# Feasibility of Recycling ULAB Slag into Fired Building Clay Bricks

A laboratory and Pilot Scale Study

*Submitted to*

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Fig. 1: Recycling of used lead acid battery (ULAB) slag to fired clay bricks and tiles

## 1. OVERVIEW

Waste slag, a by-product from used lead acid battery (ULAB) smelting operations normally contains lead (Pb) in varying proportions depending on the efficacy of the smelting process and separation of molten Pb from the slag. The concentration of Pb in ULAB slag from IBETO Recycling plant already studied ranged from 1.70 to 66.1%. The common practice of disposing of this slag, not only at IBETO, but all over most African countries is either to dump on the recycling plants' premises, in near-by bushes or submitted to local vendors who possibly use the slag for pothole filling and other purposes not well known. These practices are highly environmentally unsustainable because there is a high possibility of leaching of Pb from the slag at favourable conditions to both surface and underground soils and water with concomitant deleterious consequences on human health and the entire ecosystem. Therefore, there is a need to find other alternative methods of managing ULAB slag in a more environmentally sustainable manner.

Natural raw materials used in the fabrication of clay-based ceramic products have demonstrated a wide range of compositional variations and the resulting products are very heterogeneous. Therefore, such products can tolerate further compositional fluctuations and raw material changes, allowing different types of wastes to be incorporated to make fired ceramic products like bricks and tiles.

Many success stories indicating recycling of different kinds of solid wastes in ceramic industry already have been reported. Examples include recycling of waste glasses, which can easily be incorporated as an alternative ceramic raw material or as a fluxing agent in stoneware, tiles, bricks and concrete, wastes such as coal combustion ash, fly ash, filter dusts from waste incinerators, mud from metal hydrometallurgy, different types of sludge and glass cullet or their mixture, paper mill sludge, waste slag from PbS smelting etc have been considered in traditional ceramic and construction industries [1-11].

With this background, this study was conceived with the aim of investigating the feasibility of recycling waste ULAB slag obtained from IBETO Recycling plant with Pb concentration < 10% in fired clay construction materials with the intention of immobilizing the Pb in the inert glassy material. The specific objectives of the study were:

1. Investigating the feasibility of recycling ULAB slag into fired heavy-clay products like building bricks and tiles thereby immobilizing the Pb present.
2. Optimizing the clay/slag mixture to obtain the optimum composition.

3. Determining the physic-chemical, technological and microscopic properties of both raw and fired products.

4. Conducting leaching tests (TCLP and SPLP) on the fired products to check the extent of inertization of Pb in the products.

5. Ascertaining the class and grade of construction building products made from clay/slag mixture by comparing with ASTM standards for building products.

6. Test running the production of commercial bricks using a commercial ceramic production outfit.

## 2. EXPERIMENTALS

### 2.1 Raw materials acquisition

ULAB slag was obtained from IBETO ULAB Recycling Plant at Nnewi, Anambra State. Brick clay was sourced from a local ceramic/brick manufacturing outlet.

### 2.2 Sample preparation

Waste ULAB slag samples were pulverized and sieved using 2mm mesh size for mixing with clay.

### 2.3 Mix Proportions

Seven mix proportions were formulated with slag/clay ratio ranging from 0 to 30% replacement of clay with slag and 0% slag serving as control. For each series, an average of ten replicate Test Probes (TPs) were made. Physico-chemical, technological and microscopic properties of both the green (dry, but not fired) and fired products were conducted on these TPs.

### 2.4 Preparation of Test Probes (TPs)

Calculated amounts of slag and clay were manually mixed for each series and the TPs arising from them were made by employing the dry compression method, which was available. After this, the TPs were air dried, oven dried and fired up to 1000$^0$C using a furnace. The glassy TPs at this time were ready for further characterization. The pictorial procedure indicating the major steps is shown in Plate 1.

(a) Weighing of starting materials (b) Dry compression moulding (c) Air drying

(e) Fired Test Probes (d) Further Drying and Firing

Plate 1: Major laboratory steps of producing fired test probes

## 2.5 Analyses of raw materials and TPs

(1) The raw composite slag sample and raw clay sample were analysed for Pb and other heavy metals present using X-Ray Fluorescence (XRF) Spectrophotometric Technique.

(2) The green (dry, but unfired) and fired products for selected series were analysed using XRF technique to know the amount of metals present. This was used to estimate the emission profile of Pb during firing.

## 2.6 Determination of the technological and microscopic properties

The major mechanical properties namely; Bulk Density, Linear Shrinkage, 24 hour soaking water absorption, 5 hour boil Water Absorption, Compressive Strength, Saturation Coefficient were determined on the TPs. Furthermore, microscopic properties namely X-Ray Diffraction and Scanning Electron Microscopy were conducted on selected TPs to study the micro properties.

