

DUNAREA DE JOS" UNIVERSITY OF GALATI
Doctoral School of Fundamentals and Engineering Sciences



PHD Thesis Summary

CONTRIBUTIONS ON THE VALORIZATION IN THE CERAMIC MATERIALS INDUSTRY FOR GLAZES OF METAL IONS EXTRACTED FROM SLUDGES RESULTING IN THE METAL COATING PROCESSES

Phd student,

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PhD Supervisor,

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Series I 5: Materials Engineering No 17

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KEYWORDS

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INTRODUCTION

Industry is a fundamental part of modern society, the production of industrial waste in significant quantities being the inevitable result of development activities in recent years. Among the most dangerous inorganic pollutants for the environment, heavy metals from anthropogenic sources which are found in certain categories of waste, play a special role. Heavy metal pollution has been a major global problem since the early 1970s due to its extremely toxic effect even at low concentrations. One of the biggest risks for the environment is the ubiquity of heavy metals due to toxicity, persistence and lack of biodegradation.

Heavy metals are discharged into the environment from several industrial activities, such as surface treatments and metal coatings, metallurgy, mining, textiles or electronics industry. The metal surface treatment is one of the most hazardous areas of industry. This activity requires the use of hazardous chemicals which are subsequently discharged in the form of technological solutions and wastewater containing heavy metals such as chromium, iron, copper, cadmium, nickel, zinc, as well as organic solvents, cyanides, acids, bases. All these wastewater containing heavy metals, cyanides, are treated together, resulting a sludge with a complex chemical composition, which is a mixture of hydroxides of the following heavy metals: copper, iron, nickel, chromium, cadmium and zinc. Due to its chemical composition, this type of waste is classified as an ecotoxic hazardous waste because it contains substances that present immediate or delayed risks to the environment. Galvanic sludge can be an important source of secondary raw materials, especially valuable metals, used to replace natural resources [1-6].

The speciality literature specifies the following processes for neutralization and recovery of galvanic sludge, namely: sludge incorporation/inertization processes (implicitly of hazardous heavy metals) into stable matrices and valuable components extraction processes (metal ions) and their recovery in various industries.

Based on these considerations, glass and glass-ceramic materials can be made using hazardous waste containing incorporated metals, whose physico-chemical and mechanical properties recommend them as very stable, so they can be used in the construction materials industry. Vitrifying as such or together with other raw materials is a promising technological solution because organic pollutants can be destroyed at high temperatures (dioxins and furans are transformed into carbon dioxide and water), glass matrix incorporates heavy metals in its structure. Recent research of the hazardous or toxic waste inertization by vitrification has focused, in particular, on obtaining useful products such as: glazes for decorative ceramics, glass fibers, cellular glass, decorative glass, paving slabs, floors, aggregates for roads etc.

The Ph.D. thesis entitled "**Contributions on the valorization in the ceramic materials industry for glazes of metal ions extracted from sludges resulting in the metal coating processes**" addresses a current issue concerning the reduction of the negative impact of sludge with a complex chemical composition (in particular heavy metals) resulting from the treatment of waste water from metal surface coating processes by extraction of metal ions and their use as heavy metal compounds in the ceramic glazes manufacture.

The main objective of the research was to obtain useful compounds, through selective extraction processes specific to each compound, which can be reintroduced into the economic circuit in the form of metal hydroxides or salts in stable vitreous matrices such as ceramic glazes, thus achieving the detoxification of hazardous sludge.

The specific objectives aimed the synthesis and characterization of pigments based on metal ions selectively extracted from galvanic sludge and the obtaining, characterization of glazes for decorative ceramic materials, colored with the studied pigments.

The experimental researches carried out in order to achieve the objectives of the thesis were carried out in the laboratories of the National Research and Development Institute for Environmental Protection Bucharest (INCDPM) and in the laboratory of the Center for Research and Eco-Metallurgical Expertise (ECOMET), University POLITEHNICA of Bucharest and "Dunărea de Jos" University of Galati.

The doctoral thesis is structured in 6 distinct chapters as follows:

Chapter 1 entitled "***Current state of knowledge on the metal ions extraction from sludges resulted in metal coating processes and their valorization in the ceramic materials industry for glazes***", presents the current state of knowledge on the recovery of metal ions extracted from galvanic sludge in the ceramic materials for glazes. The liquid and solid waste resulting from the metal coatings processes are presented, as well as the current stage regarding the extraction and recovery in various industries of metal ions extracted from galvanic sludge. Notions on decorative ceramics, obtaining and characterizing glazes as well as the toxicity of heavy metals and their compounds are also presented.

Chapter 2 entitled "***Materials, methods and experimental procedures***", is an introduction to the experimental research section of the doctoral thesis. The chapter summarizes all the elements related to the conditions for conducting experimental studies: the raw materials used to obtain ceramic materials, their chemical and structural characterization, reagents used, as well as methods of analysis, experimental procedures and investigation means used for physical, chemical, thermal and structural of the obtained materials characterization are presented.

Chapter 3 entitled "***Experimental research on the selective extraction of metal ions from galvanic sludges in order to obtain pigments***" presents experimental research on the methods of selective extraction of chromium and iron metal ions from galvanic sludge and establishing optimal technological parameters extraction temperature (reaction temperature, reaction time, excess reagent versus stoichiometric consumption). The aim was to obtain the highest possible metal extraction yields. The research results highlighted the following metal extraction yields between: 84.20% - 93.19% for chromium and 95.20% - 98.5% for iron.

Chapter 4, entitled "***Experimental research on the synthesis and characterization of some chromium and iron pigments extracted from galvanic sludges***", contains experimental research on the synthesis of pigments based on metal ions extracted from galvanic sludge. The pigments obtained in the experiments are hydroxides/salts of heavy metals, such as trivalent chromium, hexavalent chromium and trivalent iron, namely: chromic hydroxide - green chromium pigment $[\text{Cr}(\text{OH})_3]$, lead chromate - yellow chromium pigment (PbCrO_4), barium chromate - yellow chromium pigment (BaCrO_4) and ferric hydroxide - red-brown iron pigment $[\text{Fe}(\text{OH})_3]$.

X-ray fluorescence spectrometry (XRF) was used in order to determine the oxidative chemical composition of the pigments synthesized from galvanic sludge. The structural analysis of the pigments and their purity were determined by X-ray diffraction (XRD) analyzes. The stability of the pigments at high temperatures was studied by simultaneous thermal analysis TG/DSC. The pigments characterization before and after their heat treatment was performed by Scanning Electron Microscopy method (SEM), since the compositional variety of the synthesized inorganic pigments as well as the different process of their extraction from sludge led to various microstructures.

In **Chapter 5 "Experimental results on the obtaining and characterization of colored glazes for decorative ceramic materials by using the studied pigments"**, experimental researches on obtaining colored glazes for decorative ceramic materials using studied pigments are presented. Various quantities of pigments introduced into the composition of different glazes (opaque and transparent) were used. The structural characterization of heat treated glazes was performed using various methods such as: X-ray diffraction (XRD) and scanning electron microscopy (SEM). The appearance of the sample surfaces after heat treatment was analyzed by optical microscopy (OM) method. The chapter also addresses the issue of solidified glazes toxicity, which are subjected to stability tests under different conditions. Leaching tests to check the toxicity of glazed ceramic samples and tests to determine the lead and cadmium given off by glazed ceramic samples were performed. The obtained results indicated a good stability of the analyzed ceramic samples and highlighted the fact that the metals were fixed in the glass structure of the solidified ceramic glaze with fixing yields of over 99%.

Chapter 6, entitled **"General conclusions, original contributions and perspectives"**, presents the general conclusions resulting from the research carried out and highlights the original contributions to solving and develop the thesis research theme, as well as the perspectives and new research directions.

The dissemination of the obtained results was achieved by participating in various scientific events, especially national and international conferences, organized in the field of the studied topic. The author has published some of the experimental results in specialized journals indexed in international databases (BDI), ISI Proceedings volumes and WoS (Web of Science) indexed journals.

CHAPTER 1. CURRENT STATE OF KNOWLEDGE ON THE METAL IONS EXTRACTION FROM SLUDGES RESULTED IN METAL COATING PROCESSES AND THEIR VALORIZATION IN THE CERAMIC MATERIALS INDUSTRY FOR GLAZES

1.1. Waste that may result in the flow of metal coatings

Metal surface treatment processes lead to the generation of two main types of hazardous waste:

→ liquid waste: from pickling, degreasing, treatment and washing baths and depleted technological solutions;

→ solid waste: sludge resulting from the treatment of liquid waste, various solid waste from surface pre-treatment, anodic sludge, etc.

1.3. Heavy metal sludge forming as a result of wastewater treatment

Among the treatment processes of wastewater resulting from the metal coating activity, chemical precipitation requires a large quantity of chemicals in order to reduce the metals concentration to an acceptable level for discharge. One of the disadvantages of the process is the generation of large quantities of ecotoxic sludge, with complex chemical composition (a mixture of water, soluble salts, process additives and especially metal species) that require neutralization/detoxification treatments for disposal.

1.5. Studies on heavy metals extraction methods from galvanic sludge

1.5.2. Hydrometallurgical methods for the extraction of heavy metals from galvanic sludge

The hydrometallurgical methods used for heavy metals extraction are based on leaching (solubilization of metal ions) in acidic or alkaline solutions, followed by selective separation of metals from these solutions by solvent extraction methods, electrochemical methods and appropriate precipitation processes. One of the most studied techniques for heavy metals (chromium, copper, iron, zinc etc.) recovery from galvanic sludge is the recovery technique by acid solubilization with sulfuric acid [143,144] or hydrochloric acid and precipitation, obtaining good yields of recovery, or by solubilization in acid-ammoniacal and combined medium, alkaline medium and acidic medium [145,146].

1.6. Recovery of metallic compounds from galvanic sludges as pigments in the ceramic industry for glazes

1.6.3. Stages of ceramic products manufacture

The process of ceramic product manufacturing generally includes the following steps: preparation of raw materials (dries or wets), modeling, drying, grinding, decorating, glazing and firing. The firing of traditional ceramic products can be done either in a single stage (single firing) or in several stages (double, triple firing).

1.6.4. Ceramic body behavior in progressive heating

In the firing process of a ceramic mass, the material undergoes both exothermic and endothermic transformations. In order to avoid the appearance of permanent defects in the final product, they must take place gradually and in a controlled manner. After firing, physical, chemical and mineralogical transformations occur in the ceramic mass, which are irreversible and confers them an increased resistance [165].

1.6.6. Factors influencing the action of chromium and iron pigments in ceramic glazes

For the use of chromium and iron compounds as pigments in the coloring of ceramic glazes, their compatibility with glaze and, implicitly, with the firing temperature, is very important. The color and quality of the solidified glaze depends on several factors: the composition of the glaze, the proportion of oxide in the glaze mass, the action of the pigments, the firing temperature, the firing atmosphere of the oven, the sample color of the raw ceramic material, the type of glaze structure (crystalline or amorphous).

1.6.7. Current state of the pigments synthesis from galvanic sludges and their recovery in the ceramic industry for glazes

In recent years, various methods for pigment synthesis from high metal ion containing sludges were described in the specialty literature, such as: green and pink pigments synthesized from high-chromium galvanic sludge [169]; black pigments for ceramics based on chromium-iron-nickel-black spinel $(\text{Ni,Fe})(\text{Fe,Cr})_2\text{O}_4$, by using galvanic sludge as a source of nickel and chromium and sewage sludge from wire production as a source of iron [170]; red pigment synthesized from sludge resulting from the neutralization of spent acid pickling solutions [171]; red, green, pink ceramic pigments synthesized from sludge from various metal coating processes and having high aluminum and chromium content and tested in ceramic glaze [167]; red-brown and black pigments obtained from high chromium and iron sludge resulting from the treatment by electrocoagulation of wastewater from metal coatings and tested in transparent ceramics [172]; gray-black ceramic pigments synthesized from sludge resulted from chromium/nickel/cooper metal coating activities [173], yellow and brown pigments obtained from metallurgical dust and tested in glazes and angobes [174]. The latest

research in the field has focused on the synthesis of ceramic pigments from tannery wastewater treatment sludge [175-177].

1.7. Toxicity of chromium and iron and inorganic pigments based on chromium and iron.

1.7.6. Toxicity of glazes with chromium and iron pigments synthesized from galvanic sludge

According to the specialty literature, almost all ceramic products, especially those decorated with colored glaze with pigments recovered from galvanic sludge or other similar waste, contain heavy metals in various concentrations that may pose a danger to human health and the environment [207]. This is due to both the composition of the glazes and the pigments used.

Ceramic materials and articles, in particular those that may come into contact with food, are subject to specific legislation at European Union level (Council Directive 84/500 / EEC as amended by Directive 2005/31/EC) which requires specific limits on potential emissions of hazardous substances. For ceramics, there are limits for lead (Pb) and cadmium (Cd) [207, 209].

1.8. Partial conclusions

Galvanic sludge contains, in various concentrations, a variety of potentially valuable and commercially important elements, such as chromium, nickel, cobalt, copper, zinc, cadmium, but also impure elements without commercial value such as iron and calcium, which must be eliminated because they would contaminate valuable recovered products.

Several studies on the sludge neutralization and recovery by incorporating/inerting them into stable matrices are reported in the specialty literature, as well as studies on various technologies for metals extraction, based on hydrometallurgical, pyrometallurgical or two combined methods and their valorization in various industries.

Metal oxides recovered from galvanic sludge can be used as pigments for coloring ceramic glazes, studies on both obtaining pigments from hazardous industrial waste and studies on the use of these pigments in the ceramic industry are described in the specialty literature.

CHAPTER 2. MATERIALS, METHODS AND EXPERIMENTAL PROCEDURES

2.1. Overview

Chapter 2 presents the used materials (galvanic sludges, chemical reagents, pigments, glazes), their preparation for experiments, as well as their physico-chemical and structural characterization. Also, the methods and procedures for investigating the raw materials used and the obtained materials, laboratory equipment and other equipment necessary for conducting experimental research are presented.

2.2. Materials and equipment used for metal ions extraction

2.2.1. Galvanic sludge

For the experimental studies, two types of sludges resulting from wastewater treatment from various chemical and electrochemical surface finishing processes, were used, shown in Figure 2.1 a, b.

- Fresh sludge (sample code: **N1**), collected from the treatment, by the Lancy type process, of wastewater (washing water and used technological solutions) resulting from a surface coating plant using electrolytic processes for the corrosion protection of metals, from Romania
- Stored sludge (sample code: **N2**), collected from a decanter of a decommissioned treatment plant, originate from the physico-chemical treatment of wastewater (washing water and wastewater solutions) derived from various metal surfaces coating processes (zinc plating, copper plating, cadmium plating etc.). The sludge was stored for over 20 years in the decanter.

2.2.2. Chemical reagents used for metal ions extraction

Analytical reagents, having the role of neutralizing, oxidizing or solubilizing agents, were used in order to perform the metal ions extraction experiments from galvanic sludge

2.2.3. Description of the experimental installation for metal ion extraction

For chromium and iron ions solubilization and extraction, an experimental installation was designed, composed of the following elements:

- water bath, GFL Model, thermoregulable, equipped with graduated temperature regulator and sensor for each hole, placed in a chemical niche
- Berzelius glasses with a capacity of 1000 mL for samples
- agitators located on stands with clamp

→ thermometers for temperature control in order to establish the optimal parameters for extraction

2.3. Preparation of sludge for metal ion extraction

2.3.1. *Drying of sludge samples*

The first sludges preparation operation for metal ions extraction consisted in drying the two samples N1 and N2, in a Binder oven at 105 °C to a constant mass, about 6 hours, in order to remove the humidity and to obtain concentrated materials.

2.3.2. *Grinding and sieving of sludge samples*

The grinding of sludges samples was performed in a ball mill, Planetary Mill PULVERISETTE 5 type. After grinding, powders with particles with average diameters of about 20 μm were obtained. The sieving was performed manually, at the size of 20 μm with standardized stainless steel analytical sieve, with a diameter of 150 mm and a height of 50 mm.

2.4. Experimental procedures for metal ions extraction from galvanic sludge

2.4.1. *Chromium ions extraction*

Chromium ions extraction was performed from dehydrated, dried, grinded and rehydrated in a ratio S/L = 1/1 sludges samples, by the method of solubilization of trivalent chromium ions (Cr^{3+}) with sodium hypochlorite (NaOCl 12%) in a strongly alkaline medium, at a pH=12.0-12.5 provided by the addition of sodium hydroxide in the form of a solution with a concentration of 20% (NaOH 20%), obtaining a solution of sodium chromate containing hexavalent chromium (Cr^{6+}) and a wet sludge cake, subsequently processed for the extraction of iron ions.

