UNIVERSITY POLITEHNICA of BUCHAREST

SUMMARY
DOCTORATE THESIS

EXPERIMENTAL RESEARCH ON THE CAPTURE AND RECOVERY OF FINE GRANULATED OXID WASTE GENERATED IN THE CERAMIC AND REFRACTORY MATERIALS INDUSTRY

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Foreword

The justification for the choice of the doctoral thesis is given by the need to solve a particularly important problem for agents producing large or special series refractory products, namely, the efficient recovery of silico-alumina dusty waste, captured in treatment plants, by incorporating this waste, in special, recipes for the manufacture of ceramic and refractory products.

The doctoral thesis addressed both the identification of the types of pollutants generated in the economic activity of an economic agent producing ceramic and refractory materials, the identification of pollutant emission sources, the quantities of pollutants, the finding of real solutions to reduce pollutant emissions, but and the completion of a technology that allows the recovery of recyclable waste from the refractory materials industry with the production of new construction materials, which can be used successfully in civil or even industrial construction.

The durability of a construction material and, implicitly, of the construction, is affected by factors of physical, chemical and biological nature from the external environment, the duration of exploitation of the constructions depending on the way in which the materials resist such destructive agents. As a result of the study carried out in this paper, respectively, based on the results obtained, it was concluded that this type of construction material - ceramic blocks - is very well suited for construction of: interior masonry for houses, industrial halls, gas hot results from the burning of industrial processes or thermal power plants, other places that do not come in direct contact with aggressive agents (moisture, acids, etc.).

The proposed theme of the doctoral thesis was the design and realization of a new technology that would allow the manufacture of ceramic blocks at SC CCPPR SA Alba Iulia using in the recipe of raw materials refractory waste generated at SC Helios Aştileu.

The doctoral thesis was developed based on research conducted in the laboratories of the Research Center for Design and Refractory Production in Alba Iulia and within the Polytechnic University of Bucharest, Faculty of Materials Science and Engineering.

At the end of this stage, my gratitude and all my love go to my mother, Tonia, to whom I dedicate this thesis, as well as to my beloved partner, Sergiu, as well as to all those who supported me in the elaboration and completion of the doctoral thesis, especially, my colleague and bestfriend, Cristina.

On this occasion I would like to express my thanks to Dr. Miron Buzduga and Dr. Eng. Radu Buzduga from S.C. CCPPR S.A. Alba Iulia for the competence with which they coordinated my entire activity carried out during the elaboration of the thesis and the entire support offered for fulfilling the objectives of this thesis.

I thank them at the same time for accepting me as a doctoral student in their research team, for the trust placed in me and for the suggestions and indications without which this work would not have been done.

I thank the scientific director of the paper, the members of the Steering Committee who offered me their support and competent advice for the elaboration and completion of the thesis.

I thank my colleagues from the IMOMM department at the Polytechnic University of Bucharest, for helping me with recommendations in all the activity I have carried out, so far, in the research team of the ERAMET laboratory.

Elisa-Florina PLOPEANU

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CONTENTS Doctoral thesis

THE PROJECT OF THE SCIENTIFIC RESEARCH PROGRAM

IN VIEW OF THE REALIZATION OF THE DOCTORAL THESIS WITH THE TITLE: "EXPERIMENTAL RESEARCH ON THE CAPTURE AND RECOVERY OF FINE GRAIN OXIDE WASTE GENERATED IN THE CERAMIC AND REFRACTORY MATERIALS INDUSTRY"

In order to complete the first stage of training within the in-depth doctoral studies, I took **three specialized exams, with the titles**:

1. **Identification of the types of noxious substances, wastes and by-products generated in the refractory materials industry,**
2. **Identification of the types of noxious substances, wastes and by-products generated in ferrous metallurgy,**
3. **Methods of recovery of waste and by-products generated in the ferrous metallurgy and refractory industries.**

All exams were passed with the grade Admitted, (grade ten) and 10 credit points each.

In order to report on the achievement of the objectives committed through the proposed research program, during the internship years, five scientific research reports were presented to the scientific director and the steering committee with the titles:
Scientific report no.1: Noxaes identified in the industry producing silico-aluminum refractory materials.
Scientific report no.2: Identification of the possibilities of control and reduction of pollution at the dispersion chimneys of the economic agents producing silico-aluminum refractory materials.
Scientific report no.3: Solutions for control and reduction of dust emissions in economic agents producing silico-aluminum refractory materials.
Scientific report no.4: Analysis of the possibilities of recycling refractory waste with a fine granulation to obtain heat-resistant ceramic blocks.
Scientific report no.5: Finalizing the technology for obtaining heat-resistant ceramic blocks by recycling refractory waste with a fine granulation.

All scientific reports were submitted on the scheduled date and were ADMITTED.

PART I

DOCUMENTARY ANALYSIS REGARDING THE CURRENT STATE OF POLICY IDENTIFICATION, CAPTURE AND RECYCLING IN THE CERAMIC AND REFRACTORY INDUSTRY

Chapter 1. IDENTIFIED CATEGORIES IN THE INDUSTRY PRODUCING SILICO-ALUMINUM REFRACTORY MATERIALS

Recoverable products resulting from the activity of companies in the refractory products sector are accompanied by emissions that are in solid, liquid and gaseous form, pollutants that affect in various ways the quality of environmental factors.

The reduction and / or elimination of these emissions is imposed by the continuation of production processes, the solution currently practiced being most of the times, the evacuation in the environment of large quantities of noxious substances and large quantities of raw materials. [1-3]

The main environmental factors affected by the interaction with these emissions are air, water, soil, vegetation and, of course, man, both as a result of direct pollution in the area, as well as air, water, soil pollution.

