Possibilities of Recovery of Industrial Waste and By-Products in Adobe-Brick-Type Masonry Elements †

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Abstract: The purpose of this study is to search for possibilities to capitalize on industrial waste, which occupies huge storage spaces. This paper presents an experimental study on the possibility and efficiency of this industrial waste in the composition of clay mixtures suitable for making unburned clay bricks. Living in harmony with nature is part of sustainable development. For this purpose, six compositions based on clay and industrial waste were made. The studied industrial wastes were: ash from the Mintia thermal power plant, Romania, limestone sludge, gypsum sludge, and damped waste from the processing of imported ore.

Keywords: adobe bricks; thermal power plant ash; dumped waste; limestone sludge; plaster sludge

1. Introduction

It is known that the cement industry produces air pollution due to CO₂ emissions, which constitute 4–8% of total greenhouse gas emissions. Other non-negligible emissions that occur in the cement industry are dust emissions and emissions of NO₂, CH₄, SOₓ, NOₓ, NH₃, and CO [1]. All this results in a depletion of the ozone layer and, therefore, global warming. Under these conditions, the elimination or substantial reduction of cement consumption is desirable. By replacing classic building materials with environmentally friendly materials wherever possible, a considerable contribution is made to protecting the environment. The possibilities of recycling, reuse, reintegration in nature, environmental protection, and efficient management of natural resources are essential indicators in the context of sustainable development. Living in harmony with nature is part of sustainable development. Products that successfully meet all these requirements are the elements of unburned clay masonry.

Another important quality of ecological materials is the fact that they offer a healthy and pleasant climate to users. Clay-based building materials used in construction allow a natural and efficient ventilation of the walls, permeability to water vapor, thermal constancy, and a constant humidity of the indoor environment. In addition, these walls made of clay-based bricks have no toxic emissions, a factor that plays a very important role in reducing the risk of respiratory diseases, allergies, and more. Studies are presented in the specialized literature that demonstrate the durability of constructions made with local materials and local techniques in different geographical and climatic conditions [2–4].

Nine thousand years ago, construction techniques with clay bricks were used. Clay bricks were discovered in Turkistan, dating from 8000–6000 BC. Clay was used as a building material in all
ancient cultures for religious buildings and houses; 5000-year-old foundations were discovered in Assyria [5].

Houses made of ecological materials have started to become more and more known and pleasant in Romania, and more and more specialists are interested in this type of construction [6,7]. The specialized literature presents the results of some research carried out in view of the possibility of realizing such constructions from clay. These results, in addition to the many benefits, also point out some drawbacks due to the clay [1,8–10]. The main drawbacks are that, in order to obtain the minimum conditions of mechanical and thermal resistance, a large wall thickness is required. There is also a high risk of cracking during drying due to significant axial contractions. The ideal clay soil to be used in construction must contain at least 15–16% clay because it has the right plasticity and workability to obtain a quality finished product [9,10]. In order to obtain a workable mixture, a certain amount of water is needed to induce the phenomenon of thinning of the clay sheets, but it must be dosed so as not to reach significant axial contractions and the appearance of cracks during drying. Thus, a linear contraction between 3% and 12% is accepted for bricks from soft mixtures or between 0.4% and 2% in the case of drier mixtures [1,8,9,11].

In order to obtain a good thermal insulation, the specialized literature indicates an apparent density of the material between 1600 and 2000 kg/m³ [1,8,11,12].

The studies presented until now in the literature do not adequately show the influence of various additives on the physical–mechanical characteristics of products made of clay (mechanical strength, thermal resistance, water behavior and water vapor, etc.). Among the additives that could be used for the clay matrix, but which have been insufficiently studied until now, is industrial waste. Every year, after burning coal in order to obtain thermal energy, large quantities of power plant ash are produced. The use of coal in the thermal energy production process in Romania has a share of over 38% of the entire electricity production in the country [13,14].

The ash resulting from the burning of coal can be of two types: fly ash, which is evacuated with the flue gases, and coarse ash, which is collected centrally and transported to specially arranged places in dumps. Both types of ash have a major impact on pollution; flying ash pollutes the air, and coarse ash occupies huge areas of land. In Romania, over 80% of industrial waste is stored in places arranged in nature; this is the main method for so-called ash disposal. A single thermal power plant in Romania produced almost 650,000 tons of ash, 50,000 tons of slag, and 50,000 tons of gypsum in 2017. Of the total industrial waste produced at the national level, only 0.06% is currently recovered [13,15].

