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STABILIZATION OF RED MUD WITH NATURAL MINERALS

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ABSTRACT

This work aimed to examine the possibility of stabilizing red mud with a natural mineral, namely pyrophyllite shale, to the extent that it is not harmful to the environment, as well as the use of such a stabilized composite for the production of building materials such as bricks, to ultimately achieve a complete circular economy, where, on the one hand, there would be the utilization of waste material, the preservation of the environment and natural resources, and, on the other hand, the production of products of the same quality. Based on the set goal, the results for the composition of red mud and pyrophyllite shale, as well as the stabilized composite before and after thermal treatment at 900 °C, are presented in the work, and they show that there is a decrease in the proportion of all oxides present in the mixture except silicon, because it is over 63% in pyrophyllite shale. Based on the stabilized composite, building block samples were formed. After the firing process, the samples cracked, and as such, they could not be analyzed further. Based on this, it could be concluded that only the stabilized composite cannot be used to make bricks.

Keywords: red mud; pyrophyllite shale; stabilization; composite; building block

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1. INTRODUCTION

1.1. Red mud

Bauxite residue, or red mud, is a solid waste product resulting from the processing of bauxite ore into alumina. Red mud is mainly collected from the Bayer process, which uses sodium hydroxide to dissolve aluminum silicates. Approximately 35–40% of the processed bauxite ore is discarded as alkaline red mud, which consists of 15–40% solids, and 1 to 1.5 t of red mud is left over from the production of 1 t of alumina [1]. As a solid

waste, red mud is usually disposed of in sludge ponds as sludge deposits or in ponds as dry sludge near alumina production plants, or it is directly discharged through pipelines into the nearby sea. Due to its fine particle characteristics, high alkalinity (pH 10–12.5), and metal content, the disposal of large quantities of red mud has caused serious environmental problems, including soil pollution, groundwater pollution, and marine fine particle suspension. The storage of red mud in lakes or ponds takes up huge areas, and the storage of dry red

mud can also lead to dust pollution, which is a serious health problem for people living near red mud dumps, because breathing brings in small particles that accumulate in the body, and they have a very bad effect on human health. The cost of red mud disposal is relatively high and accounts for about 2% of the cost of alumina [2].

On the other hand, red mud consists of valuable materials such as rare earth elements, titanium, iron, and aluminum. Typical amounts of Ti, Si, Fe, Na, and Al in red mud are 2–12%, 1–9%, 14–45%, 1–6%, and 5–14%, respectively [3]. However, despite the invaluable results obtained from research related to the use of red mud, they are not practically applicable for recycling large quantities of red mud (i.e., currently 150 million tons per year [3,4]). Of all the elements present in red sludge, iron occupies the largest share in the form of oxides or hydroxides, and by disposing of and not using red sludge, large amounts of iron are also disposed of, approximately 20 Mt per year [5].

1.2. Pyrophyllite schist

Pyrophyllite schist is a hydrated aluminum silicate with the chemical formula $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ and is commonly associated with other minerals such as quartz, mica, kaolinite, epidote, and rutile. Pure pyrophyllite shale consists of 28.3% Al_2O_3 , 66.7% SiO_2 , and 5% H_2O by mass. Pyrophyllite shale, when pure, is desirable for many applications because of its unique properties. For example, pyrophyllite provides low thermal and electrical conductivity; high refractive behavior; low coefficient of expansion; high corrosion resistance; low bulk density; and low hot load deformation. Therefore, this mineral is widely used in the refractory, ceramic, and pharmaceutical industries, but also in the production of pesticides, fertilizers, paper, paints, plastics, rubber, cement, etc. [6]

1.3. Building block

Building materials are understood as natural or artificial materials, which are used in the form of raw materials, semi-finished products, or finished products for the construction of buildings. In addition to the binding layer, the essential construction material is a building block, as a unit element for masonry, with dimensions and mass adapted to the handling of workers; most often in the form of a cube, with or without cavities. The simplest building block is essentially a traditional material called brick. The term brick refers to small units of building material, often made of baked clay and attached with mortar, a binding agent consisting of cement, sand, and water.

Today, bricks are produced from brick clay or loam with additives. Clay is the basic plastic raw material. The most common additives can be stone sand, limestone or marl clay, and iron hydroxide. Clays with a large number of impurities absorb water poorly, which is one of the disadvantages. The basic property of clay is its plasticity. This allows it, when mixed with water, to produce a dough that does not crack or tear during shaping, while retaining its shape after drying and baking. The brick production process begins with the mixing and grinding of raw materials in mills. After grinding in coarse mills, scattering, aging, and homogenization are carried out in rooms with sufficient moisture. After that, the clay is ground again in fine mills, and its shaping is carried out in a vacuum press [7].

