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New buildings materials obtained by the recovery of mining waste and red mud from the manufacture of alumina

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Abstract

In the current context of the transition to a circular economy, efforts are primarily focused on recycling, the reintegration of some wastes into the economy, as a secondary raw material. The recovery of wastes specific to the mining industry and the metallurgical industry, which through the quantities deposited and through the chemical composition put a great pressure on the environment, represents a major concern of the society. Starting from this aspect, the paper presents the results of the research carried out in order to obtain new building materials (mortars) by adding two mineral wastes - red sludge from the manufacture of alumina and mine tailings - in the basic raw material, cement. The performances of the new materials containing the two wastes prove the viability of the technical solutions so that they can be used in the field of construction, both as masonry mortars and as plastering mortars.

Keywords: waste recovery, red mud, mining waste, mortars

INTRODUCTION

Sustainable development has a determining component related to environmental issues that represent one of the European Union horizontal policies [1].

With the transition to a circular economy, the focus is on reusing, refurbishing and recycling existing materials and products. What is considered "waste" becomes a resource [2].

Europe has already prepared for this transition: "A resource-efficient Europe" is among the flagship initiatives of the Europe 2020 strategy, which coordinates actions in many policy areas to ensure sustainable growth and job creation work through a better use of resources [3].

Ideally, in a circular economy, waste streams and emissions will be used to create value, providing a secure and affordable supply of raw materials and reducing pressure on the environment [4].

The worldwide strategy is to minimize the amount of waste, respectively the amount of natural resources used and to maximize the recycling flow of matter and energy [5]

In this closed cycle, any waste is actually a new resource, so it ceases to be waste: collected waste - secondary raw material - new products.

The adequate management of waste plays a central role in the Circular Economy and must take into account both the pollution phenomena generated (impose the adoption of the most advantageous methods that minimize the impact on the environment), and the fact that this waste can be transformed into resources secondary (material and energetic), thus avoiding the depletion of resources.

The different industrial activities generate wastes from the process of exploitation of raw materials, continuing with the processing and ending with the storage of residual materials.

In Romania, the extractive industry and the metallurgical industry stand out as the largest generators of waste.

The mining sector produces large amounts of waste that induce negative effects on the environment even more important than the waste generated from any other industrial branch or human activity [6].

From the metallurgical industry, the production of alumina represents an ecological and economic responsibility at the world level, mainly due to the huge quantities of red mud produced annually (approx. 40-70 million tons) but also due to specific properties.

The waste specific to these industrial activities, mine tailings and residual sludge, put a significant pressure on the environment by storing them, but they can become an opportunity when activities involving the recovery of metals or other useful secondary materials are undertaken. [7].

Mitigating the adverse effects of mining, metallurgy and metalworking requires a holistic approach to waste management, which includes reducing the amount of waste generated, recycling processes, reuse and finding new applications in other economic sectors [8-11].

In recent years, circular economy models lead with notable steps towards the reduction, recycling and reuse of waste from the mining and metallurgical industries.

Technical solutions for the treatment of wastes are constantly sought, which can lead to the valorization as secondary resources, having the effect of optimizing the consumption of natural resources but also protecting the environment.

For example, in the case of the mining industry, the objectives of the Romanian Mining Strategy 2017-2035 aim at both the development of new processing technologies for a better extraction of useful components from ores and the development of new solutions to ensure a transformation of waste into secondary resources thus avoiding the depletion of natural resources [12].

Tailings can be reprocessed to extract metals and metal compounds, while sand-rich tailings can be mixed with cement and used as backfill when closing underground mine workings.

The tailings from ponds, which is rich in clay, can be used as an amendment for sandy soils, but also for the manufacture of bricks, cement, tiles, sanitary ware and porcelain [9].

However, the proposed reuse opportunities involve their own challenges due to the heterogeneous composition and mineralogical complex of these materials that can physically and chemically affect the products and processes where they are to be used.

In addition, mining waste can contain large amounts of pollutants, reactive elements and minerals, which can subsequently contaminate through reuse, hence a number of limitations [9, 13].