2.4.2. *Iron ions extraction*

Trivalent iron ions (Fe^{3+}) extraction was performed from the remaining sludge cake after extraction of hexavalent chromium, by solubilizing them with sulfuric acid (H_2SO_4 20%), at pH =1.0-1.5, followed by the oxidation with hydrogen peroxide (H_2O_2 30 %) of bivalent iron (Fe^{2+}) to trivalent iron (Fe^{3+}) and its precipitation with sodium hydroxide (20% NaOH), in order to obtain the iron pigment [15,17].

2.5. Experimental procedure for the synthesis of inorganic pigments based on chromium and iron

2.5.1 Synthesis method of inorganic pigments

For the synthesis of pigments based on chromium and iron ions extracted from galvanic sludges, a conventional method was used, namely precipitation, obtaining compounds such as hydroxides and metal salts.

2.6. Materials used in order to obtain the coloured ceramic glazes

2.6.1. Ceramic mass

A fine ceramic mass with the following characteristics predetermined by the manufacturer, presented in Table 2.1, was used in order to carry out the research.

Table 2.1. Main characteristics of the ceramic mass (Source: Interceram)

Characteristics	Value
Fireclay content	25%
Fireclay granulometry	< 0,5 mm
Firing temperature	1000–1240 °C

2.6.2. Glazes

The glazes used in the experiments were easily fusible glasses, deposited in thin layers on the surface of ceramic products. Two types of powdered materials were used in the experiments: opaque glaze and transparent glaze.

2.6.3. Pigments synthesized from galvanic sludge

The pigments synthesized from galvanic sludges and used to obtain colored ceramic glazes are: chromic hydroxide, also named green chromium pigment $[\text{Cr}(\text{OH})_3]$; lead chromate, also named yellow chromium pigment (PbCrO_4); barium chromate, yellow chromium pigment (BaCrO_4) and ferric hydroxide, also named red-brown iron pigment $[\text{Fe}(\text{OH})_3]$. Their synthesis and characterization are presented in Chapter 4.

2.7. Preparation of ceramic materials

2.7.2. Preparation of recipes for glazes obtaining

Research has focused on the use of varying quantities of dry and grinded pigments introduced into vitrifiable glaze compositions in order to obtain colored glazes. Two types of

glazes were used: white (opaque) and transparent glaze. In order to obtain the colored ceramic samples, quantities of 3%, 5% and 10% of each pigment were introduced in the transparent and opaque glaze mass.

2.7.3. Heat treatment of ceramic samples

The glazed ceramic materials were obtained by firing in two successive stages (double firing): raw ceramic samples firing for ceramic biscuits obtaining, followed by ceramic biscuits firing with the applied glaze. During both firing processes of ceramics, the oven followed a program of gradual increase of temperature in the first hours, then maintaining it for a certain time at maximum temperature, cooling being carried out slowly in the oven for 15-17 hours.

2.8. Methods for chemical characterization of materials

2.8.1. Flame Atomic Absorption Spectrometry (FAAS)

For heavy metals determination from the sludges samples, the GBS AVANTA PM type atomic absorption spectrometer with air-acetylene flame, from the Waste Management Department of the National Institute for Research and Development in Environmental Protection Bucharest, was used. The performed analyzes highlighted the following chemical composition of the sludges samples, expressed as a percentage (%) compared to the dry matter (DM), presented in Table 2.3.

Table 2.3. Chemical composition of N1 (fresh) and N2 (stored) sludge

SAMPLE	Chemical composition of sludge (%DM)								
	Cr	Fe	Zn	Ni	Cu	Cd	Pb	Mn	Ca, Mg, Na
N1	0.27	9.10	18.10	0.05	0.009	0.004	BDL*	BDL*	BDL*
N2	8.00	21.3	2.44	0.22	0.93	0.71	0.13	0.24	BDL*

* below detection limit

2.8.2. X-Ray Fluorescence (XRF)

Qualitative analysis of the materials oxide composition, by XRF technique, was performed using X-Ray Fluorescence Supermini analyzer within "Impact of Built Environment and Nanomaterials" Department of the National Research and Development Institute for Environmental Protection Bucharest.

2.9. Structural characterization of synthesized pigments from galvanic sludge and heat-treated glazes

2.9.1. X-Ray Diffraction (XRD)

The structural characterization of the pigments synthesized from galvanic sludge was performed using a Bruker D8 ADVANCE diffractometer, in the θ - 2θ configuration with Cu K α 1 radiation ($\lambda = 0.154060 \text{ \AA}$). The data were obtained by scanning in the range of $2\theta = 10 - 70^\circ$ with a step of 0.02° . The equipment is located in the "Impact of Built Environment and Nanomaterials" Department of the National Research and Development Institute for Environmental Protection Bucharest (INCDPM). The identification of the phases was performed through the Match! $\text{\textcircled{R}}$ software package (Crystal Impact GbR, Bonn, Germany), supported by data from the PDF-2 database (ICDD-International Center for Diffraction Data, Newtown Square, PA). The structural characterization of the heat-treated glazes was performed with an X-ray diffractometer PRO MPD X, PANalytical, equipment located in the Center for Research and Eco-Metallurgical Expertise (ECOMET UPB) laboratory.

2.9.2. Simultaneous Thermal Analysis (TG/DSC)

The heating behavior of the samples (simultaneous thermal analysis) was studied using a Netzsch STA 449 F5A device, equipment located in the "Impact of Built Environment and Nanomaterials" Department of the National Research and Development Institute for Environmental Protection Bucharest (INCDPM). The TG and DSC curves were recorded in nitrogen atmosphere using alumina crucibles. The investigated temperature range was $25 - 800 \text{ }^\circ\text{C}$ (or $850 \text{ }^\circ\text{C}$) at a heating rate of $20 \text{ }^\circ\text{C}/\text{min}$.

2.9.3. Scanning Electron Microscopy (SEM)

Within the PhD thesis, the characterization of pigments before and after heat treatment was performed by scanning electron microscopy (SEM) analysis. The scanning electron microscope HITACHI SU-70 FE-SE from the "Impact of Built Environment and Nanomaterials" Department of the National Research and Development Institute for Environmental Protection Bucharest (INCDPM) was used in order to perform the analyzes.

2.9.4. Optical microscopy (OM)

The analysis of defects and imperfections resulting from the heat treatment process of glazes containing pigments synthesized from galvanic sludges was performed using an Olympus BX 51M microscope. The equipment belongs to Center for Research and Eco-Metallurgical Expertise (ECOMET UPB). The equipment used is equipped with the possibility of investigations in light or dark field and a magnification range of $50x$ to $1000x$.

2.10. Determination of heat-treated glazes toxicity

2.10.1. Verification of glaze toxicity by leaching tests

Verification of the obtained products toxicity was carried out according to the methodology used to determine the waste degree of hazardousness, as the limits for heavy metals used as pigments for inert materials are provided. The method used to determine the leaching, as recommended in Order no. 95/2005, was taken from SR EN 12457 / 1-4: Leaching - Compliance test for leaching of granular waste materials and sludges.

2.10.2. Determination of lead and cadmium given off by ceramic tiles

Determination of the lead and cadmium quantities that can migrate from glazed ceramic materials was performed according to the international standard SR ISO 10545-15: Ceramic tiles, Part 15: Determination of lead and cadmium given off by ceramic tiles. Extraction of lead and cadmium from the surface of ceramic articles was performed by exposing the glazed samples to the action of acetic acid, a solution with a concentration of 4%, prepared in the laboratory by mixing 40 mL of glacial acetic acid with 960 mL of distilled water, thus obtaining 1 L of solution.

2.11. Partial conclusion

The raw materials used for the metal ions extraction were two types of galvanic sludges, with different composition depending on their origin: fresh sludge code N1 collected from wastewater treatment by the Lancy type process from a surface coating plant, and stored sludge code N2, collected from a decanter of a decommissioned treatment plant.

Materials chemical characterization was performed by Flame Atomic Absorption Spectrometry method (FAAS) in order to determine the chemical composition of the sludges samples and subsequently the heavy metal content of the solutions obtained from the metal ion solubilization process and the X-ray fluorescence method (XRF) in order to determine the elemental chemical composition of raw materials: sludge, ceramic mass, glazes but also of synthesized ceramic pigments.

Structural characterization of the pigments was performed by X-ray diffraction (XRD), the stability of the pigments at high temperatures was determined by simultaneous thermal analysis (TG/DSC) and their morphological characterization was performed by scanning electron microscopy (SEM). The structural characterization of heat treated glazes was performed using various methods such as: X-ray diffraction (XRD) and scanning electron microscopy (SEM). The appearance of the sample surfaces after heat treatment was analyzed by optical microscopy (OM).

Laboratory tests to determine the toxicity of solidified glazes consisted of: verifying the glazed ceramic samples toxicity by leaching tests and determining the lead and cadmium given off by glazed ceramic samples, all tests being performed in accordance with specific international SR ISO standards.

CHAPTER 3. EXPERIMENTAL RESEARCH ON THE SELECTIVE EXTRACTION OF METAL IONS FROM GALVANIC SLUDGES IN ORDER TO OBTAIN PIGMENTS

3.1. Experimental plan

The experiments were performed in order to establish the optimal extraction yields of chromium (Cr^{6+}) and iron (Fe^{3+}) ions from N1 (fresh) and N2 (stored) galvanic sludges. The used sludges had a complex chemical composition and a predominant content of chromium, iron and zinc. In the composition of N2 sludge, collected from the decanter of a decommissioned treatment plant, the presence of cyanides in 0.5% was observed.

3.2. Extraction of hexavalent chromium ions from galvanic sludge

3.2.1. Establishing the parameters of the extraction process

The analyzes carried out in order to determine the chemical composition of sludges revealed the presence of cyanides in N2 sludge, in proportion of 0,5%, therefore the experimental researches for the extraction of metal ions were oriented towards the use of a hydrometallurgical extraction process, in strongly alkaline medium, thus avoiding the release of cyan ion (CN^-) and the formation of gaseous hydrogen cyanide (HCN).

3.2.2. Solubilization of trivalent chromium by alkaline oxidation

Chromium solubilization was performed by oxidizing it from trivalent chromium (Cr^{3+}) to hexavalent chromium (Cr^{6+}), adding to the sludge hydrated with bidistilled water, sodium hypochlorite (NaOCl 12%) as oxidizing agent and sodium hydroxide (20% NaOH) as neutralizing agent, in order to ensure a strongly alkaline medium (pH = 12.0-12.5). The result of wet filtration was a solution of sodium chromate (Na_2CrO_4), containing hexavalent chromium (Cr^{6+}), which was subsequently subjected to the chromium-based pigment synthesis process.

3.2.3. Study of the temperature and reaction time influence on the hexavalent chromium ions extraction yield in solution

In the first extraction phase, only two parameters were varied, namely: reaction temperature and reaction time. The variation of the Cr^{6+} extraction yield from fresh N1 sludge in the alkaline oxidation solubilization phase is shown in Table 3.3 and Figure 3.3 [17].

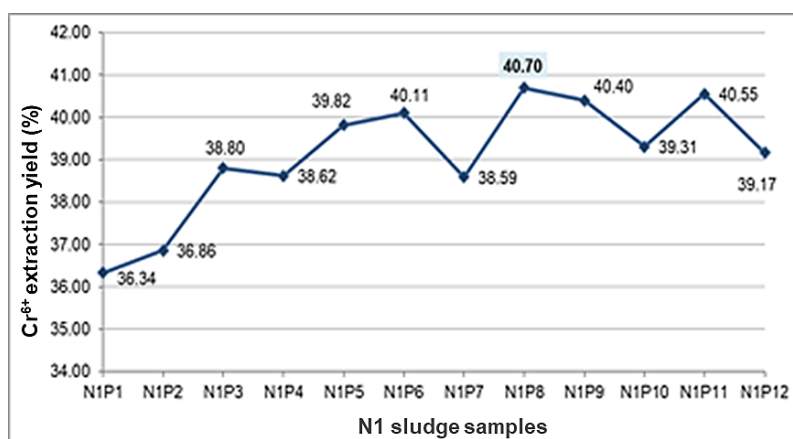


Figure 3.3. Extraction yield of hexavalent chromium ions in the first solubilization phase, for fresh N1 sludge samples (varied parameters - temperature and reaction time)

The variation of the Cr⁶⁺ extraction yield from from N2 sludge in the alkaline oxidation solubilization phase is presented in Table 3.4 and in Figure 3.4 [17].

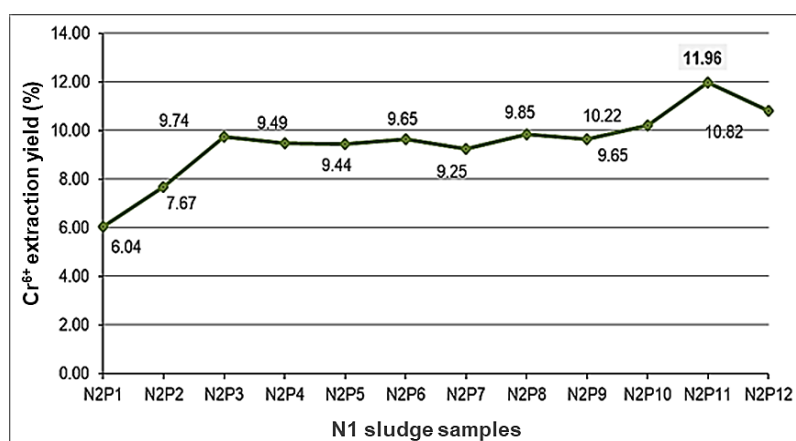


Figure 3.4. Extraction yield of hexavalent chromium ions in the first solubilization phase, for stored N2 sludge samples (varied parameters - temperature and reaction time)

Analyzing the results presented above, it is observed that the highest extraction yield of hexavalent chromium ions (Cr⁶⁺) was 40.70% from N1 sludge – obtained at a stoichiometric consumption of reagents, reaction temperature 80 °C, reaction time 30 minutes and 11.96% from N2 sludge – obtained at a stoichiometric consumption of reagents, reaction temperature 90 °C, reaction time 30 minutes.

3.2.4. Study of the influence of the quantity of oxidizing agent variation on the extraction yield of hexavalent chromium ions

Since other components of the investigated sludge and a part of bivalent iron (Fe²⁺) oxidize to hexavalent iron (Fe⁶⁺) and for the oxidation reaction of trivalent chromium to be complete, the experiments continued with the oxidizing agent quantity variation, sodium hypochlorite (NaOCl 12%). It is mentioned that the parameters previously established as

optimal (reaction temperature and reaction time) were kept. The results regarding the extraction yield of hexavalent chromium ions (Cr^{6+}) from the sludge samples are presented in Table 3.6 and Figure 3.9 for N1 sludge, respectively Table 3.7 and Figure 3.10 for N2 sludge.

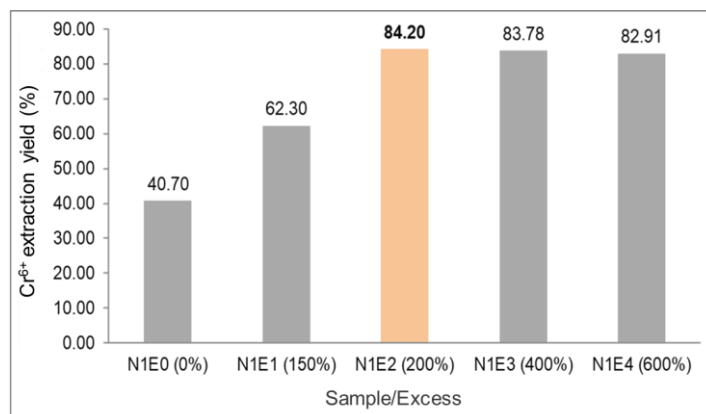


Figure 3.9. The variation of extraction yield of hexavalent chromium ions from N1 sludge, depending on the oxidizing agent excess

The results analysis shows that the extraction yield of hexavalent chromium ions (Cr^{6+}) increases with quantity increasing of added oxidizing agent, the highest value being obtained at 200% excess of sodium hypochlorite (NaOCl 12%) ($\eta_{\text{Cr}}(\text{N1}) = 84.20\%$).

