Examining the properties, behaviour in firing and potential application of coal mine overburden for stoneware ceramics

Totok Nugroho1✉, Subari1✉, Bagus D. Erlangga2✉, Supriyadi1✉, David C. Birawidha3✉, Arifin Siagian1✉

1 Research Center for Advanced Materials, National Research and Innovation Agency, Tangerang Selatan, Indonesia
2 Research Center for Geological Resources, National Research and Innovation Agency, Bandung, Indonesia
3 Research Center for Mining Technology, National Research and Innovation Agency, Lampung, Indonesia

*Corresponding author: e-mail tot004@brin.go.id

Abstract

Purpose. A binary mixture of a ceramic body was studied, incorporating overburden from a coal mine site in Bontang, East Kalimantan, Indonesia. This overburden material has been tested for the manufacture of stone-ceramic body.

Methods. The initial characterization of overburden materials includes testing the chemical composition by XRF analysis and mineral content by XRD analysis on raw materials and overburden exposed to high temperature. The composition of ceramic specimens is a mixture of 85% overburden material and 15% fine sand. Firing temperatures in the range of 900-1100°C were applied to the ceramic body specimen. Then, ceramic properties, such as physical color, plasticity, shrinkage, water absorption, and density were analyzed.

Findings. The results show that the ceramic specimen experiences densification when exposed to high temperature in this range, which in turn contributes to low water absorption and high flexural strength. This ultimately results in low water absorption below 1.0% at 1100°C, which is favorable for stoneware type of ceramics. The mechanical properties of specimen at 1000°C is in accordance with stoneware body standard. In addition to this, it is believed to be more energy efficient, since the low firing temperature is sufficient to achieve the stoneware specification.

Originality. The binary clay-based ceramic have been tested using coal mine overburden and river sand with a high Fe2O3 content. Together with the presence of alkali oxides and calcium in the raw materials, this can potentially reduce the use of fluxing agent. A comprehensive study has been conducted on the characteristics, firing effect, and application of stoneware.

Practical implications. Some ceramic prototypes from this result were also made using a rotary technique and heated at this temperature range. Since overburden is generally considered to be backfill material, the selective clay material application for ceramics can provide the potential to stimulate local product innovation by utilizing easily available overburden materials.

Keywords: coal mine overburden, clay, binary ceramic body, stoneware, high temperatures

1. Introduction

Mining operations generate a huge amount of overburden material, which refers to material that is removed to access underlying mineral deposits. Coal mining is one of the extensive mining industries that produce a huge amount of overburden during open pit excavation. In many cases, this overburden material is often considered as low valuable material and is therefore simply dumped in an area or used as a backfill material. As a backfill material, overburden can reduce the amount of natural sources such as river sand and gravel needed to close a site, which is considered economically and environmentally friendly [1]. However, coal mine overburden can be categorized into some strata based on its depth, starting from the topsoil and ending with the coal seam. This can lead to a variety of mineral and physical characteristics of overburden laid on top of the coal. The study shows that the top three layers of a coal mine overburden are composed of red soil, mudstone and shale [2]. The research findings also indicate that higher levels of overburden have lower levels of sulfuric and toxic metal contamination. This can lead to the safe utilization of such coal mine overburden.

Some research have revealed the potential of overburden material to be used as brick ceramic material [3-5] and typical aggregates for construction materials [6-8]. Such utilization can promote an extensive use of this raw material, which could benefit from the inclusion of overburden material. However, re-evaluating this overburden material as a valuable resource presents an opportunity to promote sustainable practices and explore new applications. One of the promising utilization of overburden is the production of various ceramic materials [4], including stoneware. Stoneware is a type of ceramic that is fired at high temperatures (1200-1300°C), resulting in a dense and durable product that looks like stone. In general, stoneware is made of clay, feldspar and sand.
Feldspar plays an important role as a fluxing agent, which reduces the sintering temperature [9]. Nevertheless, the significant cost of feldspar and the depletion of its resources have a notable influence on the search for more cost-effective substitute fluxes. Presently, extensive research is conducted on the investigation of other natural igneous rocks, such as granitic and basaltic minerals, whose water absorption could reach less than 1%. On the other hands, quartz sand is mostly used in ceramic body manufacture. This sand has the function of filler material that increases hardness, rigidity and reduces shrinkage [10]. Thus, the appropriate amount of fluxing and filler materials can result in optimal bending strength and low water absorption [11].

