

EXPERIMENTAL RESEARCH REGARDING THE RECOVERY OF CERAMIC WASTE FROM THE MANUFACTURING OF PIGMENTS FOR PAINTS USED IN THE CERAMICS INDUSTRY

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This paper presents the results of experimental research aimed at developing an efficient technology for recycling ceramic waste, specifically damaged chamotte crucibles originating from a paint pigment manufacturer. The study focused on the valorization of this waste, in two particle size fractions, as raw materials in recipes for ceramic and refractory materials. The research employed a 2³ experimental design matrix, with eight composition variants analysed. The optimal recipe was determined based on the physical properties obtained, demonstrating technical feasibility, economic advantages, and environmental benefits.

Keywords: ceramic waste, industrial waste, pigments for paints, electron microscopy, refractory materials

1. Introduction

The word “pigment” originates from the Latin term “pigmentum”, which initially referred to colour in the sense of coloured materials; the meaning was later extended to include decoration (coating) through coloration. By the end of the Middle Ages, the term was also used to denote products derived from plants and plant extracts, particularly those employed for colouring purposes. [1]

According to H. Kittel, the essential distinction between pigments and dyes lies in the fact that pigments are insoluble in the dispersion medium used, whereas dyes are soluble. Consequently, pigments are employed for painting, while dyes are used for dyeing.

It is understood, however, that the same-colored substance may function as a dye in one case and as a pigment in another, depending on the dispersion medium into which it is introduced. The difference lies solely in the degree of solubility. [1]

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There is a body of historical evidence documenting the use of pigments in various fields since antiquity. Mineral pigments based on copper, iron, and manganese were known and used in Babylon, Egypt, and China thousands of years before our era. [2, 3] Cobalt was introduced into Chinese porcelain during the T'ang Dynasty (618–906 BC) and in Europe from the 15th century onward. [4-6]

The use of colors and pigments, particularly by the Chinese, dates back approximately 3,000 years. Among the earliest pigments produced by humans, lead white was obtained around 400 BC, using a manufacturing method that involved the action of acetic acid on lead. [4]

Pigments used for coloring ceramic products must exhibit a range of properties common to all pigments (colouring strength, covering power, lightfastness, weather resistance, etc.), as well as specific properties, the most important of which is resistance to high temperatures and the corrosive environment encountered during the firing process. [5-7] The dissolution rate of the pigment in the melt must be very low, despite the extremely small size of its particles (~10 nm). Furthermore, the release of gaseous compounds resulting from the contact between the ceramic pigment and the melt is prohibited. [6] The severity of these conditions limits ceramic pigments to a relatively small number of compounds, while simultaneously opening a vast field of research in the area of heat-resistant ceramic pigments. Near the city of Alba Iulia, an industrial operator specializing in the production of inorganic mineral pigments is in operation. Since its opening in 2012, the investment has created 20 new jobs in Alba County. The investor is the company *Broll Pigments SRL*, owned by the Broll family from Germany. The factory produces colorants for kaolin, which is the raw material for ceramics and porcelain. [8,9]

The technology for producing ceramic pigments at this company generates ceramic waste in the form of crucibles made from refractory materials in which the pigments are obtained. These crucibles develop deposits on their walls that render them unusable in the pigment production process. Many of them break during handling after the pigments are removed. These broken crucibles with wall deposits constitute waste for which a valorization technology must be developed.

In this way, ceramic waste is generated that requires solutions for neutralization and valorization. Fine layers of deposits from the material used in pigment production are present on the walls of these crucibles.

Fig. 1 shows fragments of broken crucibles, where the deposits can also be observed.



Fig. 1. Crucible waste showing the deposits

As a result of these deposits, crucible waste has been classified as hazardous. The experimental research presented in this paper aimed to develop an efficient valorization technology for this ceramic waste.

2. Materials, equipment and method

2.1. Materials

The research on the valorization of ceramic waste, represented by crucibles out of use from ceramic pigment production, was conducted at an industrial operator specializing in the design and production of refractory and ceramic materials, SC CCPPR SA from Alba Iulia. [10]

The study focused on the valorization of ceramic waste with two different particle sizes: a fine fraction and a coarse fraction in the form of granules. These were used as raw materials in the recipes for producing ceramic blocks. The research was conducted using a 2^3 experimental design matrix, and eight recipes variants containing variable proportions of waste were established. To determine the nature of these deposits, optical microscopy investigations were conducted using the SCIAPPS X-200 spectrometer on both the crucible walls and the deposits. More information about the spectrometer used can be found at www.kimet.ro.