In general, gaseous, liquid and solid substances, which are in the atmospheric air and which are not part of its normal constituent elements, can be considered as harmful, defective elements. They are also considered vices, excessive heat and humidity. Among the noxious substances that can occur in the air can also be unpleasant odors, the presence of microorganisms that may or may not be harmful or cause infectious diseases. [4 - 7]

The microclimate at work is determined by temperature, humidity and speed of air movement, (air currents), ambient body temperature, caloric radiation in work areas, dust suspended in the air of workspaces. These are very important for the health of employees.

Industrial pollution is currently considered the most important source of pollution.

The horizon of the tangents of industrial pollution is very wide, ranging from pollution problems in the workplace to ecological consequences that affect the entire globe.

Pollution at work is characterized by the presence of substances or physical factors in the workplace and can have important consequences for occupational diseases. It is important to remember that in almost every job there are harmful factors, which in most cases cause only mild irritation or dermatitis. [8]

Industrial pollution of the environment spreads mainly through air and water.

Almost all industries are to blame for air pollution, especially some branches such as: metallurgy, cement, lime, refraction, thermoelectric, etc., in which the "visible" sign of air pollution is given by industrial emissions of dusty materials sometimes large very fine, micronic that spread over very large areas.

Water pollution is also quite important. The importance of this pollution increases with the specific industrial consumption of water, because, the higher this consumption, the higher are the possibilities of spreading harmful substances in the environment.

Harmful substances removed from industrial processes by water are very varied in effect. [8-11]

Chapter 2. CONCRETE IDENTIFICATION OF POLLUTION SOURCES AND TYPES OF POLLUTANTS IN AN ECONOMIC AGENT PRODUCING REFRACTORY MATERIALS

2.1. Overview

The effects of industrial activity in the refractory products sector on the environment can be estimated depending on the pollutants emitted, pollutants that affect in various ways the quality of environmental factors. [11-19]

This chapter presents the sources of pollution and the type of pollutants emitted by an economic agent producing refractory materials SC HELIOS SA Aștileu Romania. [20,21]

The company SC HELIOS SA Aștileu is located in the northwestern part of the country, in Bihor County, 35 km from the city of Oradea, in the eastern part of the village of Aștileu, southeast of the town of Alesd.

The paper was prepared on the basis of documentation made on site, with the consent of the company's management, field observations, based on technological data provided by the company's management and based on the determination of emissions discharged into the environment.

The recoverable products resulting from the activity of these companies are accompanied by emissions which are in solid, liquid, and gaseous form.

The reduction and / or elimination of these emissions is imposed by the continuation of production processes, the solution currently practiced being most often the evacuation into the environment of large quantities of noxious substances and large quantities of raw materials. [19]

Within the analyzed company, the entire range of sorto-tipo-dimensions of construction bricks provided in the Romanian standards is manufactured.

The methods of manufacturing construction bricks are semi-dry pressing, and the manufacture of bricks and ceramic blocks by the wet method.

The semi-dry pressing method is performed on one of the manufacturing lines of refractory bricks. The raw material, red clay, is prepared on the same flow as refractory clay.

The molding of construction bricks is done on mechanical presses of SM type, using the manufacturing line related to them.

The combustion is also performed on the tunnel furnace no. 1 at temperatures between 1130 - 1190ºC.

The manufacture of bricks and ceramic blocks by the wet method is done on an independent flow. It consists of funnels of raw materials where clay, sawdust, prepared scrap (red chamotte) are brought by car.

From the bunkers the raw materials are extracted, volumetrically dosed and transported by means of a conveyor belt to a cholergang where the crushing, wetting and homogenization of the mixture takes place.

2.6. Characterization of dust pollutants generated in the industry producing powder refractory materials from the point of view of the environment and human health

Under certain conditions, pollutants can cause direct harm to humans. This injury can occur in a variety of ways.

When the pollutant interferes with biological products at the microscopic level, alternating biochemical processes, we can talk about its toxicity, certainly the sum of the harmful consequences for the community throughout human life.

The harmful effects caused by air pollution are of several categories:

a. Irritant effects: are mainly caused by dust and some gases. The simple penetration into the respiratory tract, their presence on the ocular mucous membranes or even on the eyelids causes the reaction of the tissues, disorders of the functions, pathological processes.

Powders without toxic or irritating properties exert actions and phenomena of intolerance, the stronger the more traumatizing their size and shape. The name "inert" powders should not be confused with no harmful actions, because any kind of powder is an irritating factor, harmful, at least for an excess of function, and sometimes by histological reactions.

b. Allergic effects: determined mainly by some substances of an organic nature and by those that generate new substances with allergenic properties through contact with the tissues of the human body.

c. Infectious or infesting effects are caused by powders containing microorganisms, or spores or eggs of parasites. They cause diseases of the respiratory tract or other organs, wound infection, etc.

d. Immunological effects: represent changes in the functions of defense against infections (phococytosis, production of antibodies, ability to fix and neutralize antigens, etc.) indirectly favoring the production of diseases.

e. Carcinogenic effects: characteristic of a large category of pollutants whose number continues to increase.

Air pollution causes, in those exposed, repeated aggressions followed by restorative restorations that slowly and gradually reach a series of clinical manifestations, forms of disease, of which the best known and most present are chronic bronchitis, pulmonary sclerosis and asthma.

Air pollutants also cause the degradation and damage of various objects, materials and substances with which they come into contact through complex physico-chemical phenomena, defined by the nature of the pollutants and the material substrate on which they act.

2.7. Conclusions

The specificity of the industrial activities in the branch producing refractory materials generates dust as the main pollutant emitted into the atmosphere.

These dusts are captured by various technological installations and only a small part is emitted in a controlled way into the atmosphere, through chimneys.

As a result of the determinations made, it was found that the largest amount of dust is released into the atmosphere in the grinding, granulation, dosing and pressing mixing sectors.

It is found that the dust removal equipment did not work at the designed parameters due to physical and moral wear.

There are also important quantities of dust that are emitted due to leaks, lack of doors, windows, due to the natural ventilation of the production halls but also due to the malfunction of the dusting equipment.