Regarding the red mud resulting from the manufacture of alumina, several technological options for processing and valorization have been tested, but an economic-feasible industrial solution has not yet been identified.

In a similar way, a series of researches were carried out that followed the addition of red mud from the manufacture of alumina in the processes of obtaining a cement, as a secondary raw material [14].

The concerns of the researchers for the valorization of the red mud were channeled towards the identification of some possibilities of use in the construction materials industry (production of bricks, concrete blocks, concrete aggregates, and different ceramic materials).

A successful pilot project of red mud embankment construction in Greece was carried out by the Road Engineering laboratory of the Aristotle University of Thessaloniki, Greece [15]. The performance, the quality of the embankment in terms of deformability was studied through the theory of elastic behavior.

The solution, through the high potential of reusing the large volume of red sludge, is an attractive option considering the environmental impact problems generated by their storage.

Several researchers have studied the fact that red mud, which belongs to the category of pozzolanic materials, mixed with lime, in the presence of water, forms compounds that give the material stability and durability [16, 17].

The compositions of the two mineral wastes highlighted the opportunity of valorization by introducing them into various building materials, instead of raw materials from natural resources.

In this context, the purpose of this paper was to analyze the possibilities of valorization of two mineral wastes as an addition to the basic raw material -cement, in order to obtain new building materials.

Mining tailings (S) and red mud from the manufacture of alumina (NR) were chosen for the consideration of generation in significant quantities, currently are stored in dumps that occupy large areas and due to their composition, and create pollution problems.

EXPERIMENTAL PART

The presence of the oxides of the major elements identified in appreciable quantities (Figure 1) in the red mud (Fe_2O_3 and Al_2O_3) and in the mine tailings (SiO_2 and Al_2O_3), confers increased reactivity on the waste surface [18-20]. In addition, through the recognized quality of these oxides as activators of the hardening process, the opportunity of research with the aim of valorizing this waste as an addition to construction materials is justified, but also the opportunity of research with the aim of reducing the polluting effect of waste.

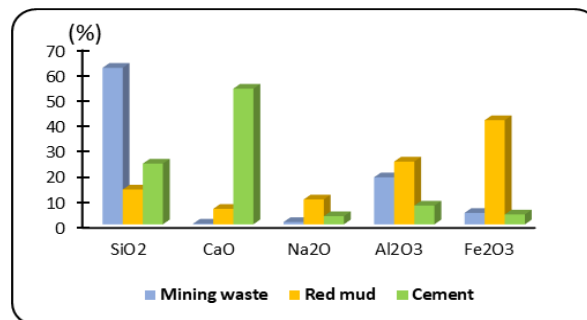


Fig. 1. The oxide composition of the main elements in the three materials (%)

The stages related to the experimental program applied in the conducted researches are presented in the following diagram (fig. 2).

