DOCTORAL THESIS

Thesis Title:

CONTRIBUTIONS TOWARD THE UPGRADED UTILIZATION OF CERTAIN SECONDARY STEEL RESOURCES IN THE CONTEXT OF THE CRITICAL RAW MATERIALS PARADIGM

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THESIS ABSTRACT

Chapter 1. PROLEGOMENA

1.1. Presentation of the Topic and Justification for the Approach Taken

Raw materials play a vital role in the European Union (EU) economy, serving as the foundation of a strong industrial base necessary for the manufacture of a wide range of products and equipment used in everyday life, as well as for the development and application of modern technologies [1]. Consequently, access to raw materials is a major concern for the EU, as international supply chains have become unreliable [1,2]. In this context, secondary resources are part of the solution for increasing the EU's resilience to disruptions in the raw materials supply chain [3]. The secondary resources paradigm is based primarily on transforming waste into useful materials. According to clause no. 1 of Article 3 of the Waste Framework Directive, **"waste"** means "*any substance or object which the holder discards or intends or is required to discard*" [4]. According to Directive 2008/98/EC, the status of a substance as waste is not defined by the chemical, physical, or mechanical properties of a material or substance, nor by the composition or lifespan of the product, but rather by the holder's attitude. On the other hand, according to the same directive, a substance ceases to be considered waste once it has undergone recovery, recycling, or primary processing that confers properties meeting specific criteria in accordance with clause 1 of Article 6 of the Waste Framework Directive [4]. In this context, given that Romania's metallurgical industry has generated a vast secondary resource and that this resource remains untapped and unexploited, it was deemed more than justified to address the topic of maximizing the value of this resource within the scope of this thesis.

1.2. How the topic fits within the specific field of the doctoral program and a brief overview of the main challenges

The thesis topic - namely, the creation of know-how, acquisition of data, and the development of projects that contribute to the utilization of secondary resources within the Romanian steel industry, including the challenge of identifying critical materials (which are, in most cases, metals) - effectively falls within the specific scope of the Doctoral School of Materials Science and Engineering (SD-SIM) within the Organizing Institution for Doctoral Studies (IOSUD) at the National University of Science and Technology "Politehnica" Bucharest (UNSTPB). In this regard, the thesis, by its very nature, addresses theoretical and experimental research aspects in the field of ***Materials Engineering*** (according to www.sdsim.ro), namely:

1. fundamental and applied investigations into the processes and technologies for the production and processing of metallic, ceramic, and composite materials;
2. advanced analyses of the composition, structural organization, and physicochemical properties of materials;
3. research aimed at the recovery through recycling of waste resulting from metallurgical activities;
4. the development and implementation of environmentally friendly metallurgical technologies, with an emphasis on the reuse of byproducts derived from polluting emissions.

As part of the thesis preparation program, fundamental research was conducted in the field of materials characterization. Given the nature of the topic, the challenge arose of characterizing large volumes of materials, which inevitably involved applying the theory of material sampling and performing statistical analysis of the data obtained from sets of collected samples. The valuable results obtained in this field were published in leading ISI-indexed journals.

1.3. Formulating research hypotheses; presenting and elaborating on the research questions used

The research hypotheses were based on the observation that secondary resources from Romania's metallurgical sector are abundant and even create problems for the village of Roman (Clause C-

301/2017, EU Regulation 1252/2024), namely: How heterogeneous is the distribution of contents estimated based on sampling in the tailings piles?

What are the batch-level (pond) concentrations of CRM and the major constituent materials?

What would be the ideal investigative infrastructure to facilitate making the correct decision regarding whether to exploit the deposit as a source of CRM or, conversely, to declare the deposit uninteresting in terms of CRM content;

Would the benefits for Romania be significant if it were to promote an appropriate project to develop expertise and infrastructure for investigating industrial and extractive waste dumps?

1.4. Presentation of the general objective of the doctoral dissertation and its specific objectives

The general objective of the research carried out during the doctoral studies was to establish the optimal recovery pathways for certain landfilled materials with waste status resulting from the activity of the iron and steel industry, and to transform them into secondary resources by changing their status from waste to by-product.

The specific objectives related to the general objective are as follows:

- Deepening knowledge regarding waste management in the steel industry;
- Deepening knowledge of sampling theory (TOS - Theory of Sampling) and its subsequent application to the sampling of waste dumps;
- Deepening knowledge of waste characterization and its subsequent application to elemental and mineralogical analyses of waste;
- Deepening knowledge of statistical inference and its subsequent application to the analysis of laboratory data to ensure the reliability of aggregate data at the batch level;
- Addressing the issue of secondary sources of CRM to align with the EU's efforts to ensure the greatest possible resilience of the supply of critical materials. It is worth noting that, during the course of the doctoral program, this issue became more pressing at the EU/EC level, and, as a result, EU Regulation 2024/1252 was enacted, which has the force of law at the EU level;
- Establishing an efficient and reliable method for the preliminary characterization (*screening*) of steel industry waste dumps in order to identify solutions for their recycling/recovery in accordance with EU practices;
- Establishing a method for the advanced recovery of blast furnace slag from the Călan slag dump;
- Disseminating the knowledge and data obtained to increase the visibility of Romanian research in the field of secondary raw material sources.

1.5. The research methodology adopted, with clear reference to each specific objective

The thesis topic involved conducting activities specific to scientific research and technological development in the field of Materials Engineering, structured around three major areas: fundamental research, applied research, and technological development with knowledge transfer. To provide a comprehensive understanding of the methodology used, the role of each category of activities is specified [35].

Fundamental scientific research, encompassing both theoretical and experimental aspects, aims to generate and consolidate basic knowledge. This is achieved through the formulation of general-purpose proofs, algorithms, methods, and computer applications in the relevant field. It is subdivided into pure fundamental research, focused exclusively on advancing knowledge, and directed fundamental research, which aims to produce knowledge useful for practical purposes, such as the assessment of a waste dump with a view to reclassifying it as a secondary resource for critical or non-critical materials.

Applied research represents the stage in which fundamental knowledge, supplemented by empirical knowledge, is integrated and transformed into products, processes, or services with the potential for economic value and practical utility.

Technological development consists of translating the results of applied research into the actual realization of the targeted product, process, or service. This can be achieved directly or through technology transfer mechanisms, including design, preparation for production, and market integration.

1.6. The impact of the doctoral dissertation's findings, highlighting its multidisciplinary and interdisciplinary nature as well as the limitations of the research conducted

Some of the findings of the doctoral dissertation were validated through publication in ISI-indexed journals in the Q2 category, in the Scientific Bulletin of UNSTPB (Q4), or were discussed in oral presentations at the international conferences RoMAT 2022 and SGCM 2025.

The purely scientific significance of certain theoretical developments regarding the sampling of powdered and granular materials will endure and serve as a valuable asset for the entire scientific community involved in this field.

Research on the screening of critical materials in steel industry tailings piles represents a completely new development at the national level and contributes to meeting the requirements of EU Regulation 2024/1252 - a regulation that will pose financial challenges for Romania if its requirements are not met on time.

Based on the data obtained - at least to date - it can be concluded that there is no risk of critical materials being lost from the investigated stockpiles in cases where the stockpiled byproducts are utilized in the cement industry or in civil and road construction.

The results obtained regarding the recycling of blast furnace slag from the Călan slag dump as a clinker precursor represent a major contribution, since using the slag for backfilling or as aggregate in concrete are inferior forms of recycling (downcycling) [36].