Measurements were performed on the outer surface of the specimens and on the inner surface (on the reddish material, which appears to be a deposit) at several locations. Additionally, a measurement was taken on the edge.

The results obtained are presented in Figs. 2–11.

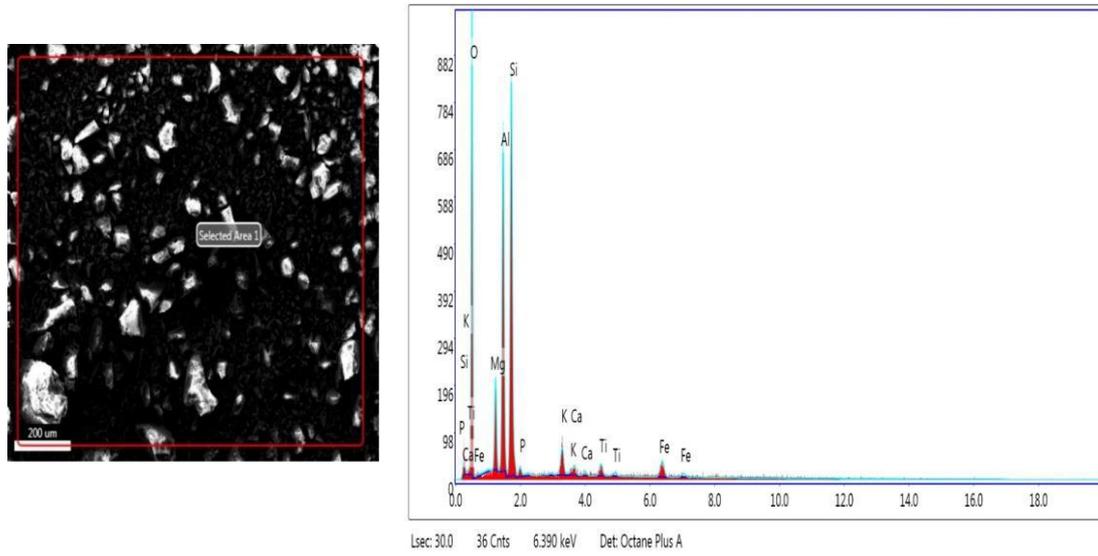


Fig. 2. EDAX report – crucible wall analysis

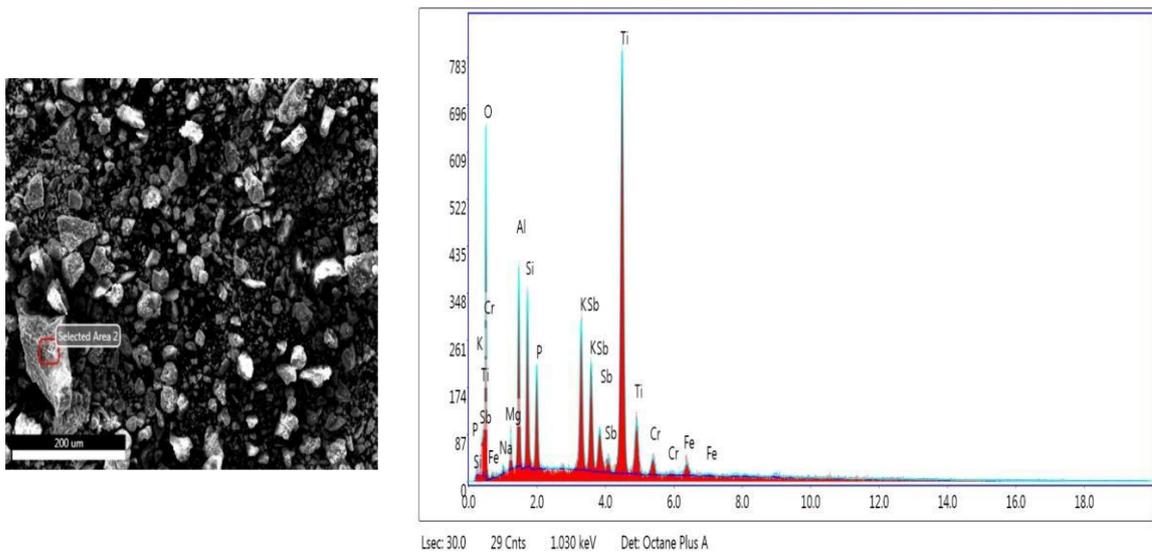


Fig. 3. EDAX report – analysis of deposit on crucible with large oxide particle

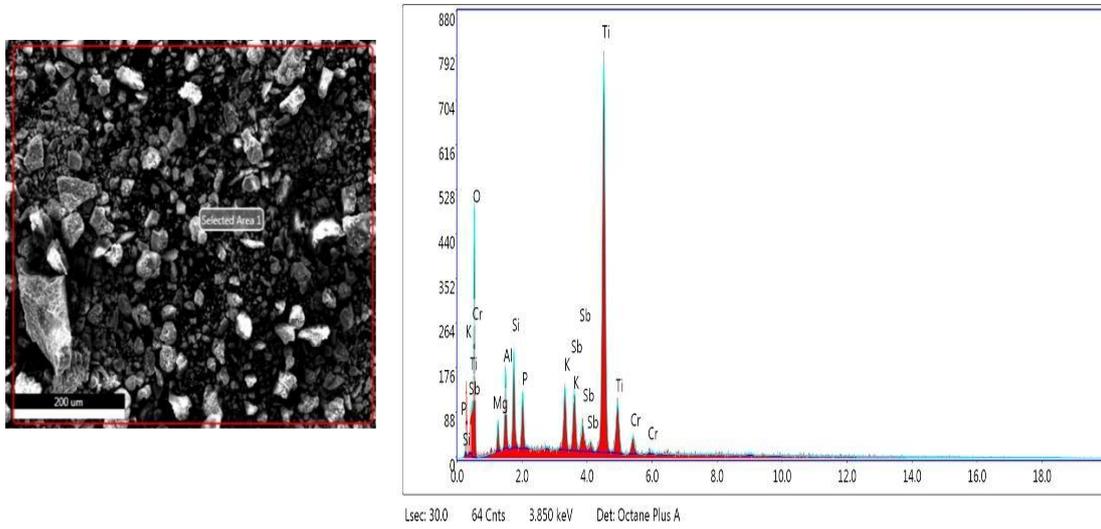