The flux effect of clay-based ceramic body sintering can also be obtained from alkaline [12], [13] and iron compounds [14]. This compound can be found inherently in particular clay and other raw materials. Therefore, the ceramic properties can still be achieved through binary mixtures [15] such as clay and filler. Quartz sands are mainly used for clay-based ceramic filler materials as they contain relatively low iron oxides. This is due to the influence of the iron content, which, when exposed to high temperature, gives clay bodies a reddish color [11], but in excess amount this can lead to deterioration of mechanical performance.

In this study, overburden rocks from coal mine located in East Kalimantan, Indonesia, were used as raw materials for traditional ceramic stoneware. Overburden from coal mining can be classified as a waste material that can be utilized as industrial raw materials, where the mineralogy of the coal overburden layer mostly contains the minerals of quartz, illite, pyrite and others [7], [16]. The wet mixture plasticity value and water absorption after firing of mixture are important criteria for traditional ceramic materials [17]. For the manufacture of ceramic stoneware, the material used must have plastic properties and a relatively low water absorption value. Stoneware is mainly produced by mixing ingredients such as kaolin clay, silica and feldspar to achieve typical ceramic properties [18]. Since clay potentially contains significant amounts of alkalies and iron oxides, research is aimed at creating a binary stoneware body consisting of the clay overburden and local river sand. In terms of the potential application of coal mine overburden as raw materials for stoneware ceramics, characteristics and mechanical properties are studied. This overburden area is known for its significant coal reserves and extensive open-pit coal mining activities. Along with the rapid development and infrastructure in this area, this research can contribute to promising local product innovation based on overburden materials.

2. Materials and method

2.1. Materials

The raw materials studied for this activity were the overburden layers of coal deposits from PT Indomincio Mandiri (coal mine) as the main raw material, and fine sand as an additive for the manufacture of ceramic products, both building materials and ceramic pottery or terracotta. The steps taken in the experiment of making ceramic product prototypes are as follows: overburden material samples were subjected to a drying process in a drying oven at a temperature of 100°C; after drying, the samples were manually pulverized with a porcelain mortar to a fine size of around 100 meshes, where visually the overburden material dominantly contained clay. The photograph of overburden clay can be seen in Figure 1.

In addition to overburden material, fine sand was also used, which functions as a filler material. Fine sand was obtained from the local area as river sand with particle size screen below 80 meshes.

2.2. Method

2.2.1. Material characterization

The particle size distribution, chemical composition and minerals content of overburden material were measured. Particle size analysis was performed by screening method using several sieve sizes from 4 to 400 meshes. For the chemical compound, X-ray fluorescence analysis was conducted using an Epsilon 4 XRF device from Malvern Panalytical, operating at 50 kV and 3 mA. Further, X-ray diffraction analysis of overburden samples was carried out before and after heating at 900°C to understand the thermal transformation of minerals. A Panalytical X’Pert 3 with Cu-Kα as the X-ray source operating at 40 kV and 30 mA was used to scan the material diffractogram. The XRD graph is compared to COD database to reveal mineral content using Highscore Plus 3.0.5 software from Panalytical.

2.2.2. Ceramic body preparation

The developed ceramic body composition consists of 85% overburden and 15% of fine river sand. Body composition refers to previous research of Stolboushkin et al., 2017. For the manufacture of ceramic bricks, in addition to overburden materials, sandy loam was also used, the mixture ratio of which consists of 80% overburden and 20% clay loam [3]. The ceramic body composition, consisting of 85% refined overburden and 15% fine sand, was mixed until homogeneous, after which about 20 wt. % of tap water was added while stirring until a plastic mass is formed. The plasticity properties of the ceramic mixture were determined using the Atterberg method, which refers to SNI 03-1323-1989 [19], Plasticity Index (PI), as an indicator of a material plasticity, was obtained by calculating the difference between liquid limit and plasticity limit. Then, a specimen in the form of a rectangle (10×20×120 mm) was formed from this plastic mass to measure physical-mechanical properties (Fig. 2).