2. EXPERIMENTAL RESEARCH

The experimental plan was to investigate the possibility of using pyrophyllite shale, as a natural mineral, to stabilize red mud to a form that is not harmful to the environment, as well as the use of such a formed composite for the production of building blocks or bricks. A mass ratio of 1:1, 1:2, and 1:3 was used to form the composite of red mud and pyrophyllite shale. Before forming the building block

samples, with the specified proportions of red mud and pyrophyllite, it was first necessary to convert the components into the same shape, so a ball mill was used for this. The samples were formed in a mold measuring 4x4x20 (cm) under the same conditions. The specified dimensions for forming the building block represent standard dimensions for subsequent analyses of the finished samples for further testing. After mixing the composite with water and filling the molds, the samples were air-dried for three days at room temperature to release moisture, leading to a volume decrease. The drying continued in an oven at 105 °C for 32 hours before firing in an annealing oven, which included an initial half-hour at 550 °C to evaporate residual moisture and prevent cracking, followed by a two-hour duration at 900 °C, and concluded with a cooling phase before the final samples were removed. The finished samples are shown in Figure 1.



Figure 1. Finished samples of the building block

3. RESEARCH RESULTS WITH DISCUSSION

In order to determine the success of the stabilization of red mud with pyrophyllite shale, the composition of red mud, pyrophyllite shale, and the formed composite was analyzed before and after thermal treatment at 900 °C, while the formed building block samples were subjected to analysis to determine the compressive strength. The pH value of the

red mud was in the alkaline range, as in the case of pyrophyllite shale, but with pronounced buffer properties. The forms of metal elements in a stable state with lower mobility and reactivity in the alkaline range were recorded. In the next step of the experiment, when the composite was subjected to the firing temperatures of the building block, the conversion of the present metal components into an inert oxide form was performed. The composition of the components used in the oxide form is shown in Tables 1 and 2.

Table 1. Analysis of the composition of pyrophyllite schist

Oxide	mas. %
SiO ₂	63.08
Al ₂ O ₃	27.42
CaO	4.44
Fe ₂ O ₃	1.54
K ₂ O	1.24
MgO	0.79
Na ₂ O	0.63
TiO ₂	0.27
ZnO	0.05

Table 2. Analysis of the composition of red mud

Oxide	mas. %
Fe ₂ O ₃	43.93
Al ₂ O ₃	17.91
SiO ₂	6.79
TiO ₂	10.2
Na ₂ O	6.9
CaO	8.96

For the sake of easier comparison, Figure 2 shows the composition of red mud and pyrophyllite shale, where it can be seen that in the pyrophyllite shale, the oxides SiO₂ and Al₂O₃ are present in the largest proportion, while in the red mud, Fe₂O₃, Al₂O₃, SiO₂, and TiO₂ are present, while the remaining oxides are present in smaller, negligible amounts.

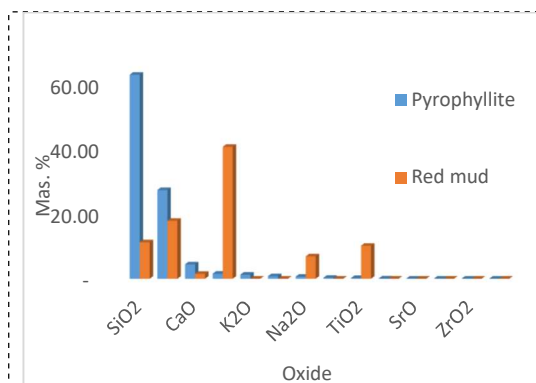


Figure 2. Graphic representation of the presence of metals in red mud and pyrophyllite shale

In Table 3, the composition of the formed composite is shown for three samples, i.e., three different ratios of pyrophyllite and red mud (Sample A 1:1, Sample B 1:2, Sample C 1:3). Of all the oxides in the analysis, only SiO₂ shows a trend of increasing concentrations (28.58 – 35.6 – 41.69 %) with an increase in the proportion of the pyrophyllite component, which is logical because pyrophyllite shale has 66.7 % SiO₂ in its composition. Other oxides generally decrease, indicating selective dilution and chemical inertness of certain components such as Al₂O₃ (25.99 – 20.05 – 24.11 %).