Recycling blast furnace slag as a clinker precursor has two major advantages:

1. It conserves limestone, which is a valuable rock in Romania;
2. It reduces the carbon footprint associated with cement production, as it saves the energy required for quarrying as well as that required for clinkerization.

The research for this thesis is multidisciplinary, as it integrates elements of materials science and engineering, waste management, instrumental analysis, metrology, and mathematical statistics. The thesis topic is comprehensive, ambitious, and pressing, since if waste dumps (tailings piles) are not properly closed, Romania will face financial penalties [8, 27].

On the other hand, the thesis topic is broad and cannot be fully covered in a single thesis. Thus, the research undertaken had limitations regarding the scope of the sample set; specifically, more samples needed to be collected to improve the reliability of the synthesized results. Furthermore, limited access to investigative and measurement equipment constituted an impediment that restricted the final quality of the research results.

Chapter 2. METHODS AND TECHNIQUES FOR INVESTIGATING THE PHYSICAL AND CHEMICAL PROPERTIES OF TARGET MATERIALS

2.1. Introduction

It is evident that "there is no engineering research without measurements"; the value of knowledge is essentially determined by the exactness (precision and accuracy) of measurement results. Thus, the effort to conduct meaningful research in the field of advanced recycling of secondary metallurgical resources cannot be successfully achieved without measurements that are appropriate for the purpose and that yield numerically exact results. I emphasize the importance of the exactness (precision and accuracy) of numerical results by referring to the well-known remark by the scientist William Thomson, also known as Lord Kelvin, namely "*When you can measure what you are talking about and express it in figures, then you know something about the subject; when you cannot express it in figures, your knowledge is poor and unsatisfactory; it may be the beginning of knowledge, but you have scarcely advanced, in your thoughts, to the stage of science.*"[40].

2.2 Methods and Techniques for the Elemental and Mineralogical Characterization of the Investigated Materials

2.2.1. General Considerations

According to the literature [41, 42, 47, 48, 50, 53, 54], the characterization of metallurgical waste in the laboratory is carried out using three main categories of methods. The first category comprises methods for assessing the pollution impact by means of leaching tests, used to determine the mobility of contaminants in aqueous media (eluates, leachate, acid mine drainage). The second category consists of analytical methods designed to quantify pollutants associated with heavy metals and other toxic substances, such as X-ray fluorescence spectrometry (XRFS), atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), inductively coupled plasma mass spectrometry (ICP-MS), or high-performance liquid chromatography (HPLC). The third category includes methods for assessing recovery and recycling potential by determining the content of valuable elements and their exploitation characteristics.

2.2.2. Summary of the Methods Used

2.2.2.1. The Electrical Resistivity Method

The electrical resistivity method, one of the oldest geophysical techniques, is notable for its non-invasive nature and its ability to collect a large volume of data in a short period of time. ERT (Electrical Resistivity Tomography) is widely used in environmental and engineering studies [56 - 58]. In the case of tailings ponds, ERT-based studies have primarily focused on identifying the internal structure of the tailings, delineating the interface with the geological substrate, detecting discontinuities (faults, fractures) that may affect stability, and identifying preferential migration pathways for heavy metals or acid drainage [59, 60].

2.2.2.2 X-ray Fluorescence Spectrometry

XRFS Spectrometry is a well-established analytical method characterized by accuracy and reproducibility. XRFS measures elemental concentrations without being sensitive to the structures in which the atomic species are found.

2.2.2.3. Method for Investigating Materials via X-ray Diffraction

X-ray diffraction (XRD) is a fundamental analytical technique used to investigate crystalline structure, perform mineralogical identification of solid materials, and conduct quantitative phase analysis. The technique is sensitive to the fine structure of phases and to crystalline defects.

2.2.2.4. Optical microscopy methods and techniques

Optical microscopy (OM) is a fundamental and widely used technique for the microstructural characterization of materials, including metallurgical wastes such as tailings. OM has two subcategories: conventional OM and metallographic OM. Conventional OM is used to observe microscopic details (texture, morphology) at magnifications of 20 - 1,000X without altering the sample's morphology, while so-called metallographic OM is used to examine flat, ground, and polished surfaces

2.2.2.5. SEM-EDS Microscopy Method and Technique

For the micro and nanostructural analysis of materials at magnifications ranging from 100× to $2*10^5$×, scanning electron microscopy (SEM) is the most widely used technique because it provides relevant images at a reasonable cost. In most cases, SEM microscopes are often equipped with X-ray analyzers - EDS (Energy Dispersive Spectrometer) - that detect X-rays generated by the interaction of the electron beam with the sample [70]. EDS results are indicative/semi-quantitative because they depend on the morphology and orientation of the sample relative to the EDS detector.

2.2.2.6. LIBS Microscopy Method and Technique

LIBS (Laser-Induced Breakdown Spectroscopy) has demonstrated its ability to measure, with reliable accuracy, the concentrations of elements in rocks, slag, and other materials of interest, ranging from ppm levels to high concentrations [73 - 76]. In addition, LIBS can detect and quantify elements that are not detectable by XRFS and XRD, such as Li, B, Be, C, etc. [75, 76]. LIBS is a form of atomic

emission spectrometry that measures the radiation emitted by quantum transitions of valence electrons that occur when these transitions are excited by appropriate laser radiation. To date, the LIBS technique has not been applied in the field of slag analysis in our country.

Chapter 3. STUDIES AND RESEARCH ON THE UPCYCLING OF AIR-COOLED BLAST FURNACE SLAG IN LINE WITH THE "ZERO WASTE" APPROACH

3.1. The Importance and Relevance of the Topic in the Current Trend

In Romania, there are still huge piles of air-cooled blast furnace slag (ACBFS) in Galati, Hunedoara, Calan, and elsewhere. This slag is occasionally used for backfilling or filling pits, which constitutes a lower-value use (down-cycling) compared to other potential applications, such as a cement precursor or a potential source of CRM. Up-cycling this slag is a major challenge and the subject of this chapter. The value/economic difference between up-cycling and down-cycling amounts to more than 10 euros per metric ton of slag, which, at a volume of millions of metric tons, can yield substantial benefits!

3.2. Physicochemical Characteristics of Steel Slags

The utilization of metallurgical slags depends critically on their mineralogical and physicochemical characteristics, such as crystalline and amorphous phases, inert element contents, toxic element contents, etc. In fact, the first step toward the optimal utilization of slag of any kind is its elemental, mineralogical, and dispersional characterization—i.e., distribution in the stockpile, impurities, etc.

3.3. Current Status of Steel Slag Utilization

3.3.1. Methods of Utilizing Steel Slag

From the very beginnings of the steel industry, it was recognized that residual slag could be used in various fields as a substitute for genuine materials, both to conserve those materials and to reduce the slag piles accumulating around steel mills. Obviously, in the early days of the steel industry, environmental considerations did not play a significant role in the strategy for utilizing slag. The following section will briefly outline the classification of blast furnace slag utilization/recycling to provide a clear picture of what conventional recycling, upcycling, and downcycling, and to place the Călan resource in the context of its utilization according to the new paradigm established by EU Regulation 1252/2024 and the "zero waste" approach mandated by the EU's circular economy policy.

3.3.2. The Current State of Blast Furnace Slag Recycling in Europe

The recycling of blast furnace slag produced by the steel industry is primarily achieved through forced cooling to produce GBFS (Granulated Blast Furnace Slag). Approximately 90% of the blast furnace slag produced in Europe in recent years has been recycled in the cement industry (Fig. 3.6) [101].