Chapter 3. IDENTIFICATION OF THE POSSIBILITIES OF CONTROL AND REDUCTION OF POLLUTION IN THE DISPERSION EXHAUSTER OF ECONOMIC AGENTS PRODUCING SILICO-ALUMINOUS REFRACTORY MATERIALS.

3.2. Laboratory analytical methods applied in practice for the main pollutants encountered in the refractory materials sector

Carbon monoxide (CO) can be detected and measured by physical and chemical methods. Infrared absorption and spectrometric determination are commonly used as a physical method.

Chemical detection methods:

a) the method with palatal chloride

$PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl$ (1)

Due to the appearance of the metallic palladium, a black coloration will occur.

b) Tille method

$AgO + CO = Ag + CO_2$ (2)

Due to the appearance of metallic silver, the solution at first colorless, turbid and darkens.

c) Method with iodine pentoxide (I_2O_5).

Carbon monoxide acts as a reducing agent and the blue coloration of free iodine appears.

The detection of carbon monoxide is done by observing the color change. Carbon dioxide can be determined by the infrared absorption spectrometric method in water absorption, which must be removed by passing the sample over solid absorbents.

Chemically use a solution of barium chloride ($BaCl_2$) in water through which the sample is bubbled with carbon dioxide.

Barium carbonate ($BaCO_3$) precipitates. The amount and concentration of CO_2 will be deduced from the amount of $BaCO_3$ determined gravimetrically.

Nitrogen dioxide is absorbed into the Saltzman reagent. In the presence of nitrogen dioxide will result in a red coloration that will be read spectrophotometrically.

Nitrogen oxide is obtained by difference, ie the amount of nitrogen dioxide in the air is determined initially, according to the above method, then a new determination is made on a new air sample, after it has been passed - by bubbling - by a solution of 5% potassium permanganate in 5% sulfuric acid. In this way the oxide of nitrogen is converted into nitrogen dioxide and a new result will be obtained at the spectrophotometric reading.

3.3. Continuous methods of controlling atmospheric pollutants

As air pollution with toxic agents poses an immediate risk to employees as well as to the surrounding population, it is necessary to design and manufacture devices for the continuous control of the state of pollution of the atmosphere and workspaces.

This is to see on the one hand the exposure of organisms to the respective pests, and on the other hand to alarm and take the necessary measures for each situation.

In principle, such a device for continuous control consists of:

- a system of circulation, or absorption of air (gas).
- a transducer that converts the characteristic property of the pollutant concentration into an electrical or optical signal.
- an apparatus for measuring this signal.

For the field of refractory materials, continuous pollutant control systems are rather poorly presented, with widespread discontinuous control systems.

The use of continuous control methods must be introduced in the combustion furnaces, in the grinding drying mills, in the fine grinding mills, etc. Parameters used are flue gases (CO, CO_2, NO_x, dust).

3.4. Experimental methods for determining water pollution

For drinking water, which can become a very important vector in the injection of certain pollutants into human food, determinations are made according to standard 1342-71 for organoleptic properties, physical and chemical properties, radioactivity, bacteriological properties, biological properties.

Industrial wastewater includes wastewater resulting from various industrial processes (washing, cooling, etc.) as well as domestic wastewater.

Both categories must be treated.

The control of the purification degree is performed by determining certain parameters before and after purification:

a) Determination of oxygen content

The presence of organic substances in water and their influence on organisms is very important.

For fish mollusks, microorganisms, etc. from the aquatic environment the presence of organic substances in water is a food source without which they cannot exist.

Increasing the content of organic matter in water means on the one hand a higher standard of living for certain populations in the biocenosis.

But it also has a negative effect by the fact that organic substances, with a reducing chemical character, consume oxygen dissolved in water, which is also necessary for anaerobic organisms.

In other words, although the organic substances represent a food for the respective biocenosis, nevertheless, blocking another important environmental factor - namely oxygen - acts as a dangerous pollutant.

The content is determined according to standard 6536-82, the water content in dissolved oxygen is determined based on the oxidation reaction of dissolved manganese hydroxide Mn (OH) 2 in strongly alkaline solutions.

b) Determination of biochemical oxygen consumption

The concentration of dissolved oxygen still does not tell us about the risk of suffocation in the aquatic environment because the organic substances may be in greater quantities than they could be oxidized by the oxygen dissolved in water and then they could continue to block oxygen, even if I have air.

To determine this total oxygen requirement for the oxidation of organic substances there is a procedure to leave the samples at a sufficient time to perfect the biological decomposition.

This time, usually five days, is sufficient to improve the biological decomposition.

This time is perfected internationally, at 5 days, but the use of other incubation methods is not excluded.

In Romania, the determination of biochemical oxygen consumption after 5 days is done according to standard 6560-82.

c) Determination of chemical oxygen consumption

Determined according to standard 6954-84.

Chemical oxygen consumption (OCC) refers not only to the oxidation of organic substances but also to oxidizable inorganic substances.

Oxidation is done with potassium dichromate in an acid medium.

In the Romanian specialized literature this sample is symbolized CCO-Cr and in the international specialized literature COD (Chemical Oxygen Demand).

The determination of specific pollutants (detergents, ammonia) can be determined by classical or modern chemical methods (chromatography, spectrophotometry).

3.6. Technological control of pollution

The technological control of pollution refers to the totality of measures, methods and means of detecting polluting agents, as well as to the tasks incumbent on companies resulting from the legislation in force regarding the pollution resulting from the flows and the applied technology.

Technological control of pollution is quite closely linked to controls to ensure labor protection within companies.

Because of this, certain measures in the field of labor protection directly help to reduce environmental pollution.

Efficient technological control necessarily requires the existence of laboratories to perform physical and chemical analyzes essential for determining the concentrations of pollutants so that the measures can be applied operatively.