## 2.7 Preparation of Standard Size Brick

A pilot study was carried out in a local ceramic/ brick manufacturing plant to produce standard size fired bricks from optimum clay/slag mixtures to appreciate a real life mass production scenario of brick manufacture. Tiles were not made because the mould was not easily available. The bricks from our mixtures were made using the conventional brick making process of drying raw materials, grinding, sieving, moulding, drying and firing using a locally fabricated kiln with firewood.

Plate 3: Moulding of commercial size brick from our optimum composition

Plate 4: Firing of commercial size bricks in a local ceramics/brick making outfit

## 2.8 Leaching Studies

Toxicity Characteristic Leaching Procedure (TCLP, US EPA Method 1311)[12] and Synthetic Precipitation Leaching Procedure (SPLP, US EPA Method 1311)[12] to ascertain environmental friendliness of the products were conducted on TPs from each series to mimic the impact of municipal landfill conditions (TCLP) and exposure to products to natural precipitation using a locally fabricated rotary shaker(Plate 2). The leachates were analysed for Pb using Atomic Absorption Spectrometric Technique.

Plate 2: Locally Fabricated Rotary Shaker (28 rpm)

# 3. RESULTS and their IMPLICATIONS

## 3.1 Elemental composition of Raw Materials

Table 1 indicates the concentrations of major elements in raw clay and slag samples used in this study

Table 1: Elemental Composition of Raw Materials

| Element | Raw Clay | Raw Slag |
|---|---|---|
| Mg | ND | ND |
| Al | 17.20 | 1.655 |
| Si | 30.67 | 3.34 |
| P | 0.180 | 0.277 |
| S | 1.24 | 21.02 |
| K | 2.26 | 0.0285 |
| Ca | 3.15 | 0.835 |
| Ti | 0.306 | ND |
| V | 0.0125 | 0.0156 |
| Cr | 0.0001 | 0.0297 |
| Mn | 0.0448 | 0.108 |
| Co | 0.251 | 0.941 |
| Fe | 11.28 | 33.88 |
| Ni | 0.0307 | 0.0146 |
| Cu | 0.0234 | 0.0235 |
| Zn | 0.2500 | 0.0720 |
| As | ND | 0.478 |
| Pb | 0.0295 | 4.431 |
| W | 0.2679 | ND |

| | | |
|---|---|---|
| Au | ND | 0.515 |
| Ag | ND | 0.0005 |
| Rb | 0.0082 | ND |
| Nb | 0.0100 | ND |
| Mo | 0.168 | 0.181 |
| Cd | ND | ND |
| Sn | 0.779 | 1.627 |
| Sb | 0.773 | 0.174 |

ND – Not Detected

The raw materials contain an appreciable concentrations of Si and Fe which provide strength and colour, making them appropriate for brick making.

## 3.2 Technological Properties

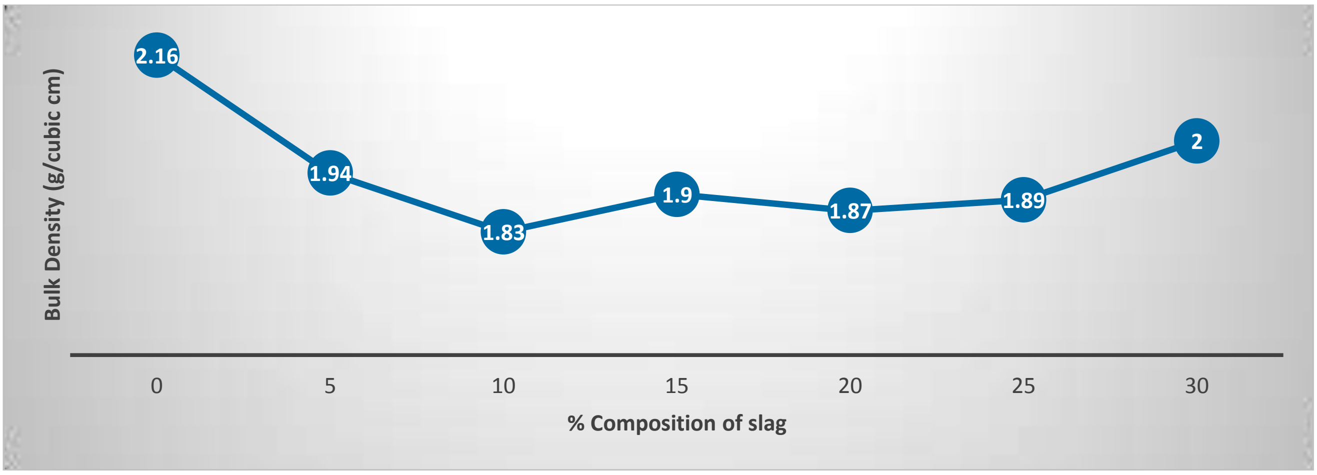


Figure 1: Bulk Density of Test Probes of 0 – 30% clay replacement with ULAB slag

The average bulk density (n = 5) of the fired test probes fluctuated between 2.16 and 2.00 g/cm$^3$. The bulk density for all TPs of the clay/slag mix proportions studied fell within the range of 1.5 – 2.4 g/cm$^3$ set for building purpose in developing countries[13] . The fluctuation in bulk density of the fired test probes could be attributed to variable complex channelling in the pore system of the fired products.