3.3.3. Current Status of Steel Slag Recycling in Romania

In Romania, there is no official documentation attesting to the use of ACBFS as a material for highway foundations or other infrastructure projects, although this option would be technically feasible. Environmental authorities and local businesses have emphasized, for several years now, that road infrastructure development projects - such as the construction of Pan-European Corridor IV - could represent a viable solution for utilizing these quantities of slag accumulated in stockpiles. Furthermore, companies specializing in slag processing have indicated that they have the capacity to supply several million metric tons of such material annually, which could meet the potential demand from the construction sector.

In contrast, there is clear evidence regarding the utilization of granulated blast furnace slag (GBFS) in Romania.

3.4. Experimental Results on the Advanced Utilization of Slag from the CĂLAN slag dump

The utilization/recycling of stockpiled ACBFS slag involves at least four unavoidable processes: 1) breaking up the slag (especially the "slag lumps "; 2) crushing; 3) iron removal; 4) sorting. These processes are resource-intensive (infrastructure, energy, labor, technical and economic management).

The level of processing costs relative to the market price of the resulting fractions determines the choice between:

- immediate utilization of the slag or
- postponing it until a market opportunity arises.

In this context, studies and research were conducted in two areas:

1. Optimizing the slag processing technology at the Călan slag dump;
2. Investigating the possibility of further valorization of the sorted fractions, where such an opportunity exists.

The results obtained in these two areas are presented below.

3.4.1. The efficient "DESTRO" technology for processing ACBFS slag based on the "zero waste" approach, applied at the Călan slag dump

3.4.1.1. Overview of the Călan blast furnace slag dump

Starting in 2012, the Călan slag dump came under private ownership, and some of the stored materials - particularly slag and associated waste - were excavated and reused as fill material in road infrastructure and civil engineering projects through 2021. Subsequently, the owner decided to begin a recycling process for the remaining material, estimated at 1,000,000 m³. Field observations indicate that slag is the predominant material in the tailings pile. In the northern part of the pile, there are massive blocks of slag ("giant logs"), while the central area is characterized by larger aggregates mixed with various ceramic waste, bricks, fragments of lining materials, plastics, and other industrial debris. An important point to note is the presence of spontaneous vegetation across the entire surface of the slag heap, which suggests that the stored materials have low toxicity.

3.4.1.2. DESTRO Technology for Superior ACBFS Recycling

The advanced recycling of ACBFS and ceramic waste identified in the Călan landfill involves the following steps: a) de-rocking (removal of large compact materials), b) crushing (breaking up large aggregates); c) deferritization (separation of metallic components); d) screening/fractionation of the crushed material by particle size: 20-50 mm, 50-63 mm, and over 63 mm.

Obviously, to maximize the recovery of the entire contents of the old metallurgical waste deposit in Călan, research must be conducted on the mineralogical composition of the valuable mineral fractions in order to assess their potential for being utilized as efficiently as possible as secondary resources - whether in the cement industry, in civil and industrial construction, in agriculture, but especially as CRM or strategic resources, or for the production of geopolymers. To this end, research has been conducted on the chemical and mineralogical composition of the contents of the Călan slag dump, as follows.

3.4.2. Laboratory Research on the Utilization Potential of the Contents of the Historic Călan Metallurgical Slag Dump

Note. *Blast furnace slag is not considered waste under current definitions; however, the contents of the Călan slag dump can be classified as waste because, prior to the implementation of Destro technology, there was no practical use for these materials that would grant them non-waste status[4]. Furthermore, the mixing of slag with municipal solid waste and construction waste reinforces the waste status of the overall contents of the slag heap. Thus, referring to the contents of the Călan slag dump as "waste" is not inappropriate.*

XRFS, XRD, and SEM-EDS analyses were performed on the slag that had been crushed, ground, and mechanically sorted into size fractions using DESSTRO technology

Conclusions regarding the composition of the analyzed fractions

The mineralogical compositions of the 20-50 mm and 50-63 mm fractions are similar. Apart from quartz (SiO_2), no oxides such as CaO, MgO, Al_2O_3, etc., were identified in the phase composition of the slag. Consequently, the assessment of opportunities for higher-value utilization of the investigated fractions must consider only the mineralogical composition, since the oxide composition is scientifically unreliable. One might argue that there are numerous articles in which the composition of

steel slags is presented as an oxide composition and that this validates the approach of analyzing slag composition at the oxide level. However, the XRD evidence is consistent, and there is no other way to justify presenting the slag composition as a mixture of oxides. Nevertheless, the XRFS method and techniques are valuable for characterizing slags, but only when elemental concentrations are measured or estimated.

The mineralogical compositions and XRFS data lead me to believe that the most promising routes for the value-added utilization of ACBFS slag from the Călan slag dump may be: 1) **a precursor in the cement industry**; 2) **a secondary source of critical raw materials; 3) - material for CO_2 capture and storage.**

Route 1 will be investigated because it can accommodate a very large quantity of sorted material in a relatively short time. Route 2 will be explored simultaneously with Route 1 through detailed laboratory analyses. Route 3 exceeds my current capabilities and will be set aside for the time being.

3.4.3. Studies and Research on the Advanced Recycling of ACBFS from the Călan Slag Dump in the Cement Industry

3.4.3.1. Current Status of Industrial-Scale Cement Production

Linking the current state and challenges of the cement industry with the potential for advanced utilization of ACBFS is key to utilizing the slag from the Călan slag dump. Cement is the main ingredient in concrete and is an essential material in civil, industrial, and road construction. Consequently, the cement industry has developed on a global scale. Total global cement production is estimated at 4.1 billion metric tons in 2023 [113]. Cement production in Romania in 2022 was estimated at 10.2 million metric tons, while in 2023 it was estimated at 9.5 million metric tons [114].

3.4.3.2. Experimental Results

a). Materials and Test Methods

Currently, the manufacture of Portland cement clinker involves the use of raw materials (precursors) such as limestone, clay, marl, and composition correctors, such as pyrite ash or iron ore (as a corrective additive of Fe_2O_3) [117]. For these reasons, the experiments utilized limestone and clay from the Medgidia area, which is a traditional supplier of precursors for Portland clinker. ACBFS slag was extracted from the Călan slag dump, crushed, de-ferrized, and sorted by screening. The mechanized processing of the material from the Călan slag dump is described earlier in this chapter. The screening process was adjusted to produce five size fractions, namely: 1) Fraction 1: 32-63 mm; b) Fraction 2: 16-32 mm; c) Fraction 3: 8-16 mm; d) Grade 4: 4-8 mm; and e) Grade 5: 0-4 mm

Fractions 3 and 4 were selected for this study because they meet one of the requirements for clinker production, namely, an apparent diameter of less than 25 mm. Sampling and preparation of specimens for XRFS measurements are also described in detail in subsection 3.2.

Particle size measurements are used in experiments to estimate technological properties, such as grindability and clinkerization ability. The particle size analysis of slag fractions and fine-grained clinkers was performed using sieving methods with appropriate sieve sets, employing sieving machines and calibrated Mettler Toledo balances. The raw materials were analyzed by XRFS to determine the chemical composition of the materials in the clinker precursor recipes. An XEPOS energy-dispersive X-ray spectrometer with 3D X-ray irradiation geometry, manufactured by Spectro-AMETEK, was used to measure the elemental composition of the samples. The XEPOS software can provide results in the form of mass concentrations of elements or in the form of oxides (% by weight). The XRFS technique is widely accepted as the standard method for characterizing waste in terms of oxide content [134]. The results of research in this field are presented in the paper |*"Research concerning the upcycling of aircooled blast furnace slag from old Călan dump as admixture in clinker precursor*" ,Timiș, A.L. et.al, 2024, UPB Sci. Bull. Ser. B, v.86, pp.231-244.