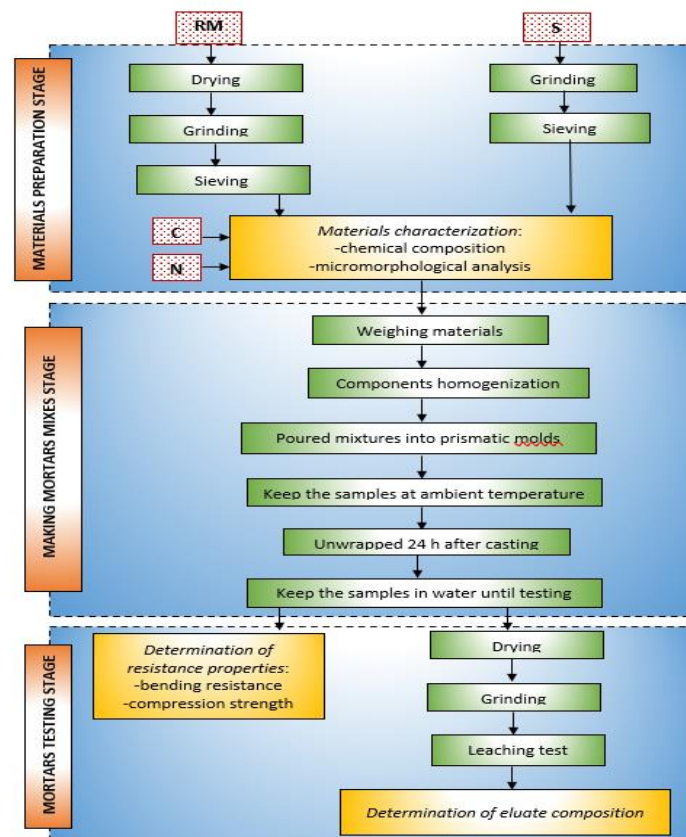


Fig. 2. Flow diagram of the experimental program stages

Materials preparation stage

The removal of moisture was achieved by drying in a thin layer in plastic trays, at an ambient temperature of 25-30°C, for 72 hours, in a specially arranged room, provided with ventilation for air circulation and external exhaust of excess moisture. Grinding was carried out in a vibrating mill with RS 200 discs, at 900 rpm, for 8 seconds. Sieving was done with a sieve up to a material size below 20 µm.

The characterization from the point of view of the chemical composition of the materials that were used in the constitution of the new mortar mixtures was carried out as follows: *metals* were determined by X-ray fluorescence (EDXRF) using a Rigaku CG analyzer (Japan), equipped with a 50W X-ray source with a Pd anode and Al, Mo, Cu, RX9 secondary targets. The detection was carried out with the help of an SDD detector (silicon drift detector) maintained at the optimal temperature by means of a Peltier system. For *the other indicators*, specific current analytical techniques were used electrochemical, gravimetric, GC, etc. In order to analyze the appearance of the surface of the materials used, *the micromorphological analysis* was carried out with the help of an x-ray electron dispersive analyzer Quanta 250 FEG (SEM).

Making mortar mixes stage

Weighing the materials was done with the help of an analytical balance. The materials were homogenized in a special laboratory mixer. The mixtures were poured into prismatic molds (40x40x160mm), followed by passing on a vibrating table to achieve the uniformity of the mixtures. The samples were unwrapped 24 hours after casting. Keeping the samples in water at 20 °C until the testing time.

The mortar mixtures were made in 6 experimental variants (PC1÷PC6) following the substitution of a quantity of cement with different quantities of tailings waste (10%, 20%, 40%) simultaneously with red mud (10%, 20%). The amounts of water and sand were kept constant. For comparison, a MC control sample was also made in which the cement was not substituted by any waste.

Mortar testing stage

Testing experiment was performed on the strengthened materials (specimens) in terms of bending resistance and compression strength at: 48h±30 min, 7 days±2h and 28 days±8h; with the help of a mechanical press for the bending test, respectively with the help of a compression device placed in a SERVOTRONIC compression testing machine. To highlight **the polluting potential**, the hardened mortar samples were crushed and then subjected to the leaching process in a batch system, in accordance with romanian specific legislation [21], at a ratio S:L of 1:10 kg/L [22].

The composition of the eluates resulting from the leaching tests, after filtration, was determined using the Agilent 7900 Technologies ICP-MS equipment - for metals and using current analytical methods (volumetric, gravimetric) - for the other indicators provided in romanian specific legislation [21].

RESULTS AND DISCUSSION

The main chemical characteristics of the materials (red mud NR, mine tailings S, cement C), presented in table 1, revealed the following important aspects: the red mud has an alkaline pH (10.90), while the mining waste has an acid pH (4.20); the pH of cement is very alkaline (13.0); as major elements (with a concentration greater than 10 g/kg) identified were: Si, Fe, Al, Ca, Na.