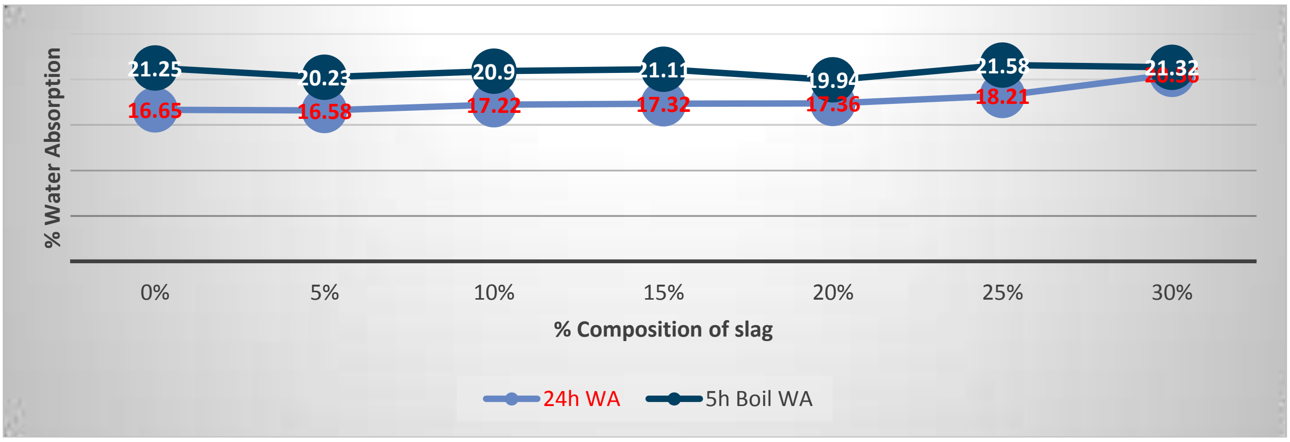


Figure 2: 24 Hour-Soaking and 5-Hour Boil Water Absorptions (%) of Test Probes of 0 – 30% clay replacement with ULAB slag

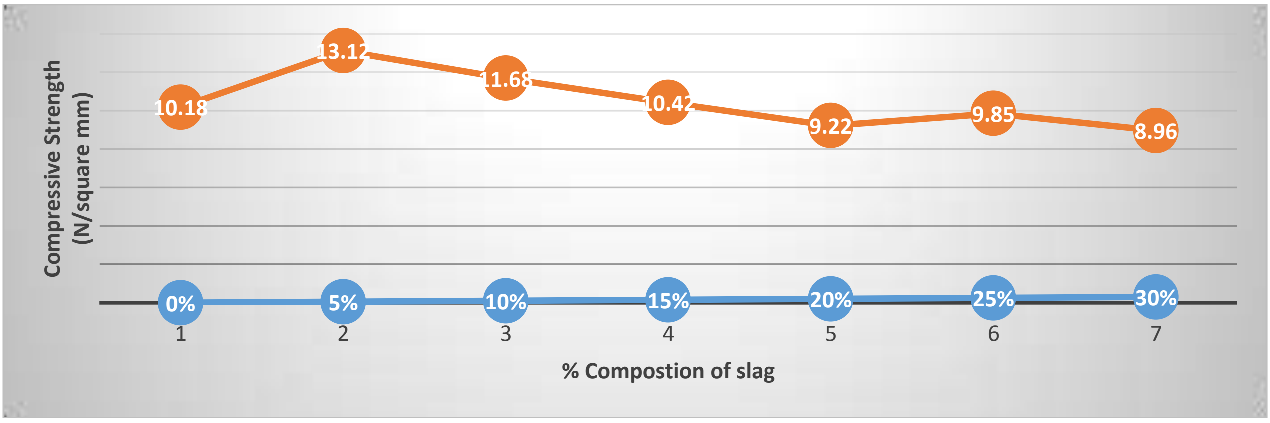


Figure 3: Compressive Strengths of Test Probes of 0 – 30% clay replacement with ULAB slag