Chapter 4. RESEARCH ON THE POTENTIAL FOR UPGRADED UTILIZATION OF TAILINGS FROM THE TELIUC POND IN ACCORDANCE WITH THE NEW PARADIGM ESTABLISHED BY EU REGULATION 2024/1252

4.1. Rationale for Choosing This Topic

The primary steel industry - that is, the production of primary cast iron - developed in symbiosis with the mining industry, which provided it with raw materials and its main energy source: coking coal. During the extraction and processing (concentration, beneficiation) of ore, very large quantities of waste are produced (approximately 40% of the mass of the processed ore), usually consisting of residues, namely [145]: (1) solid waste in the form of tailings, dust, and sludge; (2) liquid waste in the form of wastewater and effluents; and (3) gaseous emissions.

In the national context, waste from mining and metallurgical activities represents one of the most significant sources of environmental pollution [147-150].

4.3. Studies on the Assessment of Secondary Resources in the Teliuc 2 Pond

Methodology for Investigating Potentially Contaminated and Contaminated Sites, developed on July 16, 2020, and included in ***Order No. 1423/2020*** [176], hereinafter referred to as the Methodology, provides a unified and coherent framework for identifying, inventorying, and assessing ponds. It serves as an essential tool for both authorities and researchers, particularly in the context of screening secondary sources. The document stipulates that the first step is **conducting a preliminary investigation**, which includes an analysis of existing documents, supplemented by interviews with individuals who possess relevant information about the site's history. Subsequently, an on-site inspection is recommended, and based on the results obtained, a decision is made as to whether it is necessary to proceed to the **detailed investigation stage**.

Detailed investigation involves collecting samples from the geological environment and analyzing them in a laboratory accredited according to the SR EN ISO 17025:2018 standard, so that the site's physicochemical properties can be characterized as accurately as possible and the presence of any contaminants can be identified. In addition, the Methodology stipulates that sampling techniques, as well as procedures for the preservation and handling of samples, must comply with applicable national, European, and international standards to ensure the accuracy and comparability of the results.

4.3.1 Documentary Investigation Regarding the Teliuc Tailings Pond

Iron ore mining in the Teliuc-Ghelari area has a history stretching back more than two millennia. Mining activity continued into the Middle Ages and intensified during the Communist era. The preliminary investigation, in accordance with the Methodology, was based primarily on the following documents: M.M.D.D., Report on the Results of Technical Inspections and Control at Tailings Ponds in the Mining Industry, No. 111509/June 22, 2007; Report: Inventory and Visual Inspection of Waste Dumps and Tailings Ponds in Romania, No. 60440/Sty/July 12, 2017, Issued by the Interministerial Commission for the Nationwide Inventory of Waste Dumps and Tailings Ponds in Romania; Daniel Guţă, "The Curse of a Collapsed Industry: Polluted Ponds, Waste Dumps, and Toxic Wastelands Surround Hunedoara," Adevarul, Published: August 6, 2013; Last updated: August 11, 2022, 12:36 a.m.; Adrian Stoica, "Mountains of Tailings and Toxic Waste: The Curse We Can't Escape," Jurnalul, March 31, 2022. The preliminary investigation led to the conclusion that there is a very important secondary resource in the form of metallurgical tailings. I specifically investigated the iron ore tailings (IOT) found in the Teliuc-Ghelari area in three massive tailings ponds. Furthermore, the preliminary investigation indicated that it is appropriate to conduct the secondary investigation provided for in the Methodology.

4.4. Experimental Results

The results of the investigations conducted on samples from the Teliuc 2 pond were analyzed in five areas:

1) estimation of the morphological heterogeneity of the waste rock at various scales;

2) estimation of the concentrations of both high-concentration elements (such as quartz and iron oxides) and trace elements from the EU CRM list, which may prove extremely valuable in the context of the application of EU Regulation 2024/1252, which has the force of law for member states;
3) implementation of the mathematical model "Balanced replicated sampling with three-level split ANOVA analysis"
4) finding solutions for the enhanced utilization of tailings from the pond;
5) prevention of passive loss of CRMs through improper recycling of tailings (downcycling).

4.4.1. Results of optical microscopy (OM) tests

Optical microscopy (OM) images show that the matrix consists of various minerals, some of which are transparent and are most likely quartz particles. Other particles are brown or reddish-brown in color and are most likely iron oxides. Analyses performed using optical microscopy (OM) reveal that the waste rock has a heterogeneous granular structure, composed of particles with varied morphologies and color shades. The translucent appearance of a significant portion of the grains indicates the predominant presence of silica, while the reddish and dark-colored particles suggest iron compounds in the form of oxides.

4.4.2 Results of SEM-EDS and XRD Analyses

SEM-EDS investigations were conducted in two laboratories with extensive experience in the field of electron microscopy. At the Laboratory for Morphological-Structural Investigations and Elemental Analysis (LIMSAE), part of the National Institute for Research and Development in Materials Physics (INCDFM), SEM-EDS tests were performed on unembedded powder samples. LIMSAE is RENAR-accredited for testing activities in accordance with SR EN ISO/IEC 17025, as specified in accreditation certificate no. LI 1281.

The mineralogical tests were performed at the Geological Institute of Romania, GEOECOLAB Laboratory, which is a leading authority in the field of mineralogical analysis.

Preparing samples for SEM-EDS analysis is a complex undertaking because the primary samples are heterogeneous on a sub-millimeter scale, as revealed by the MO investigations. For this reason, secondary samples (subsamples) weighing approximately 200 g were taken from the primary sample, which had been homogenized by mixing.

4.4.2.1. Results of the microscopic and mineralogical analysis for sample 1

In the fine fraction (micron-sized particles) of sample 1, code P1, particles with faceted 3D geometry are observed, which is typically attributed to crystallites. Given the process of pre-grinding the waste rock prior to SEM observation, it is clear that only crystals can withstand fragmentation and retain a polyhedral geometry. Fig. 4.22 also shows submicron particles, or dust, which may originate from the fragmentation of amorphous particles and growths on the surfaces of the crystallites.