PART II
OWN EXPERIMENTAL RESEARCH ON THE POSSIBILITIES OF CONTROL AND REDUCTION OF DUST EMISSIONS IN ECONOMIC AGENCIES PRODUCERS OF SILICO-ALUMINOUS REFRACTORY MATERIALS AND VALORIZATION OF EARTHFUL WASTE.

Chapter 4. MEASUREMENT OF NOXIDANT QUANTITIES AND IDENTIFICATION OF DUST CONTROL AND REDUCTION SOLUTIONS TO AN ECONOMIC AGENT PRODUCING SILICO-ALUMINOUS REFRACTORY MATERIALS. Case study SC HELIOS SA Aștileu.

In this chapter of the doctoral thesis, are presented solutions for control and reduction of toxins for the company S.C. HELIOS S.A. Aștileu.

The paper was prepared based on documentation made on the spot, respectively of observations made in the field, based on technological data provided by the management of company, and based on the determinations of noxious substances discharged into the environment.

The effects of the activity of S.C. HELIOS S.A. Aștileu, as well as of the other studied companies, on the environment will be estimated depending on the pollutants emitted and which affect the quality of the environmental factors. [20, 21]

The recoverable products from the activity of this company are accompanied by emissions that are in gaseous, solid, and liquid form.

The reduction or elimination of these emissions is required by environmental legislation and is the basic condition for the continuation of technological processes, the solution currently practiced being generally the emission into the environment of noxious substances and significant quantities of raw materials.

4.1. General description of the analyzed company

The company S.C. HELIOS S.A. Aștileu is located in the northwestern part of the country, in Bihor county, 35 km from the city of Oradea, in the eastern part of the village of Aștileu, southeast of the town of Alesd.

The company's industrial waste dump is located at a distance of 500 m from the company's boundary to the town of Alesd, along the Crisului Repede valley in the eastern part of the village of Aștileu.

4.2. Description of production sections and technological processes

At present, the chamoting section no longer works, the unit using only refractory waste.

The methods of manufacturing building bricks are:

- Manufacture of construction bricks by pressing method.
- Manufacture of bricks and ceramic blocks by the wet method.

S.C. HELIOS S.A. Astileu operates at low capacity, however, managing in 2018 to produce a range of products required by the domestic market with several 350 employees.

The activity in this company is carried out on one shift (8 h/day), or two shifts / day depending on the production needs, five days / week, 280 days / year.

The raw materials used in 2018 are given in table 4.1.

Table 4.1. Raw materials used in the production of silico-aluminum refractory materials [21]

Assortment	Quantity consumed, t/an 2018
Butane gray argil	10.864,771
Argil Groza sort I	10.025,203
Argil Groza sort II	1.520,051
Red argil	19.685,857
Refractory waste	7.131,320
Red waste	4.895,162
Sand	1.784,995
Novolac	0,867
Intensifier	0,485
Micronized argil	621,131
Feldspart	111,164
Sawdust	1.051,447
Calcined diatomitis	24,056
Sodium silicate	23,087

The products manufactured in 2018 are given in table 4.2.

Table 4.2. Ceramic and refractory products manufactured by the economic operator analyzed [21]

Assortment	U.M.	Designed capacity, t/an	The production obtained, t/an 2018
Refractory bricks	t / an	105.000	10.238,357
Silica - aluminous	t / an	-	18.693,494
Red brick	t / an	-	574,174
Antacid tiles	t / an	-	8.573,387
Ceramic blocks	t / an	-	36,650
Film-coated sand	t / an	27.000	19,110
Thermal insulation boards	t / an	-	352,214

4.3. Description of the waste dump

The total area of the dump is 27,839 sqm. The dump has a length of 1,150 m and an average height of 8.5 m with a slope of 60^o. The large base of the dump is on average 18 m, and the small base is on average 12 m. The volume of waste stored is approx. 150,000 m^3.

Between 1948-1992 (44 years old) approx. 147,600 m^3 of industrial waste was stored. Of these approx. 70% is the ash resulting from the burning of coal and coal slag from the gas gasogen preparation section, the remaining 30% is refractory waste that could not be reused in the manufacturing process as well as other waste.

Since 1992, because of the abandonment of the use of gasogen gas as a fuel and its replacement with fuel oil, the biggest problems with pollution due to tar gases resulting from the process of transforming coal into gasogen gas, have been removed. After the start of the production of construction bricks and later of the ceramic blocks, in the waste dump approx. 300 m^3 of sterile argile, resulting from the impurity of red argile.

In the last 10 years,wa stored approx. 3,000 m^3 of sterile dump. From the above data it results that only 16% of the total volume of waste was deposited in this landfill.

Taking into account the characteristics of the dump, respectively the tank climbing ramp, the turning radius, a maximum storage capacity of 175,000 m^3 is estimated. At a maximum storage volume of 1,000 cubic meters / year, the maximum capacity of the landfill would be reached in a maximum of 25 years.

Sterile argile resulting from the impurity of red argile is transported to waste dumps.

The dump occupies an appreciable area of land, the area removed from the agricultural circuit. The materials in the dump are an important source of pollution because the fine ones can be easily entrained by the wind. Acidic materials, poor in nutrients, can contribute over time to the impoverishment of the soils on which they are deposited.

From the industrial activity carried out in the company in 2018 resulted important quantities of waste (table 4.1.), A part of them being delivered to other companies for recovery, another part being deposited on the waste dump.

Table 4.3. Quantities of waste resulting in 2018 at the analyzed economic agent [21]

The type of waste	**Quantity**	**UM**
Ferrous waste	168,040	T
Non-ferrous waste	2,09	T
Used tires	74	Piece
Worn batteries	24	Piece
Waste refractory materials	496,03	T
Waste red building materials	3.772,24	T
Used oil	0,639	T
Sludge from water treatment	10,0	T
Industrial waste in the form of rubble	550,0	T

The technological processes that take place in the manufacture of refractory and construction materials produced by SC Helios SA Aștileu, are accompanied by significant dust releases, which lead to exceeding the maximum concentrations allowed for both total powder and sedimentary powder. The main cause that leads to this situation is the failure of existing dusting equipment, damage or lack of housings related to dust generating equipment, physical and long wear of technological equipment, etc.