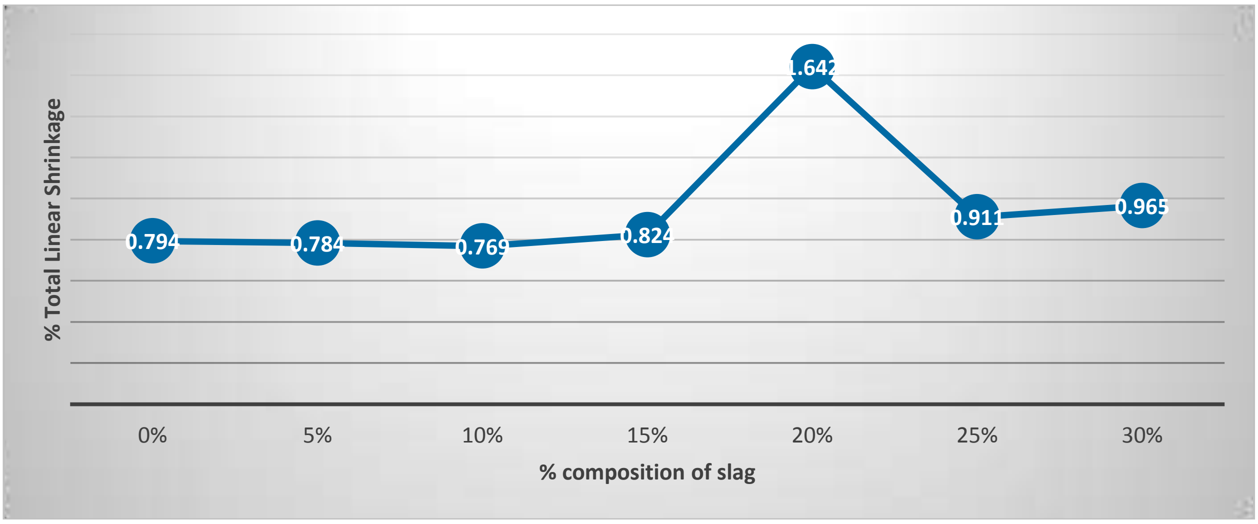


Figure 4: % Total Linear Shrinkage of Test Probes of 0 – 30% clay replacement with ULAB slag

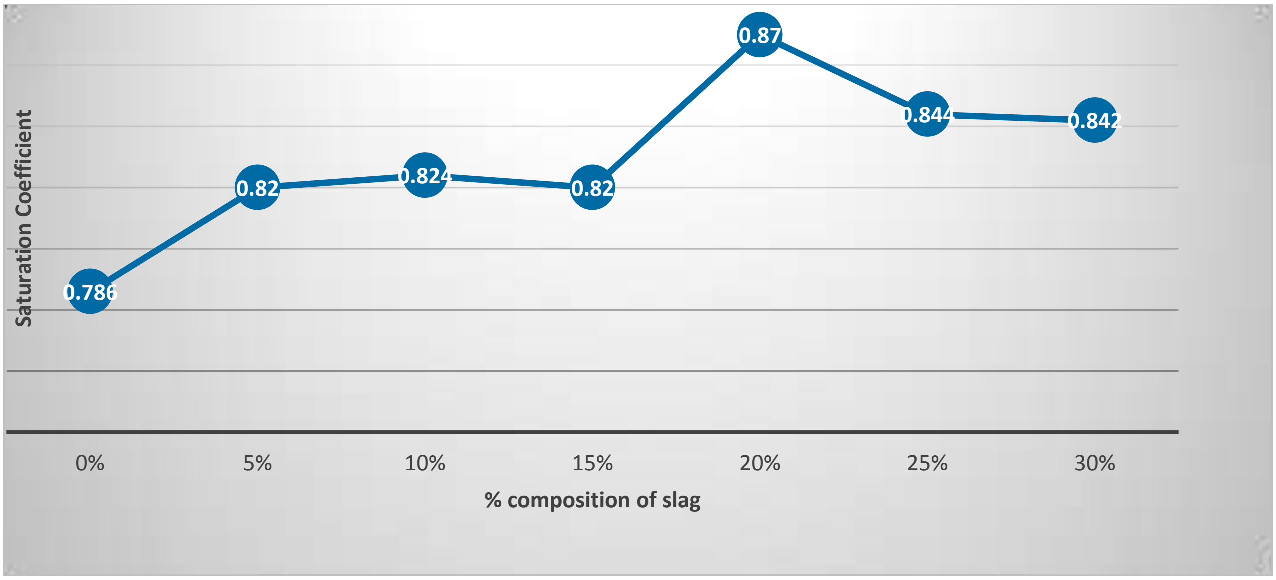

Figure 5: Saturation Coefficient of Test Probes of 0 – 30% clay replacement with ULAB slag

The three most relevant technological properties that determine the class and durability of fired material used for building purposes are water absorption (WA), total linear shrinkage (TLS) and the compressive strength (CS). Furthermore, the grade and durability of a fired clay product vary depending on factors like the type of clay used, compaction method, position of material in the firing furnace and final firing temperature. Table 2 shows the average ranges of some important technological properties compare with American Standards for Testing Materials (ASTM) limits.