To conduct physical and mechanical tests at each designated temperature, three samples were made from the prism ceramic bodies. The resulting ceramic product is subjected to natural air-drying, a process that lasts up to 6 days. The ultimate stage entails the firing the ceramic body specimen at a range of temperatures, specifically 900, 1000 and 1100°C, for 10 hours in an electric furnace. The cooling process was allowed to proceed naturally inside the furnace until it reached ambient temperature. This experiment was also conducted in a bowl-shaped prototype exposed to the same high temperature range. This will further evaluate the physical appearance of such a product.
2.2.3. Measurement of linear shrinkage, water absorption and flexural strength

When determining the shrinkage value, the change in the bulk specimen length was divided by the initial length and expressed as a percentage. The formula used for calculating the shrinkage data is as follows:

\[ \text{Linear shrinkage} = \frac{\text{dry length} - \text{fired length}}{\text{dry length}} \times 100\% . \]  

(1)

To assess water absorption, the specimens were immersed in water for 24 hours. The specimens were weighed before (dry weight) and after immersion (wet weight). The water absorption percentage is determined by dividing the difference between dry weight \( (D) \) and wet weight \( (S) \) by dry weight \( (D) \), as illustrated in the formula below:

\[ \text{Water absorption} = \frac{S - D}{D} \times 100\% . \]  

(2)

The rupture modulus, also known as flexural strength or bending strength, is a measure of a material ability to resist failure under bending or flexural stress. In this study, the rupture modulus is determined by applying a force to a material specimen in a three-point bending test [20]. The specimen is supported at two points while a force is applied at the center, causing it to bend. The maximum stress experienced at the outer of the specimen, at the point of failure, is recorded as the load force. The rupture modulus was calculated by the following formula:

\[ \sigma_r = \frac{3LD}{2bd^2} \times 100\% , \]  

(3)

where:

- \( L \) – the breaking load, N;
- \( D \) – the distance between supports, mm;
- \( b \) – the breadth or width of the specimen, mm;
- \( d \) – the depth or thickness of the specimen, mm.

3. Results and discussion

3.1. Mineral and oxide content

The overburden material from the coal deposit is first tested for its chemical composition before being used as a raw material for making ceramic products. The overburden layers tested for chemical composition are raw overburden rocks and river sand. Chemical composition data from the XRF analysis can be seen in Table 1.

This significant presence of \( \text{K}_2\text{O} \) (4.13%) in overburden clay has a noticeable impact on the thermal characteristics and ultimate qualities of ceramic products. This is achieved by enhancing the fluxing capability and lowering the temperature required for vitrification [21].

<table>
<thead>
<tr>
<th>Table 1. Oxide content of coal mine overburden and river sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide compounds</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{TiO}_2 )</td>
</tr>
<tr>
<td>( \text{CaO} )</td>
</tr>
<tr>
<td>( \text{MgO} )</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{P}_2\text{O}_5 )</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
</tr>
<tr>
<td>( \text{MnO} )</td>
</tr>
</tbody>
</table>

The \( \text{K}_2\text{O} \) compound can also be attributed to the existence of illite mineral. Besides that, the \( \text{Fe}_2\text{O}_3 \) content of the overburden and sand material was 14.34 and 21.60%, respectively. This significant amount of iron oxides could potentially result in a red color similar to the terracotta product. On the other hand, the \( \text{CaO} \) content in the sand could help maintain low firing shrinkage and porosity of ceramic body [22].

Data from the XRD test results on overburden material before and after firing at a temperature of 900°C can be seen in Figure 3. The diffractogram indicated the content of clay minerals of the kaolin group and illite types, as well as iron minerals of the pyrite (\( \text{FeS}_2 \)) and quartz types. Pyrite can be associated with sulfur content, and illite may be associated with potassium oxide content, as indicated in the XRF analysis. This illite clay could impart beneficial properties to clays that make them suitable for ceramic application [23].