4.7. Conclusions of the case study at the analyzed economic agent

The effects of industrial activity in the refractory products sector on the environment can be estimated depending on the pollutants emitted, pollutants that affect in various ways the quality of environmental factors.

The exploitabled products resulting from the activity of these companies are accompanied by emissions that come in solid, liquid and gaseous form.

The reduction and / or elimination of these emissions is imposed by the continuation of the productive processes, the solution currently practiced being most of the times the evacuation in the environment of large quantities of noxious substances and large quantities of raw materials.

The main environmental factors affected by the interaction with these emissions are air, water, soil, vegetation, and of course human beings both as a result of direct pollution in the area and due to air, water, soil pollution.

The industry producing refractory materials, along with other industries: construction materials, metallurgy is energy-intensive and polluting.

The main environmental factor affected is air and the main noxae generated is dust. Regardless of the physico-chemical characteristics of each type of powder, their presence beyond the limits imposed by current legislation is an important alarm signal both for those responsible for the production processes and the entire population.

Chapter 5. EXPERIMENTAL RESEARCH ON THE RECYCLING OF FINE-GRANULATED REFRACTORY WASTE IN THE PRODUCTION OF HEAT-RESISTANT CERAMIC BLOCKS

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 fairly 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 despite to the fine fraction (0.02-0.002 mm), because a too high proportion of fine, determines a decrease of the mechanical resistance with deformation effect of the ceramic block core. [37,38]

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 densifying the product, a decrease of the porosity, therefore a lower water absorption.

Following a maximum compaction, another 6 variants of variation of the percentages of refractory waste, 28 A, presented in figures 5.6-5.11 were tried.

Fig. 5.6. Sample test nr.1

Fig. 5.7. Sample test nr.2

Fig.5.8 Sample test nr.3

Fig.5.9 Sample test nr.4

Fig.5.10 Sample test nr.5

Fig.5.11 Sample test nr.6

In table 5.4 the chemical compositions of the raw materials are presented, and Table 5.5 shows the manufacturing recipes.

Table 5.4. 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	3,0	-	-	60,0	-	-	-
Cement	20,73	5,32	4,91	61,36	1,98	0,47	0,93

Table 5.5 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	-

Determining the physical characteristics of the resulting products, the values recorded in table 5.6 were obtained.

Table 5.6. Results of determining the physical properties of recipes 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.

Because 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 S.C. CCPPR S.A. Alba Iulia [12].

The location of the equipment does not undergo any change compared to the existing one at present, the flow of raw materials being the one indicated in figure 6.1.