Table 2: summary of selected properties of fired clay products compared with ASTM Standards

| S/N | Selected Technological Properties | ASTM Standards | | | |
|---|---|---|---|---|---|
| | | Range (standard deviation) | Class 1 | Class 2 | Class 3 |
| 1 | Compressive Strength ($N/mm^2$) | 8.96 (±1.59) - 13.12(±3.04) | ≥20.7 | ≥15.5 | ≥10.3 |
| 2 | 5 hour- Boil Water Absorption (%) | 19.94(±1.65) - 21.58(±0.36) | ≤17 | ≤22 | No limit |
| 3 | Linear Shrinkage (%) | 0.784(±0.015) - 1.642(±0.242) | ±3.125 | ±3.125 | |
| 4 | Saturation Coefficient | 0.786 (±0.510) - 0.870 (±0.069) | ≤0.88 | ≤0.78 | |

From Table 2, and Figures 2-5, the grade of bricks made up to 15% clay replacement with slag were between class 2 and 3. This grade falls generally within the quality of fired clay bricks made by dry compression method which demonstrate moderate strengths and water absorption. Considering the aforementioned and the colour of the fired products, which was getting darker with increasing slag addition, one could confidently say clay replacement with slag till 10 % will give products that are desirable both in quality and aesthetics (colour).

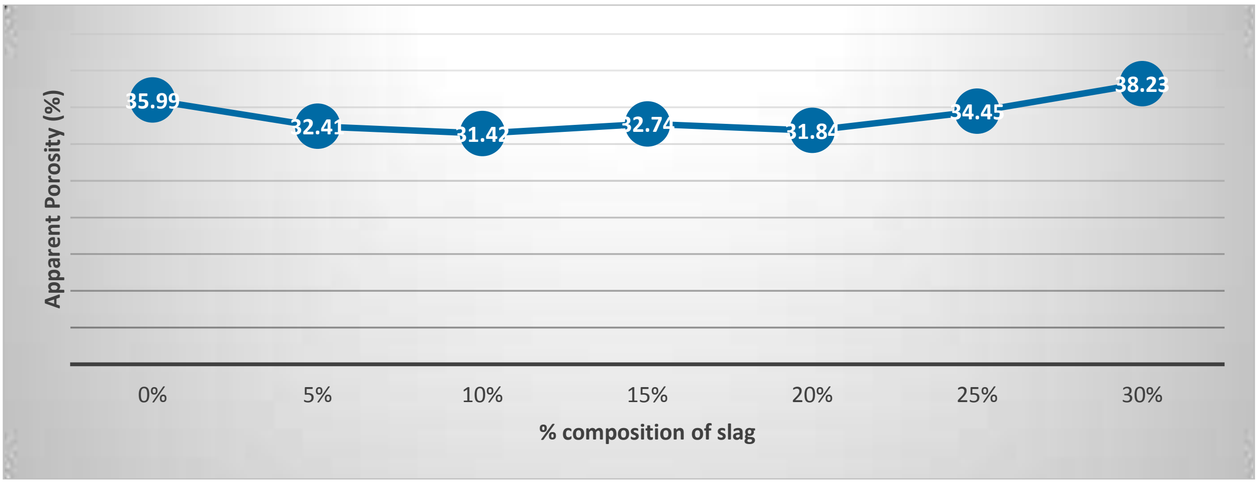


Figure 6: Apparent Porosity of Test Probes of 0 – 30% clay replacement with ULAB slag

Apparent Porosity (AP) and Saturation Coefficient (SC) are used to indicate the complexicity of the pore system of the fired material. The APs and SCs generally conform to fired products made by dry compression method.

