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EXPERIMENTAL RESEARCH REGARDING THE RECYCLING OF FINE GRANULATE REFRACTORY WASTE FROM ECONOMIC AGENTS PRODUCING CERAMIC AND REFRACTORY MATERIALS

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Abstract: In this paper, the authors present a technology that allows the manufacture of ceramic blocks using refractory waste at the raw material recipe. The research was carried out within the Refractory Design and Production Research Center in Alba Iulia. In these researches we studied various types of possible raw materials used for the preparation of recipes that include different proportions of refractory waste. Several manufacturing recipes were studied which led to the obtaining of heat–resistant ceramic blocks, determining the physical and chemical properties of the finished products obtained, which can be accepted by beneficiaries in the construction materials industry. The comparative analysis of the manufacturing recipes and of the characteristics of the heat–resistant ceramic blocks obtained, determined the optimal recipe.
Keywords: building materials, ceramic materials, refractory materials, silico aluminous waste, and waste recycling

1. INTRODUCTION

Currently, there are many companies that manufacture ceramic blocks but, from the documentation performed there is none that includes in the manufacturing recipe, refractory brick waste.

The main objective of the research was the refractory bricks waste, which in a small proportion are resumed in the technological flows in the refractory sector, but a large part can be capitalized in the construction materials sector. [1, 2, 3, 6]

At the same time, from the refractory materials used to build the furnaces and thermal melting aggregates and which meet the respective melt (metal, slag, glass, etc.), strongly contaminated waste with slag and traces of melts are obtained.

This waste can only be reused in the refractory industry after a difficult cleaning process, which raises the cost to close to the value of the new raw material.

Under these conditions, large quantities of such waste that do not find use are collected at steel plants, glass factories, etc. [4, 5, 7, 8]

By grinding the raw materials, an uniformization of the composition is achieved, obtaining a base of raw materials suitable for the technological process.

2. EXPERIMENTS

— Experimental research to determine the composition and properties of raw materials likely to be used in the manufacture of ceramic blocks

Starting from the main groups of raw materials that contribute to the manufacture of a ceramic block: binder, aggregate, additives or fluidifies, are chosen for testing:

1. Binding raw materials:

a) ceramic binder raw materials such as argil and kaolin;

b) inorganic binder raw materials such as sodium silicate, colloidal silica and aluminium chloride;

c) hydraulic binder raw materials, such as plaster, aluminous cement and Portland cement, presented in figure 1.

Portland Cement | White Cement for construction | Dry mortar Multibat

Figure 1. Hydraulic binder raw materials used in the manufacture of ceramic blocks

2. Degreasing raw materials, such as refractory waste, calcined alumina, chamotte, slag, diatomite, perlite and vermiculite, some of which are shown in Figure 2.

Slag (Burnt argil) | Sand | Refractory waste 28A

Figure 2. Degreasing raw materials used in the manufacture of ceramic blocks

From these raw materials were made by forming and pressing cubes for testing, shown in Figure 3.

Figure 3. Test cubes made of raw materials

These starting materials were analysed chemically, determining the percentage of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O.

Calcination losses, particle size, density and moisture were determined. The results of analyses are shown in Table 1.

From the raw materials analysed from a physical and chemical point of view, recipes were established according to table 2. The components of each recipe were gravimetrically dosed and then mixed in the laboratory in the paddle mixer. In these first recipes, the use of the plaster–based hydraulic binder was tried in a larger proportion in the first phase.

Wetting of the mixture was done at a humidity of 10–15%. The obtained mixture was pressed in a friction press of 120 tF/m2, in 4 stages following the most advanced deaeration of the mass. 100 x 100 mm cubes were obtained.

From all the prepared mixtures, it was found that those mixtures based on plaster and cement were characterized by a better workability. The marked cubes were dried, naturally 7–14 days.

Following the external aspect of the sample, recipes 1, 2, 5, 9, 17 were selected in order to follow through a physical and chemical analysis the characteristics of the finished product.

In table 3 the obtained results can be followed.