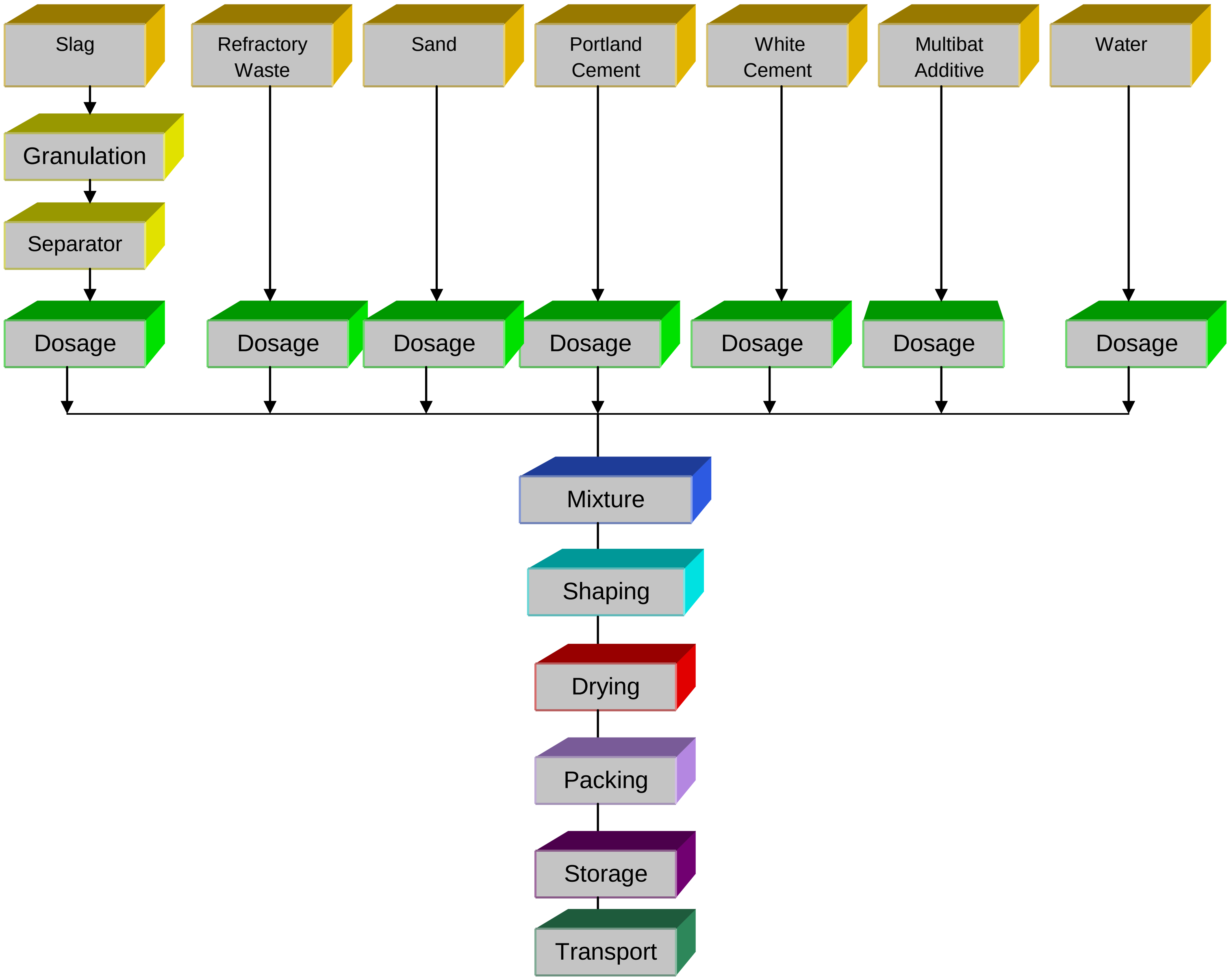

Fig. 6.1 Technological flow for the production of heat-resistant ceramic blocks using refractory waste

Figure 6.2 shows the ceramic blocks obtained without refractory waste in the manufacturing recipe, and in figure 6.3 ceramic blocks obtained using refractory waste in the manufacturing recipe.

	
Fig.6.2. Ceramic blocks without refractory waste in the manufacturing recipe	Figure 6.3. Ceramic blocks obtained using refractory waste in the manufacturing recipe

6.4. 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, considering the products currently manufactured on the technological flow from S.C. CCPPR S.A. Alba Iulia.

The average results corresponding to the two types of products were notified and in accordance with the regulations imposed by the Romanian standards, the results were tabulated.

In tables 6.5 and 6.6 can be compared the production characteristics of the standard ceramic blocks, without refractory waste and of the batch produced at S.C. CCPPR S.A. Alba Iulia using refractory waste.

Table 6.5. Comparative presentation of the physico-chemical properties of ceramic blocks, products 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 6.6. Comparative presentation of the dimensions of ceramic blocks, products 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 hardening is better.

Regarding the use of slag, its fairly 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 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 ceramic block used in construction.

7.1. Economic aspects regarding the manufacture of ceramic blocks using refractory waste in the recipe

Referring to the recipes for the manufacture of ceramic blocks according to the work and the products made at S.C. UNIREA MATCONS SCHELA S.A. Tg.Jiu, the cost price was established for the two types of products.

The cost price of raw materials is shown in table no.7.1.

Table 7.1. Cost price of raw materials used in the manufacture of ceramic blocks

Raw material	Price, Ron/t	Value, Ron/t			
		Ceramic block produced at S.C. CCPPR S.A. Alba Iulia		Ceramic block produced at S.C UNIREA S.A. Târgu Jiu	
		%	Ron/t	%	Ron/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 batch SC CCPPR SA Alba Iulia) and without refractory waste in the manufacturing recipe S.C. UNIREA MATCONS SCHELA S.A. Targu Jiu, is shown in table 7.2.

Table 7.2. 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 S.C. CCPPR S.A. Alba Iulia	**Ceramic block produced at S.C. UNIREA S.A. Târgu 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, ron /t	950.0	935.0
Delivery price, ron /piece	3.63	3.50

From table 7.2. it is observed that the cost price of the product proposed in accordance with the technology proposed in this paper is about 15 ron /ton (0.13 ron/piece) higher than the one currently manufactured on the flow from an economic agent producing ceramic blocks S.C. UNIREA MATCONS SCHELA S.A. 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 involves another aspect, which is 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.

This waste can no longer be reused in the refractory field due to impurities (slag) remaining from the furnaces or steel equipment to which it was built. 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.

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 fairly 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 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 achieve for a ceramic building block.The environmental effects of refractory waste recycling are obvious and extremely important.

C. FINAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE RESEARCH DIRECTIONS

C.1. Summary final conclusions

The proposed theme of the doctoral thesis was, the design and realization of a new technology that would allow the manufacture of ceramic blocks at S.C. CCPPR S.A. Alba Iulia, using in the recipe of raw materials, refractory waste generated at S.C. Helios S.A. Aștileu.

The doctoral thesis addressed first of all the identification of the types of pollutants generated in the economic activity of an economic agent producing ceramic and refractory materials, the identification of pollutant emission sources, the quantities of pollutants, the finding of real solutions to reduce pollutant emissions, and secondly, the completion of a technology that allows the recovery of recyclable waste from the refractory materials industry with the production of new construction materials, which can be used successfully in civil or even industrial construction.

The refractory industry is cited as a polluting industry.

The most important noxaes encountered in this field are dust, flue gases, waste resulting from technological processes.

The refractory materials industry differs quite a lot from the other sectors of the ceramic industry.

The field of silico-alumina refractories studied in this doctoral thesis is somewhat related to that of construction bricks for mixture-pressing-combustion flows, as well as to that of cement production, especially in the flow part of obtaining chamotte.

The most important component of pollution in this area is that of dust removal. Emissions and dust imissions from technological processes of manufacturing refractory products take a very important form because they contain free crystalline silicon dioxide or heavy metals.

Obtaining silico-alumina refractory materials involves the use of raw materials with a high content of free silicon dioxide, which is particularly harmful to human health.

In the first part of our own research conducted to meet the objectives of the doctoral thesis was conducted a case study on identifying sources of pollution in an economic agent producing refractory materials and ceramics.

The case study aimed to identify the types and quantities of pollutants, as well as to identify solutions to reduce pollutant emissions by improving technological flows, by introducing special facilities for capturing and neutralizing pollutants emitted into air, water and soil.

Technological control of pollution refers to all measures, methods and means of detecting pollutants, as well as to the tasks of companies resulting from the legislation in force regarding the pollution resulting from the flows and the applied technology.

Technological control of pollution is quite closely linked to controls to ensure labor protection within companies.

Because of this, certain measures in the field of labor protection directly help to reduce environmental pollution.