In addition, within the technological process of the processing of natural stones and marble (limestone blocks), there are significant quantities of sludge—an average of 20 tons/day [13]. The resulting limestone sludge, which is partially dry, is stored in heaps in the form of cakes, drying naturally.

Another category of industrial waste is gypsum sludge resulting from the processing of imported ore. This plaster slime is stored in heaps, occupying large spaces as well. Therefore, studies and research are needed for the possibility of recovering this waste. One way of recovery of industrial waste can be by using is as an additive in clay mixtures intended for the manufacture of unburned clay bricks. The aim of this study is to establish optimal clay-based mixtures for the manufacture of unburned bricks, using four types of industrial waste as an addition to clay, as follows: power plant ash and limestone sludge on the one hand, and scrap waste from the processing of imported ore and gypsum sludge on the other.

The purpose of these experimental studies is to find sustainable ways to capitalize on industrial waste.

2. Materials and Methods

The raw materials used to make the experimental mixtures were: clay that was extracted from Valea Draganului, Cluj Napoca, Romania, ash from the Mintia thermal power plant, Romania, limestone sludge from limestone processing, scrap waste from imported ore processing, and gypsum sludge. These wastes were used simultaneously, two by two: ash with limestone sludge and scrap
waste with gypsum sludge. The sandy clay used was characterized by particle size distribution (Figure 1) and oxide composition (Table 1) [16,17].

![Figure 1. Granulometry of sandy clay [16].](image)

Table 1. Oxide composition of clay, determined according to romanian standard STAS 9163.

| Oxides   | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | TiO₂ | PC  |
|----------|-------|-------|-------|-----|-----|-----|------|------|-----|
| Content [%] | 74.17 | 12.74 | 4.38  | 0.7 | 1.0 | 1.43| 0.73 | 0.05 | 4.78|

The power plant ash was characterized by the oxide composition (presented in Table 2) and the apparent density (Table 4) [18].

Table 2. The composition of the ash from the Mintia thermal power plant, determined by XRF (X-ray fluorescence) analysis.

| Oxides | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | P₂O₅ | TiO₂ | MnO₂ |
|--------|------|-------|-------|-----|-----|-----|------|-----|------|------|------|
| Content [%] | 53.75 | 53.75 | 26.02 | 7.91 | 0.35 | 0.59 | 1.54 | 2.54 | 0.09 | 0.12 | 0.05 |

The fineness of the ashes from the Mintia thermal power plant, determined on a sieve of 0.045 mm, was 39.20%.

The limestone sludge used had the particle size composition shown in Table 3 and the apparent density shown in Table 4 [18].

Table 3. Particle size distribution of limestone sludge.

| Sieve Size (mm) | 0.063 | 0.125 | 0.250 | 0.500 | 1 |
|-----------------|-------|-------|-------|-------|---|
| Through the sieve (%) | 69 | 93 | 95 | 99 | 100 |

The apparent densities of all wastes used in this study, determined in the laboratory, are shown in Table 4 [18].

Table 4. Apparent density of the filler materials used.

| Type of Industrial Waste | Ashes from Mintia Thermal Power Plant | Landfilled Waste from Imported Ore Processing | Gypsum Sludge | Limestone Sludge |
|--------------------------|------------------------------------|---------------------------------------------|---------------|-----------------|
| Apparent density (mg/m³) | 1.67 | 1.26 | 1.26 | 1.78 |

Three compositions of clay, ash, and limestone sludge were made in different proportions, as well as another three compositions of clay, scrap waste, and gypsum sludge in other three proportions. The dumped waste and gypsum sludge came from the same working point for processing the imported ore, and the ash and limestone sludge came from the same area. The
compositions of the six mixtures made, as well as that of a control sample (made of clay material without additives), are presented in Table 5. Prismatic specimens measuring $40 \times 40 \times 160$ mm were made from each mixture and kept until the equilibrium humidity was reached. The parameters that were examined on these specimens, after a visual control of possible cracks appearing in the specimens that reached the equilibrium humidity, were:

- Axial contractions according to Romanian standard STAS 2634;
- The apparent density in the hardened state when the equilibrium humidity is reached according to European standard harmonized in Romania SR EN 1015-10;
- Mechanical strengths according to European standard harmonized in Romania SR EN 1015-11.