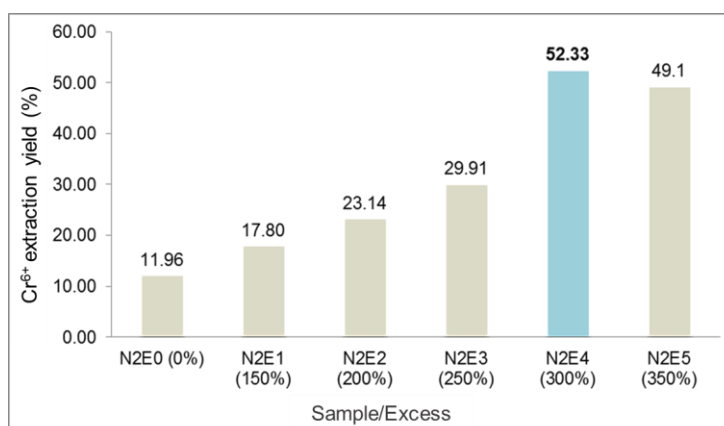


Figure 3.10. The variation of extraction yield of hexavalent chromium ions from N2 sludge depending on the oxidizing agent excess

It is observed from the results analysis that the extraction yield of hexavalent chromium ions (Cr^{6+}) increases with quantity increasing of added oxidizing agent, the highest value being obtained at 200% excess of sodium hypochlorite (NaOCl 12%) ($\eta_{\text{Cr}}(\text{N2}) = 52.33\%$).

3.2.5. Second stage of hexavalent chromium ions extraction from the landfilled sludge N2

The sludge destabilization in the first extraction stage, allowed the extraction yield to increase in second extraction stage. The total extraction yield of hexavalent chromium ions (Cr^{6+}) from the N2 sludge was 93.19% in the two extraction stages.

3.3. Extraction of trivalent iron ions

3.3.1. Preparation of sludge cakes for the extraction of iron ions

In the sludge cakes resulted after the extraction of hexavalent chromium ions, iron is found in the form of bivalent iron (Fe^{2+}), trivalent iron (Fe^{3+}) and hexavalent iron (Fe^{6+}) compounds.

3.3.2. Solubilization of iron ions from sludge cakes in acidic medium

Solubilization of iron ions from sludge cakes was performed with sulfuric acid (20% H_2SO_4) addition, in order to ensure a pH=1.0-1.5, reaction temperatures and reaction times that varied and with continuous stirring throughout the reaction period [232].

3.3.3. Oxidation of bivalent iron to trivalent iron

For iron ions recovery from the solution in the form of hydroxide it was necessary to oxidize bivalent iron (Fe^{2+}) to trivalent iron (Fe^{3+}). In the first phase of chromium ion recovery, a part of the bivalent iron (Fe^{2+}) was oxidized to trivalent iron (Fe^{3+}) with sodium hypochlorite (NaOCl 12%) and sodium hydroxide (NaOH 20%). In the second stage, the oxidation of bivalent iron (Fe^{2+}) to trivalent iron (Fe^{3+}) was achieved by adding hydrogen peroxide (30% H_2O_2), in accordance with other previous studies [233].

3.3.4. Study of the extraction parameters influence on the extraction yield of trivalent iron ions

Trivalent iron (Fe^{3+}) extraction yield variation, depending on the varied parameters: reaction temperature and reaction time - for the two investigated sludges is shown in Figure 3.12.

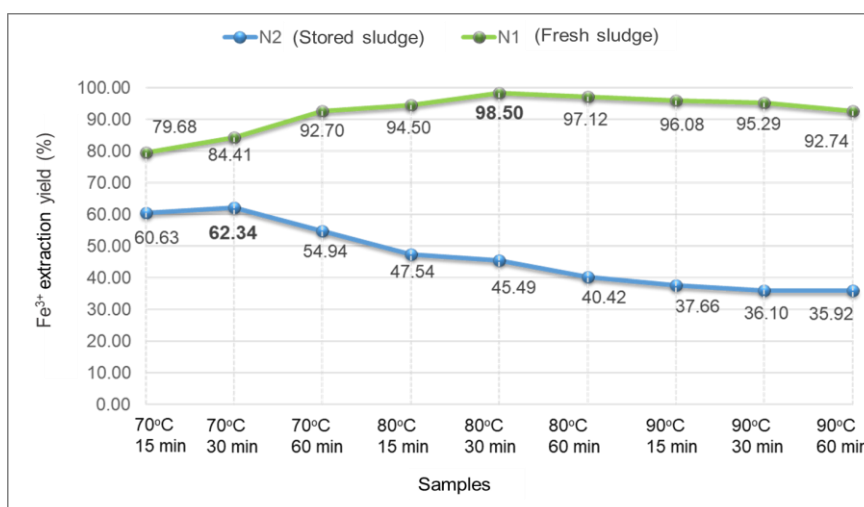


Figure 3.12. The variation of extraction yield of trivalent iron ions from N1 and N2 sludges

- the highest iron ions extraction yield from N1 sludge was obtained at 80 °C reaction temperature and 30 minutes reaction time. $\eta_{Fe(N1)} = 98.50\%$;
 - the highest iron ions extraction yield from N2 sludge was obtained at 70 °C reaction temperature and 30 minutes reaction time. $\eta_{Fe(N1)} = 62.34\%$;
- Iron ions extraction yield was 32.87% in the second extraction stage. The total extraction yield of iron from N2 sludge was $\eta_{Fe(N2)} = 95.20\%$.

3.4. Partial conclusions

The best chromium extraction yield from N1 sludge ($\eta_{Cr(N1)} = 84.20\%$) was obtained in one extraction stage at a reaction temperature of 80 °C, reaction time of 30 minutes and 200% excess of oxidizing agent, sodium hypochlorite (NaOCl 12%).

The best chromium extraction yield from N2 sludge ($\eta_{Cr(N2)} = 93.19\%$) was obtained in two extraction stages at a reaction temperature of 90 °C, reaction time of 30 minutes and 300% excess of oxidizing agent, sodium hypochlorite (NaOCl 12%).

The best trivalent iron ions extraction yield ($\eta_{Fe(N1)} = 98.50\%$) from N1 sludge was obtained at a reaction temperature of 80 °C and reaction time 30 minutes.

The extraction of trivalent iron ions from N2 sludge was performed in two steps, the total extraction yield being $\eta_{Fe(N2)} = 95.20\%$ at a reaction temperature of 70 °C and reaction time 30 minutes.

CHAPTER 4. EXPERIMENTAL RESEARCH ON THE SYNTHESIS AND CHARACTERIZATION OF SOME CHROMIUM AND IRON PIGMENTS EXTRACTED FROM GALVANIC SLUDGES

4.1. Experimental plan

The experimental plan aimed the recovery of chromium and iron from the solutions obtained in the solubilization stage, by precipitation in the form of hydroxides and metal salts potentially usable as pigments for coloring ceramic glazes. The recovery yield of metals by precipitation varied depending on the metal concentrations in the solution, the pH provided but also the precipitation reagent quantity used.

4.2. Synthesis and characterization of chromic hydroxide [Cr(OH)₃].

4.2.1. Synthesis of chromic hydroxide

Due to the fact that the chromium is present in the of hexavalent oxidation form in sodium chromate solution obtained after the solubilization process, two phases were required for the synthesis of chromic hydroxide Cr(OH)₃, also named green chromium pigment, namely: hexavalent chromium (Cr⁶⁺) reduction to trivalent chromium (Cr³⁺) and (Cr³⁺) trivalent ion precipitation with chromium hydroxide formation. In the first step, the reduction of hexavalent chromium (Cr⁶⁺) to trivalent chromium (Cr³⁺) was performed with sodium pyrosulphite (20% Na₂S₂O₅). The reduction reaction took place in an acidic medium, at a pH=2.0 which was ensured by the addition of sulfuric acid (20% H₂SO₄). The precipitation of trivalent chromium (Cr³⁺) was performed with sodium hydroxide (20% NaOH), at a pH=7.0.

4.2.2. The influence of the reducing agent on chromic hydroxide recovery efficiency

In order to test the influence of the sodium pyrosulfite (20% Na₂S₂O₅) quantity on the pigment recovery efficiency from solution, various reagent excesses were used. The results showed that the highest recovery yield of the green chromium pigment in the solution, namely 98.53%, was obtained at an excess of sodium pyrosulphite of 30%.

4.2.3. Chemical characterization of chromic hydroxide by X-ray fluorescence (XRF)

The chemical oxidic composition of chromic hydroxide Cr(OH)₃, also called green chromium pigment, obtained from N1 and N2 galvanic sludges, determined by X-ray fluorescence analysis (XRF) method, is presented in Table 4.3.

Table 4.3. Chemical oxidic composition of chromic hydroxide synthesized from galvanic sludge

Chromic hydroxide Cr(OH) ₃	
Oxide	wt %
Na ₂ O	6.0779
MgO	0.8805
Al ₂ O ₃	0.1654
SiO ₂	0.6525
P ₂ O ₅	0.1500
SO ₃	0.2649
Cl ⁻	0.1133
CaO	0.4089
Cr ₂ O ₃	89.3540
Fe ₂ O ₃	1.2335
CdO	0.1835
WO ₃	0.5156

The fluorescence spectrum of the green chromium pigment Cr(OH)₃ shows the presence of a large amount of chromium oxide Cr₂O₃ (89.354%), followed by small amounts of sodium oxide Na₂O (≈6%). Na₂O comes most probably from the process of extracting chromium ions. The presence of Fe₂O₃ ferric oxide whose amount is 1.233%, as well as the other minority oxides, are observed.

4.2.4. Characterization of chromic hydroxide by X-ray diffraction (XRD)

Figure 4.3 shows the diffraction spectrum of the chromic hydroxide pigment.

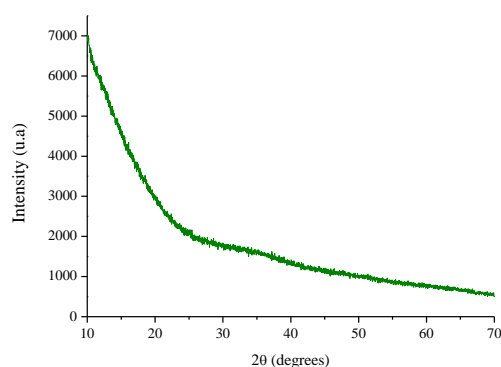


Figure 4.3. The diffraction spectrum of chromium hydroxide pigment synthesized from galvanic sludges

The diffraction spectrum of chromium hydroxide pigment highlights the amorphous character, the lack of sharp peaks along with the presence of halo within interval $2\theta = 25-40^\circ$ emphasizing this characteristic.

4.2.5. Thermal characterization of chromium hydroxide pigment by simultaneous thermal analysis (TG/DSC)

Figure 4.4 shows the TG/DSC curves obtained from the simultaneous thermal analysis of chromic hydroxide sample (green chromium pigment), synthesized from galvanic sludge.

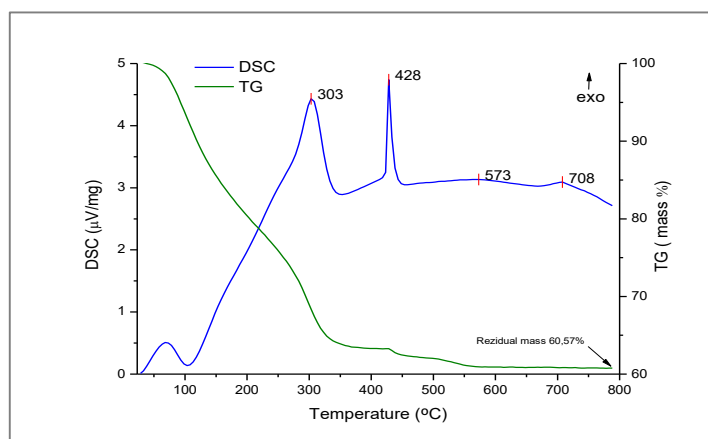


Figure 4.4. TG/DSC curves of chromium hydroxide $\text{Cr}(\text{OH})_3$

The exothermic effect recorded at the temperature of 430°C corresponds to the dehydroxylation of $\text{Cr}(\text{OH})_3$ with the change of the oxidation state of chromium from 3⁺ to 6⁺ which it has in chromic oxide (Cr_2O_3). This phenomenon occurs with a mass loss of 14.93%. Beyond this temperature the sample does not register significant changes, the peak registered at $T=708^\circ\text{C}$ being associated with the beginning of the chromium oxide (Cr_2O_3) melting process.

4.2.6. Morphological characterization of chromic hydroxide by Scanning Electron Microscopy analysis (SEM)

The morphology of newly synthesized chromic hydroxide [$\text{Cr}(\text{OH})_3$], as well as that of the heat-treated compound at 800°C, was investigated by scanning electron microscopy (SEM), using a Hitachi SU-70 FE-SEM microscope, the obtained results being presented in Figure 4.5.

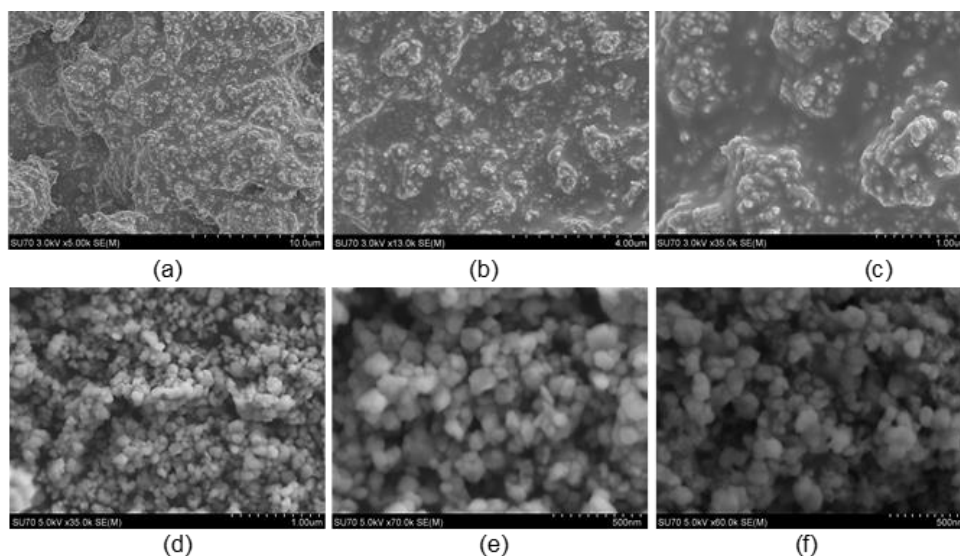


Figure 4.5. SEM images of raw chromium hydroxide $[Cr(OH)_3]$, (a) - (c) and heat-treated at $800\text{ }^\circ\text{C}$, (d) - (f), at different magnifications

SEM images of the newly synthesized chromic hydroxide highlight the presence of an amorphous matrix, in which small gel agglomerated formations, weakly crystallized, are uniformly distributed in the matrix (Figure 4.5 a-c). The heat treatment at $800\text{ }^\circ\text{C}$ causes the loss of water from the structure and the formation of nanometric crystals of chromium oxide in the shape of agglomerated hexagonal granules, these results being in good correlation with TG/DSC analyzes.

4.3. Synthesis and characterization of lead chromate ($PbCrO_4$)

4.3.1. Synthesis of lead chromate

Lead chromate ($PbCrO_4$), also named yellow chromium pigment, was synthesized by direct precipitation of hexavalent chromium (Cr^{6+}), from the solution resulting from the solubilization process, with lead acetate $[Pb(CH_3COO)_2 \cdot 3H_2O]$ having a concentration of 20%.

4.3.2. Influence of precipitating agent on lead chromate recovery efficiency from solution

The results regarding the recovery efficiency of lead chromate, also named yellow chromium pigment ($PbCrO_4$), depending on the variation of the precipitation reagent excess, are presented in Table 4.5 and Figure 4.6. The obtained results showed that the recovery yield of the yellow chromium pigment $PbCrO_4$ increased progressively with the increasing of precipitation reagent quantity.

4.3.3. Chemical characterization of lead chromate by X-ray fluorescence (XRF)

The chemical oxidic composition of lead chromate is shown in Table 4.6.

Table 4.6. Chemical oxidic composition of lead chromate synthesized from galvanic sludge

Lead chromate PbCrO ₄	
Oxide	wt %
Al ₂ O ₃	0.1013
SiO ₂	0.4849
P ₂ O ₅	0.1783
K ₂ O	0.1504
Cr ₂ O ₃	29.4208
Fe ₂ O ₃	1.0188
PbO	68.6455

The fluorescence spectrum of yellow chromium pigment PbCrO₄ highlights the presence of chromium oxide (Cr₂O₃) and lead oxide (PbO) as major components, found in a proportion of 29.42%, respectively 68.65%. Additionally, other compounds have been identified in lead chromate, but the amount does not exceed 2% of the total sample analyzed, which indicates an advanced degree of purity of this pigment.