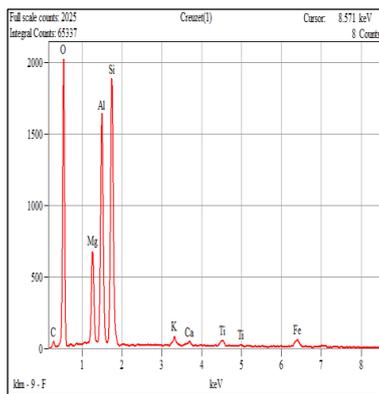
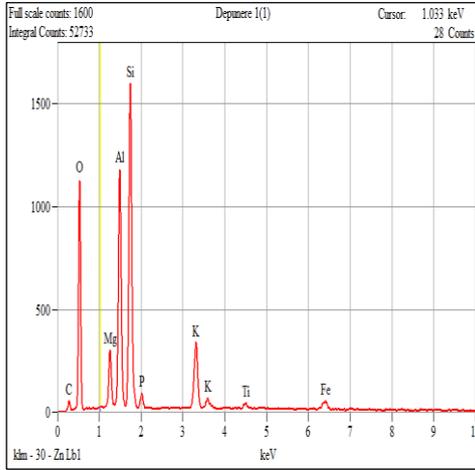


Fig. 4. EDAX Report – Analysis of deposit on crucible, small red oxide particle



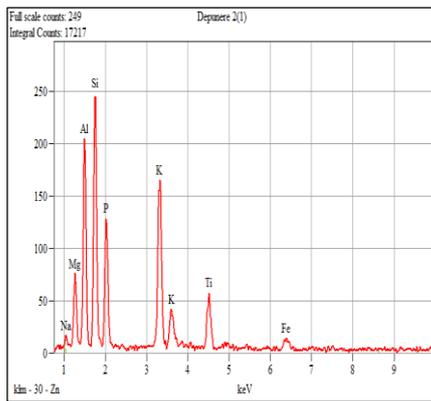
Elem.	Weight %	Weight % Error	Atom %	Atom % Error
C	2.78	± 0.21	4.43	± 0.34
O	55.83	± 0.49	66.83	± 0.59
Mg	6.71	± 0.14	5.29	± 0.11
Al	13.95	± 0.20	9.90	± 0.14
Si	18.61	± 0.19	12.69	± 0.13
K	0.53	± 0.03	0.26	± 0.01
Ca	0.24	± 0.03	0.12	± 0.01
Ti	0.42	± 0.06	0.17	± 0.02
Fe	0.93	± 0.11	0.32	± 0.04
Total	100.00		100.00	