Table 3. Analysis of the composition of pyrophyllite schist

Oxide	Unit	Sample A	Sample B	Sample C
SiO ₂	%	28.58	35.6	41.69
Fe ₂ O ₃	%	25.99	20.05	16.93
Al ₂ O ₃	%	23.36	24.97	24.11
CaO	%	13.05	11.43	10.22
TiO ₂	%	4.05	3.31	2.8
Na ₂ O	%	2.8	2.48	2.15
MgO	%	0.59	0.56	0.62
SiO ₂	%	28.58	35.6	41.69

Figures 3, 4, and 5 show XRD analysis of the mineralogical composition for samples A, B, and C, or XRD diffractograms, before and after heat treatment, with visible results, which reflect the change in the mineralogical proportion of individual components.

In all three ratios of the composite, the samples before firing have more intense peaks; they indicate a better arrangement of the crystalline state and more crystalline substances, unlike the sample that was fired at 900 °C. This relationship is recorded in the range of values of the angle $2\theta = 0 - 33$. Beyond this value, the heat-treated sample exhibits crystallinity. Better ordering of the crystalline state can be traced up to the value of the angle $2\theta = 36$, after which it significantly decreases (individual peaks of lower intensity appear). That means the crystalline state

is correlated with the increase of the pyrophyllite component in the composite. In addition to examining the composition of red mud and pyrophyllite shale before and after stabilization, the formed building blocks were to be subjected to several analyses, such as compressive strength and water absorption properties, etc.

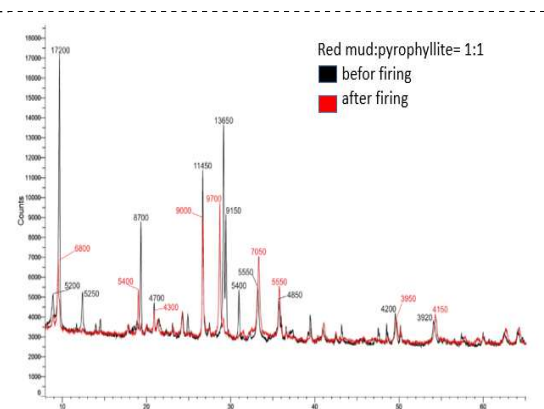


Figure 3. XRD diffractogram for sample A

However, this was not possible because the samples, after finishing the baking

process, had already cracked and, as such, could not be used for further analysis.

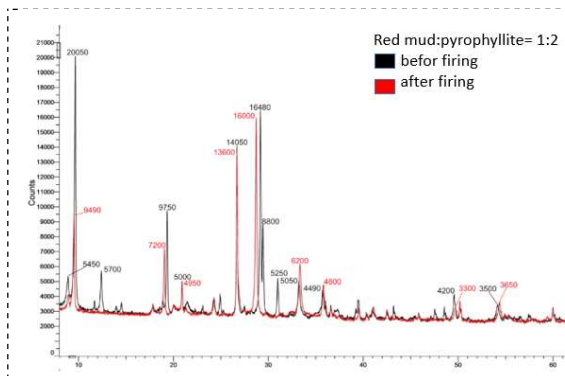


Figure 4. XRD diffractogram for sample B

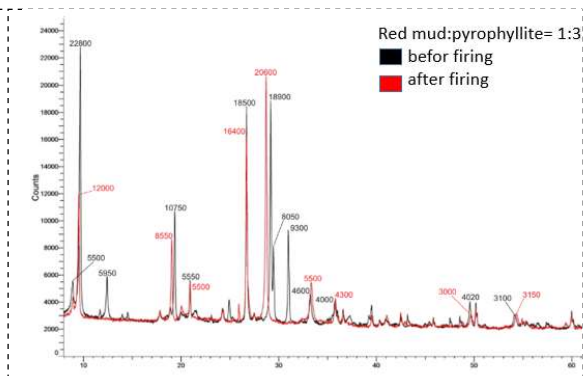


Figure 5. XRD diffractogram for sample C

Several mechanisms can explain the observed stabilization. First, the high SiO_2 and Al_2O_3 contents of pyrophyllite promote the formation of a more stable silicate matrix that can accommodate reactive components of red mud, thereby reducing their leaching. Aluminosilicate minerals have been shown to immobilize heavy metals and to stabilize alkaline wastes [2,4]. Moreover, the pre-fired composites exhibit a much higher degree of crystallinity in XRD analysis, indicating a more ordered arrangement that contributes to initial structural stability. During firing, some peaks diminish in intensity, which probably corresponds to phase transformations and partial melting, which affects the structural integrity.