4.3.4. Characterization of lead chromate by X-ray diffraction (XRD)

Compared to the diffraction spectrum of the green chromium pigment Cr(OH)₃, the diffraction spectrum of the yellow chromium pigment PbCrO₄ (Figure 4.8) looks different.

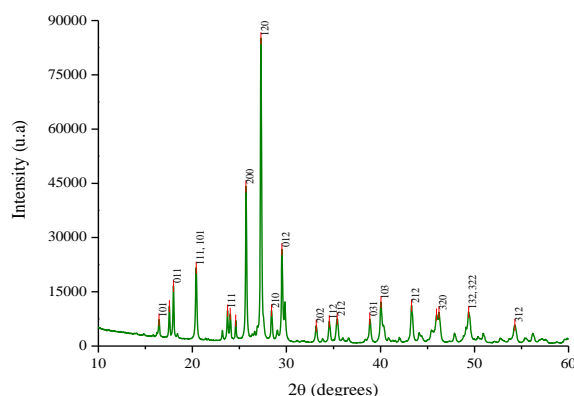


Figure 4.8. The diffraction spectrum of lead chromate synthesized from galvanic sludge [239]

The diffraction spectrum of lead chromate (PbCrO₄) shows a crystalline structure, with high-intensity interferences. All reflection peaks identify 100% the monoclinic phase of PbCrO₄, spatial group P21/n(14) with a=7.12 Å, b=7.43 Å, c=6.79 Å, and β=102.420°, perfectly matching with the spectra reported in the JCPDS archives (JCPDS 73-2059), as well as in the literature by other researchers [239-242].

4.3.5. Thermal characterization of lead chromate by simultaneous thermal analysis (TG/DSC)

The TG/DSC curves corresponding to the lead chromate synthesized from the N1 and N2 galvanic sludges are presented in Figure 4.9.

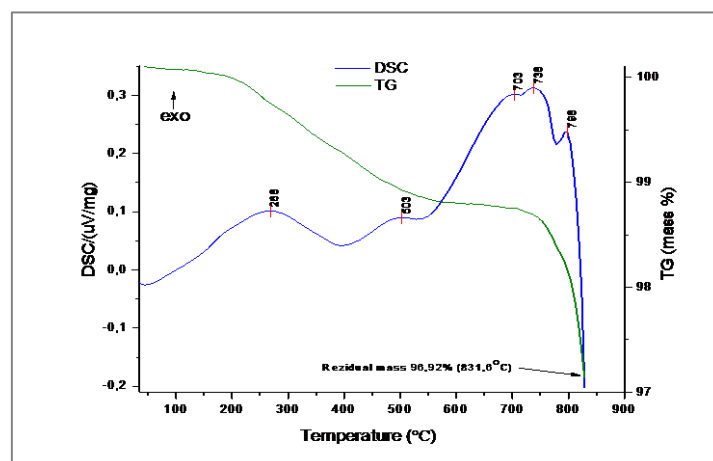


Figure 4.9. Curbele TG/DSC ale cromatului de plumb $PbCrO_4$ [239]

There is an exothermic effect indexed on the DSC curve, with a maximum of 738 °C, followed by a mass loss of 0.72%. The thermal effect corresponds to the phase transformation of the monazite structure in the barite shape at high temperatures. The total mass loss recorded on the TG curve of lead chromate was 1.96%.

4.3.6. Morphological characterization of lead chromate by Scanning Electron Microscopy analysis (SEM)

The SEM images of lead chromate ($PbCrO_4$) synthesized from galvanic sludge, before and after heat treatment, are shown in Figure 4.10.

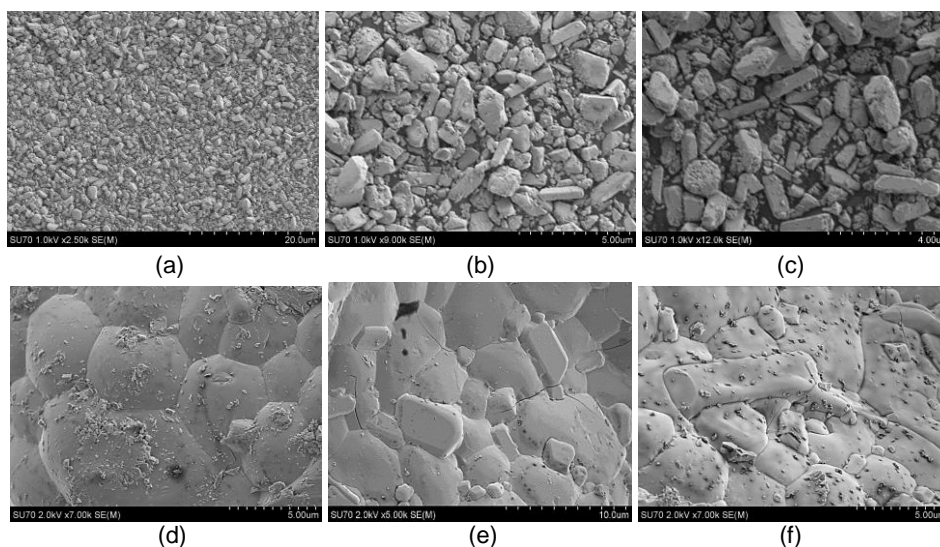


Figure 4.10. SEM images of raw lead chromate ($PbCrO_4$), (a) - (c) and heat treated at 700 °C, (d) - (f), at different magnifications

The morphological analysis results presented in Figure 4.10, (a) to (c) positions, highlights the presence of polyhedral $PbCrO_4$ particles, which have a bimodal distribution, without agglomerated particles. The size of big particles varies between 1 μm and 2 μm , and the small particles do not exceed 0.4 μm . The sintering process at 700 °C led to the formation of a compact structure, through a close connection of the particles in spherical agglomerates, with visible intergranular boundaries and triple junctions (Figure 4.10 d-f). The particle size can reach up to 8 μm , highlighting the positive effect of temperature on their growth process.

4.4. Synthesis and characterization of barium chromate ($BaCrO_4$)

4.4.1. Synthesis of barium chromate

The second yellow chromium pigment was obtained by precipitating hexavalent chromium (Cr^{6+}) in the form of barium chromate $BaCrO_4$, with barium chloride [$BaCl_2 \cdot 2H_2O$] having a concentration of 20%.

4.4.2. Influența agentului de precipitare asupra randamentului de recuperare a cromatului de bariu din soluție

Various excesses of precipitating agent were used in order to observe its influence on the precipitation reaction, respectively on the recovery efficiency of the yellow chromium pigment from the solution. The results obtained showed that the precipitation yield increased progressively with increasing precipitation reagent quantity.

4.4.3. Chemical characterization of barium chromate by X-ray fluorescence (XRF)

Table 4.9 shows the chemical oxidic composition of yellow chromium pigment $BaCrO_4$.

Table 4.9. Chemical oxidic composition of barium chromate synthesized from galvanic sludge

Barium chromate BaCrO₄	
Oxide	wt %
SiO ₂	0.6496
SO ₃	2.7408
Cl ⁻	0.1353
Cr ₂ O ₃	29.4077
CuO	0.1322
CdO	0.3044
BaO	66.6300

The second yellow chromium pigment also presents an advanced degree of purity. Thus, the fluorescence spectrum of barium chromate indicates the presence of 29.41% Cr₂O₃ and 66.63% BaO, the rest being minority compounds.

4.4.4. Characterization of barium chromate by X-ray diffraction (XRD)

Figure 4.13 shows the diffraction spectrum of the BaCrO₄ sample.

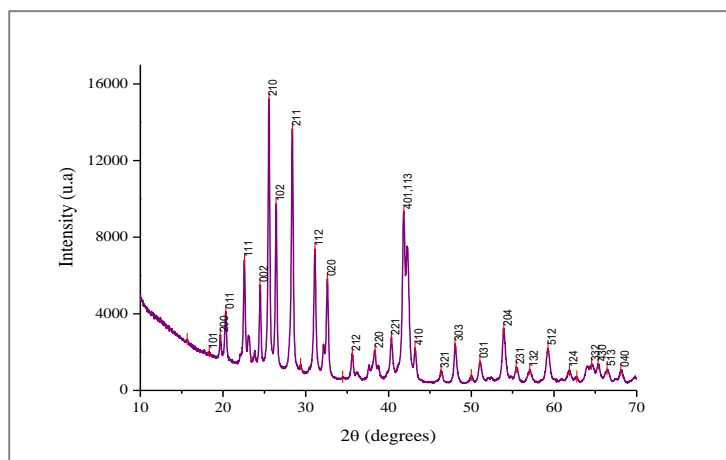


Figure 4.13. The diffraction spectrum of the yellow chromium pigment BaCrO₄ [239]

According to the ICDD (International Center for Diffraction Data) database, all the diffraction peaks are perfectly indexed as an orthorhombic phase of BaCrO₄ with the network parameters: a=9.103 Å, b=5.526 Å, and c=7.337 Å, such a structure being also identified in the specialty literature [239,245].

4.4.5. Thermal characterization of barium chromate by simultaneous thermal analysis (TG/DSC)

The DSC curve of the inorganic barium chromate pigment (BaCrO₄) recorded a thermal effect within the temperatures interval of 570 °C and 770 °C (with the maximum at 650 °C) to which it corresponds a mass loss of 0.25% (Figure 4.14).

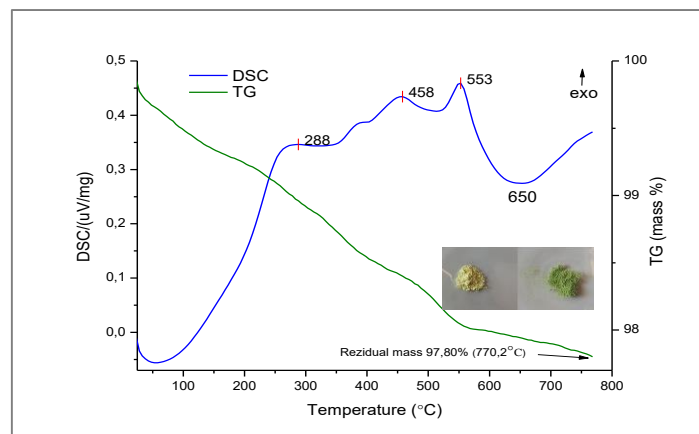


Figure 4.14. TG/DSC curves of barium chromate- $BaCrO_4$

In contrast to the lead chromate, the synthesized barium chromate powder changed its color from yellow to green at the end of the analysis (detail in Figure 4.14), which suggests the thermal instability of the compound and its decomposition into the nitrogen atmosphere [239]. The total mass loss during heat treatment is small and represents only 2.2% of the initial sample mass [239].

4.4.6. Morphological characterization of barium chromate by Scanning Electron Microscopy analysis (SEM)

Figure 4.15 shows the SEM images of barium chromate ($BaCrO_4$) synthesized from galvanic sludges, the morphological characterization being performed for both raw and heat-treated pigments at 800 °C.

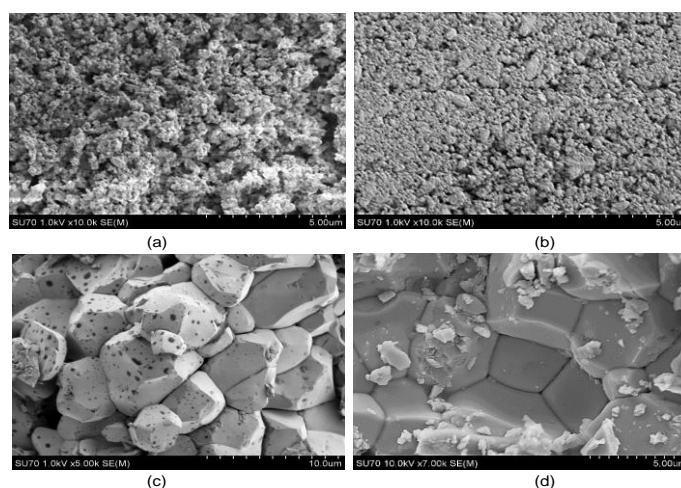


Figure 4.15. SEM images of raw barium chromate ($BaCrO_4$), (a) and (b) and heat-treated at 800 °C, (c) and (d)

From the SEM images shown in Figure 4.15, it is observed that the raw barium chromate powder has a fine texture with a unimodal particle size distribution, highlighting an agglomeration tendency of very small particles, Figure 4.15 (a) and (b). After the pigment heat treatment at 800 °C, Figure 4.15 (c) and (d), a compact and pore-free structure results in which the polyhedral granules (with well-defined sides and edges) present sizes of approximately 5 μm [239].

4.5. Synthesis and characterization of ferric hydroxide [Fe(OH)₃]

4.5.1. Synthesis of ferric hydroxide

Ferric hydroxide (red-brown pigment) was obtained by complete precipitation of trivalent iron (Fe³⁺) from the solutions resulting in the iron extraction phase. Starting from a solution with an iron concentration of 59.65 g/L, an iron precipitation yield of 99.87% was obtained.

4.5.2. Chemical characterization of ferric hydroxide by X-ray fluorescence (XRF)

Table 4.10 shows the chemical oxide composition of ferric hydroxide Fe(OH)₃.

Table 4.10. Chemical oxidic composition of barium chromate synthesized from galvanic sludge

Ferric hydroxide Fe(OH)₃	
Oxid	wt %
Al ₂ O ₃	1.2805
SiO ₂	8.3399
P ₂ O ₅	1.3731
SO ₃	9.4067
Cr ₂ O ₃	1.4645
MnO	0.3231
Fe ₂ O ₃	73.3744
NiO	0.1575
CuO	1.0452
ZnO	2.6129
CdO	0.3184
WO ₃	0.3038

The composition of ferric hydroxide Fe(OH)₃ is more varied compared to the rest of the pigments presented above and contains, in addition to 73.3744% Fe₂O₃, various proportions of silicon dioxide (SiO₂), sulfur trioxide (SO₃), zinc oxide (ZnO) etc. In this case, the amount of the SO₃ compound of 9.4067%, which comes from the pigment synthesis process and which represents an impurity, is particularly noticeable.

4.5.3. Characterization of ferric hydroxide by X-ray diffraction (XRD)

In Figure 4.17 is presented the XRD pattern of $\text{Fe}(\text{OH})_3$ ferric hydroxide sample.

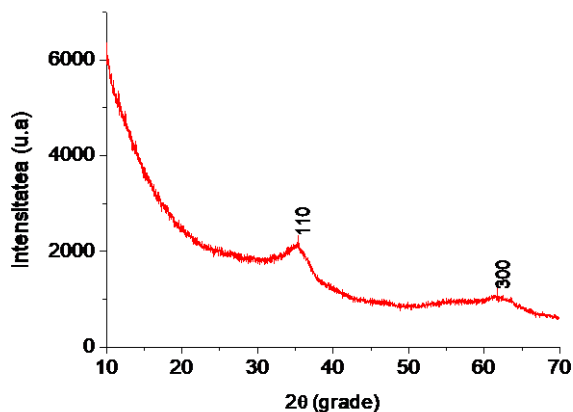


Figure 4.17. The diffraction spectrum of ferric hydroxide synthesized from galvanic sludges

The XRD pattern of $\text{Fe}(\text{OH})_3$ emphasizes a predominantly amorphous character of the powder resulted from the synthesis process, excepting the presence of the two weak interferences at $2\theta \approx 35^\circ$ and $2\theta \approx 61^\circ$ specific to the $\text{Fe}(\text{OH})_3$, having hkl (110) and (115), explained as a presence of a weakly crystalline structure in a predominantly gel structure [249,250].

4.5.4. Thermal characterization of ferric hydroxide by simultaneous thermal analysis (TG/DSC)

Figure 4.18 shows the TG/DSC curves of ferric hydroxide $\text{Fe}(\text{OH})_3$, synthesized from galvanic sludge.