— Experimental equipment used for experimental research on the characteristics of raw materials used to make heat–resistant ceramic blocks [22]

The testing of the raw materials was done in the Laboratories of SC CCPPR SA Alba Iulia using the following equipment for chemical analyses in the laboratory and of the physical properties of the raw materials:

The research equipments used is shown in Figure 4 and consists of:

– atomic absorption spectrometer, using ContrAA® 300 (Analytik Jena AG, Germany), figure 4a;
– analytical balance AL204, Mettler–Toledo International Inc., Switzerland, figure 4b;

– analyser with AS 200 Control screens (Retsch GmbH, Germany, figure 4c;
– high temperature oven – LHT 04/17 (Nabertherm GmbH, Germany), with $MoSi_2$ heating elements, figure 4d.

a b c d
Figure 4. Laboratory equipment for testing raw materials and finished products

Table 1. Physical and chemical analysis of the raw materials used

Raw material	CHEMICAL COMPOSITION							PC %	Granulation mm	Density g/cm^3	Humidity %
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O				
Ipsos	1,02	–	–	55,20	–	–	–	13,16	100% under 006	–	under 1
Slag	35,28	2,09	6,84	2,92	38,20	0,24	0,07	14,28	–	–	–
Argile	60,56	24,72	1,76	1,30	1,20	1	1	9,30	100% under 006	–	8
Pearl stone	76,28	12,50	1,75	2,47	–	6,4	6,4	–	–	–	8
Alumina	–	99,8	max. 0,01	–	–	–	–	–	100% under 004	3,6	8
Diatomite	89,75	5,36	0,32	1,26	Trash	–	–	2,36	100% under 004	1,11	8
Vermiculite	36,20	13,17	16,20	2,10	15,10	4,55	0,72	12	100% under 006	2,47	under 1
Colloidal silica	87,09	–	–	–	–	1,41	7,11	7,72	–	1,28	–
Sodium silicate–	–	–	–	–	–	–	–	–	–	–	2%
Waste silico–aluminum refractory bricks	41,75	52,5	1,55	0,8	0,65	1,1	1,65	–	–	–	–

Table 2. Recipes used to obtain the optimal ceramic material for the manufacture of ceramic blocks

No. recipe	Water	Ipsos	Perlite	Cement	Aluminium Cement	Slag	Clay	Vermi –culite	Alumina	Brick waste	Biato–mite	Na Silicate	Colo Sil.
1.	24,24	75,8	–	–	–	–	–	–	–	–	–	–	–
2.	26,76	73,3	–	–	–	–	–	–	–	–	–	–	–
3.	50,0	33,3	–	–	–	16,7	–	–	–	–	–	–	–
4.	47,0	35,3	–	–	–	17,7	–	–	–	–	–	–	–
5.	30,0	40,0	–	–	–	30,0	–	–	–	–	–	–	–
6.	40,4	47,6	12,0	–	–	–	–	–	–	–	–	–	–
7.	33,4	53,3	13,3	–	–	–	–	–	–	–	–	–	–
8.	37,5	50,0	12,5	–	–	–	–	–	–	–	–	–	–
9.	15,0	–	–	42,5	–	42,5	–	–	–	–	–	–	–
10.	40,4	–	–	–	41,6	18,88	–	–	–	–	–	–	5,8
11.	38,2	39,2	–	–	–	16,8	–	–	–	–	–	44,5	–
12.	18,0	27,0	–	–	–	13,5	–	–	–	–	–	–	–
13.	28,6	35,7	–	–	–	11,9	23,8	–	–	–	–	–	–
14.	24,0	12,9	–	–	–	35,9	–	–	–	–	–	28,2	–
15.	22,6	33,7	–	–	–	17,0	–	–	–	–	–	–	26,7
16.	34,2	–	5,2	–	–	–	7,9	–	18,5	34,2	–	–	–
17.	42,8	28,8	–	–	–	–	–	–	–	17,1	17,2	–	–
18.	–	–	–	–	–	–	–	–	–	–	–	–	–
19.	–	–	–	–	10	3	–	40,0	–	37,0	–	10	–

Table 3. Physico–chemical characterization of the recipes used to obtain ceramic blocks