![Figure 2. Ceramic body specimen](image2)

![Figure 3. XRD diffractogram of raw overburden and the river sand exposed to 900°C firing](image3)

The changes observed in the X-ray diffraction (XRD) pattern after heat treating clayey overburden at 900°C provide insight into the alterations that occur during this process. The diffractogram graph for the overburden layer after firing at 900°C contains the minerals quartz, hematite and muscovite. An increase in temperature causes the disappearance of a distinct diffraction peak corresponding to halloysite, specifically at 12°. This firing temperature effectively triggers the removal of hydroxyl groups from minerals belonging to the kaolin group [15]. In addition, the emergence of hematite after exposure to high temperature can be caused by the pyrite mineral (\( \text{FeS}_2 \)) reaction with excess oxygen during high-temperature firing process.

The river sand contained magnetite iron minerals and albite feldspar minerals, anorthite and diopside types. The feldspar mineral can function as a flux, and the iron minerals...
help sintering process. The presence of hematite (Fe₂O₃) and potential fluxes such as potassium oxide (K₂O) and feldspar from the sand may indicate that the mixture may develop into ceramic bodies.

### 3.2. Particle size distribution

The results of the grain size analysis of coal overburden material can be seen in Table 2. Based on the particle size analysis, a graph of the grain size distribution can be seen in Figure 4. The grain size distribution of overburden material according to the Wentworth 1922 scale consists of gravel size, coarse sand, medium sand, fine sand, silt and clay. The data from the grain size analysis according to the Wentworth scale can be seen in Table 3.

#### Table 2. Grain size analysis of coal overburden material

<table>
<thead>
<tr>
<th>Particle size, mm</th>
<th>Percentage, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.76</td>
<td>1.600</td>
</tr>
<tr>
<td>2.00</td>
<td>0.000</td>
</tr>
<tr>
<td>1.00</td>
<td>0.000</td>
</tr>
<tr>
<td>0.250</td>
<td>0.000</td>
</tr>
<tr>
<td>0.177</td>
<td>0.108</td>
</tr>
<tr>
<td>0.149</td>
<td>0.110</td>
</tr>
<tr>
<td>0.125</td>
<td>0.164</td>
</tr>
<tr>
<td>0.074</td>
<td>0.712</td>
</tr>
<tr>
<td>0.044</td>
<td>0.800</td>
</tr>
<tr>
<td>0.037</td>
<td>0.600</td>
</tr>
</tbody>
</table>

Based on the grain size distribution data for the overburden material listed in Table 2 for the 400 mesh (0.032 mm) size fraction of 95.906% and in Table 3, it appears that the clay size fraction < 0.002 mm is 91.900%. Thus, this overburden is a type of plastic clay and belongs to the type of roof tile clay [24].

### 3.3. Properties of ceramic body specimen

The plasticity properties of the ceramic mixture were determined using the Atterberg method, which refers to SNI 03-1323-1989 [19]. The test results are as follows: liquid limit is 44.80%, plastic limit is 21.07% and Plasticity Index (PI) is 23.73. These Figures have determined that this mixture has a medium plasticity value. The ceramic body composition with a mixture of 85% overburden and 15% fine quartz sand is made as a specimen and fired at a temperature of 900-1100°C, as shown in Figure 5.

Figure 5 shows that raw (unfired) specimens have a gray color similar to the color of the overburden material from the Bukit Asam Tampung Enim coal deposit. After firing at a high temperature (800°C), the specimen color changed to brown, then the specimen was fired at even higher temperatures (850°C), the color became reddish brown, and then when fired at 1100°C, the specimen color became dark red. Thus, the higher the firing temperature, the darker the color of the ceramic body sample will be. This is because the overburden material contains the mineral iron pyrite (FeS₂), and the Fe₂O₃ content is above 14%, which tends to produce a reddish-brown color after firing at high temperatures [25], [26]. In addition to the above observations, measurements and calculations of the physical properties of ceramic body specimens such as the percentage of dry shrinkage, burnt shrinkage, total shrinkage and water absorption percentage were also carried out, referring to the previous research [17], [27]. The data from the measurement test results and the calculation of the physical properties of the specimen can be seen in Table 4.