The fractured fired building blocks are due to the mismatch in thermal expansion as well as the high content of Fe_2O_3 from red mud. During firing, iron oxides serve as fluxes and lead to a decrease in the softening point and internal stresses due to different expansion rates and phases. Industrial wastes are a potential medium of high-iron loading that will have to be blended with plastic clays to obtain solid bricks, since iron-contaminated waste might contribute towards thermal stress on the brick of the same type [1,7]. Thus, while the solidified red mud–pyrophyllite composite provides some protection for hazardous materials, it has limited capability

of making crack-free bricks by itself. One potential strategy is to utilize the stabilized mixtures as an additive to traditional clay blending to enhance environmental safety without compromising mechanical integrity. These results add to the literature by showing the chemical stabilization of red mud with pyrophyllite, but not to new brick processes directly.

Contrary to other literature work, which works with red mud mostly for soil or pigment stabilization, this work focuses on combining stabilization mechanisms with circular economy strategies and proposes the possibility of valorization of industrial waste materials while preserving building materials' performance.

4. CONCLUSIONS

To determine the success of the stabilization of red mud with pyrophyllite shale, an analysis of the composition of red mud, pyrophyllite shale, and the formed composite was performed before and after thermal treatment at 900 °C. The composition analysis shows that pyrophyllite shale consists mainly of oxides SiO_2 (63.08%) and Al_2O_3 (27.42%), and red mud consists of Fe_2O_3 (43.93%), Al_2O_3 (17.91%), SiO_2 (6.79%), and TiO_2 (10.2%), while other oxides are present in smaller, negligible amounts.

Analysis of the composition of the formed composite for all three samples, i.e., three different ratios of pyrophyllite shale and red mud (Sample A 1:1, Sample B 1:2, Sample C 1:3), indicates that of all the oxides present, only SiO₂ records a trend of increasing concentrations (28.58 – 35.6 – 41.69%) with an increase in the share of the pyrophyllite component, which is logical because pyrophyllite shale in its composition has 63.08% SiO₂. The content of Al₂O₃ (25.99 – 20.05 – 24.11%) is quite uniform, which can be explained by its inertness, while a decrease in concentrations was recorded for other oxides.

XRD analysis of the formed composite shows that for all three composite ratios, the samples before firing have more intense peaks, which indicates a better order of the crystalline state, more crystalline substances, unlike the sample fired at 900 °C. This relationship is recorded in the range of values of the angle $2\theta = 0 - 33$. Beyond this value, the heat-treated sample exhibits crystallinity.

The initial experiment to create building blocks using red mud and pyrophyllite slate was unsuccessful because the samples cracked after firing, indicating that the proportions used were unsuitable.

However, the successful stabilization of red mud with pyrophyllite suggests a potential alternative application, warranting further

research into using the stabilized mud as an additive to clay for brick production.

Conflict of Interest

The authors declare no conflict of interest.

5. REFERENCES

- [1] L. Zhan, Production of bricks from waste materials, *Constr. Build. Mater.*, [Online], 47 (2013), pp. 643–655.
- [2] V. Feigl, A. Anton, N. Uzigner, K. Gruiz, Red mud as a chemical stabilizer for soil contaminated with toxic metals, *Water Air Soil Pollut*, [online], 223 (2012), pp.1237–1247
- [3] W. Huang, S. Wang, Z. Zhu, L. Li, X. Yao, V. Rudolph, F. Haghseresht, Phosphate removal from wastewater using red mud, *Journal of Hazardous Materials*, 158 (2008) 158, pp.35-42
- [4] Sushil, V. Batra, Catalytic applications of red mud, an aluminium industry waste: A review, *Applied Catalysis B: Environmental*, 81 (2008), 1-2, pp. 64-77
- [5] J. Mikić, D. Lazić, J. Pwnavin-Škundrić, M. Prtušić, D. Kešelj, D. Blagojević, G. Ostojić, Crveni mulj kao pigment u proizvodnji betonskih elemenata, *Reciklaža i održivi razvoj*, 6 (2013) 1, pp. 18-25
- [6] T. Mukhopadhyay, S. Ghatak, H. Maiti, Pyrophyllite as raw material for ceramic applications from the perspective of its pyro-chemical properties, *Ceram. Int.*, 36 (2010) 3, pp. 909–916
- [7] W. Bender, F. Handle, *Brick and Tile Making*, Bauverlag GmbH, 1985