The equilibrium humidity is considered to be reached when the constant mass is reached. From previous experiences, it has been found that it occurs about 40 days after making clay-based specimens.

Table 5. Compositions of experimentally tested mixtures.

| Nr. of Test | Age Test | Clay (%) | Mintia Thermal Power Plant Ash (%) | Limestone Sludge (%) | Dumped Waste from Imported Ore Processing (%) | Gypsum Sludge (%) |
|-------------|----------|----------|-----------------------------------|---------------------|---------------------------------------------|-------------------|
| 1           | 40 days  | 100      | 0                                 | 0                   | 0                                           | 0                 |
| 2           | 40 days  | 60       | 20                                | 20                  | 0                                           | 0                 |
| 8           | 1 year   | 50       | 25                                | 25                  | 0                                           | 0                 |
| 9           | 1 year   | 40       | 30                                | 30                  | 0                                           | 0                 |
| 4           | 40 days  | 70       | 0                                 | 0                   | 15                                          | 15                |
| 5           | 1 year   | 60       | 0                                 | 0                   | 20                                          | 20                |
| 11          | 1 year   | 50       | 0                                 | 0                   | 25                                          | 25                |

These compositions were tested at 40 days and at one year in order to appreciate the variation of the parameters over time. Samples 1 to 7 were tested at 40 days, and samples 8 to 13 were tested at one year.

3. Results and Discussion

Analyzing the appearance of the specimens at 40 days and at one year, the lack of surface cracks can be noticed, which is a very important aspect for clay-based mixtures, but it must be taken into account that the dimensions of the specimens are small (Figure 2).

Figure 2. Appearance of the surface of the hardened specimen.
The results of the axial contractions recorded are represented in Figure 3.

![Figure 3. Axial contractions of dry mixtures at equilibrium humidity.](image)

It was found that, from the point of view of the axial contractions, all the tested mixtures fell within the limits indicated as being admissible in the specialized literature [1,7,13,18]. Although the results obtained for drying shrinkage and crack evolution were satisfactory on these specimens, it can be stated that for the manufacturing of bricks from these compositions, the dimensions of the elements made must not exceed certain dimensions to avoid cracks. In order to be able to establish a correlation between the maximum permissible dimensions of the elements made from these types of clay mixtures with additions of industrial waste and the absence of cracks, a further study is needed.

Based on the results shown in the graph in Figure 3, it is observed that the additives used in the mixture had a small influence on the axial contractions compared to the control specimen made only of clay. The specimens were checked 40 days (mixtures 1 to 7) and one year (samples 8 to 13) after manufacturing, as shown in Table 5. It was observed that the waste obtained from the processing of the imported ore, as well as the dumped waste and the gypsum sludge added into the clay matrix, induced a more accentuated decrease of the axial contractions compared to when the Mintia ash and the limestone sludge were added in the same proportions.

The most accentuated decrease of the axial contractions was presented by the mixture with 50% clay, 25% dumped waste, and 25% gypsum sludge (sample no. 7), which was from 9.4 mm/100 mm of the control specimen up to 8.6 mm/100 mm. Axial contractions after one year remained constant. There was no significant decrease or increase in axial contractions from 40 days to one year after manufacturing.

The values of the apparent densities are presented in Figure 4.

According to the specialized literature, the materials whose apparent density is between 1600 and 1690 kg/m³, as shown in the graph, have the ability to store heat, which then yields when the temperature drops [1,7,12,13,18]. According to the graph, all compositions fall within this limit. Materials with densities between these values have a good thermal index, which causes a room to have constant temperature. This is an important quality of natural materials.

The mixtures with the lowest values of apparent density at 40 days, 1650 kg/m³, were samples 2 and 5. Sample 2 contained 60% clay and 40% waste (20% ash and 20% limestone sludge), and sample 5 contained 70% clay and 30% waste (15% waste and 15% gypsum sludge).

The sample with the highest apparent density was sample 4, which contained the maximum percentage of added waste (40% clay and 60% other additives). This composition probably had the
highest density due to the addition of limestone sludge, which has the highest bulk density compared to other raw materials.

After one year, the sample with the highest apparent density was sample 10 which contained 40% clay and 60% waste (30% ash and 30% limestone sludge). In all mixtures, after one year, a small increase of the values of bulk density could be observed, probably due to the reaction between Ca and CO$_2$ from the air that formed the limestone.