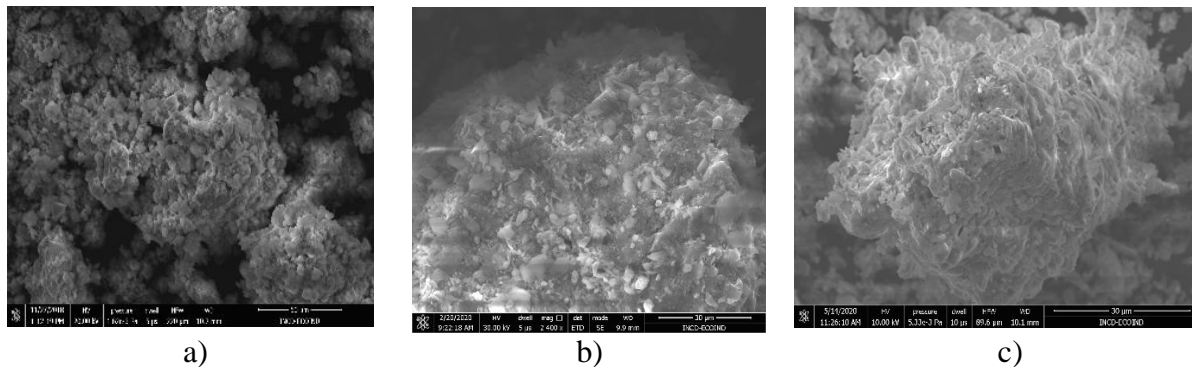
The SEM images (morphological analysis) obtained for the three component materials of the mortars (fig. 3) showed: a homogeneous appearance, with low porosity for cement C, particles with a crystalline appearance, with some smooth portions for mine tailings S, relatively free microstructures, with some cavities in the NR red mud, defining aspects in the structure of the materials.

The purpose of the mortar making experiments was highlighting the influence of the two mineral wastes addition in the cement base matrix on the resistance properties of the new materials.

The mixture recipes for the 6 experimental mortar variants made, including the control sample with only cement, are presented in table 2.

Table 1. The main chemical characteristics of the materials (*dry matter)

Characteristics	UM	RM	S	C
pH	pH unit	10.9	4.20	13.0
Carbonates	% d.m.*	4.40	-	18.5
Chlorine	mg/kg d.m.	36	43	157
Sulphates	mg/kg d.m.	125	126	224
Aluminum	mg/kg d.m.	131100	98290	39220
Silicon	mg/kg d.m.	64310	288450	112070
Iron	mg/kg d.m.	286960	31690	27580
Titanium	mg/kg d.m.	13550	4620	2070
Calcium	mg/kg d.m.	43850	1850	381720
Sodium	mg/kg d.m.	72760	6590	23730
Magnesium	mg/kg d.m.	<25	5680	9810
Potassium	mg/kg d.m.	196	68070	10680
Arsenic	mg/kg d.m.	10.0	217	6.00
Chromium	mg/kg d.m.	1030	128	203
Nickel	mg/kg d.m.	35	<25	38
Copper	mg/kg d.m.	111	74	163
Zinc	mg/kg d.m.	57	1160	840
Lead	mg/kg d.m.	34	2650	116
Barium	mg/kg d.m.	<25	990	258

**Fig. 3.** The SEM images for the three component materials of the mortars,
a) red mud NR, b) mine tailings S, c) cement C**Table 2.** Experimental variants of mortar mixes

Samples	Mine tailing (g)	Red mud (g)	Cement (g)	Sand (g)	Water (g)	Ratio W/C
MC	-	-	450	1350	250	0.56
PC1	45	45	360	1350	250	0.69
PC2	45	90	315	1350	250	0.79
PC6	90	45	315	1350	250	0.79
PC5	90	90	270	1350	250	0.92
PC3	180	45	225	1350	250	1.11
PC4	180	90	180	1350	250	1.39

The samples removed from the molds in which they were made, for all materials, can be seen in fig. 4.

From the figure, you can see the different color of the samples due to the presence of different amounts of red mud waste. Compared to the MC control, which does not contain any of the mineral waste, all the others have a reddish color. The most intensely colored samples are PC2, PC4, PC5, which have the highest percentage of red sludge introduced into the mixture with cement.