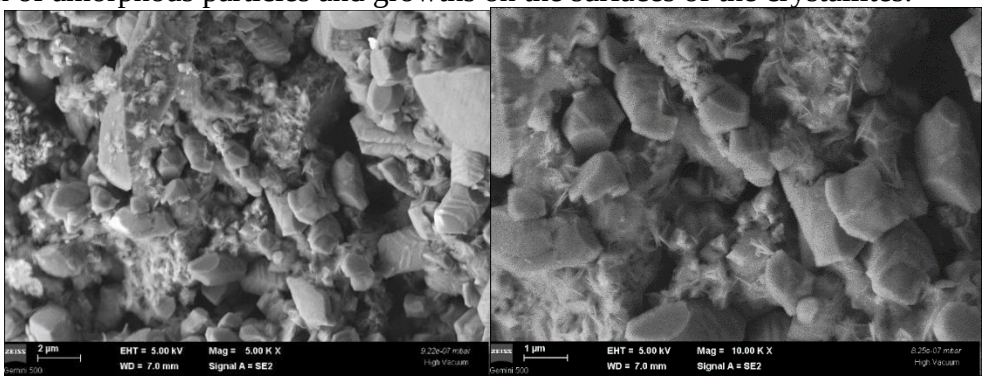
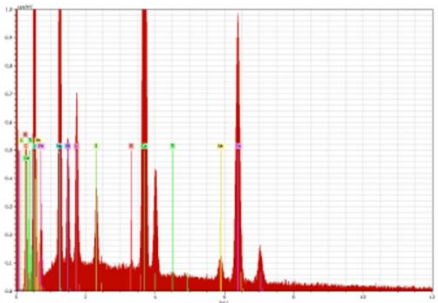


Fig.4.22. SEM images obtained from sample P1: a) image of the micron-sized fraction; b) detailed view associated with image a)

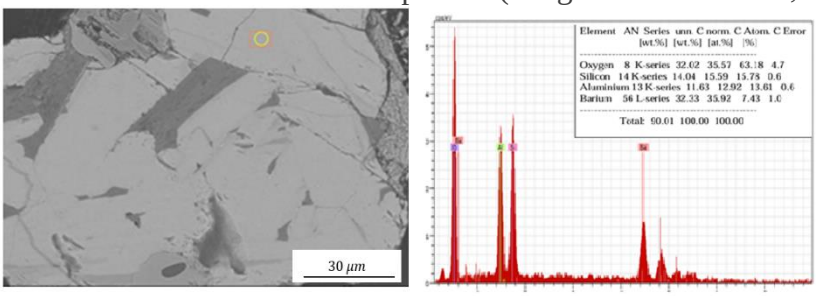


a)

El	AN	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Error [%]
C	6	K-series	3.13	2.77	5.03	0.6
O	8	K-series	57.16	50.56	68.85	25.1
Mg	12	K-series	7.56	6.69	6.00	0.4
Al	13	K-series	1.64	1.45	1.17	0.1
Si	14	K-series	1.98	1.75	1.36	0.1
S	16	K-series	1.22	1.08	0.73	0.1
K	19	K-series	0.17	0.15	0.08	0.0
Ca	20	K-series	21.24	18.79	10.21	0.7
Ti	22	K-series	0.17	0.15	0.07	0.0
Mn	25	K-series	1.41	1.25	0.50	0.1
Fe	26	K-series	17.37	15.37	6.00	0.5
		Total:	113.06	100.00	100.00	

b)

Fig.4.23. a) The EDS spectrogram obtained from sample P1; b) The mass and atomic concentrations of elements in a selected area of sample P1. (image code EDS Pb 1, 1-3)



a) b)

Fig.4.24. a) SEM image of the celsian mineral; b) spectrum and EDS analysis results corresponding to the area marked in the adjacent SEM image

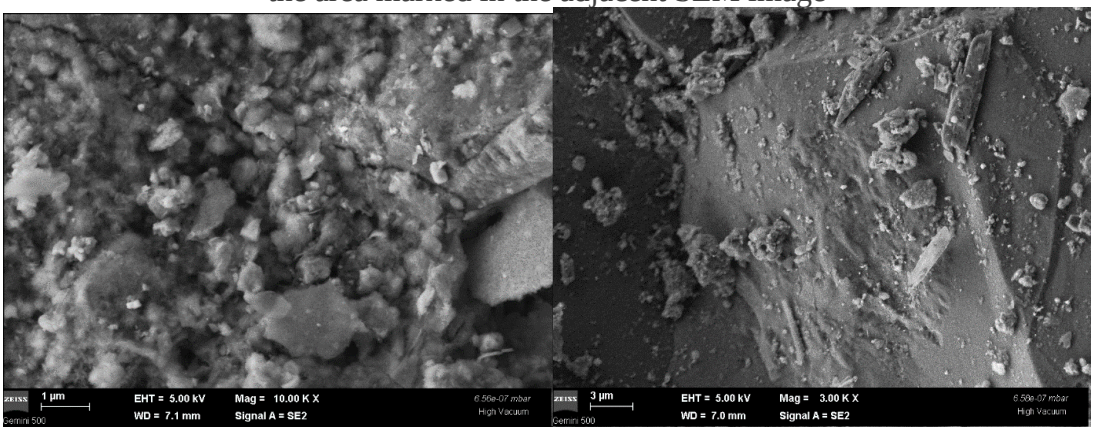


Fig.4.31. SEM images obtained from sample P2: a) image of the micron-sized fraction; b) detailed view associated with image a);

4.4.2.2. Results of the microscopic and mineralogical analysis of sample P2

The morphological heterogeneity of the particles comprising sample P2 is high (Fig. 4.31.a); specifically, the sample contains submicron particles ***with a fractal texture*** as well as faceted particles, indicating a crystallized structure of those particles. Fig. 4.31.b reveals the presence of particles with a diameter of approximately 20 µm to which submicron faceted particles, as well as those with irregular geometry, adhere.

4.4.2.3. Results of the microscopic and mineralogical analysis for sample P3

The SEM images used for the textural and morphological analysis of the constituent particles of the sample corresponding to sample P3 (Fig. 4.37.a, b) show distinctive features that were not observed in samples P1 and P2

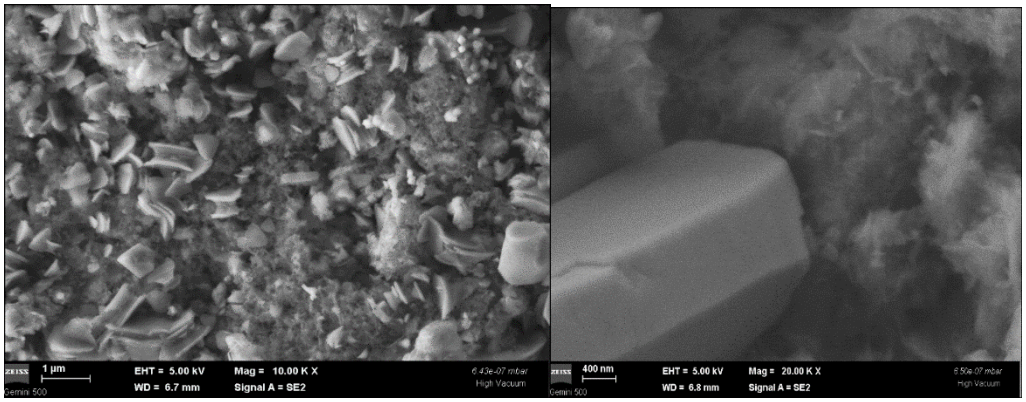
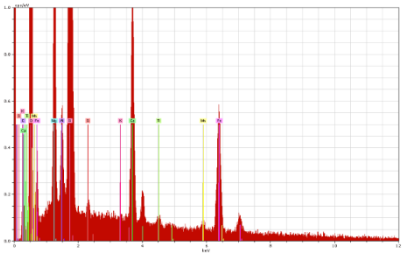


Fig.4.37. SEM images obtained from sample P3: a) image of the micron-sized fraction; b) detailed view associated with image a);



El	AN	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Error [%]
C	6	K-series	1.97	1.96	3.29	0.5
O	8	K-series	55.22	55.01	69.39	22.9
Mg	12	K-series	3.87	3.86	3.20	0.2
Al	13	K-series	0.95	0.95	0.71	0.1
Si	14	K-series	24.70	24.61	17.68	1.1
S	16	K-series	0.18	0.18	0.11	0.0
K	19	K-series	0.15	0.15	0.08	0.0
Ca	20	K-series	5.06	5.04	2.54	0.2
Ti	22	K-series	0.23	0.23	0.10	0.0
Mn	25	K-series	0.62	0.62	0.23	0.1
Fe	26	K-series	7.42	7.39	2.67	0.2
		Total:	100.38	100.00	100.00	

a) b)

Fig.4.38. a) The EDS spectrogram obtained from sample P1; b) The mass and atomic concentrations of elements in a selected area of sample P1. (image code: EDS Pb 3 P3-2)

4.4.2.4. Results of the microscopic and mineralogical analysis of sample P4

The SEM images in Fig. 4.44.a, b show that the waste rock comprising the sample taken from sample P4 has a matrix richer in submicron-sized particles, which constitute a larger amorphous fraction than in samples P1-P3. In the SEM images in Fig. 4.44a and b, particles with faceted polyhedral geometries - which are characteristic of crystallites - can be observed. Acicular particles and fine/small particles that appear to result from the fragmentation of the acicular particles are also observed.