#### Table 4. Some physical properties of the specimen exposed to high temperatures

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Linear shrinkage, %</th>
<th>Water absorption, %</th>
<th>Density, g/mm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>11.21</td>
<td>3.45</td>
<td>1.82</td>
</tr>
<tr>
<td>1000</td>
<td>11.67</td>
<td>1.01</td>
<td>2.25</td>
</tr>
<tr>
<td>1100</td>
<td>15.61</td>
<td>0.31</td>
<td>2.23</td>
</tr>
</tbody>
</table>

According to Table 4, it appears that the higher the firing temperature, the higher the specimen shrinkage value. This volume reduction was also accompanied by greater densification, ultimately decreasing the apparent ceramic body porosity [18]. This could also lead to reduction in water absorption value since the specimen had denser and lower porosity as the temperature increases in this range. The water absorption of ceramic body specimens at firing temperature of 900-1000°C were ranging from 3.45-1.09%, which can
be classified as the type of semi-vitreous China body. Mean-while, the average water absorption value of the ceramic body specimen fired at 1100°C was 0.31%, which can be classified as a stoneware ceramic body based on SNI 7275:2018 [28]. The advantage of this ceramic body is that it is more efficient or energy-effective because the firing temperature can be lower than 1200°C to achieve the stoneware body type, which can practically be achieved at temperatures between 1200-1300°C [29]. This can be attributed to the presence of significant Fe₂O₃ and K₂O, which could enhance the formation of a liquid phase at lower temperatures [30]. Subsequently, the densification occurred through a further consolidation process.

The rupture modulus or flexural strength of the ceramic specimen can be seen in Figure 6. It is clear that at 1000°C the optimum strength of 28.79 MPa is reached. This flexural strength complies with the standard of stoneware ceramics according to SNI 15-1327-1989 [31]. This high flexural strength can be attributed to the emergence of glass-like phase, which occurred from alkaline and ferric oxide contents, creating low porous matrix at that temperature [32]. However, when the specimen was exposed to 1100°C, there was a marked decrease, which may be an indication that excessive liquid phase was formed. This glass-like phase could emerge from high amount of alkaline and ferric oxides at such temperature. This can be compromised by the lower water absorption of less than 1%. The flexural strength pattern may not be linearly related to the physical properties in Table 4. This could be due to the complex association between flexural behavior and stoneware material brittleness.

3.4. Prototype ceramic stoneware

The test results of properties of the ceramic body based on overburden materials show that the studied ceramic bodies include solid fine earthenware to stoneware. Then, a prototype mold was made from the ceramic body composition, which was fired at 900, 1000, and 1100°C. A ceramic body made from a single component of overburden material without adding sand was fired at 1100°C for a comparison (Fig. 7).

It can be seen that ceramic bowls in ambient condition are gray in color, and those that fired at 900-1000°C – brown and at 1100°C – dark red, and their shape is still relatively perfect. This phenomenon of intense color change of the ceramic body exposed to high temperature is consistent with the previous study [26]. Meanwhile, a single component of clayey overburden ceramic bowls fired at 1100°C had an imperfect shape, with a bloating effect on the surface.

This intricate occurrence of a defective body could be due to a combination of factors stemming from both the expansion of gases within the enclosed pores, leading to bloating, and the specimen collapse due to its insufficient viscosity and inability to support its own weight [33]. It is also worth noting that during the firing process, the water trapped by the clay body begins to evaporate. This release of water vapor could create inner pressure within the clay, which can cause the clay to expand or bloat. This can be deteriorated by the lack of support from structural filler material, such as sand to maintain thermal stability [34]. Therefore, in this experiment, the use of 15% sand can effectively prevent the phenomenon of bloating.

The importance of further research is in its potential to optimize firing behavior and economic opportunity. The firing behavior of ceramics made from coal mine overburden could be optimized in greater detail. This includes the optimization of composition, particle distribution and firing duration to achieve the desired stone-ware characteristics, such as strength, porosity and color. A thorough cost-benefit analysis can be considered to determine the economic viability of ceramic products. This will ultimately lead to sustainable and economically viable solutions in applying this material in the ceramic industry.