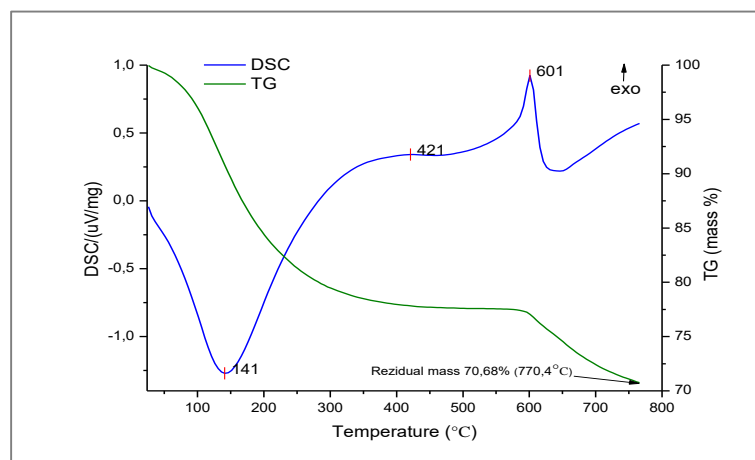


Figure 4.18. TG/DSC curves of ferric hydroxide $\text{Fe}(\text{OH})_3$

A detailed evaluation of the $\text{Fe}(\text{OH})_3$ heating behavior shows that the mass loss of 22.39% can be attributed to the loss of physically and chemically bonded water, the endothermic/exothermic phenomena that occur at temperatures below 450 °C. The last stage of the $\text{Fe}(\text{OH})_3$ transformation represents the conversion of hydroxide into amorphous oxide (the loss of OH^- bonds and the Fe_2O_3 crystallization), an exothermic phenomenon recorded in this case at 601°C with a mass loss of 4.09%.

4.5.5. Morphological characterization of ferric hydroxide by Scanning Electron Microscopy analysis (SEM)

As in the case of the other synthesized pigments presented above, the SEM images of ferric hydroxide $\text{Fe}(\text{OH})_3$, highlight the morphological transformations that occur as a result of the heat treatment up to 800 °C.

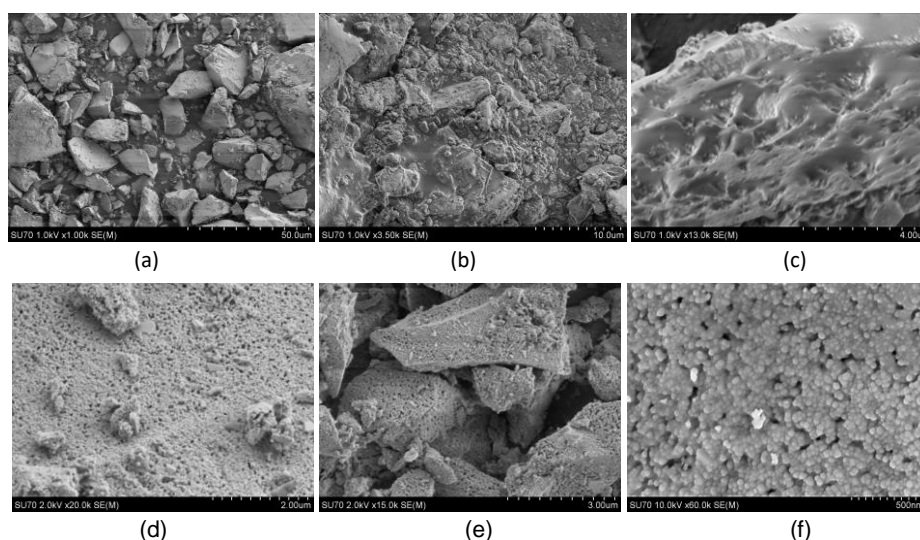


Figure 0.1. SEM images of raw ferric hydroxide [$\text{Fe}(\text{OH})_3$], (a) - (c) and heat treated at 800 °C, (d) - (f), at different magnifications

Thus, by thermal treatment of the red-brown iron pigment, a predominantly amorphous mass (matrix) results in which weakly crystallized polyhedral formations are dispersed, defined by sharp edges and corners (Figure 4.19 a-c). Such microstructures have been reported by other researchers, identified as $\gamma\text{-FeOOH}$, obtained by hydrolysis of a solution of $\text{Fe}(\text{ClO}_4)_3$ [250]. The applied treatment favored the formation of $\alpha\text{-Fe}_2\text{O}_3$ pseudosphere particles with nanometric dimensions (Figure 4.19 d-f).

4.6. Partial conclusions

The green chromium pigment $\text{Cr}(\text{OH})_3$ was obtained by reducing hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}) in acid medium and precipitating it with sodium hydroxide (20% NaOH), at pH=7.

From the solutions resulting after the solubilization of chromium ions, two yellow chromium-based pigments were synthesized: lead chromate PbCrO_4 and barium chromate

BaCrO₄ by precipitating hexavalent chromium (Cr⁶⁺) with two salts, lead acetate and barium chloride.

Ferric hydroxide Fe(OH)₃, the red-brown iron pigment, was obtained by complete precipitation of trivalent iron (Fe³⁺) from the solutions resulting in the iron extraction phase, with sodium hydroxide (NaOH 20%), precipitation yield being about 99.87%.

Chemical analyzes by the X-ray fluorescence method (XRF) showed the purity of the synthesized pigments: the main component of the green chromium pigment Cr(OH)₃ is chromium in proportion of 89.3%; of the yellow chromium pigment PbCrO₄ is lead (75.2%), followed by chromium (23.6%). The second yellow chromium pigment BaCrO₄ contains mainly barium (72.8%) and chromium (25.1%) and the red-brown iron pigment Fe(OH)₃ has Fe₂O₃ as the main component 73.37% and various proportions of SiO₂, SO₃, ZnO.

The diffraction patterns obtained by XRD analysis showed the amorphous character of the chromic hydroxide Cr(OH)₃ and the predominantly amorphous character of the Fe(OH)₃ hydroxide. The diffraction patterns of barium chromate BaCrO₄ and lead chromate PbCrO₄ revealed crystalline structures, perfectly indexed as the orthorhombic phase of BaCrO₄ and the distinct monoclinic phase of PbCrO₄.

The TG/DSC curves of chromic hydroxide Cr(OH)₃ showed the endothermic and exothermic effects during the heat treatment up to 800 °C, an important mass loss of 14.93% being registered at 430 °C. The TG/DSC analysis of ferric hydroxide Fe(OH)₃ revealed the appearance of an endothermic effect at a temperature below 450°C and an exothermic one at 601 °C determining the loss of the OH⁻ bonds and Fe₂O₃ crystallization.

Additionally, the TG/DSC curves showed an exothermic effect for the lead chromate PbCrO₄ with a maximum at 738 °C, accompanied by a mass loss of 0,72% corresponding to the phase transformation of the monazite structure in the barite form.

For BaCrO₄, the DSC curve recorded a thermal effect between 570 °C and 770 °C, with a mass loss of 0.25%. At the end of the treatment, the color of BaCrO₄ changed from yellow to green, which suggests its decomposition. The total weight loss was 2.2%.

The SEM images of raw chromic hydroxide Cr(OH)₃ showed the presence of weakly crystallized granular formations embedded in an amorphous matrix. After the heat treatment at 800 °C, a granular texture was highlighted in which the crystalline granules with small dimensions (less than 100 nanometers) are agglomerated in clusters.

The SEM images of the raw lead chromate PbCrO₄ showed dispersed polyhedral particles, with a bimodal distribution, while the heat-treated pigment has a compact structure, with visible intergranular boundaries and triple junctions.

The SEM analysis of raw barium chromate BaCrO₄ revealed a fine-textured powder with a unimodal particle distribution, presenting the tendency of very small particles towards agglomeration. The heat treated sample at 800 °C showed a pore-free structure, in which the polyhedral granules (with well-defined sides and edges) have approximately 5 μm size.

The last but not least, the SEM images of raw ferric hydroxide Fe(OH)₃ showed the presence of weakly crystallized polyhedral formations in a predominantly amorphous mass and the heat treatment emphasized the formation of pseudosphere particles, of nanometric dimensions.

CHAPTER 5. EXPERIMENTAL RESULTS ON THE OBTAINING AND CHARACTERIZATION OF COLORED GLAZES FOR DECORATIVE CERAMIC MATERIALS BY USING THE STUDIED PIGMENTS

5.1. Experimental plan

The experimental researches aimed the possibility of obtaining colored ceramic glazes, by introducing various amounts of chromium and iron pigments, synthesized from galvanic sludge, in their compositions.

5.2. Preparation of ceramic body samples

The ceramic mass with a water content of about 20%, was modeled by hand and processed in order to obtain both large samples (5x5 cm) and smaller samples (1x1 cm) for firing in oven and for their subsequent analysis. The samples were subjected to the drying operation in order to increase their resistance and to avoid the deformation phenomenon, as a result of the sudden evaporation of water in the firing process.

5.3. Heat treatment of dry ceramic body

The firing of the naturally dried ceramic samples was carried out in a special oven, in a neutral atmosphere, without oxygen supply. The oven followed a program of gradual increase of temperature in the first hours, then maintaining it for a certain time at maximum temperature, cooling being carried out slowly in the oven.

5.4. Structural characterization of heat-treated glazes

Regarding the glazes used in the experimental researches, the elemental quantitative analysis by the X-ray fluorescence method (XRF) revealed the presence, in the composition of the opaque glaze, of cerium oxide (CeO_2) in a proportion of 14.7% and zirconium oxide (ZrO_2) in a proportion of 9.57%, these compounds having the role of opacifiers (Table 5.2).

Table 5.2. Oxidic composition of glazes, opaque (GO) and transparent (GT)

Oxide	SiO ₂	CeO ₂	Al ₂ O ₃	ZrO ₂	HfO ₂	Na ₂ O	CaO	K ₂ O	MgO	MnO	ZnO	Alții
GO (%)	48.500	14.700	10.800	9.570	4.820	3.660	3.480	1.480	0.890	0.634	0.639	0.826
GT (%)	65.200	-	15.500	0.514	-	7.300	6.950	1.280	1.630	0.072	0.751	0.803

24 compositions of opaque glaze and transparent glaze in which the four pigments synthesized from galvanic sludges were introduced in various amounts, were prepared, (presented in Figure 5.1).

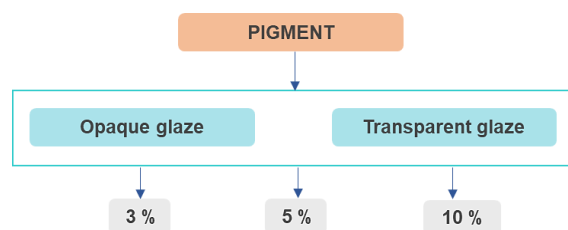


Figure 0.1. Amounts of pigments used in glazes

The glazing operation was performed by uniformly applying colored glazes with a brush on the surface of the gheat treated ceramic mass. The samples were marked with a natural pigment of ferric oxide.

5.5. Heat treatment of colored glazes

The glazing operation was followed by a second firing by which the ceramic biscuit was heated to the vitrification temperature of the glaze applied on its surface. The oven, as in the first firing, followed a special program of gradual and controlled heating until it reached the temperature of 1030 °C, followed by a 15 minutes at this temperature, the subsequent cooling being carried out slowly, in about 15 hours in order to avoid cracks.

5.6. Structural characterization of heat-treated glazes

5.6.1. Characterization of heat-treated glazes by X-Ray Diffraction (XRD)

The glazes used in the mixture with the synthesized pigments were initially characterized by XRD analyzes, the results being presented in Figure 5.4.

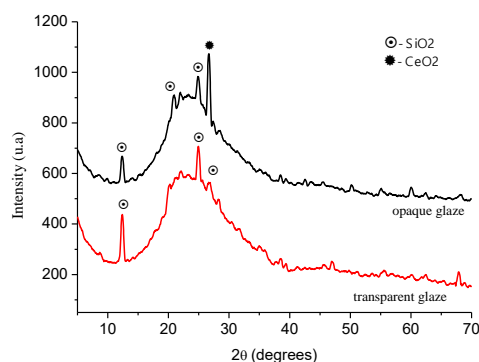


Figure 5.4. XRD patterns corresponding to glazes used in the experimental research (opaque and transparent)

The predominantly vitreous character of the glazes is highlighted by the presence of the halo in the range $2\theta=15-35$ degrees. Additionally, small amounts of fine crystals of silicon dioxide SiO_2 are identified in the diffraction spectrum of glazes besides of a characteristic peak of cerium oxide CeO_2 detected on the XRD pattern of the opaque glaze, conferring to this material the opacifying character, these analyzes being in good correlation with the results of XRF analysis.

Figure 5.5 shows the diffraction spectrum of the ceramic specimens obtained with transparent or opaque glaze in which different proportions of barium chromate (PbCrO_4) - yellow chromium pigment was added, namely 3%, 5%, and 10%, heat-treated at 1030 °C.

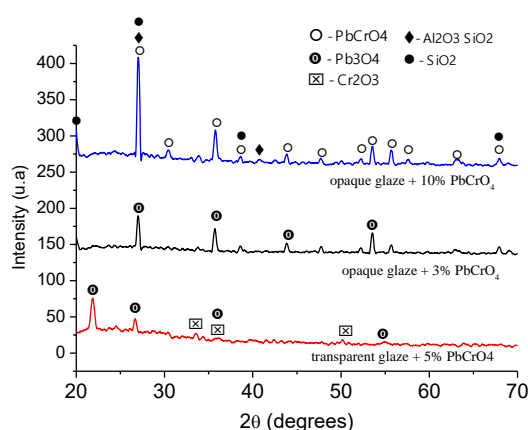


Figure 5.5. XRD patterns of ceramic glazed materials (opaque and transparent) with PbCrO_4 content in proportions of 3%, 5% and 10%, heat treated at 1030 °C

The diffraction spectrum of the ceramic specimen with opaque glaze and 10% of lead chromate highlights the presence as the majority phase of PbCrO_4 (monoclinic crystallization system, with the network parameters: spatial group P21/n, $a=7.12 \text{ \AA}$, $b=7.43 \text{ \AA}$ and $c=6.79 \text{ \AA}$), along with the spectral lines attributed to silicon dioxide SiO_2 from the glaze composition and weak interferences attributed to metakaolin, the main component of the ceramic body.

The XRD spectrum of the ceramic specimen with opaque glaze and 3% lead chromate highlights the formation as the main phase of lead tetraoxide or lead minium Pb_3O_4 (tetragonal crystallization system, with network parameters: space group P-4b2, $a=8,778 \text{ \AA}$, $b=8,778 \text{ \AA}$ and $c=6,551 \text{ \AA}$). The XRD spectrum of the sample with transparent glaze and 5% lead chromate evidenced the amorphous nature of the glaze and small amounts of crystalline phases, identified as lead oxide (II, IV) – also called the red lead or lead minium Pb_3O_4 (tetragonal crystallization system, space group P-4b2, with $a=8.86 \text{ \AA}$, $b=8.86 \text{ \AA}$ and $c=6.66 \text{ \AA}$) and chromic oxide Cr_2O_3 (rhombohedral crystallization system, space group R-3c, with $a=4.96 \text{ \AA}$, $b=4.96 \text{ \AA}$ and $c=13.59 \text{ \AA}$) detected through the presence of low-intensity interferences.

By the histograms analysis, it can be observed that the opaque glaze with 10% lead chromate contains 100% by weight crystalline phase of lead chromate PbCrO_4 while the opaque glaze with 3% lead chromate contains 100% by weight of crystalline phase of lead minium Pb_3O_4 (Figure 5.6 a, b). The crystalline phases present in the transparent glaze with

5% lead chromate were: 84% chromic oxide Cr_2O_3 as the majority phase and 16% of lead minium Pb_3O_4 (Figure 5.6 c).

Figure 5.7 shows the diffraction spectrum for two ceramic specimens covered with opaque and transparent glaze with 10% of barium chromate BaCrO_4 content, heat-treated at 1030°C .

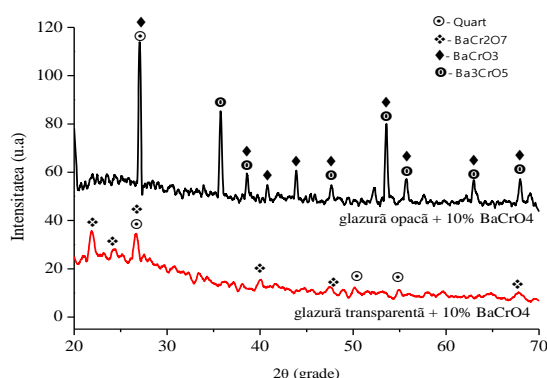


Figure 5.7. XRD patterns of the glazed ceramic materials (opaque and transparent) with 10% of BaCrO_4 content, heat-treated at 1030°C

On the XRD pattern corresponding to the ceramic body covered with the opaque glaze, two main crystalline phases were identified by specific interferences, namely BaCrO_3 (rhombohedral crystallization system, R-3m space group, with $a=5.65 \text{ \AA}$, $b=5.65 \text{ \AA}$ and $c=62.75 \text{ \AA}$) and Ba_3CrO_5 (tetragonal crystallization system, space group 14 / mcm with $a=7.3 \text{ \AA}$, $b=7.3 \text{ \AA}$ and $c=11.67 \text{ \AA}$). As it was expected the transparent glaze has a predominantly amorphous character, presenting thus a much more adequate aptitude for homogenization than the opaque one.