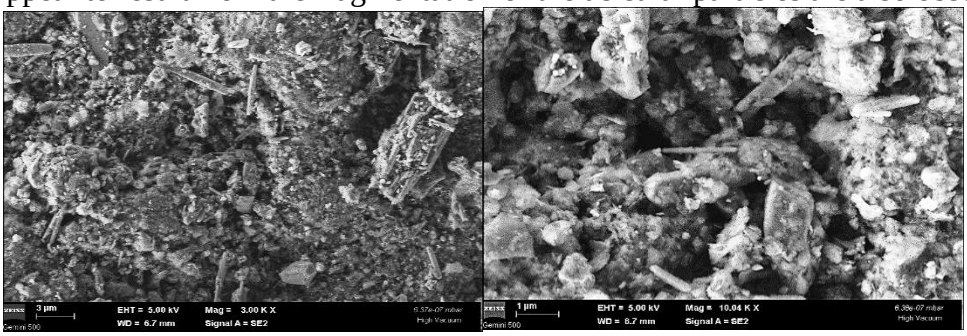


Fig.4.44.SEM images obtained from the sample taken from sample P4: a) image of the micron-sized fraction; b) detailed view associated with image a);

4.4.2.7. Results of the microscopic and mineralogical analysis for sample P7

Subsample P7 exhibits distinctive and relevant features of the interweaving of amorphous and crystallized phases in Fig. 4.62.a, b, which unmistakably highlight agglomerations of particles with fractal geometry - which are most likely amorphous - and particles with well-defined 3D geometry. Fig. 4.62.b) shows a detailed image of a stack of lamellar crystallites embedded in a mixture of aggregated (cemented) submicron particles with a globular morphology (most likely an amorphous fraction) intertwined with faceted particles that may be crystallized.

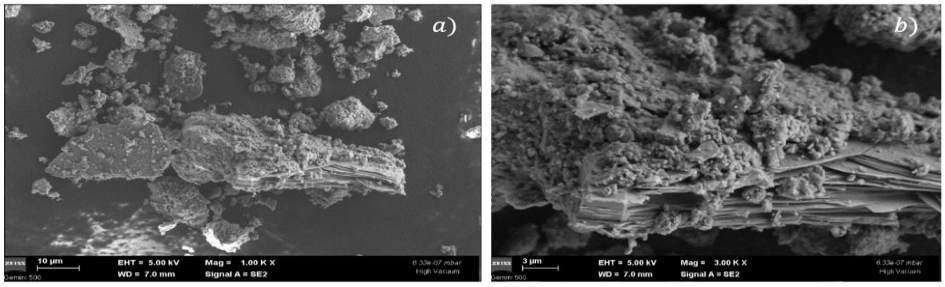


Fig.4.62. SEM images obtained from the sample corresponding to P7: a) image of the micron-sized fraction; b) detailed view associated with image a);

4.4.2.8. Results of the microscopic and mineralogical analysis for sample P8

The SEM image shown in Fig. 4.68 (a) highlights the metamorphic nature of the tailings resulting from the iron ore concentration process by flotation. The observed texture is marked by structural degradation and successive fragmentation, indicating an advanced disintegration process caused by the combined action of geological and environmental factors. The platelet-like morphology of the micron-sized particles suggests a mechanism of progressive detachment from the initial mineral matrix, reflecting an active stage of alteration. This tendency toward exfoliation and fragmentation promotes both an increase in the material's specific surface area and the mobilization of associated chemical elements. The high dimensional variability, ranging from grains on the order of 100 μm to nanometric particles, reveals a heterogeneous material susceptible to migration and chemical transformation processes. This characteristic gives the waste significant potential for interaction with the environment, amplifying both the risks of fine particle dispersion and the opportunities for valorization through selective recovery technologies. As mentioned, this can be an advantage when considering its utilization in the cement or geopolymer industries, since the issue of grinding it no longer arises. The presence of crystallized phases is not advantageous for recycling in the cement industry or for the extraction of critical elements, as it requires a great deal of energy to transform them into cement-specific minerals (allite, belite, felite) or to hydrolyze them.

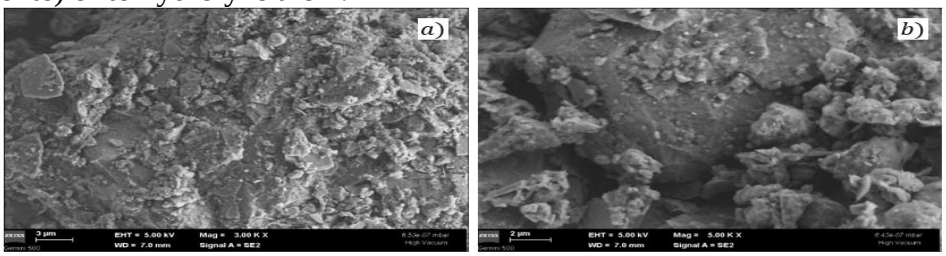


Fig.4.68.SEM images obtained from sample P8: a) image of a metamorphic structure; b) detailed view associated with image a);

4.4.2.9. Results of the microscopic and mineralogical analysis for sample P9

The matrix of subsample P9 appears to be a heterogeneous mixture of minerals in terms of both the size and crystalline state of its constituent particles (Fig. 4.73.a); specifically, the matrix of sample P9 is a mixture of phases consisting of both parallelepiped and acicular crystallites.

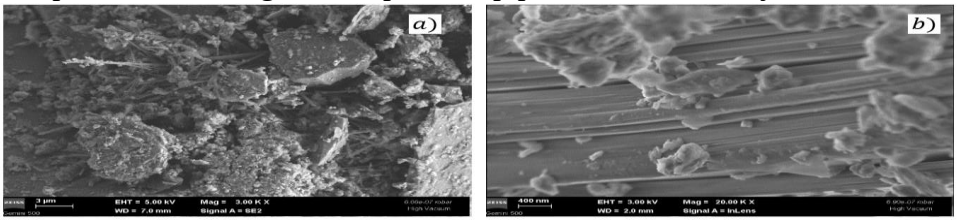


Fig.4.73. SEM images obtained from subsample P9: a) image of the matrix; b) close-up image of an atypical crystallite with adherent nanometer-sized particles;

4.4.2.10. Results of the microscopic and mineralogical analysis for sample P10

The matrix of subsample P10 is similar to that of sample P9. In this case as well, the SEM images (Fig. 4.78.a) reveal a microcomposite matrix with heterogeneities manifesting on three levels: dimensional, morphological, and structural (crystalline structure, also referred to as fine structure in the field of metallurgy).