An efficient technological control necessarily requires the existence of laboratories to perform the physical and chemical analyzes essential for determining the concentrations of pollutants, so that the measurements can be applied operatively.

The specificity of the industrial activities in the branch producing refractory materials generates powder, as the main pollutant emitted into the atmosphere.

These powders are captured by various technological installations and only a small part is emitted in a controlled way into the atmosphere, through chimneys.

It is found that the dust removal equipment did not work at the designed parameters, due to physical wear and tear and service life.

There are also significant amounts of dust that are emitted due to leaks, lack of doors, windows, due to natural ventilation of production halls, but also due to malfunction of dusting equipment.

From the analysis of the soils and the measurements carried out on the soils of the company's vacancy, it appears that they have not undergone any essential structural or chemical changes.

Dust pollution being the most important factor of society does not affect the soil or vegetation, it affects over time the health of people producing occupational diseases such as fibrosis and silicosis.

Also, even if it does not reach occupational diseases, it affects health by generally decreasing the immunity of human bodies.

The dusts emitted by the refractory production companies are largely (70%) large dusts, with diameters of 0.1-1 mm and they are deposited in the immediate vicinity of the emission sites. The suspended powders have small diameters of up to 20 microns, so we can consider that a relatively small fraction of the powders with diameters between 0 - 0.5 mm is the suspended powders.

As a result of the determinations made, it was found that the largest amount of dust is released into the atmosphere in the sector of grinding, granulation, dosing, mixing, pressing and pneumatic transport. It is found that the dust removal equipment did not work at the designed parameters due to physical and moral wear.

Consequently, it is necessary to execute some technical projects for the modernization of the dedusting installations, of the technological flows, to follow the connection of all the noxious generating equipment to the capture installations.

The category of solid waste identified at S.C. Helios S.A. Aştileu, is represented by the silico-alumina refractory powders captured in the treatment plants and, by the small residue of refractory material resulting from the shaping of the products manufactured by this company.

Continuing our own experimental research within the doctoral thesis, the objective was to establish a technology for capitalizing on refractory waste by introducing it in the manufacturing recipes of construction materials such as ceramic blocks.

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

The main objective of the research was the waste of refractory bricks, which, in a small proportion, are resumed in the technological flows in the refractory sector, but a large part can be recovered in the construction materials sector.

Following the study carried out in this paper, respectively, based on the results obtained, it was concluded that this type of construction material - ceramic blocks - is very suitable for construction of: interior masonry for houses, industrial halls, hot gas chimneys from burning industrial processes or thermal power plants, other places that do not come into direct contact with aggressive agents (moisture, acids, etc.).

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 fairly 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, a too high 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.

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.

But the particle size distribution should not be neglected. In this sense, the coarse fraction (2.5-0.2 mm) is preferred instead of the fine one (0.02-0.002 mm), because a too high proportion of fine, determines a decrease of the mechanical resistance with the effect of core deformation ceramic block.

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 densifying the product, a decrease of the porosity, therefore a lower water absorption.

Following a maximum compaction, another 6 variants of variation of the refractory waste percentages, 28 A, were tried.

Analyzing the results, the recipe R5 for the manufacture of the ceramic block was chosen, based on which an experimental batch of ceramic blocks was manufactured, which were tested in terms of quality and proved to be appropriate.

From an economic point of view, the recycling of refractory waste is technologically possible, analyzing the costs and benefits.

The effects are also noteworthy.

The cost price of the product proposed in accordance with the technology defined in the doctoral thesis, is 15 ron/ton (0.13 ron/piece) higher than the one currently manufactured on the flow from an economic agent producing ceramic blocks S.C. UNIREA MATCONS SCHELA S.A. Târgu Jiu, while its characteristics are better, obtaining higher durability (double resistance in frost-thaw conditions). This justifies the delivery price, and the proposed solution is economically advantageous.

At the same time, the use of refractory waste implies another aspect, which is related to environmental protection, by capitalizing on some wastes that do not find a rational reuse in the economic circuit.

This waste can no longer be reused in the refractory field due to impurities (slag) remaining from the furnaces or steel equipment to which it was built.

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.

The environmental effects of refractory waste recycling are obvious and extremely important.

C.2. Personal, original contributions

The research undertaken within the doctoral thesis aimed at establishing a technology for the recovery of solid silico-alumina waste resulting in the activity of producing ceramic materials and refractory to specialized economic agents.

The topic of the doctoral thesis was proposed and accepted in order to identify pollutants emitted into air, water, soil, to find solutions to reduce emissions to the production of ceramic and refractory materials, but also to design and finalize a technology to recycle waste silico-alumina dusts in the manufacture of refractory products corresponding to the requirements imposed by the current requirements of the beneficiaries in the construction materials industry.

To fulfill the committed objective of the doctoral thesis, during the doctoral internship I performed scientific documentation activities, laboratory experiments and experiments on pilot installations, I collaborated with researchers and specialists from SC CCPPR SA Alba Iulia, SC Helios SA Aștileu Oradea, University POLITEHNICA from Bucharest - Faculty of Materials Science and Engineering, with specialists from the metallurgical sector, the ceramics industry, refractories, etc.

The original, own contributions made in the doctoral thesis are supported by the following activities:

1. We conducted a documentary study based on the literature on the types of pollutants emitted in water, air, soil in the production of ceramic and refractory materials, as well as the harmful influences that these pollutants have on the environment, vegetation, animal kingdom and not in last line on people's health.

2. We carried out a documentary study of the current situation regarding the possibilities of control and reduction of pollution at the dispersion chimneys of the economic agents producing silico-aluminum refractory materials.

3. We have carried out our own research at an economic agent producing ceramic and refractory materials, finalized with the measurement of the quantities of noxious substances and the identification of solutions for control and reduction of dust emissions at an economic agent producing silico-alumina refractory materials, the rules imposed a case study at S.C. HELIOS S.A. Aștileu Oradea.