It is observed that the BaCrO_3 crystalline phase represents the main component (71%) of the opaque glaze with 10% of barium chromate content, followed by the Ba_3CrO_5 compound with 29% (Figure 5.8 a). In the case of transparent glaze with 10% barium chromate content, the BaCrO_7 represents a single crystalline phase (Figure 5.8 b).

Figure 5.9 illustrates the diffractograms of two ceramic specimens with opaque and transparent glaze and 10% of ferric hydroxide content heat-treated at 1030°C .

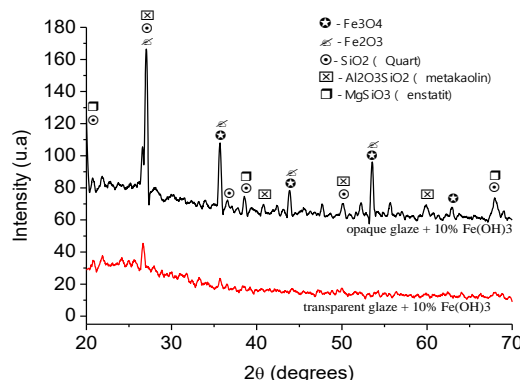


Figure 0.2. XRD patterns of glazed ceramic materials (opaque and transparent) with 10% of $\text{Fe}(\text{OH})_3$ content, heat-treated at 1030°C

The XRD spectrum of the ceramic specimen with opaque glaze and 10% red-brown iron pigment addition, evidences the presence of ferric oxide or iron (III) oxide Fe_2O_3 (tetragonal crystallization system, space group P43212 with $a=8,346 \text{ \AA}$, $b=8,436 \text{ \AA}$ and $c=25,0340 \text{ \AA}$), respectively of iron oxide (II, III) Fe_3O_4 (cubic crystallization system, space group Fd-3m with $a=b=c=8,375 \text{ \AA}$), as the main mineralogical compound with the greatest abundance. The main interference and with the highest intensity is attributed to silicon dioxide SiO_2 , whose line in the XRD pattern overlaps with both metakaolin (resulted from the heat treatment of kaolin - the first combustion) and Fe_2O_3 chemical compounds. Additionally, the amorphous character imprinted by the glaze to the analyzed powder is emphasized by the spectrum halo in the range $2\theta=20\text{-}35$ degrees. The transparent glaze seems to be more suitable for obtaining a homogeneous glaze/pigment mixture, since, unlike the diffraction spectrum of the powder mixture with opaque glaze / red-brown iron pigment content, it has a predominantly amorphous character, in the XRD pattern a less intense interference of SiO_2 ($2\theta=26$ degrees) and a weak interference of Fe_2O_3 (rhombohedral crystallization system, R-3C space group with $a=5.0342 \text{ \AA}$, $b=5.0342 \text{ \AA}$ and $c=13.7483 \text{ \AA}$) being presented. The semi-quantitative percentage analysis of the crystalline phases identified in the opaque glaze with 10% ferric hydroxide revealed a percentage of 91% ferric oxide (Fe_2O_3), followed by 9% iron oxide Fe_3O_4 (magnetite). In the transparent glaze with 10% ferric hydroxide, a single crystalline phase of ferric oxide (Fe_2O_3) was identified.

5.6.2. Structural characterization of basic ceramic material and heat-treated glazes by Scanning Electron Microscopy (SEM)

Figure 5.11 illustrates the SEM images of ceramic body with transparent glaze and 10% of ferric hydroxide $\text{Fe}(\text{OH})_3$ content, heat treated at $1030 \text{ }^\circ\text{C}$.

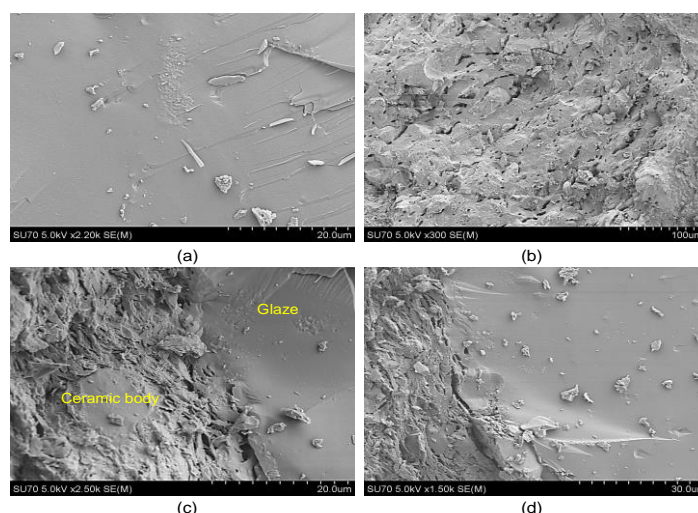


Figure 5.11. SEM images of ceramic body with transparent glaze and 10% of $\text{Fe}(\text{OH})_3$ content heat treated at $1030 \text{ }^\circ\text{C}$: a) glaze; b) ceramic body; c) and d) the interface of ceramic body/glaze

The microstructures presented in Figure 5.11 (a, b, c, d) reveal the transition zone from the porous, crystalline ceramic to the amorphous glaze layer, as well as a narrow area representing the interface of ceramic body / glaze, where as a result of the glaze diffusion into the surface layer of ceramic material, a good adhesion between these two components was achieved.

Figure 5.12 shows the SEM images of the ceramic material with transparent glaze and 10% of chromium hydroxide $\text{Cr}(\text{OH})_3$ content, heat treated at 1030 °C.

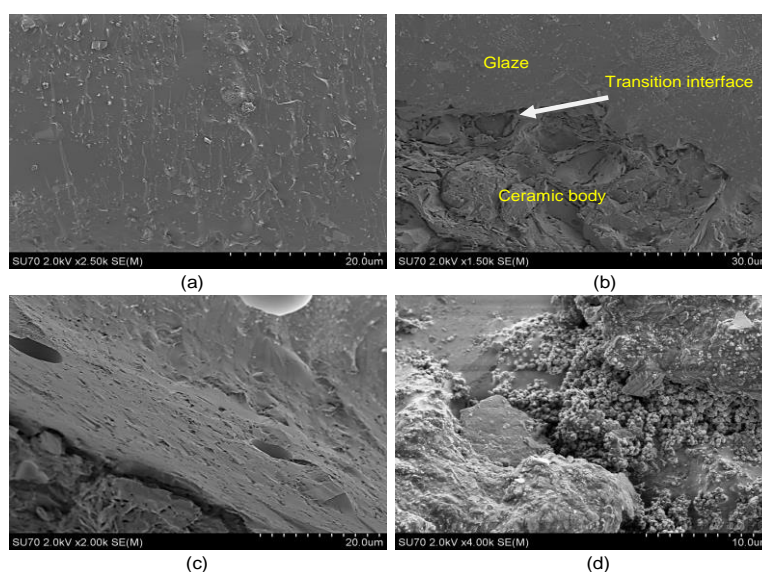


Figure 5.12. SEM images of ceramic body with transparent glaze and 10% of $\text{Cr}(\text{OH})_3$ content, heat treated at 1030 °C: a) glaze; b and c) the interface of ceramic body / glaze; d) defective glaze

As in the case of ceramic glazed specimens containing ferric hydroxide $\text{Fe}(\text{OH})_3$, the ceramic specimens covered with glaze which contains 10% of chromic hydroxide $\text{Cr}(\text{OH})_3$ pigment show similar microstructures in terms of the identified metallographic constituents, respectively, there are very well distinguished the three areas, namely: ceramic body, the interface (the transition zone ceramic body / glaze) and the glaze, Figure 5.12 (a - c).

SEM images of the ceramic body covered with transparent glaze which contains 10% of barium chromate BaCrO_4 , heat treated at 1030°C are shown in Figure 5.13.

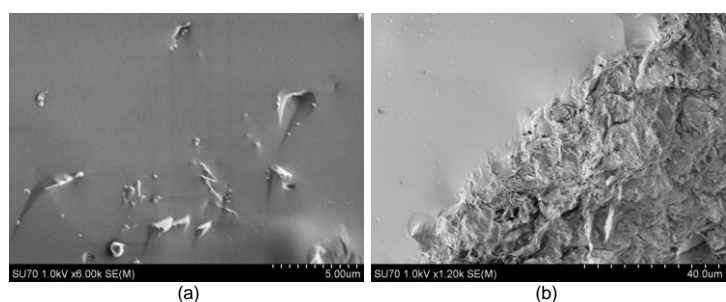


Figure 5.13. SEM images of ceramic body with transparent glaze and 10% BaCrO_4 heat treated at 1030 °C: a) glaze and b) the interface ceramic body / glaze [239]

Regarding the ceramic body covered with transparent glaze which contains 10% of barium chromate BaCrO_4 , the microstructure particularities are similar to those of ceramic specimens with $\text{Fe}(\text{OH})_3$ pigment present in the mixture.

5.6.3. Heat-treated glazes surface analysis by optical microscopy method

Both heat treated glazes (opaque and transparent) containing 10% lead chromate respectively 10% barium chromate, had presented the small surfaces defects, such as holes or bubbles, but visible to the naked eye. Figure 5.14 shows the glazes macrostructures obtained after the optical examination of ceramic samples, heat-treated at 1030°C , by using an optical microscope with a 50x magnification [253].

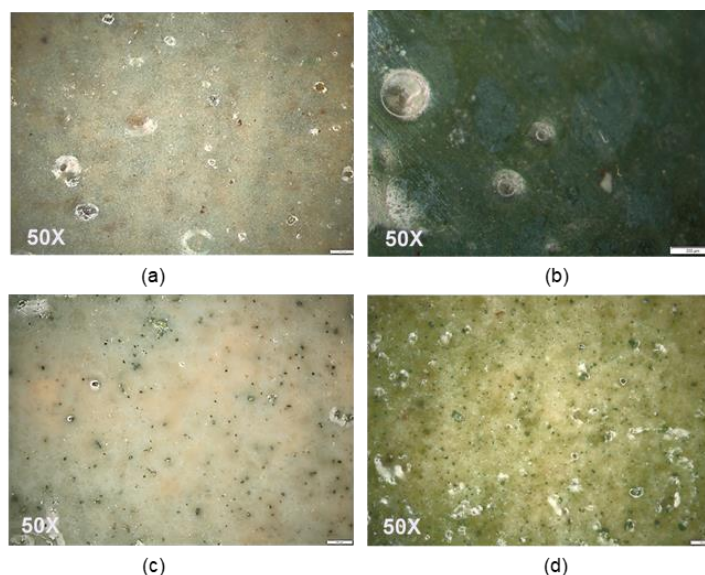


Figure 5.14. The macrostructure of heat-treated glazes at 1030°C : (a) opaque glaze with 10% PbCrO_4 ; (b) transparent glaze with 10% PbCrO_4 (c) opaque glaze with 10% BaCrO_4 ; (d) transparent glaze with 10% BaCrO_4 : 50x magnification

Within the specialty literature it is specified that these types of surface defects can be caused by a too high content of aluminum oxide or silicon dioxide, this being the main compounds of the glaze composition that play a very important role in increasing the melting temperature and glaze viscosity as well as improving the adhesion of the raw glaze.

Another cause of these defects may be the lack of lead oxide in the glazes composition. Additionally, an inadequate heat treatment program can also lead to the appearance of such surface defects.

The opaque and transparent glaze with 10% of ferric hydroxide content, showed after the heat treatment stage a distinctiveness defect namely the presence of small pigment grains within the solidified glazes, visible to the naked eye. (Figure 5.15).

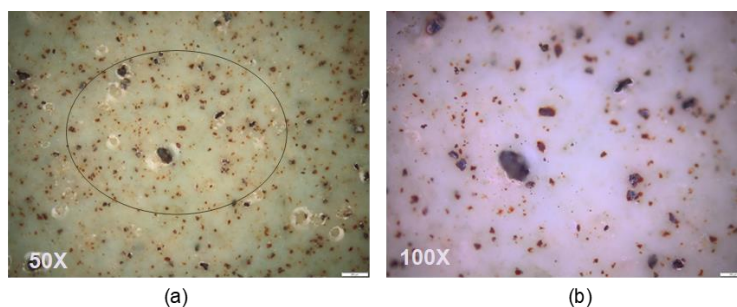


Figure 5.15. Macrostructure of the opaque glaze with 10% of ferric oxide content heat treated at 1030°C: a) 50x magnification; b) 100x magnification

A similar defect was observed for the ceramic specimen with opaque glaze and 10% of chromic hydroxide addition, and, to a lesser extent, these inclusions were present in the structure of solidified opaque glaze with 3% of lead chromate content. The appearance of this defect may be due to the melting points of the pigments synthesized from the galvanic sludges, used to color the ceramic glazes, are higher than the glazes melting point.

All ceramic specimens with both transparent and opaque glaze showed color changes after the heat treatment at 1030°C (see Figure 5.3). The occurrence of this phenomenon can have different causes depending on the compositional characteristics of the pigments, the existence of impurities, the burning conditions or the compatibility of the pigments with the two glazes used in the experimental research.

5.7. Determination of toxicity of heat-treated glazes

5.7.1. Determination of glaze toxicity by leaching tests

The toxicity verification was performed on glazed ceramic samples, for both types of glaze, the selection criterion being the absence of defects or the most visible defects, as well as the lowest and highest pigment content introduced in the glazes. Table 5.4 shows the ceramic samples with heat-treated glazes that have been tested for toxicity [255].

Table 5.4. Ceramic samples with heat-treated glazes, analyzed for toxicity

Sample code	Glaze type	Pigment	Pigment content (%)
P1	Opaque	Ferric hydroxide	10%
P2	Transparent	Ferric hydroxide	10%
P3	Opaque	Lead chromate	3%
P4	Transparent	Lead chromate	10%
P5	Opaque	Chromic hydroxide	10%
P6	Transparent	Chromic hydroxide	10%
P7	Opaque	Barium chromate	3%
P8	Transparent	Barium chromate	10%

Figures 5.16 to 5.18 graphically present the results of leaching tests performed on heat-treated ceramic samples with heavy metals: zinc, total chromium and lead, compared to the maximum permissible limits for waste acceptance on inert landfills, in accordance with the Order no.95/2005 establishing acceptance criteria and preliminary procedures for the acceptance of waste storage and the national list of waste accepted in each class of landfill, amended and supplemented.

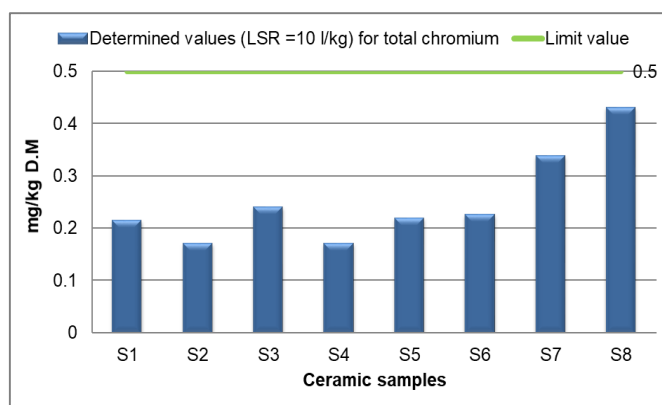


Figure 5.16. Leaching tests for glazed ceramic samples - Total chrome

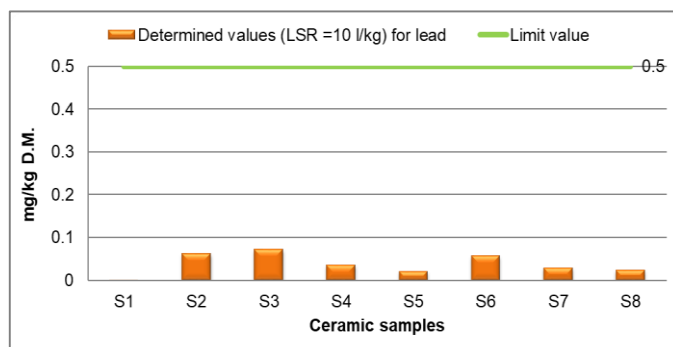


Figure 5.17. Leaching tests for glazed ceramic samples – Lead

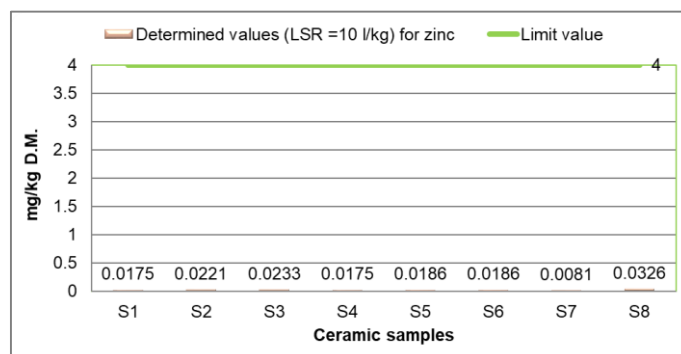


Figure 5.18. Leaching tests of glazed ceramic samples - Zinc

For all glazed ceramic samples subjected to leaching tests, the total amount of chromium was lower compared to the maximum permitted limit provided by the legislation in force for inert waste and which is 0.5 mg/kg DM.