## 3.3 Emission of Pb during Firing

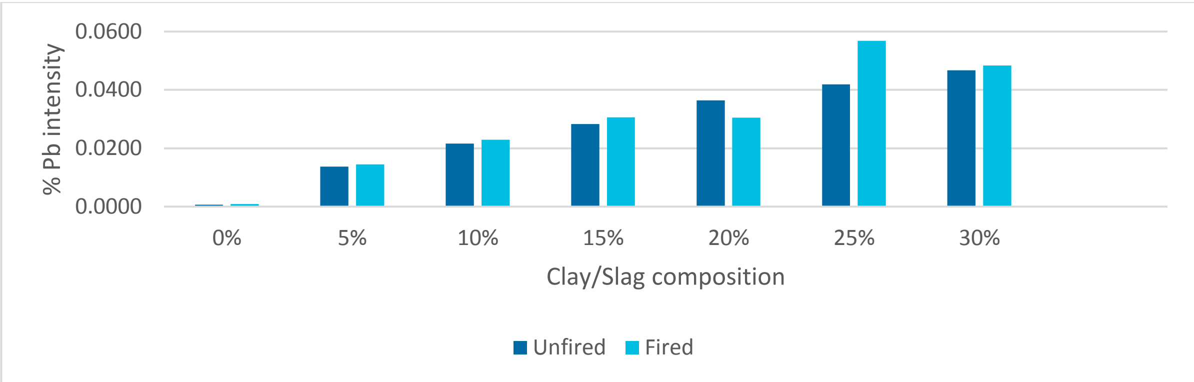


Figure 7: Comparison of Pb level in green (unfired) and fired products

The comparison of green and fired products of the different series was carried out to study the emission profiles arising from the firing. There seem to be little or no Pb emission from the products during firing as there is no significant difference in Pb level between green and fired products. It is thought that this could be possible as demonstrated in our previous study[12] where Pb was found to be immobilised in a fired glassy matrix in the form of Lead alumina-silicate, a new crystal found to be insoluble in water and stable in the environment. However, a confirmatory test could still be necessary where emissions arising during firing are scrubbed using appropriate reagents to study Pb levels.

## 3.4 Microscopic Properties of fired and unfired products

Figure 8a – 8e show micrographs arising from Scanning Electron Microscopy (SEM) analysis of selected fired clay/slag mix proportions to study the surface morphology, to qualitatively determine

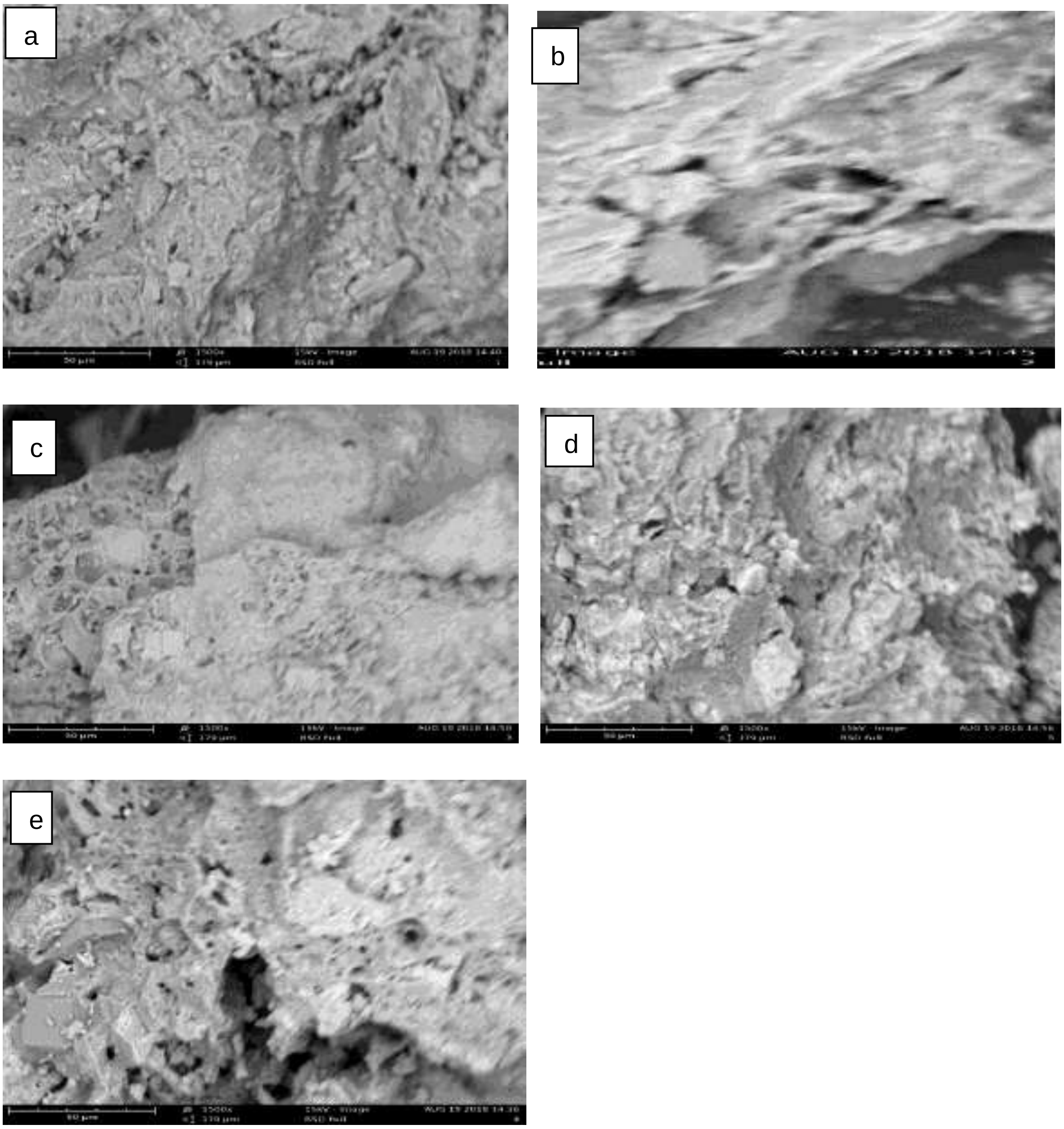


Figure 8a:100% fired clay, b: Fired product with 5% slag, c: Fired product with 10 % slag
d: Fired product with 30 % slag e: Unfired product with 30% slag

the porosity of the products.