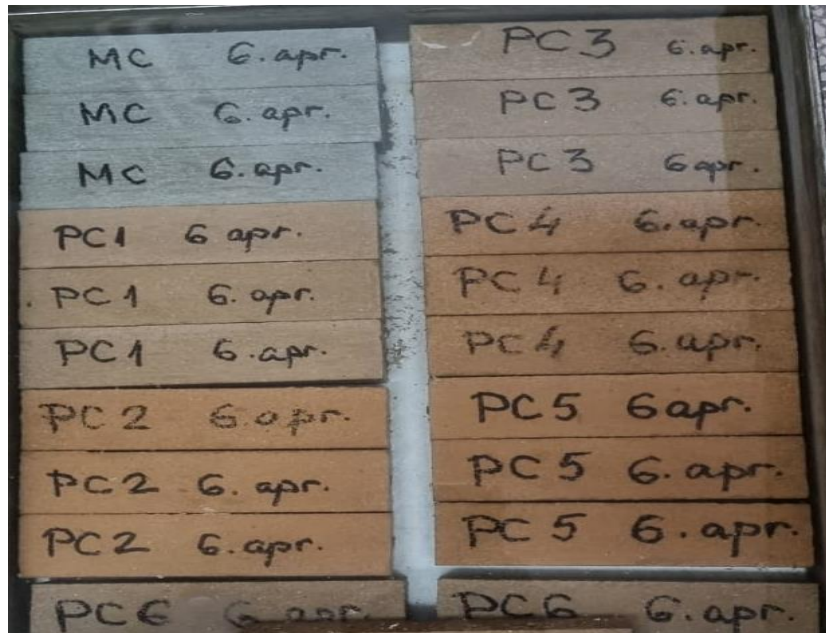


Fig. 4. The samples removed from the molds

The water/cement ratio (W/C, table 2) shows the correlation between the amounts of water (as an activator of the hydration-hydrolysis reactions of cement) and cement (the reacting binder). It is the important indicator of the durability, resistance of the construction material, respectively of the class.

A small W/C ratio indicates a small porosity and therefore a high resistance of the material. In this way, a higher class of construction material is obtained.

The recipes in which cement was substituted with the highest amounts of mineral waste (PC3 and PC4) presented the highest values of the W/C ratio (1.11 and 1.39).

Resistance properties testing

Fig. 5 show the variation of the bending strength (as arithmetic averages of the results obtained on 3 samples) at 2 days, 7 days and 28 days.

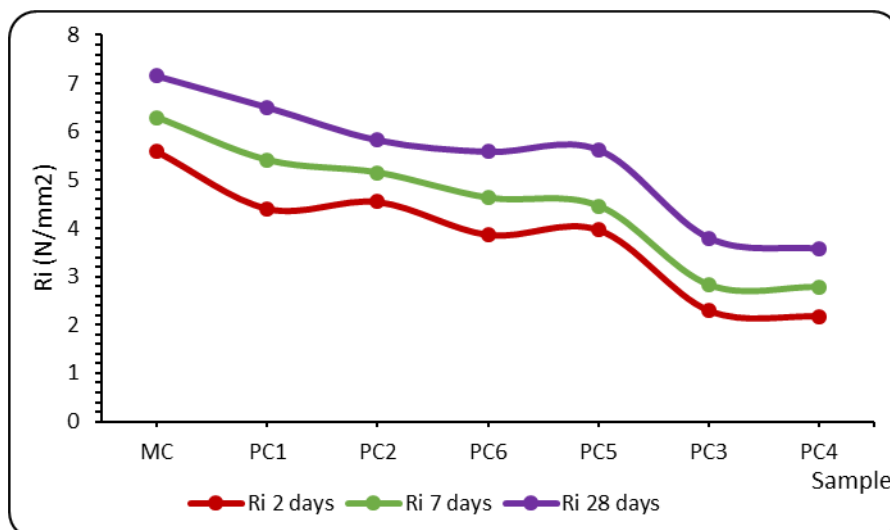


Fig. 5. Average bending strengths at 2, 7, 28 days

Similarly, in fig. 6 can be seen the variation of the compressive strength (as arithmetic averages of the results obtained on 3 samples) at 2 days, 7 days and 28 days.