Analyzing the results of the leaching tests obtained for lead and zinc (Figures 5.17 and 5.18) it can be observed that the glazed ceramic samples analyzed were safe and non-toxic, the results determined for the analyzed metals falling well below the lowest maximum concentration allowed by legislation in force, namely for the acceptance of waste on landfills: 0.5 mg/kg DM for lead and 4 mg/kg DM for zinc.

5.7.2. Determination of lead and cadmium given off by ceramic tiles

Figures 5.19 and 5.20 graphically present the results of the test for determination of lead and cadmium given off glazed ceramic samples, compared to the maximum permissible limits provided in Government Decision No. 1197/2002 for approval of Norms regarding the food contact materials, amended and supplemented.

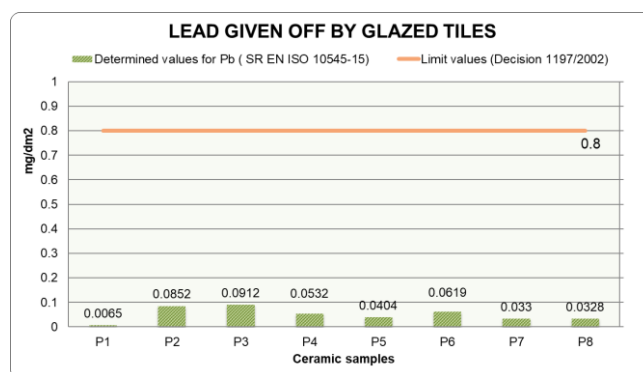


Figure 5.19. The results of the test for determination of lead given off from glazed ceramic samples

The results indicate a good chemical stability of the analyzed samples in terms of lead emission and highlight the fact that the metal was successfully fixed in the vitreous structure of solidified ceramic glazes.

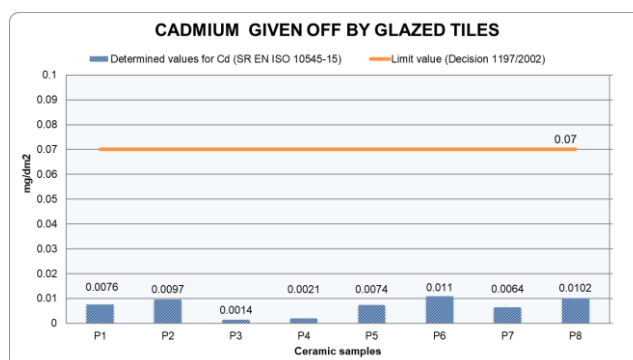


Figure 5.20. The results of the test for determination of cadmium given off from glazed ceramic samples

The results indicate a good chemical stability of the analyzed samples in terms of cadmium emission and highlight the fact that the metal was successfully fixed in the vitreous structure of solidified ceramic glazes.

5.8. Partial conclusions

The diffraction spectrum of the heat-treated ceramic specimens, containing lead chromium and barium chromate, showed a similar crystallization tendency. They also highlighted the presence of silicon dioxide SiO_2 , the major component of the two types of glazes, as well as the predominantly amorphous glazes structure with small crystalline phases.

The diffraction spectrum of the heat treated ceramic specimens with opaque and transparent glaze and 10% of ferric hydroxide content, revealed the presence of two iron oxides as main compounds of the opaque glaze and the predominantly amorphous character of transparent glaze with weak interferences attributed to silicon dioxide and iron oxide.

SEM images of ceramic specimens covered with transparent glaze and 10% of ferric hydroxide, 10% of chromium hydroxide and 10% of barium chromate, heat treated at 1030 °C, highlighted the transition areas from the crystalline ceramic body at the amorphous glaze layers, as well as the diffusion areas of glazes into the support material, respectively the obviousness of glazes fixing on the surface of ceramic body.

Some ceramic specimens with heat-treated glazes showed some surface defects associated with visible bubbles or holes in the layers of solidified glazes or the presence of pigment grains in the solidified glazes.

All glazes showed discoloration, either due to vaporization of the oxidizing compounds (eg chromium oxide) or due to inadequate combustion temperature, generally too high, or the furnace atmosphere.

The leaching tests results regarding the study of heavy metals migration (Cr, Pb, Zn, Fe, Cd) from heat-treated glazes, demonstrate the compatibility between glazes and the incorporated heavy metals. The results also showed the chemical stability of the solidified glaze. The amounts of chromium, lead and zinc leached into distilled water as a test solution among with the amounts of lead and cadmium in 4% acetic acid as a test solution were significantly lower compared to the maximum permitted limits specified in the applicable national legislation.

CHAPTER 6. GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND PERSPECTIVES

6.1. General conclusions

The PhD thesis entitled "*Contributions on the valorization in the ceramic materials industry for glazes of metal ions extracted from sludges resulting in the metal coating processes*" aimed to obtain useful compounds in the form of chromium and iron hydroxides or metal salts, by selective extraction procedures of metal ions from galvanic sludges, in order to reintroduce them in the form of pigments into stable vitreous matrices such as glazes.

The aim was also to detoxify the galvanic sludge considered to be hazardous, in order to ensure its safe landfilling, both for the environment and for human health.

The general conclusions resulting from the PhD thesis elaboration are presented below.

1. The galvanic sludges used for the development of the hexavalent chromium (Cr^{6+}) and trivalent iron (Fe^{3+}) extraction procedures came from different sources, namely a fresh sludge resulting from the wastewater treatment process from a metal surface treatment plant (code: N1) and sludge stored for more than 20 years in a decanter of a decommissioned wastewater treatment plant resulting from various processes of metal surfaces treatment (code: N2).

2. For (Cr^{6+}) and (Fe^{3+}) ions extraction from the two galvanic sludges, an experimental installation was designed at laboratory level which allowed the continuous stirring of the samples and the variation of some technological parameters influencing the solubilization process, such as the reaction temperature and the reaction time.

3. Since chromium is found in galvanic sludge in the form of an insoluble compound of trivalent chromium [$\text{Cr}(\text{OH})_3$], the solubilization of chromium ions was achieved by its oxidation from trivalent chromium (Cr^{3+}) to hexavalent chromium (Cr^{6+}), the oxidizing agent used being sodium hypochlorite (12% NaOCl), in a strongly alkaline medium, at a pH = 12.0-12.5, provided by the addition of sodium hydroxide (20% NaOH).

4. The presence of cyanides in percentage of 0.5% in the N2 sludge composition, led to the orientation of experimental research towards a hydrometallurgical process of chromium ions extraction in strongly alkaline medium, in order to avoid the risk of cyanide ion (CN^-) release in atmosphere, so conditions of its oxidation were ensured simultaneously with the oxidation of chromium.

5. The study of the technological parameters (reaction time, reaction temperature, oxidizing agent excess) influence on the solubilization reaction of hexavalent chromium ions (Cr^{6+}), respectively on their extraction yield from galvanic sludges highlighted the following aspects: the best extraction yield of hexavalent chromium ions from N1 sludge ($\eta_{\text{Cr}(N1)}=84.20\%$) was obtained in a single extraction step, at reaction temperature 80 °C, reaction time 30 minutes and 200% excess of NaOCl 12% oxidizing agent, and the best extraction yield of hexavalent chromium ions from N2 sludge ($\eta_{\text{Cr}(N2)}=93.19\%$) was obtained in two extraction

steps, at the reaction temperature of 90 °C, reaction time 30 minutes and 300% excess of NaOCl 12%.

6. Experimental research has highlighted the fact that the reaction temperature is a technological parameter that influences the chromium ions extraction from galvanic sludge, the extraction yield increasing with temperature increasing.

7. Iron is found, in the sludge cakes resulted after the extraction of hexavalent chromium ions, in the form of bivalent iron (Fe^{2+}), trivalent iron (Fe^{3+}) and hexavalent iron (Fe^{6+}). Trivalent iron ions (Fe^{3+}) were extracted in a strong acid medium, at a pH=1.0-1.5 obtained by the addition of sulfuric acid (20% H_2SO_4), followed by oxidation of bivalent iron (Fe^{2+}) to trivalent iron (Fe^{3+}) with hydrogen peroxide (30% H_2O_2), for N1 sludge and without the addition of hydrogen peroxide, for N2 sludge.

8. The study of technological parameters (reaction time and reaction temperature) influence on the extraction yield of trivalent iron ions (Fe^{3+}) revealed that the best extraction yield of iron ions from N1 sludge was obtained at reaction temperature 80 °C and reaction time 30 minutes ($\eta_{\text{Fe(N1)}}=98.50\%$) and the best extraction yield of iron ions from N2 sludge was obtained at reaction temperature 70 °C and reaction time 30 minutes, in two extraction steps ($\eta_{\text{Fe(N2)}}=95.20\%$).

9. Low extraction yields of both hexavalent chromium and trivalent iron were obtained in the case of N2 sludge, which is a sludge stored for over 20 years in a decanter. This aspect highlights the correlation between the process of solubilization of metal ions and the age of sludge, the solubilization of metal ions, respectively their dissolution in solution being achieved with difficulty due to the stable structure of old sludge.

10. The synthesis of pigments based on chromium and iron, from the solubilization solutions, was performed by precipitating them from the solution, thus obtaining compounds such as hydroxides and metal salts of trivalent chromium (Cr^{3+}), hexavalent chromium (Cr^{6+}) and trivalent iron (Fe^{3+}).

11. Four pigments were synthesized, namely: chromic hydroxide [$\text{Cr}(\text{OH})_3$] also called chromium green pigment, ferric hydroxide [$\text{Fe}(\text{OH})_3$] or red-brown iron pigment, lead chromate (PbCrO_4) also called yellow chromium pigment and barium chromate (BaCrO_4) another yellow pigment.

12. The green chromium pigment $\text{Cr}(\text{OH})_3$ was synthesized by reducing hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}) in an acid medium, at a pH between 2.0 and 2.5 and its complete precipitation with hydroxide sodium (20% NaOH) at pH=7. Experimental studies have shown that the addition of reducing agent, sodium pyrosulfite, in excess influences the precipitation reaction of chromium as a hydroxide, its recovery yield from the solution being 98.50%, to an excess reagent of 30%.

13. Yellow pigments based on chromium, lead chromate (PbCrO_4) and barium chromate (BaCrO_4) were synthesized by precipitating them with lead acetate and barium chloride. The investigation of precipitating reagents excess variation highlighted that the precipitation efficiency, respectively chromium ions recovery from the solution increased with the increasing of precipitation reagent quantity, being almost 100%.

14. Ferric hydroxide, the red-brown iron pigment, was obtained by complete precipitation of trivalent iron (Fe^{3+}) from the solutions resulting in the extraction phase of iron with sodium hydroxide (20% NaOH).

15. The analysis of the elemental chemical composition by the X-ray fluorescence (XRF) method highlighted the purity of the synthesized pigments. The main component of the green chromium pigment $\text{Cr}(\text{OH})_3$ is chromium (89.354%), for the yellow chromium pigment (PbCrO_4) the main component is lead in proportion of 75.2%, followed by chromium in proportion of 23.6%. The yellow chromium pigment BaCrO_4 contains mainly barium (72.8%) and chromium (25.1%) and the red-brown iron pigment $\text{Fe}(\text{OH})_3$ has iron as the main component (73.37%) and various proportions of SiO_2 , SO_3 , ZnO . Impurities from the extraction process of metal ions, were identified for chromic oxide, namely $\text{Na}_2\text{O} \approx 6\%$ and for ferric oxide $\text{Na}_2\text{O} \approx 9.4\%$.

16. The pigments synthesized from galvanic sludge were characterized from a structural point of view by X-ray diffraction and scanning electron microscopy (SEM) analyses. Simultaneous thermal analyses (TG/DSC) were performed in order to determine how temperature variation produces endothermic/exothermic effects that occur in pigments during heat treatment, respectively associated mass loss and calorimetric effects, and to highlight the thermal stability of pigments at high temperatures.

17. With regard to chromic hydroxide $\text{Cr}(\text{OH})_3$, also known as green chromium pigment, the diffraction pattern revealed its entire amorphous structure.

18. The TG/DSC curves of chromic hydroxide showed endothermic and exothermic effects during heat treatment (up to $800\text{ }^\circ\text{C}$), the loss of mass being 14.93% at $430\text{ }^\circ\text{C}$, when an exothermic effect occurred which corresponded to the dehydroxylation of $\text{Cr}(\text{OH})_3$, with the change of the oxidation state of chromium from Cr^{3+} to Cr^{6+} . Accordingly, in chromic oxide (Cr_2O_3), chromium has the 3^+ valence. At a temperature of $708\text{ }^\circ\text{C}$ a peak was recorded which was associated with the onset of the chromium oxide (Cr_2O_3) melting process.

19. SEM images of raw chromic hydroxide showed the presence of small, gel-like and poorly crystallized agglomerated formations, uniformly incorporated in an amorphous matrix. Following the heat treatment at $800\text{ }^\circ\text{C}$ and the loss of water from the structure, a granular, crystalline texture was highlighted, the results being in accordance with the TG/DSC analyses.

20. For PbCrO_4 lead chromate, the diffraction pattern revealed a crystalline structure, with high intensity interferences, a single monoclinic phase of PbCrO_4 lead chromate being identified, which can thus highlight that the pigment has a high degree of purity, this result being consistent with the results of the XRF analysis.

21. The simultaneous thermal analysis of TG/DSC of lead chromate revealed the presence of an indexed exothermic effect on the DSC curve, with a maximum of $738\text{ }^\circ\text{C}$, accompanied by a mass loss of 0.72% which corresponded to the phase transformation of barite-shaped monazite structure. The total mass loss recorded on the TG curve for the lead chromate was 1.96%.

22. SEM images of raw lead chromate showed the presence of dispersed polyhedral particles of PbCrO_4 , with dimensions varying from $0.4\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m}$, while the pigment subjected to heat treatment at $700\text{ }^\circ\text{C}$ showed a compact structure with agglomerated spherical particles measuring up to $8\text{ }\mu\text{m}$, strongly connected and with visible intergranular boundaries with junctions, being thus highlighting the effect of temperature on particle growth.

23. The diffraction spectrum of barium chromate BaCrO_4 showed a high degree of crystallinity of this compound, all diffraction peaks being perfectly indexed as the orthorhombic phase of BaCrO_4 , the minor components appeared during synthesis were poorly crystallized,

so it can be concluded that this pigment has an advanced degree of purity, the results being in good correlation with the XRF data.

24. The barium chromate DSC curve recorded a thermal effect at temperatures between 570 °C and 770 °C, when a mass loss of 0,25% occurred, the total weight loss being 2.2%. Unlike the other pigments, at the end of the heat treatment, the color of barium chromate changed from yellow to green, which suggested the thermal instability of the compound and its decomposition.

25. SEM images of raw barium chromate showed a fine particle texture, with a tendency of the very small ones to agglomerate and a unimodal distribution. The thermal treated sample at 800 °C had a pore-free structure, in which the polyhedral particles, measuring approximately 5 μm, showed well-defined sides and edges.

26. For the ferric hydroxide, also called red-brown iron pigment, the diffraction pattern revealed a predominantly amorphous character and the presence of poorly crystalline structures in a broadly gel formation.

27. TG/DSC analysis of ferric hydroxide revealed the presence of endothermic effects at temperatures below 450 °C, where due to the loss of physically and chemically bonded water from the structure and loss of OH- bonds the mass loss was 22.39%, but also at 601 °C where due to Fe₂O₃ crystallization an exothermic phenomena appeared along with a mass loss of 4.09%.

28. SEM images of ferric hydroxide showed the morphological transformations that took place, induced by the heat treatment performed up to 800 °C. Thus, if the raw pigment had a predominantly amorphous structure with poorly crystallized polyhedral formations, dispersed in the amorphous matrix, the heat treatment of the pigment led to the appearance of nanometer-sized particles of α-Fe₂O₃.

29. The valorization of metal ions extracted from galvanic sludges was carried out by embedding them as pigments in glazes. As the lead chromate (PbCrO₄) and barium chromate (BaCrO₄) are two toxic compounds, being salts of the hexavalent chromium, it is recommended to use them in ceramic materials for decorative use that do not come in contact with food.