Fig. 5. Crucible wall analysis 1



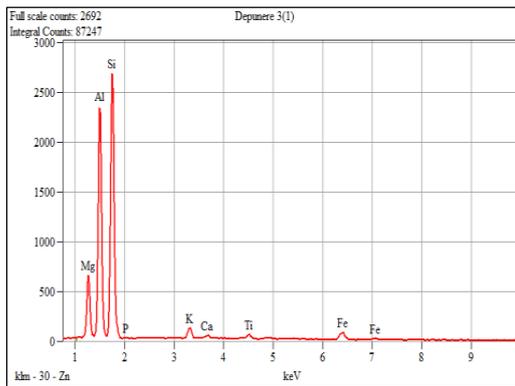
Elem.	Weight %	Weight % Error	Atom %	Atom % Error
C	4.72	± 0.31	7.60	± 0.49
O	52.54	± 0.61	63.55	± 0.74
Mg	3.69	± 0.14	2.94	± 0.11
Al	12.96	± 0.21	9.29	± 0.15
Si	19.59	± 0.23	13.50	± 0.16
P	0.97	± 0.10	0.60	± 0.06
K	3.86	± 0.11	1.91	± 0.05
Ti	0.48	± 0.04	0.19	± 0.02
Fe	1.19	± 0.15	0.41	± 0.05
Total	100.00		100.00	

Fig. 6. Analysis of Area 1 – deposit on crucible



Elem	Weight %	Weight % Error	Atom %	Atom % Error
C	2.65	± 0.40	4.51	± 0.69
O	49.61	± 1.23	63.44	± 1.57
Na	1.03	± 0.20	0.91	± 0.18
Mg	4.56	± 0.21	3.84	± 0.18
Al	9.72	± 0.40	7.37	± 0.30
Si	12.36	± 0.46	9.01	± 0.34
P	6.96	± 0.33	4.60	± 0.21
K	8.35	± 0.29	4.37	± 0.15
Ti	3.42	± 0.24	1.46	± 0.10
Fe	1.35	± 0.19	0.49	± 0.07
Total	100.00		100.00	

Fig. 7. Analysis of Area 2 – deposit on crucible



Elem.	Weight %	Weight % Error	Atom %	Atom % Error
C	2.65	± 0.21	4.29	± 0.33
O	53.53	± 0.47	65.11	± 0.57
Mg	4.77	± 0.11	3.82	± 0.09
Al	15.37	± 0.18	11.09	± 0.13
Si	20.98	± 0.18	14.53	± 0.13
P	0.19	± 0.03	0.12	± 0.02
K	0.74	± 0.06	0.37	± 0.03
Ca	0.20	± 0.03	0.10	± 0.01
Ti	0.49	± 0.06	0.20	± 0.02
Fe	1.08	± 0.11	0.38	± 0.04
Total	100.00		100.00	