Recipe	CaO %	Al_2O_3 %	SiO_2 %	Fe_2O_3 %	Absorption %	Density g/cm^3	Porosity %
1.	54,2	–	2,02	Urme	13,24	1,66	21,98
2.	55,4	–	1,01	Urme	13,98	1,64	22,90
5.	58,12	2,09	37,3	2,49	81,6	0,71	66,97
9.	16,92	40,2	39,2	0,62	41,45	0,76	36,4
17.	25,73	17,18	27,22	1,84	154,4	0,45	69,4

— **Technology to produce ceramic blocks**

For the manufacture of ceramic blocks, with basic hydraulic binder, it is necessary to use cement, opting for the equal use of 5% aluminous cement and 5% Portland cement. [27, 30, 36, 37, 38]

Regarding the use of slag, its good workability, accompanied by its low–cost price, recommends it. But the particle size distribution should not be neglected. In this sense, the coarse fraction (2.5–0.2 mm) is preferred to the fine fraction (0.02–0.002 mm), because a too large proportion of fine, determines a decrease of the mechanical resistance with deformation effect of the ceramic block core. [8, 9]

By introducing the refractory waste in the slag fine deficit, the increase of the mechanical resistance in the first phase is offset and with subsequent effect in its use by densification of the product, a decrease of the porosity, therefore a lower water absorption.

For the manufacture of ceramic blocks, with basic hydraulic binder, it is necessary to use cement, opting for the equal use of 5% aluminous cement and 5% Portland cement. [10, 11, 12]

Following a maximum compaction, 6 more variants of variation of the percentages of refractory waste, 28 A, shown in figures 4–9 were tried.

Figure 4. Sample test no.1

Figure 5. Sample test no.2

Figure6. Sample test no.3

Figure7. Sample test no.4

Figure8. Sample test nr.5

Figure 9. Sample test no.6

Table 4 shows the chemical compositions of the raw materials, and table 5 shows the manufacturing recipes. Determining the physical characteristics of the resulting products, the values recorded in table 6 were obtained.

Table 4. Chemical compositions of raw materials

Raw material	Chemical composition						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Slag	35,28	2,09	6,84	2,92	38,20	0,24	0,07
Brick waste	41,75	52,5	1,55	0,8	0,65	1,1	1,65
Sand	87,09	–	–	–	–	1,41	7,11
Multibat							
Cement	20,73	5,32	4,91	61,36	1,98	0,47	0,93

Table 5. Manufacturing recipes for ceramic blocks

Raw material	Slag	Waste 28A	Sand	Portland Cement	White Cement	Multibat
R1	60	20	5	5	–	–
R2	50	30	10	10	–	–
R3	40	40	10	10	–	–
R4	50	15	15	5	–	5
R5	50	15	15	–	5	10
R6	–	60	20	–	20	–

Table 6. Results of determining the physical properties of networks 1–6

Recipe	Absorption	Density	Porosity
R1	14,3	1,86	27,3
R2	14,3	1,77	25,3
R3	14,7	1,81	26,6
R4	12,3	1,92	23,6
R5	8,8	2,0	17,6
R6	13,4	1,93	25,8

Analyzing the results, the recipe R5 for the manufacture of ceramic blocks was chosen.
Considering the fact that the technology of production of heat–resistant ceramic blocks requires a preparation of raw materials such as natural slag, refractory waste, identical to that for the production of refractory bricks according to classical technology all equipment in that stream exists within SC CCPPR SA Alba Iulia [12].
The location of the machines does not undergo any change compared to the existing one at present, the flow of raw materials being the one indicated in figure 10.