No pronounced differences were observed in the images for the various series examined confirming the results from water absorption and apparent porosity which showed similar trends. This suggests that there was no obvious modification of the surface of the fired products with slag addition.

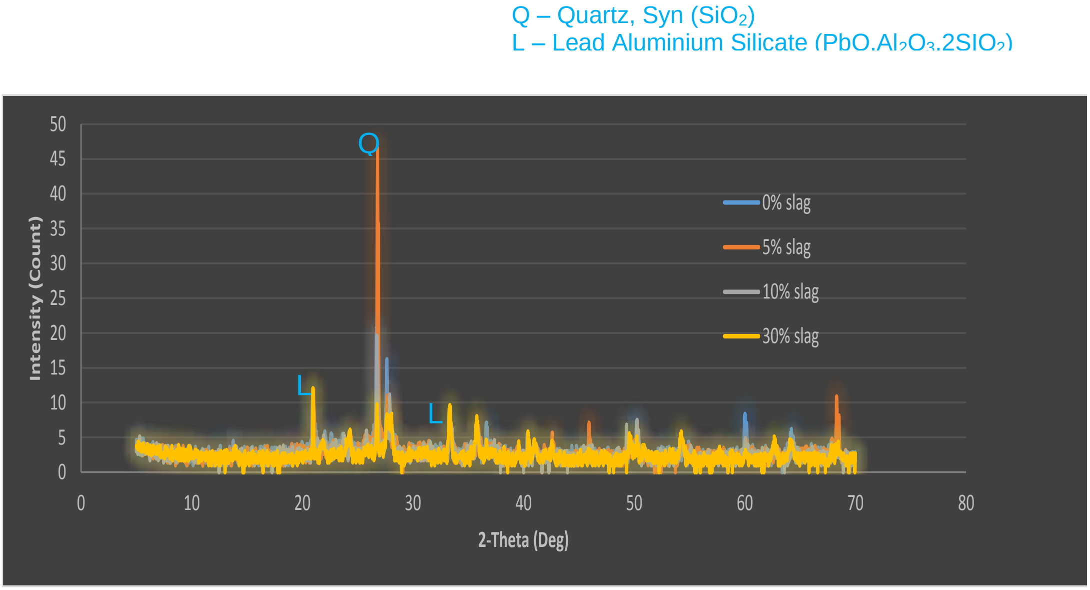


Figure 9a: XRD charts of different Clay/Slag Mix Proportions

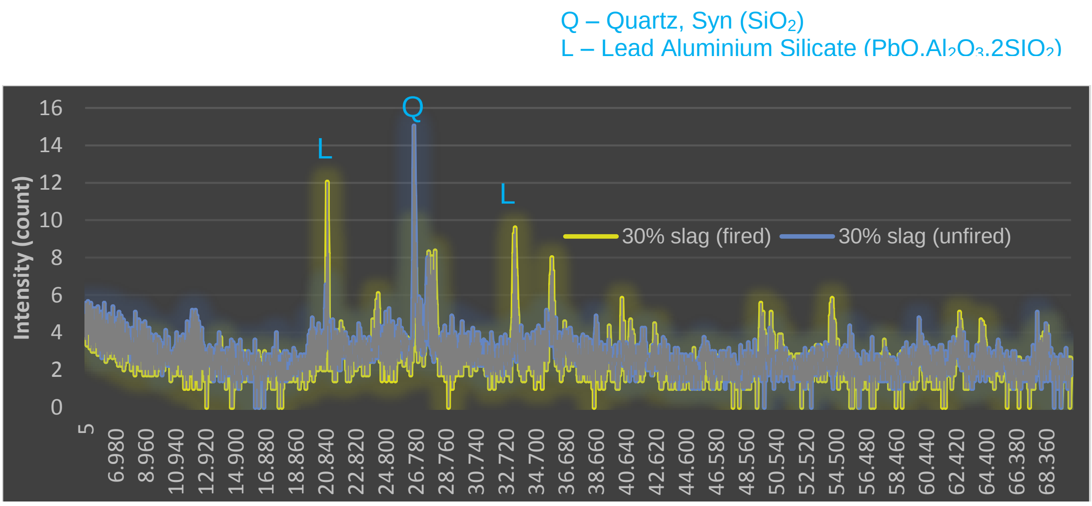


Figure 9b: XRD charts of unfired and fired 30% Clay/Slag Mix Proportion

Figure 9a indicates the XRD charts of fired products with different slag compositions ranging from 5-30% slag replacement with 0% as control while Figure 9b compares the XRD charts of green and fired products. This analysis was carried out to investigate the influence of slag composition and heat of firing on major crystal transformation in the products. Interestingly, it was observed as seen in Figure 9a the conspicuous formation of a new crystal (Lead Aluminium Silicate, $PbO.Al_2O_3.2SIO_2$), which was absent in the sample without slag. This new crystal was not conspicuous in compositions with lower slag content possibly because the amount of Pb present was small to show visible line corresponding to the crystal phase. The Pb containing crystal was obvious in composition with 30% slag. Furthermore, Figure 9b also indicate Lead Aluminium Silicate ($PbO.Al_2O_3.2SIO_2$) crystal in the fired product which was not visible in the unfired product. This as we earlier observed in our previous study[12] could be as a result of the formation of new crystal phase from a reaction of Pb and Pb containing compounds in the slag with alumino-silicate in the clay to form this stable, water insoluble crystal.

## 3.5 Pilot Study of Optimum Compositions

The technological properties of the fired products containing up to 10% clay replacement carried out in an identified small scale ceramic/brick making outlet were found to be within the same ranges as the laboratory experiments except the strengths which were a bit lower (7.22-9.43 $N/mm^2$), but still much higher than the minimum strength of 3 $N/mm^2$ for fired bricks to be used for building. There was no significant difference between products with slag and without slag studied. All samples passed the leaching experiments also as the laboratory made samples.

## 3.6. Results of Leaching Studies

Fired products with different Clay/Slag mix proportions were subjected to Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) tests to determine the influence of municipal landfill and exposure to atmospheric precipitation conditions, respectively. The levels were within the maximum limit of 5 mg/L as specified by US EPA.

It was interesting to note that Pb level in leachates arising from samples with slag up to 30% using the TCLP solution was less than 1.00% and was not detected in all samples using the SPLP solution. This demonstrates that the fired products will be safe and stable in the environment.

## 3.7 Economic Viability of the Fired Products

From the interaction with the staff and owner of the outlet the products were made, the incorporation of slag in brick is a welcomed idea as slag is a waste and is replacing the clay which is bought, thereby saving cost (provided the cost of transportation of slag is not considered).Furthermore, with proper mixing and drying, slag has a tendency of improving the strength of the fired products.