Fig. 8. Analysis of Area 3 – deposit on crucible

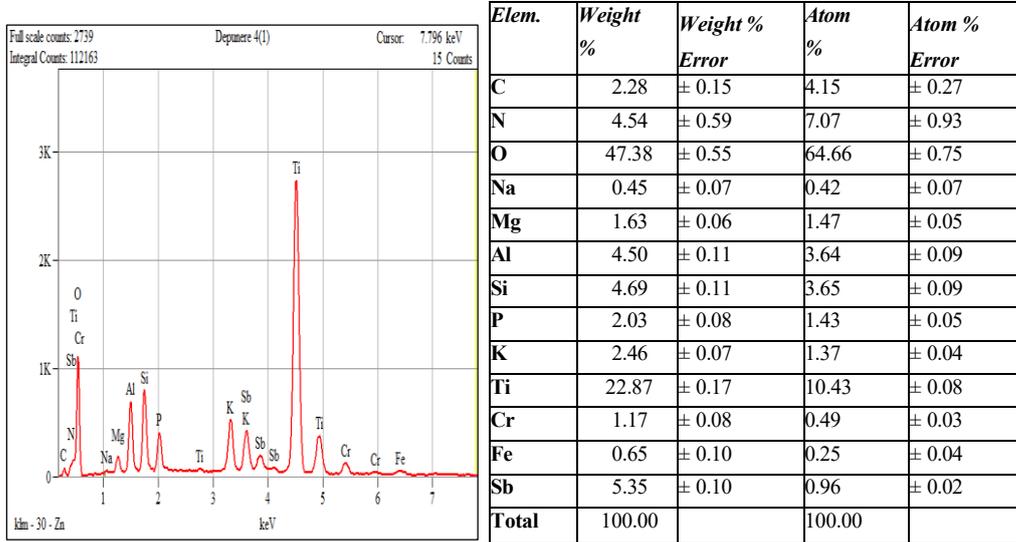


Fig. 9. Analysis of Area 4 – deposit on crucible

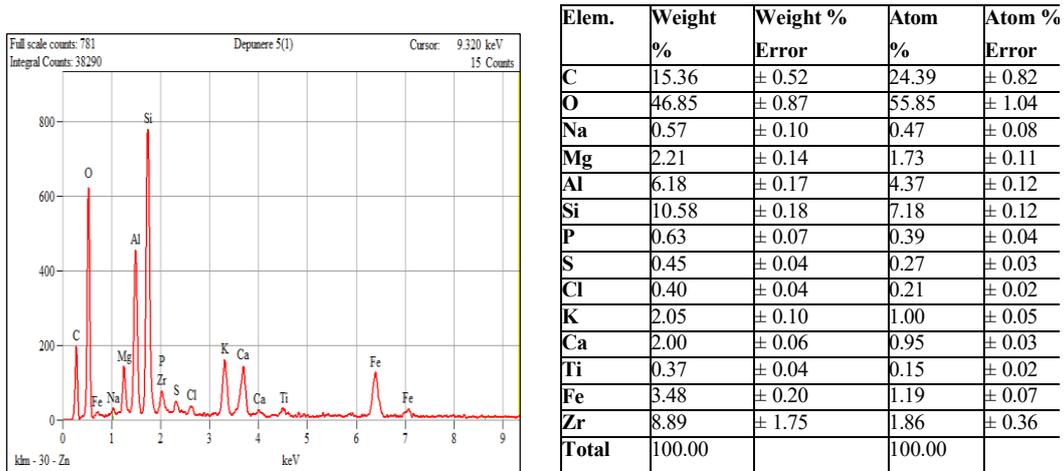


Fig. 10. Analysis of Area 5 – deposit on crucible

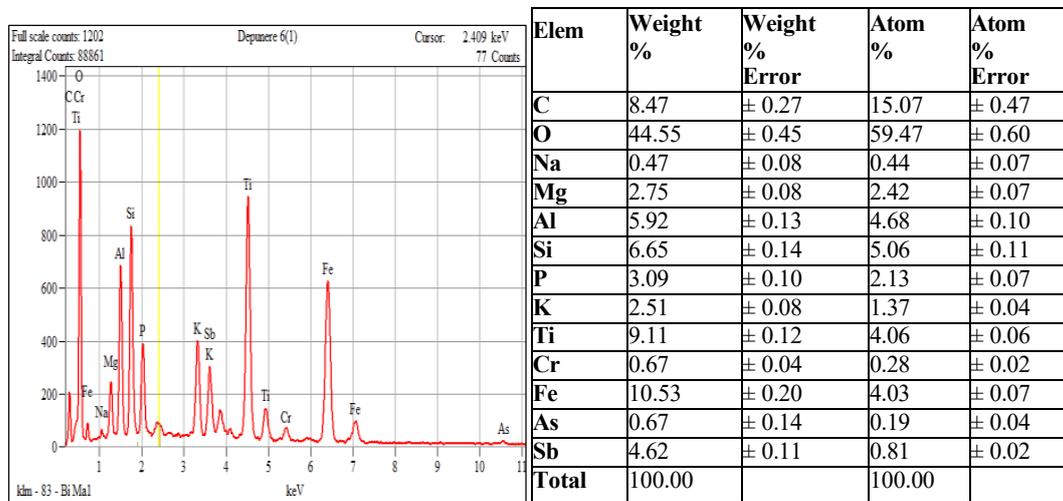


Fig. 11. Analysis of Area 6 – deposit on crucible

Analyzing the results of the investigations on the composition of the crucible walls, and especially of all the zones examined for pigment deposits, it was found that there are no elements conferring toxic characteristics to this waste. Their structure is very similar to that of the chamotte used in the production of refractory and ceramic materials. Based on this observation, research was conducted on the valorization of this waste at the industrial operator SC CCPPR SA in Alba Iulia, by incorporating the waste in varying proportions into the manufacturing recipes of ceramic blocks.