30. Various glaze compositions (opaque and transparent) with pigments synthesized from galvanic sludges were established and it was analyzed the influence of controlled incorporation and the use of different concentrations of pigments containing chromium and iron on the behavior of glazes. The amount of pigments were added in proportions of 3%, 5% and 10% in solutions prepared with opaque and transparent glaze.

31. Obtaining glazed ceramic materials was achieved through a double heating program: heating the naturally dried ceramic mass, in a neutral atmosphere, for 7 hours at a temperature of 1070 °C, with 15 minutes of maintaining the maximum temperature and afterwards slow cooling for 17 hours, followed by heat treatment of glazed ceramic samples under similar conditions, but at a temperature of 1030 °C.

32. XRD analysis of the glazes (opaque and transparent) revealed their predominantly vitreous character and the presence of fine silicon dioxide crystals in both types of glazes or other specific compounds such as cerium oxide in the opaque glaze, the results being in good correlation with the XRF data.

33. The degree of crystallinity and the mineralogical composition of the glazes with pigment additions, heat treated at a temperature of 1030 °C, changed due to the compositional diversity, which was highlighted by the XRD analyses of some randomly selected samples.

34. Thus, the diffraction patterns of the ceramic samples heat treated at 1030 °C, with the studied glazes and varied lead chromate content highlighted the following: in the opaque glaze with 10% lead chromate - the presence of lead chromate (PbCrO_4) as the majority monoclinic phase, in the opaque glaze with 3% lead chromate - the presence lead tetraoxide (Pb_3O_4) as the majority tetragonal phase along with SiO_2 from the composition of the glaze and weak interferences attributed to metakaolinite. The spectrum of the sample with transparent glaze and 5% lead chromate, highlights the amorphous character of the glaze and small crystalline phases, identified as red lead Pb_3O_4 (tetragonal crystallization system) and chromic oxide Cr_2O_3 (rhombohedral crystallization system).

35. The diffraction spectrum of the ceramic materials with opaque glaze and 10% barium chromate highlighted the presence of two main crystalline phases, namely BaCrO_3 (rhombohedral crystallization system) and Ba_3CrO_5 (tetragonal crystallization system). For the transparent glaze with 10% barium chromate, the presence of BaCr_2O_7 monoclinic phase was emphasized. The transparent glaze had a predominantly amorphous character, having a much more adequate disposition for homogenization than the opaque one.

36. Regarding the XRD analyses of basic ceramic materials with opaque glaze and 10% ferric hydroxide as well as transparent glaze with 10% ferric hydroxide, the diffraction patterns highlights the presence of Fe_2O_3 iron oxide (tetragonal crystallization system) and respectively of iron oxide Fe_3O_4 (in which Fe has a valence of 2⁺ or 3⁺) which has a cubic crystallization system. The transparent glaze has a predominantly amorphous character, as the diffraction pattern differentiates only a less intense interference attributed to silicon dioxide and weak interferences of iron oxide Fe_2O_3 (rhombohedral crystallization system).

37. SEM images of the ceramic bodies with transparent glaze and 10% ferric hydroxide, transparent glaze and 10% chromic hydroxide and transparent glaze and 10% barium chromate, heat treated at 1030 °C, clearly highlighted the transition areas from the crystalline ceramic body to the amorphous glaze layers, as well as the diffusion and bonding areas of the glazes on the ceramic body surface.

38. In the case of ceramic body with glaze and 10% chromium hydroxide addition, crystalline formations similar to Cr_2O_3 chromium oxide crystals appear in the amorphous mass of the glaze as inclusions, caused by insufficient homogenization between the glaze and pigment or due to the high heat temperature of the glaze.

39. Certain samples with heat-treated glazes showed some surface defects that can be attributed to several causes.

40. Both transparent and opaque glazes containing 10% lead chromate, as well as transparent and opaque glazes containing 10% barium chromate showed defects associated with visible bubbles or holes in the layers of the solidified glazes, the appearance of which may have various causes, most likely being caused by emissions of H_2O and CO_2 vapors during heat treatment.

41. Both opaque and transparent glazes, containing 10% ferric hydroxide, opaque glaze containing 10% chromic hydroxide and opaque glaze with 3% lead chromate addition showed a defect characterized by the presence of pigment grains in the solidified glazes, most likely due to the pigments' granulometry and their higher melting points compared to that of the glazes.

42. All glazes showed discoloration, either due to vaporization of the oxidizing compounds (e.g. chromium oxide) or due to an inadequate, generally too high calcination temperature or the atmosphere in the furnace.

43. The emission of toxic substances is of great importance for the hygienic and sanitary conditions of ceramic products, the verification of the solidified glazes toxicity being carried out by leachate tests (in distilled water) and tests to determine the lead emission of glazed ceramic bodies (in 4% acetic acid solution).

44. The toxicity verification was performed for both types of glaze, the selection criterion being the lack of defects or of the most visible defects, as well as for the lowest and highest pigment content introduced into the glazes.

45. The results of the leaching tests showed that the studied ceramic bodies with heat-treated glazes and various quantities of pigments were safe and non-toxic, and the determined results were well below the lowest maximum concentration allowed by the national legislation.

46. The results of the test for determining lead and cadmium emissions showed that the values were well below the maximum permissible limit of 0.8 mg/dm² for lead and 0,07 mg/dm² for cadmium, provided by Decision no. 1197 / 2002, with its subsequent amendments and supplements.

47. The obtained results indicated a good stability of the analyzed glazed ceramic bodies and highlighted the fact that the metals were successfully fixed in the vitreous structure of the solidified glazes. Calculations of heavy metals fixating yields for each analyzed sample showed values of over 99.99%.

48. The results of the present research are of particular importance as they demonstrate the possibility of fixing the pigments extracted from galvanic sludge in the vitreous structure of solidified glazes and the use of ceramic products as decorative products, without toxic effects on the environment and human health.

6.2. Original contributions

The research topic approached in the PhD thesis is part of current concerns for the useful compounds recovery from hazardous waste in various industries and reducing the negative impact of heavy metals on the environment and human health.

The experimental researches that contributed to this PhD thesis elaboration, presents novelty elements compared to the current state of knowledge regarding the metal ions extraction from sludges resulting from metal coatings and their introduction in the form of pigments in glazes for decorative ceramic materials, since they led to the obtaining of new materials (different types of colored glazes) and to the reduction of environmental pollution.

The main contributions of the author of the PhD thesis are presented below.

1. Elaboration of a bibliographic study, based on specialty literature, regarding the valorization in the ceramic materials industry, for glazes, of metal ions extracted from sludges containing heavy metals, resulted from metal coatings technologies.

2. The use and characterization of two types of galvanic sludge, with different origin, for the extraction of metal ions: a fresh sludge collected from the treatment of wastewater derived from a metal surfaces treatment plant, and a sludge stored for more than 20 years in a decanter of a decommissioned wastewater treatment plant, resulting from various metal coating processes.

Experimental researches have highlighted that the structure and chemical composition of sludge stored over a long period of time have been much more stable than the structure of fresh sludge, and metal ions solubilization has been slower, and their extraction yields have been lower.

3. Design and realization of the experimental laboratory installation for the solubilization of chromium and iron metal ions in order to extract them from galvanic sludge.

4. Development of a procedure for hexavalent chromium ions (Cr^{6+}) extraction from galvanic sludges, in a strongly alkaline medium, simultaneously with the oxidation of cyanides identified in the composition of one of the used sludges, thus avoiding the release of cyan ion (CN^-) and hydrocyanic acid formation (HCN) gaseous, very toxic.

5. Development of a procedure for trivalent iron ions (Fe^{3+}) extraction, in a strongly acidic medium, from sludge remaining after the hexavalent chromium ions (Cr^{6+}) extraction.

6. Investigation of the influence of different extraction parameters (reaction temperature, reaction time and oxidizing agent - reagent excess) on the solubilization reaction of hexavalent chromium ions (Cr^{6+}), respectively on their extraction yield from galvanic sludge. It has been established that the reaction temperature is an important parameter during the oxidation process, therefore better dissolution yields of hexavalent chromium ions (Cr^{6+}) in solution were obtained with increasing of temperature.

7. The influence of precipitating agents excess on the precipitation reactions and, implicitly, on the efficiency of pigments recovery from the solution resulting in solubilization process was analyzed.

8. The pigments were synthesized: chromic hydroxide [$\text{Cr}(\text{OH})_3$], also called chromium green pigment, ferric hydroxide [$\text{Fe}(\text{OH})_3$] or brown iron pigment, lead chromate (PbCrO_4) also called chromium and chromium yellow pigment of barium (BaCrO_4) which is also a yellow pigment. These pigments contain hexavalent chromium (Cr^{6+}) or trivalent iron (Fe^{3+}) ions, extracted from galvanic sludge.

9. The detoxification of some galvanic sludges considered as hazardous waste was aimed, by selective extraction of chromium and iron metal ions in the form of hydroxides or chromium salts, in order to reintroduce them in the form of pigments in vitreous, stable matrices, such as glazes for decorative ceramic materials.

10. The chemical, structural characterization of the pigments synthesized from galvanic sludges, their thermal stability at high temperatures, were achieved by performing XRF, XRD, SEM and TG/DSC analyzes.

11. Obtaining colored glazes for decorative ceramic materials by using two types of glazes (opaque and transparent) and introducing the pigments extracted from galvanic sludge in different concentrations in the composition of glazes has been investigated.

12. Research on obtaining and characterization of glazes colored with varied content of inorganic pigments synthesized from galvanic sludge focused on determining the chemical, structural properties, through modern investigation methods, such as XRF, SEM, XRD analyzes.

13. The determination of glazes eco-toxicity was performed by leaching tests or tests in order to determine the lead and cadmium given of from them. The obtained results indicated a good stability of the glazed ceramic samples and highlighted the fact that the metal ions were fixed in the vitreous structure of the solidified glazes, which supports the presented research contribution to obtain new materials and reduce environmental pollution.

6.3. Perspectives

The experimental researches carried out within this doctoral thesis, opens the opportunity and the possibility to develop new research directions, the following being mentioned.

- Deepening of studies regarding the application of metal ions extraction process from galvanic sludge, developed in the PhD thesis, to other categories of sludge with complex chemical compositions, similar to that of the studied sludges.
- Study regarding the evaluation of galvanic sludges for the development of extraction processes of other heavy metal ions present in their chemical composition, such as: copper, zinc, lead, cadmium, etc.
- Deepening of study regarding the obtaining of glazes with the addition of synthesized pigments from galvanic sludge, by varying the amounts of pigments used to color glazes but also the technological parameters of ceramic mass and glaze firing operations, such as: time, firing temperature, firing atmosphere etc.
- Study of the use of chromium and iron metal ions extracted from galvanic sludges for other applications, other than the ceramic materials industry.

SCIENTIFIC ACHIEVEMENTS

Scientific publications in the field of research theme

Publications in WoS indexed journals

1. **Maria-Iuliana Marcus**, Mihaela Andreea Mitiu, Maria Vlad, Mariana Mincu, Gina Ghita, Ana Maria Anghel, ***Influence of different electroplating sludge types on the iron ions recovery yield***, Rev. Chim. (Bucharest), Vol. 69, Issue 3 (2018), 618-620, ISSN: 0034-7752, <https://doi.org/10.37358/RC.18.3.6161>, WOS:000430946500018, Factor de Impact: 1.605.

2. Mihaela Andreea Mitiu, **Maria-Iuliana Marcus**, Maria Vlad, Cristina Mihaela Balaceanu, ***Stability of ceramic glazes obtained by valorification of anorganic pigments extracted from electroplating sludge***, REV. CHIM. (Bucharest), Vol. 69, Issue 3 (2018), 571-574, ISSN: 0034-7752, <https://doi.org/10.37358/RC.18.3.6151>, WOS:000430946500008, Factor de impact: 1.605

3. **Maria-Iuliana Marcus**, Maria Vlad, Maria Andreea Mitiu, Ana-Maria. Anghel, Florica Marinescu, Lucian Laslo, Mihaela Ilie, Robert Szep, Gina Ghita, Monica Matei, Elena Holban, Florina Diana Dumitru, ***Recovery of galvanic sludge by physicochemical mechanisms***, Journal of Environmental Protection and Ecology (JEPE), 18, No 3 (2017), ISSN:1311-5065, <http://www.jepe-journal.info/vol-15-no-2-2014>, Factor de impact: 0.774

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1. **Maria-Iuliana Marcus**, Maria Vlad, György Deák, Andreea Moncea, Ana-Maria Panait, Gelu Movileanu, ***Thermal stability of inorganic pigments synthesized from galvanic sludge***, REV. CHIM. (Bucharest), Vol. 71, Issue 8 (2020), 13-20, Indexare revistă: SCOPUS, SJR, LetPub, CAS, <https://doi.org/10.37358/RC.20.8.8274>

2. **Iuliana Marcus**, Maria Vlad, Ileana Mițiu, Mihaela Andreea Mițiu, ***Selective recovery by solubilization of metals ions of chromium, iron and zinc from electroplating sludge to develop pigments for ceramics industry***, The Annals Of "Dunarea De Jos"

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3. Maria Vlad, Gelu Movileanu, **Iuliana Marcus**, Gheorghe Florea, Alina Cantaragiu, **Neutralization of hazardous waste in vitreous mass of glass**, The Annals Of "Dunarea De Jos" University Of Galati, Fascicle IX METALLURGY AND MATERIALS SCIENCE, NO. 2 – 2012, ISSN 1453 – 083X, Categoria B+ Cod CNCSIS 2015, Indexări revistă: CSA/EBSCO/Copernicus

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Participation in International Conferences:

1. **Maria-Iuliana Marcus**, Mihaela-Andreea Moncea, Maria Vlad, Ana-Maria Panait, Mihaela Mitiu, György Deák, **Thermal stability of inorganic pigments synthesized from galvanic sludge**, *The 12th European Symposium on Thermal Analysis and Calorimetry, ESTAC12, Braşov* (prezentare orală), August 2018

2. **Marcus Maria-Iuliana**, Vlad Maria, Panait Ana-Maria, Moncea Andreea, Mîțiu Mihaela Andreea, Movileanu Gelu, **Chemical and structural characterization of chromium-based pigments extracted from hazardous sludge**, *International Conference on Material Science & Engineering, UGALMAT 8th edition*, (poster), octombrie 2018

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5. **Marcus Maria-Iuliana**, Vlad Maria, Mitiu Ileana, Mitiu Mihaela Andreea, Toba Francisc, **Recovery of heavy metals from electroplating sludge in order to reduce their harmfulness**, *B.EN.A. International Conference - MACODESU, Trabzon, Turkey* (poster), septembrie, 2015

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1. **Maria-Iuliana Marcus**, Maria Vlad, Andreea Moncea, Ana-Maria Panait, Gelu Movileanu, **Applications in ceramic glazes of iron hydroxide pigment synthesized from galvanic sludge**, *Scientific Conference of Doctoral Schools SCDS-UDJG 2019, Universitatea „Dunărea de Jos”, Galați (poster), iunie 2019*

2. **Maria-Iuliana Marcus**, Maria Vlad, Andreea Moncea, Mihaela Andreea Mitu, Gelu Movileanu, **Characterization of ceramic pigments obtained by extraction from galvanic sludge**, *Scientific Conference of Doctoral Schools SCDS-UDJG 2018, Universitatea „Dunărea de Jos”, Galați (poster), iunie 2018*

3. **Maria-Iuliana Marcus**, Maria Vlad, Mihaela Andreea Mițiu, Andreea Moncea, Gelu Movileanu, **Valorisation potential of the inorganic compounds recovered from galvanic sludge in decorative ceramic glazes**, *Scientific Conference of Doctoral Schools SCDS-UDJG 2017, Universitatea „Dunărea de Jos”, Galați (poster), iunie 2017*

4. **Maria-Iuliana Marcus**, Vlad Maria, Radu Tamara, Balint Lucica, Constantinesu Stela, **Selective extraction of metal compounds from electroplating sludge**, *Scientific Conference of Doctoral Schools SCDS-UDJG 2016, Universitatea „Dunărea de Jos”, Galați (poster), iunie 2016*

5. **Maria-Iuliana Marcus**, Maria Vlad, Ileana, Mihaela Andreea Mitu, **Selective recovery by solubilization of metals ions of chromium, iron and zinc from electroplating sludge to develop pigments for ceramics industry**, *Scientific Conference of Doctoral Schools SCDS-UDJG 2015, Universitatea „Dunărea de Jos”, Galați (poster), iunie 2015*

Participation in Workshop:

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