4. As a result of identifying the important quantities of silico-alumina dusty waste generated as a result of the economic activity of the company S.C. HELIOS S.A. Aștileu, Oradea County, we carried out experimental research for recycling this waste with the production of heat-resistant ceramic blocks.

The research was carried out within the Refractory Design and Production Research Center in Alba Iulia. Within this research we studied types of possible raw materials used for the preparation of recipes that include different proportions of refractory waste collected from S.C Helios S.A. Aștileu, and from S.C. CCPPR S.A. Alba Iulia.

We studied several manufacturing recipes that led to obtaining 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 analyzes of the manufacturing recipes and of the characteristics of the heat-resistant ceramic blocks obtained, we determined the optimal recipe.

5. Based on this optimal recipe we obtained, with the support of researchers from SC CCPPR SA Alba Iulia, a pilot batch of ceramic blocks, we performed experimental research using the equipment from S.C. CCPPR S.A. Alba Iulia for the physico-chemical characterization of the manufactured batch.

6. We have carried out on the basis of the data from the finalized manufacturing technology an economic analysis to establish the cost price of the products made, proving that these products fall within the manufacturing costs that allow them to be marketed.

7. We made the specifications that complete the designed technology, confirmed both technologically and economically.

The main objectives of the thesis were reflected in articles and papers presented at symposia and published in specialized journals. The research results were presented, discussed and approved at a series of specialized scientific forums.

C.3. Future directions for the development of research in the doctoral thesis

1. The experimental research carried out in the doctoral thesis allowed the identification of solutions to reduce pollution at the emission source.

It is considered necessary to purchase modern equipment to capture and neutralize pollutants before they are emitted into the atmosphere, or in the groundwater as wastewater.

2. Further research is needed in order to modernize the manufacturing technologies of ceramic and refractory materials, so that the quantities of waste are minimized and fully recycled.

3. It is necessary to continue the experimental research with the realization of manufacturing recipes as diverse as possible in which the share of recycled waste is as high as possible.

4. It is recommended to continue experimental research with recipes containing recycled waste and leading to the obtaining of other required products on the market of construction materials or the metallurgical industry.

5. It is necessary to monitor the exploitation in the beneficiaries of ceramic and refractory products made from raw materials that also contain recycled waste, so that, through the obtained results, it is possible to return, if necessary, to improve the manufacturing networks.

DISSEMINATION OF THE RESULTS FROM THE DOCTORAL THESIS

Papers published in journals in the field of the thesis:

1. **Elisa–Florina PLOPEANU**, Cristian PANDELESCU, Nicolae CONSTANTIN, Elena Madalina VLAD, Radu Vasile BUZDUGA, Dorica MIRON BUZDUGA; Identification of pollution sources and types of pollutants in an economic agent producing refractory materials, ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering, Tome XVIII [2020] | Fascicule 3 [August], pag 99-106, indexata B+, BDI, http://annals.fih.upt.ro/indexes.html
2. C. Mititelu, M. Hritac, N. Constantin, **E.-F. Plopeanu**, A. Ioana, M. Ciurdas, C. Pandelescu, Analysis of the recycling possibilities of ferrous waste with small granulation in cupolas furnace, U.P.B. Sci. Bull., Series B, Vol. 82, Iss. 3, 2020 ISSN 1454-2331, pag 221-230 , **indexata ISI**, **WOS:000610098500019**
3. Marian Simion Stratescu, Nicolae Panait, **Elisa-Florina Plopeanu**, Mariana Ciurdaș, Analysis of the possibilities of transformation a used industrial oil in general use grease; U.P.B. Sci. Bull., Series B, Vol. 82, Iss. 3, 2020 ISSN 1454-2331, pag 261-270, **indexata ISI, WOS:000610098500022**
4. Cristian PANDELESCU**, Elisa–Florina PLOPEANU**,Nicolae CONSTANTIN, Elena Mădălina VLAD; Remedy by reconditioning the metal parts defects from the component of pumping aggregates; ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering, Tome XVIII [2020] | Fascicule 2 [May], pag 169-175, indexata B+, BDI, http://annals.fih.upt.ro/indexes.html
5. Cristian PANDELESCU, **Elisa-Florina PLOPEANU**, Nicolae CONSTANTIN, Elena Mădălina VLAD; Analysis of the current situation concerning the duration of use and the main defections of the pumping aggregates, ACTA TECHNICA CORVINIENSIS – Bulletin of Engineering [e–ISSN: 2067–3809], TOME XIII [2020] | FASCICULE 2 [April – June], pag 147-152, indexată B+, BDI , http://acta.fih.upt.ro/index.html
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7. **Elisa-Florina PLOPEANU,** Radu Vasile BUZDUGA, Nicolae CONSTANTIN, Bogdan FLOREA, Experimental research on the recycling of fine-granulated refractory waste in the production of heat-resistant ceramic blocks, ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering, Tome XVIII [2020] FASCICULE 4,pag. 74-82 indexata B+, BDI , http://annals.fih.upt.ro/indexes.html
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Papers submitted and accepted at ISI and BDI indexed journals, being published in the thesis field:

1. E M Vlad, V E Caloian, C Pandelescu, **E F Plopeanu**, V Oancea, V Rucai, N Constantin and M Hritac, Experimental research on the effect of additives on the sintering process of alumina-based refractory materials, Conferinta Internationala, International Conference on Applied Sciences – ICAS 2020, May 22, 2020, Hunedoara, Romania, indexata ISI, http://icas.science/forms/Program_ICAS2020.pdf

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STAS 10331/1992- Privind principii și reguli generale de supraveghere a calității aerului;

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[6] ***HG 152/2018***- Privind prevenirea, reducerea și cotrolul integrat al poluării;

[7] ***Ordinul 462/1993***- Pentru aprobarea condițiilor tehnice privind protecția atmosferei și norme metodologice privind determinarea emisiilor de poluanți atmosferici;

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