2.2 Equipment

Laboratory equipment for testing raw materials and finished products

The main laboratory equipment used is shown in Fig. 12.

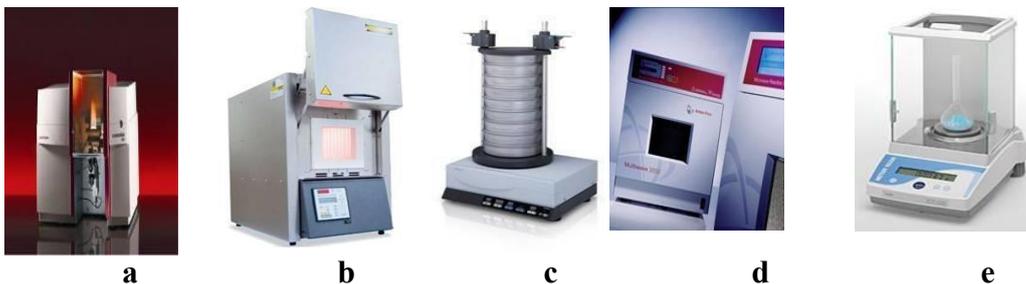


Fig. 12. Laboratory equipment for testing raw materials and finished products [10] a – High-resolution spectrometer, b – Compact high-temperature furnace, c – AS 200 Control sieve analyser, d – Microwave system for pressure-assisted mineralization, e – AL204 analytical balance, Mettler-Toledo. [10]

2.3. Method

Following an experimental study using a 2³ factorial design, eight variants of slag proportions were developed in the manufacturing recipes. Considering that the technology for producing ceramic and refractory materials using industrial waste, such as slag from secondary aluminum production, requires a raw material preparation process identical to that used for producing refractory bricks by the conventional method, all the necessary equipment for this production flow is available at SC CCPPR SA, Alba Iulia. [10]

The raw materials were chemically analysed, with the content of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, and K₂O determined as percentages. The loss on ignition, particle size distribution, density, and moisture content was determined.

Based on the physicochemical analysis of the raw materials, recipes were established as shown in table 1.

Table 1

Manufacturing recipes of the experimental ceramic samples					
Recipe	Crucible waste, fine particle size%	Crucible waste, coarse granules%	Fine SA 40A chamotte, fine grains %	SA 40A chamotte, coarse granules %	Water with chemical binder, mL
R1	25	-	15	60	300
R2	30	-	10	60	250
R3	35	-	5	60	250
R4	40	-	2	58	300
R5	-	25	15	60	300
R6	-	30	20	50	300
R7	-	35	15	50	350
R8	-	40	15	45	300

The graphical variations of the raw material components in the experimental samples are shown in Fig. 13.