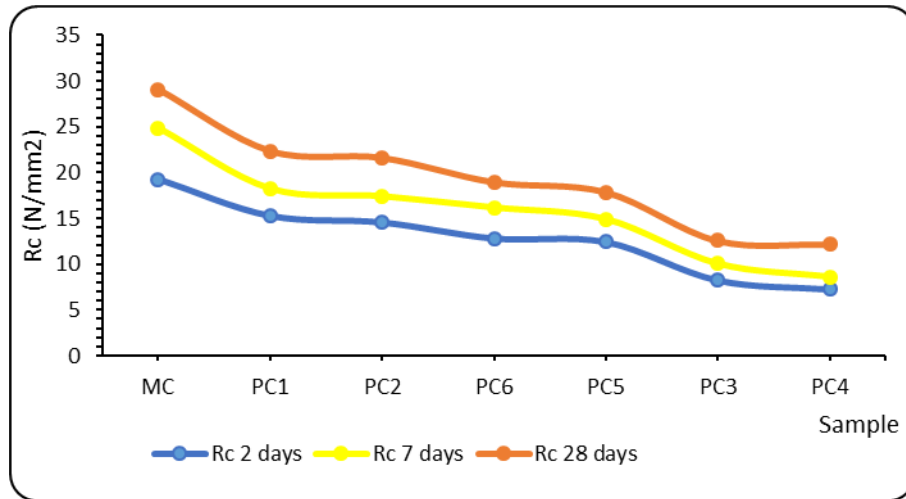


Fig. 6. Average compressive strengths at 2, 7, 28 days

The addition of mine tailings in the highest percentage of 40% (samples PC3, PC4), regardless of the percentage of red mud (10 or 20%), led to the lowest values of the bending strengths and compressive strengths of those materials. There is a good correlation with the W/C ratio which presented the highest values, therefore a high porosity. This statement is also supported by the SEM analysis of the material obtained from the addition of mine tailings (40%) and red mud (10%) - PC3 - which shows a high porosity of the surface (fig. 7).

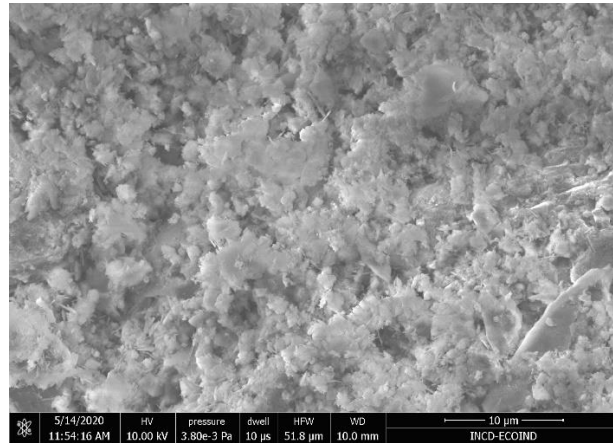


Fig. 7. The SEM image of the material obtained from the addition mine tailings (40%) and red mud (10%)

Compared to the control sample, regardless of the test time, both the bending and compressive strengths of the samples decrease with the increase in the amount of added waste, so with the increase in the water/cement ratio, due to the decrease in the amount of binder (water being constant).

All mortars made, regardless the mine tailings and red mud content, have a compressive strengths corresponding to class CS IV (compressive strengths ≥ 6 N/mm²) of plastering mortars according to specific standards. For use as a masonry mortars, depending on the compressive strength, the mortars can be classified as M10 (compressive strength ≥ 10 N/mm²) or even higher: M15 (compressive strength ≥ 15 N/mm²), M20 (compressive strength ≥ 20 N/mm²).

In this context, all the obtained and tested mortars can be used for this purpose.

Pollutant potential testing

The leaching tests carried out on the newly created materials highlighted the fact that the pollutants specific to the mineral waste used are retained in the matrix of the material, which demonstrates the beneficial effect from the environmental point of view.

CONCLUSIONS

The experiments demonstrated the possibility of using the two mineral wastes (mine tailings and red mud) mixed with cement to obtain building materials such as mortars, with similar properties to those currently obtained from cement.

In this way, the research results corroborated with the analysis from the point of economic feasibility, demonstrate the viability of the reuse solution of the two wastes as secondary raw material in obtaining new products.

The conducted research constitutes a circular economy model through the reuse of two important industrial wastes in terms of the quantities stored and the pressure put on the environment.

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