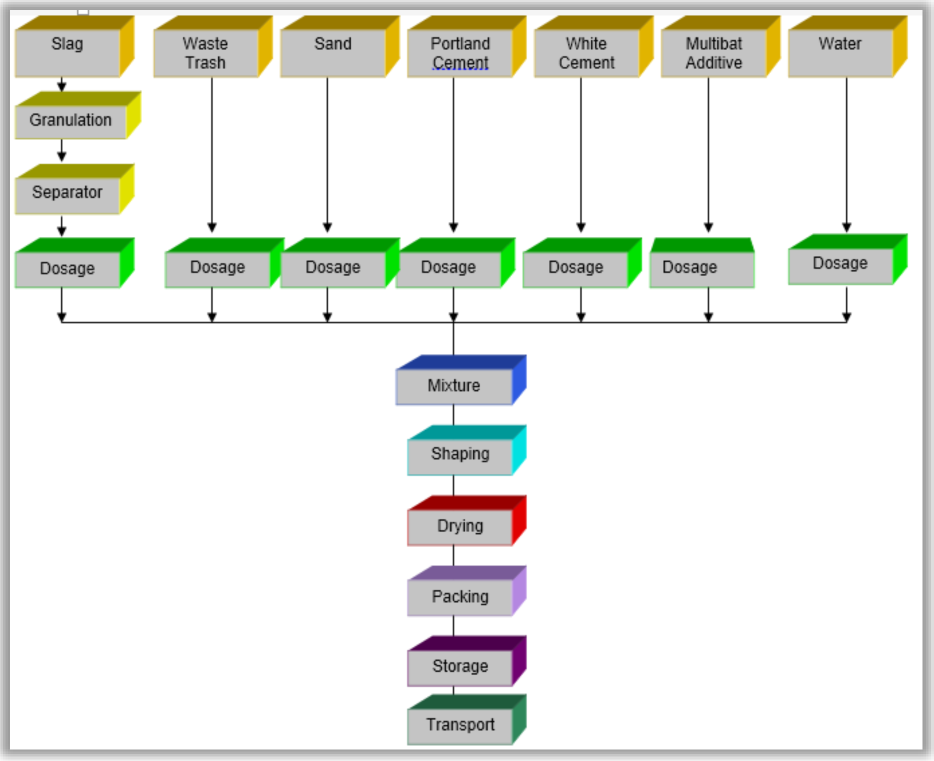

Figure 10. Technological flow to produce heat–resistant ceramic blocks using refractory waste

In figure 11 are presented ceramic blocks obtained without refractory waste in the manufacturing recipe and in figure 12 ceramic blocks obtained using refractory waste in the manufacturing recipe.

Figure 11. Ceramic blocks without refractory waste in the manufacturing recipe

Figure 12. Ceramic blocks obtained using refractory waste in the manufacturing recipe

— **Experimental research for the physico–chemical characterization of the manufactured batch**

The batch of ceramic products obtained was analyzed from a physico–chemical point of view, taking into account the products currently manufactured on the technological flow from SC CCPPR SA Alba Iulia. The average results corresponding to the two types of products were notified and in accordance with the regulations, imposed by Romanian standards, results were tabulated.

Tables 7 and 8 present the main characteristics of the standard ceramic blocks, without using refractory waste as raw material and those produced at SC CCPPR Sa Alba Iulia using refractory waste.

Table 7. Comparative presentation of the physico–chemical properties of ceramic blocks, produced without refractory waste in the recipe and with refractory waste.

Characteristics	Ceramic block obtained without refractory waste in the manufacturing recipe	Ceramic block obtained with refractory waste in the manufacturing recipe CCPPR experimental lot
Silicon dioxide, (SiO_2), %	38	36.5
Aluminium trioxide, (Al_2O_3), %	9	10
Iron thrioxide, (Fe_2O_3), %	5	5,5
Calcium oxide (CaO), %	8	9
Magnesium oxide (MgO), %	20	15
Calcination loss, (PC),%	20	25
Bulk density after drying at 105 ± 5°C, g / cm^3	2,0	1.8
Compressive strength 7 days after pressing, N / mm^2	16.8	15.2
Compressive strength 28 days after pressing, N / mm^2	20.8	19.1
Porosity, %	17.8	27.6
Freezing after 25 cycles, % loss	5	12

Table 8. Comparative presentation of the dimensions of the ceramic blocks, produced without refractory waste in the recipe and with refractory waste

Name	Ceramic block produced at CCPPR	Standard ceramic block
Length (mm)	245	245
Width (mm)	118	118
Height (mm)	66	66
Mass (kg)	3,760	3,870
Volume (dm^3)	1,923	1,923

The manufacture of ceramic blocks as a basic hydraulic binder requires the use of cement, as the strength of the product after curing is better.

Regarding the use of slag, it is good workability, accompanied by its low–cost price, recommends the use of up to 50% of the mass.

Particular attention must be paid to the grading of the slag because a too large proportion of fine, determines a decrease of the mechanical resistances, a deformation of the nuclei.

In the case of using refractory waste, the use of fractions that give a structural skeleton to the ceramic mass is considered.