The tailings shown in Fig. 4.78a is a mixture of micron-sized crystals with a faceted 3D geometry, TO the surface of which submicron particles have adhered - most likely resulting from the grinding process, which caused extensive fragmentation. For this reason, what can be stated with certainty is the specific appearance of certain fragmented crystallites, as also highlighted in Fig. 4.78b. EDS analyses performed on several selected micron-scale areas showed that the analyzed tailings exhibit a composition similar to that of samples P1 - P9, in that the dominant element in all the spectra obtained is O, followed by Ca or Si depending on the mineralogical nature of the dominant particle in the selected area. Since the most important elements that would confer greater utility to the tailings are Ba, first and foremost, and Mg, secondarily, an effort was made to identify the compositions that reveals CRM.

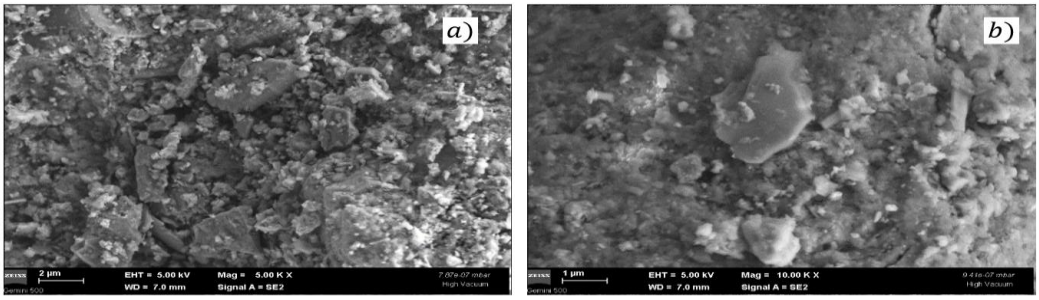


Fig. 4.78. SEM images obtained from the subsample taken from sample P10: a) an overview of the matrix; b) a detailed image showing a crystallized particle surrounded by an area of particles that appear amorphous.

4.4.3. Results of X-ray fluorescence spectrometry tests

4.4.3.1. Sample preparation

X-ray fluorescence spectroscopy (XRFS) has seen significant development in recent years, with several related methods and techniques now available for analyzing the elemental composition of tested materials. The ED-XRFS (Energy-Dispersive X-ray Fluorescence Spectroscopy) and WD-XRFS (Wavelength-Dispersive X-ray Fluorescence Spectroscopy) methods are the primary techniques used to analyze the elemental composition of materials. Both are based on the principles of X-ray fluorescence, in which X-rays excite the sample, causing it to emit characteristic X-rays that are specific to each element and reveal the sample's elemental composition. The choice between ED-XRF and WD-XRF depends on the specific application, the desired level of accuracy and precision, and budget constraints. If speed and cost are priorities, then ED-XRF is preferable. If accuracy and quantification limits are essential, then WD-XRF is a better choice.

4.4.4 Conservative Statistical Analysis of Numerical Results

4.4.4.1. Conservative Model for the Statistical Analysis of Numerical Results

a). General Considerations

In the case of fine-grained substances (#<1 mm), such as tailings from ore processing, ground slag, etc., random or stratified discrete sampling cannot be applied because this approach has at least three disadvantages:

(i) The concentration of an analyte (chemical element) in a fine particle is a continuous function rather than a discrete one. The continuous distribution of the analyte contradicts the assumption that some

particles contain a constant amount of the analyte, while others contain none. Consequently, discrete distributions are unsuitable for interpreting statistical data in the case of fine-grained solid waste.
(ii) An analyte may be present in different particles as part of different compounds. This contradicts the assumption that a particle contains a constant amount of analyte, making discrete probability models even less suitable.
(iii) Discrete (particle-by-particle) sampling is inadequate for fine-grained waste, such as tailings and coal combustion ash, etc. Instead, incremental sampling is the standard approach used for sampling fine-grained waste deposits [20].

4.4.4.2. Conservative Analysis of the XRFS Results Obtained from Tailings Samples from the Teliuc Pond

As shown in this chapter, 40 measurements were performed on tailings samples prepared as described in subsection 4.3. The XRFS measurements provide results that should be interpreted as average values on a scale of approximately 1 kg, since the collected sample was homogenized prior to the subsampling of the analytical sample used for testing.

4.5 Discussion

The Xepos instrument's Turboquant analytical program reported an LOQ = 0.5 ppm for Ge and an LOQ = 1.0 ppm for Bi. Five results were reported as below the LOQ for Ge and six for Bi. Robust statistical analysis of the data for Ge revealed a mean (median) of 2.2 ppm and a standard deviation of 1.9 ppm, while for Bi, a median of 3.2 ppm was obtained with a standard deviation of 1.9 ppm.

Using the conservative model, the average Ge concentration was calculated to be 2.9 ppm, which is approximately 0.7 ppm higher than the value provided by the robust statistical analysis, that is, about 32% higher. For Bi, the conservative approach yielded a mean concentration of 3.3 ppm, which is very close to the robust estimate of 3.2 ppm, representing an increase of approximately 3%. The conservative (prudent) approach revealed higher standard uncertainties in these cases - approximately 3.4 ppm for Ge and 3.9 ppm for Bi - which exceeded the concentration values themselves. In such cases, the data are not considered reliable for making decisions regarding the recovery of Ge and Bi. The conservative data analysis model we developed does not apply to Y and Ce (Table 4.8), since their concentrations exhibit a clustering trend and a unimodal distribution, respectively (Figure 4.90a, b). In contrast, the conservative model is appropriate for analyzing the data in the cases of Bi and Ge. Classical statistical analysis overestimates the Ge and Bi concentration values by approximately 59% and 15%, respectively. Similarly, robust statistical analysis overestimates the Ge and Bi concentration values by approximately 43% and 7%, respectively. Furthermore, the SDs assigned to the concentration values using classical and robust data analysis are underestimated (Table 4.8). This evidence demonstrates that both classical and robust statistical analyses of concentration values near the LOQ in a series of uniformly distributed results produce distorted values i.e., concentrations higher than the actual values and lower associated uncertainties. Such data analyses can lead to false-positive decisions regarding investments in the recovery of critical materials present in ppm concentrations or other trace elements. Therefore, when there is evidence that analytical results are uniformly distributed, it is prudent to apply a statistical analysis based on the conservative approach described above.

4.6. Conclusions

The results of the research conducted on the tailings from the Teliuc pond proved to be original and valuable, as they led to the publication of articles in Q1 and Q2 journals, namely:

A.L. Timiș et al., A New Conservative Approach for Statistical Data Analysis in Surveying for Trace Elements in Solid Waste Ponds, 2025, *Applied Sciences* 15 (8), 4246

I. Pencea, R.N. Turcu, AC Popescu-Argeș, AL Timiș, et al., 2023, An Improved Balanced Replicated Sampling Design for Preliminary Screening of Tailings Ponds Aiming at Zero-Waste Valorization. A Romanian case study, Journal of Environmental Management 331, 117260, (IF 8.0)

Timiș A.L., et al., A Comprehensive Derivation of the Expectation and Its Variance in Sampling without Replacement from a Particulate Lot with a Numerical Attribute, COJ Technical & Scientific Research 5 (1)

It can be stated without a doubt that tailings (IOT) represent a valuable secondary resource that can be recycled both through down-cycling as fill material and through up-cycling as a precursor in the ceramics industry and, of particular interest, as a precursor for CRM.