4. Conclusions

Based on the characterization and experimental results of the overburden material for ceramic stoneware application, the following conclusion can be drawn.

Before becoming backfill material, this overburden, especially extracted from the topsoil, can be used as a supply material for ceramic products. In this way, it is possible to increase the economic and sustainability value of the material.

In addition to kaolinite, illite and quartz, the overburden contains the mineral pyrite (FeS₂). This pyrite is as-sociated with sulfuric content, which transformed into hematite after the process of firing at high temperatures.

The iron oxide (Fe₂O₃) content in the overburden material is above 14%, which gives a dark or reddish color after firing at high temperatures.

From the particle size analysis, the clay content in the overburden material exceeds 90%. This clay has plastic properties, which is potentially possible for ceramic raw materials. The plasticity index of binary mixture ceramic body reached 23.73%, having medium plastic property.

The firing temperature of ceramic body specimens tends to give a reddish brown to dark red color. Densification in the specimen occurred linearly with an increase in temperature up to 1100°C. Exposure to high temperatures also led to low porosity and water absorption, but increased firing shrinkage.
Ceramic body specimens fired at 900-1000°C are classified as semi-vitreous China type ceramic bodies, and specimens fired at 1100°C include stoneware ceramic bodies, in which the overburden-based ceramic body formula can be made into ceramic items by rotating techniques.

Acknowledgements

The authors express their gratitude to PT. Indomincio Mandiri, who supported this research, as well as to colleagues from BRIN who assisted in this research activity.

References


Vивчення властивостей, динаміки при випалюванні та можливостей застосування 
роківних порід вугільних шахт для виробництва кам’яної керамики

**Т. Нугрохо, С.бурбі, Б.Д. Ерланга, Супріяді, Д.К. Бірандіха, А. Сянг**

**Мета.** Вивчення властивостей бінарної суміші керамічної маси, що включає роківні породи з ділянки вугільної шахти в Бонтапу, Східний Калімантан, Індонезія. Цей роківний матеріал пройшов випробування для виготовлення кам’яно-керамічної маси.

**Методика.** Початково характеристика матеріалів роківних порід включає визначення хімічного складу за допомогою XRF-аналізу і вмісту мінеральних речовин за допомогою XRD-аналізу на сировинні роківних порід, що зазнали впливу високої температури. Склад керамічних розчинів являє собою суміш 85% роківного матеріалу і 15% дрібнозернистого піску. До зразка

114
керамічної маси застосовували температури випалювання в діапазоні 900-1100°С. Потім були проаналізовані властивості кераміки, такі як фізичний колір, пластичність, усадка, водопоглинення та густина.

**Результати.** Встановлено, що керамічний зразок ущільнюється при впливі високих температур у цьому діапазоні, що, у свою чергу, сприяє низькому водопоглинанню та високій міцності на витин, що призводить до низького водопоглинання нижче 1.0% при температурі 1100°С і є сприятливим для кам’яного типу кераміки. Визначено, що механічні показники зразка за температури 1000°С відповідають стандарту для маси із кам’яної кераміки. Крім того, вона вважається більш енергоефективною, оскільки низької температури випалу достатньо для досягнення технічних характеристик кам’яної кераміки.

**Наукова новизна.** Оригінальністю даного дослідження є випробування бінарної кераміки на основі глини розкривних порід вугільних шахт та річкового піску з високим вмістом Fe₂O₃. Виявлено, що разом з наявністю у сировині оксидів лужних металів та кальцію зменшується використання флюсового матеріалу. Проведено всебічне дослідження характеристик ефекту випалу та застосування кам’яної кераміки.

**Практична значимість.** Розкривні відвалові породи, зазвичай, вважаються матеріалом для зворотного засипання, а вибіркове застосування глинистого матеріалу для керамічних виробів може забезпечити потенціал для стимулювання місцевої інноваційної продукції за рахунок використання легкодоступних розкривних матеріалів.

**Ключові слова:** розкривні породи вугільних шахт, глина, бінарна керамічна маса, кам’яна кераміка, високі температури