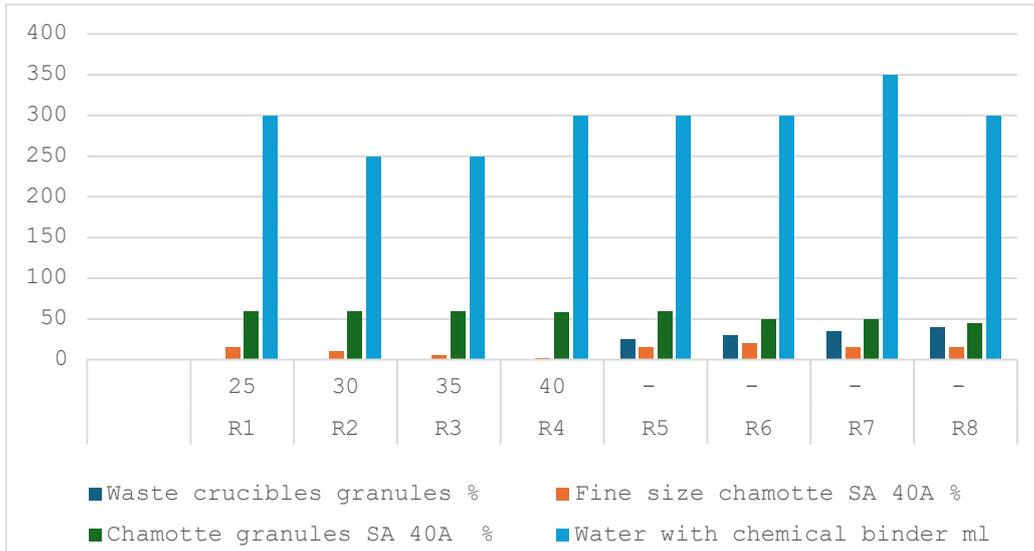


Fig. 13. Proportion of components in the experimental manufacturing recipes

The components of each recipe were weighed gravimetrically and then mixed in the laboratory using a paddle mixer. The resulting mixture was pressed in a friction press at 120 tF/m^2 in four stages, aiming for maximum deaeration of the mass. Cylinders with a diameter of 60 mm and a height of 60 mm were obtained. Images of the experimental samples are shown in Fig. 14.



Fig. 14. Examples of experimental samples for different recipes

The experimental samples were air-dried naturally for 10 days. It can be observed that the batch recipes are diversified, being developed based on the experience of the industrial operator SC CCPPR SA from Alba Iulia, where the experimental research was conducted.

3. Experimental results and their interpretation

3.2. Values of the main quality characteristics of the obtained ceramic products

For all eight experimental samples, the main qualitative properties were determined through laboratory measurements of water absorption, density, and porosity, as well as optical microscopy investigations of their structure. The results of the physical properties of recipes 1–8 are presented in table 2.

Table 2

Results of the physical properties for recipes 1–8			
Recipe	Absorption %	Density g/cm ³	Porosity %
R1	15,73	2,1204	29,484
R2	15,73	2,0178	27,324
R3	16,17	2,0634	28,728
R4	13,53	2,1888	25,488
R5	9,68	2,28	19,008
R6	14,74	2,2002	27,864
R7	15,95	2,394	28,782
R8	16,06	2,5422	30,024

The graphical variations of the main qualitative characteristics of the ceramic and refractory materials for the experimental samples are shown in Fig. 15.

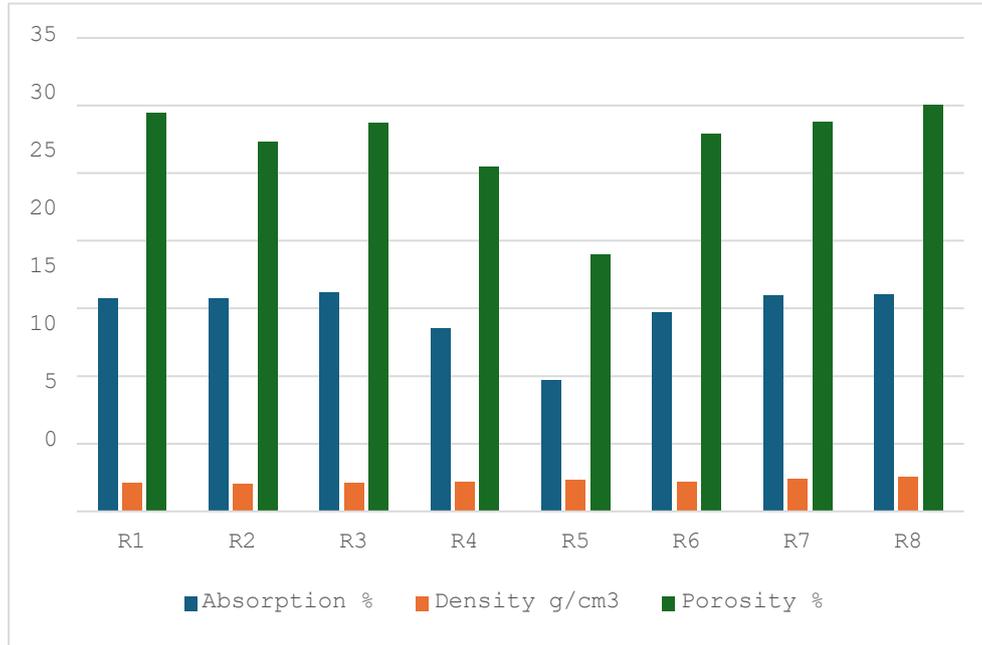


Fig. 15. Variation of the specific qualitative characteristics of ceramic and refractory materials for the eight experimental samples

Analysing the results in terms of the main qualitative characteristics of ceramic and refractory materials, recipe R8 is considered the most suitable for the valorization of crucible waste from pigment production.