The mechanical resistances determined on hardened prisms at the equilibrium humidity after one year are presented in Figure 5. In Figure 6, the appearance of the specimen after breaking can be observed.

A first observation is that all mixtures with added waste have increased mechanical strength compared to the control sample, which was made only with clay. Another important observation is that mechanical strength increases over time. All values of one-year resistance are higher than 40-day resistance.

In the case of the addition of ash and limestone sludge, samples 3 and 9 (25% ash, 25% limestone sludge, and 50% clay) had the highest mechanical strength at 40 days and one year, with 8.2 N/mm$^2$ (sample 3) and 8.9 N/mm$^2$ (sample 9), respectively. With a greater or lesser addition of this type of waste, the strengths are lower compared to that of this mixture. There is an increase in mechanical strength by 47% compared to the control sample at 40 days and by 8% at one year, compared to the
same mixture tried at 40 days. For sample 2 (addition of 20% ash and 20% limestone sludge) as well as at sample 4 (30% ash and 30% limestone sludge), there was a small decrease in resistance compared to sample 3, but nevertheless, the mechanical strengths were higher than the strength of the clay without addition.

![Figure 6. Appearance of test specimens after breaking.](image)

In the case of the addition of dumped waste and gypsum sludge, the sample with the best mechanical resistance at 40 days was sample 6 with 20% dumped waste, 20% gypsum sludge, and 60% clay. The value of the mechanical strength of sample 6 was with 40% higher than that of the control sample. The same mixture tested at one year (sample 12) had a value of compressive strength 10% higher than at 40 days. A higher proportion of piled waste and gypsum sludge reduced the mechanical strength compared to sample 6 when tested 40 days after manufacture. The same mixture tested at one year, sample 12, also had the highest mechanical strength among mixtures with this type of waste. The samples with the addition of 30% and 50% mixtures of dumped waste and gypsum sludge had mechanical strengths of approximately 6% lower than that of sample 6.

The best mixtures analyzed from the point of view of mechanical strength were the mixtures marked with 3 or 9 (50% clay, 25% Mintia ash, and 25% limestone sludge) and samples 6 or 12 (20% dumped waste, 20% plaster sludge, and 60% clay).

4. Conclusions

After this study, the following conclusions can be drawn.

All mixtures have a good workability, which allows a necessary homogenization.

Axial shrinkage is not negatively influenced by the addition of industrial waste, and no mixtures showed cracks when drying. The largest length of a side of the specimens made was 160 mm, so it can be stated that when making bricks with a side of 160 mm, no cracks appear, but for a brick with a larger side, there is a probability of cracks; therefore, an additional study to establish the maximum possible dimensions without cracks is necessary. Due to the results obtained at 40 days and at one year, it can be stated that the axial contractions remain constant over time.

All the values obtained for the densities in the hardened state were within the interval of 1600–2000 kg/m³. According to the literature, this range is satisfactory in terms of thermal efficiency, so the addition of industrial waste does not negatively influence the values of apparent densities in the hardened state. The apparent density increases very slightly over time.

The mechanical strengths were positively influenced by the addition of waste. The composition with the addition of 25% ash and 25% limestone sludge had the highest mechanical strength of all mixtures. The mechanical strength of this mixture increased by 8% after one year.

The mechanical strength of the sample with the addition of 20% bulk waste and 20% gypsum sludge was also higher than the mechanical strength of the control sample. This mixture had the highest resistance in the case of dumped waste and gypsum sludge.

The resistance value of this sample was 12% lower compared to the sample with 25% ash and 25% limestone sludge. In the test with the addition of 20% dumped waste and 20% plaster sludge, the value of the resistance after one year increased by 10%.
All the conclusions confirm the fact that, in terms of physical–mechanical characteristics, industrial waste can be successfully used as an addition in clay matrixes intended for the production of unburned clay bricks, and it is very welcome to capitalize on industrial waste in this way, resulting in ecological and healthy materials at the same time.

The bricks made according to the studied recipes can be successfully used to make constructions that are environmentally friendly and energy efficient, and that provide a pleasant and healthy climate for the inhabitants; at the same time, nature is protected from pollution by reducing cement consumption. This also preserves the basic principles of traditional vernacular architecture that is modeled according to current technological progress.

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