The use of fired clay bricks and tiles for building compared to cement based system is still low, possibly because of the initial cost of purchase (between N130 – N500, depending on the grade) of the products. Due to this, there are still very few outlets that are engaged in full time brick making for commercial purposes. There could be need for more advocacy by government and private stakeholders and media to promote the use of bricks in building as there are some long term benefits such as:

(i) With a brick house, painting is not required
(ii) There are hardly any cracks on the building

(iii) The durability is more guaranteed compared to cement blocks
(iv) The building is always cooler during the hot season and warmer during the cool season because of the ability of the bricks to trap and release heat in a slower manner compared with cement systems.
(v) The building is usually more secured in terms of breaking and entry.

## 4. Concluding Remarks

(i) This study investigated the feasibility of recycling ULAB slag with about 5% Pb in fired clay bricks that could be used for building/construction.
(ii) The grade of bricks obtained was generally within second to third class, complying with the grade normally obtained by dry compression method used for moulding.
(iii) The results obtained indicate that this recycling option of ULAB slag is environmentally sustainable as Pb was proven to be chemically immobilised in the glassy matrix of the fired product and cannot leach out given commonly available conditions the material could be exposed to. Therefore, this is a promising management option for waste ULAB slag that needs to be explored since Nigeria and many parts of the world are endowed with clay deposits suitable for brick making.

## 5. Recommendations

(i) There is need for advocacy and commitment by both private sectors and government on the use of bricks arising from impregnation with waste ULAB slag. This can be done by possibly engaging in low cost housing projects with socio-economic dividends.
(ii) ULAB recycling enterprises could add or modify their plants' blue prints to include this management option to operate in a greener manner.
(iii) Plants to recycle waste ULAB slag into fired bricks and other clay based products could be cited as close as possible to the ULAB recycling plants to reduce cost of transportation.
(iv) More brick making industries that produce better quality products that can be used for engineering works should be encouraged.
(v) It is recommended that this procedure should be repeated to produce first class fired bricks using extrusion method to mould not dry compression to study the dynamics that could arise.

## 6. Challenges

(i) It was a challenge getting the green products to dry to acceptable moisture content before firing due to the high humidity in the air during the rainy season. It took far longer time than the estimated time to make the commercial size products.

## 7. Acknowledgement

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