3.3. Experimental research for testing the compressive behaviour of ceramic samples

The compression test was carried out on a Walter + Bai LFV 300 universal testing machine, Walter + Bai AG, Switzerland. The test was displacement-controlled, with a constant crosshead speed of 5 mm/min. The stopping criterion for the test was reaching 75% of the maximum recorded force. The curve was adjusted to eliminate the initial region in which the specimen settles between the compression platens. The stress-strain curves are shown in Fig. 16.

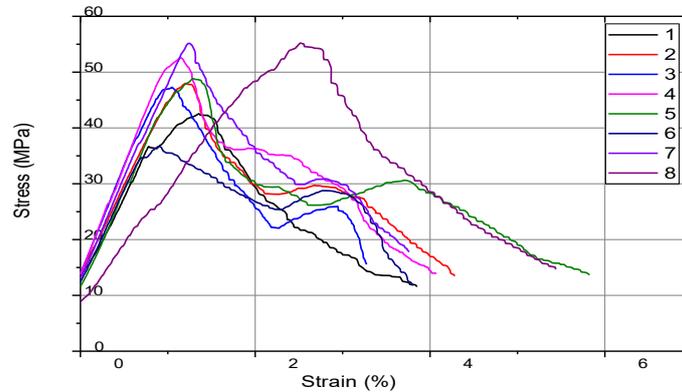


Fig. 16. Stress–strain curves in compression for the experimental specimens

The experimental results are presented in Table 3.

Table 3

Results of mechanical testing of the ceramic samples

Specimen	E[MPa]	σ_1 [MPa]	σ_c [MPa]
1	3196.83	36.516	42.553
2	3172.27	44.497	47.979
3	3878.08	38.265	47.293
4	4053.77	26.736	52.52
5	3847.84	30.308	48.845
6	3398.83	34.67	36.689
7	3703.83	37.887	55.15
8	2311.42	25.404	55.208

Where:

E [MPa] – represents the equivalent modulus of elasticity of the specimen

σ_1 [MPa] – represents the stress at the first failure, observable on the curve as a drop or short plateau, corresponding to the point where a crack initiates, leading to failure

σ_c [MPa] – represents the compressive strength, the maximum stress during the test

According with data from the table, it can be observed that all samples exhibit suitable values for the studied parameters. The highest modulus of elasticity is recorded for sample 4, where the proportion of fine crucible waste is 40%. The best stress at which cracks appear is recorded for sample 2, while the highest compressive strength is observed for sample 4.

These results indicate that a significant amount of crucible waste, up to 40% of the recipe components, can be used in the manufacturing recipes for ceramic blocks. It is also recommended that the crucible waste be crushed before the homogenization of the raw materials in the production recipes.

4. Conclusions

The use of secondary raw materials and recycled refractory materials in refractory production was the focus of the experimental research. Ceramic crucible waste resulting from the ongoing production of a major industrial operator was used as a raw material in the recipes for producing experimental samples, with varying proportions of crucible waste from pigment production, either fine-grained or coarse granules.

Following an experimental study using a 2³ factorial design, eight variations of crucible waste proportions were developed: four using fine-grained crucible waste and four using coarse crucible granules.

According to the standards for defining the quality of ceramic and refractory materials, the analyzed quality indicators are the water absorption of the finished product (measured in %), the density of the finished product (measured in g/cm³), and the porosity of the finished product (measured in %). It was found that crucible waste can be successfully used in recipes for producing market-demanded refractory materials. The maximum proportion of crucible waste, both fine-grained and coarse granules, that can be used in the recipes is 40%.

The obtained finished products exhibited good values for the main tested quality characteristics, considering their intended use: a water absorption of 16.06 %, a density of 2.54 g/cm³, and a porosity of 30.024 %.

The results of the experimental research demonstrated the feasibility of efficiently recycling crucible waste from pigment production by incorporating these wastes into the manufacturing recipes of products at SC CCPPR SA Alba Iulia, such as ceramic blocks used in refractory masonry for equipment operating at high temperatures ranging from over 1000 °C up to 1400 °C. The results of the conducted research demonstrated the possibility of efficiently valorizing these ceramic wastes, with significant economic benefits as well as enhanced environmental protection.

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