The use of refractory waste also aims at the fact that it is a burned product and its absorption is very low, reducing the absorption capacity of the ceramic product.

The immediate effect is an increase in the freeze–thaw cycles of the final ceramic product, a very important goal to be achieved for a building ceramic block.

3. ECONOMIC ASPECTS REGARDING THE MANUFACTURE OF CERAMIC BLOCKS USING REFRACTORY WASTE IN THE RECIPE

Having as reference the recipes for the manufacture of ceramic blocks according to the project and the products made at S.C UNIREA MATCONS SCHELA S.A. Targu Jiu, the cost price for the two types of products was established. The cost price of raw materials is shown in table 9.

Table 9. Cost price of raw materials used in the manufacture of ceramic blocks

Raw material	Price lei/t	Value, Ron/t			
		Ceramic block produced at SC CCPPR SA Alba Iulia		Ceramic block produced at S.C UNIREA S.A. Targu Jiu	
		%	lei/t	%	lei/t
Portland cement	2500	5	125.0	16	400.0
White cement	2930	5	146.5	–	–
Slag	10	50	5.0	70	7.0
Sand	400	15	60.0	14	56.0
Refractory waste	650	15	97.5	–	–
Multibat	400	10	40.0	–	–
Total		100	474.0	100	463.0

The estimated cost price of the two types of products made with refractory waste in the manufacturing recipe (experimental lot SC CCPPR SA Alba Iulia) and refractory waste in the manufacturing recipe SC UNIREA MATCONS SCHELA SA Targu Jiu, is shown in table 10.

Table 10. Comparative cost price of the two types of ceramic blocks produced with and without refractory waste in the manufacturing recipe

Calculation elements	Value, Ron/t	
	Ceramic block produced at SC CCPPR SA Alba Iulia	Ceramic block produced at S.C UNIREA S.A. Targu Jiu
Raw materials	474.0	463.0
Supply and transport costs, 10%	47.4	46.3
Electricity and fuel	200.0	200.0
TOTAL Raw Materials	721.4	709.3
Total labor	17.5	17.5
Section expenses, 60%	10.5	10.5
Section cost	749.4	737.3
Enterprise expenses, 15%	112.4	110.6
Factory cost	861.8	847.9
Sales expenses, 5%	43.1	42.4
Benefit 5%	43.1	42.4
TOTAL	948.0	932.7
Delivery price, lei / t	950.0	935.0
Delivery price, lei / piece	3.63	3.50

In table 10 it is observed that the cost price of the product proposed in accordance with the technology proposed in this paper is about 15 lei / ton (0.13 lei / piece) higher than the one currently manufactured on the flow from a economic agent producer of ceramic blocks SC UNIREA MATCONS SCHELA SA Targu Jiu, while its characteristics are better, obtaining higher durability (double resistance in frost–thaw conditions).

This justifies the delivery price, as the proposed solution is economically advantageous.

At the same time, the use of refractory waste, however, involves another aspect, related to environmental protection, both by eliminating a more advanced exploitation of slag quarries and by eliminating waste that does not find a rational reuse in the economic circuit.

Their storage at ground level or in pits is not possible, due to the sterile nature of the waste, with effect on the plant and animal kingdom.

4. CONCLUSIONS

The manufacture of ceramic blocks as a basic hydraulic binder requires the use of cement, as the strength of the product after curing is better.

Regarding the use of slag, its good workability, accompanied by its low–cost price, recommends the use of up to 50% of the mass.

Particular attention must be paid to the granulometry of the slag because too large a proportion of fine–grained material causes a decrease in mechanical strength and a deformation of the solidification cores.

In the case of using refractory waste, the use of fractions that give a structural skeleton to the ceramic mass is considered.

The use of refractory waste also aims at the fact that it is a burned product and its absorption is very low, reducing the absorption capacity of the ceramic product.
The immediate effect is an increase in the freeze–thaw cycles of the final ceramic product, a very important goal to be achieved for a building ceramic block.
For the manufacture of ceramic blocks, with basic hydraulic binder, it is necessary to use cement, opting for the equal use of 5% aluminous cement and 5% Portland cement.
The environmental effects of refractory waste recycling are obvious and extremely important.

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