The electromagnetic surveys conducted by BRANTAX (brantax.ro) and presented in this thesis are merely illustrative, in the sense that they demonstrate effectiveness in revealing inhomogeneities deep within the pond. These investigations must be conducted systematically and supplemented with directional drilling followed by compositional and mineralogical analyses of the collected samples in order to establish a value model for this resource site. Unfortunately, by the time this thesis was completed, I had not observed any interest in exploiting this resource on the part of the relevant institutions in Romania, even though I published important data on this topic between 2022 and 2025.

Chapter 5. RECYCLING OF STEEL SLAG IN ROMANIA IN THE CONTEXT OF THE NEW PARADIGM ESTABLISHED BY REGULATION (EU) 2024/1252

5.1. Context and Paradigm

From a regulatory standpoint, ferrous slags have been the subject of debates regarding their status - that is, whether they are **waste or non-waste (residues)** [218, 219]. Thus, ferrous slag has been classified as waste according to the entries in the European Waste Catalogue [223]: entries: ***10 02 01 waste*** *from slag processing; 10 02 02 unprocessed slag*. The European Waste Catalogue has been adopted in Romania, and the above entries are referenced in a recent government document, namely Government Emergency Ordinance 92/2021, approved by Law 17/2023, Article 8, paragraph (3), Annex No. 1 [220]. EUROFER's revised 2023 position paper clearly states that "***slag is a byproduct of the steelmaking process***" [219]. The status of ferrous slag as a by-product is particularly important, since waste that ceases to be waste is no longer subject to many of the restrictions set forth in Directives 94/62/EC [4].Recently, Regulation (EU) 2024/1252, hereinafter referred to as the Regulation, has shifted the paradigm regarding historical and current slag dumps from a source of environmental pollution to a potential secondary resource of critical raw materials (CRMs) that can mitigate the risk to the EU's access to **CRMs**.

5.2. Materials and Methods

As mentioned, several times in this paper, the recovery of a byproduct, namely ACBFS slag, cannot be achieved without characterizing its composition and mineralogy. Laboratories often provide analytical results that are less than precise, particularly lacking the accuracy required for operational decisions. If an element has a low concentration, comparable to the limit of quantification (LOQ), then the expanded relative uncertainty, see ISO 98-3, associated with the result is high; that is, there are many cases where it exceeds 100%. A decision to utilize a material whose concentration has a relative uncertainty >50% is a particularly risky undertaking. In this context, to substantiate the decision to prioritize the utilization of ACBFS based on XRFS measurements, it was necessary to estimate the performance characteristics of the laboratory XRFS procedure. To evaluate the performance characteristics of the laboratory XRFS procedure, a certified reference material made from steel slag was used. Subsequently, XRFS measurements were performed on four samples of ferrous slag (2 EAF slag samples and 2 air-cooled BFS slag samples, also known as ACBFS). The first XRFS measurements were performed on the certified reference material, Certificate No. 050616-101-Slag, supplied by Brammer Standard Company, Inc. The certified reference material is a fine powder that was dried for one hour at 105 °C and thoroughly mixed before use. Subsequently, the compositions of samples taken from the

target stockpiles were measured. The steel slag samples were obtained from the slag stockpile at Târgoviște (Colanu). The samples were prepared from the 8–63 mm slag fraction (Fig. 5.1.a).



Fig.5.1. Images of the target stockpiles: a) steel slag pile, Colanu; b) the ACBFS slag pile at Călan with sorted slag (inset).

5.3. Experimental Results

5.3.1. XRFS Measurement Results

To estimate the performance characteristics of the XRFS measurement procedure, four analytical samples were prepared from the BS 101-3 MRC, codes CRM-BS-1-:-4. The results of the four measurements performed under reproducibility conditions are presented in Table 5.2.

Table5.2. Results of measurements performed on BS 101-3 certified reference material samples

Symbol	certified reference material-BS **no. 1**		certified reference material-BS **no. 2**		certified reference material-BS **no. 3**		certified reference material-BS **no. 4**	
	C*[% weight]	SD**[% weight]	C[% weight]	DS[% weight]	C[% weight]	DS[% weight]	C[% weight]	DS[% weight]
Na2O	0.027	0.027	0.031	0.0017	0.029	0.0006	0.0222	0.0254
MgO	3.212	0.006	2.757	0.0052	3.161	0.024	3.098	0.007
Al2O3	1.940	0.004	0.950	0.0033	1.507	0.01	1.455	0.004
SiO2	18.670	0.010	18.280	0.01	18.820	0.02	18.76	0.01
P2O5	0.794	0.001	0.588	0.0013	0.794	0.0029	0.782	0.0015
SO3	0.481	0.001	0.471	0.0009	0.496	0.00071	0.501	0.001
K2O	< 0,0012	0.000	< 0,0012	0	0.046	0.0033	0.046	0.0015
CaO	53.640	0.040	54.480	0.04	53.640	0.04	53.65	0.04
TiO2	1.034	0.008	0.977	0.008	0.982	0.0037	0.932	0.008
MnO	5.313	0.007	5.459	0.007	5.131	0.008	5.188	0.007
Fe2O3	15.080	0.010	15.640	0.01	14.940	0.01	15.78	0.01

*mass concentration [% weight], **standard deviation attributed to C [% weight]

5.3.2 LIBS Measurement Results

LIBS (Laser-Induced Breakdown Spectrometry) is an emerging technique that offers the significant advantage of having a broader analytical range than all known spectrometric methods. LIBS can measure the concentrations of Li, Be, B, and C, which XRFS cannot measure. Furthermore, LIBS measures the elements Na, Al, and Mg with sufficient accuracy, elements that pose challenges for XRFS analytical procedures. This thesis addressed LIBS measurements on ACBFS samples to investigate the suitability of this technique and to justify, if warranted, the need to implement a LIBS analytical procedure for the analytical investigations required for the enhanced utilization of ferrous slags and other materials.

LIBS spectrometers are supplied on the Romanian market by SC Kimet SRL (kimet.ro), which in turn sources them from SciApps in Germany. As part of the collaboration with SC Kimet SRL and SciApps Germany, it was agreed to conduct a preliminary investigation of 5 samples (slag lumps from the Călan slag dump), Fig. 5.2.

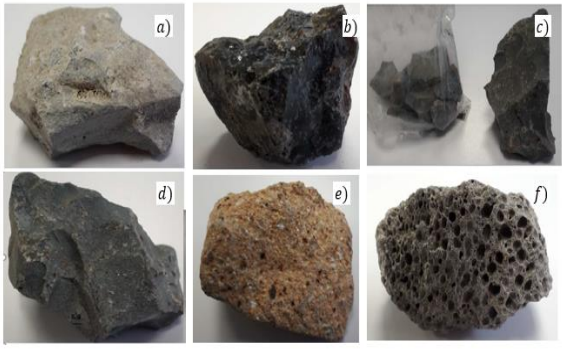


Fig.5.2. Images of the Bulgarian slag samples analyzed by LIBS: a) Sample No. 1, code S1; b) Sample No. 2, code S2; c) Sample No. 3, code S3; d) Sample No. 3, code S3 - main fragment; e) Sample No. 4, code S4; f) Sample No. 5, code S5

Test specimen No. 1 was prepared by local grinding as shown in Fig. 5.7 (inside)

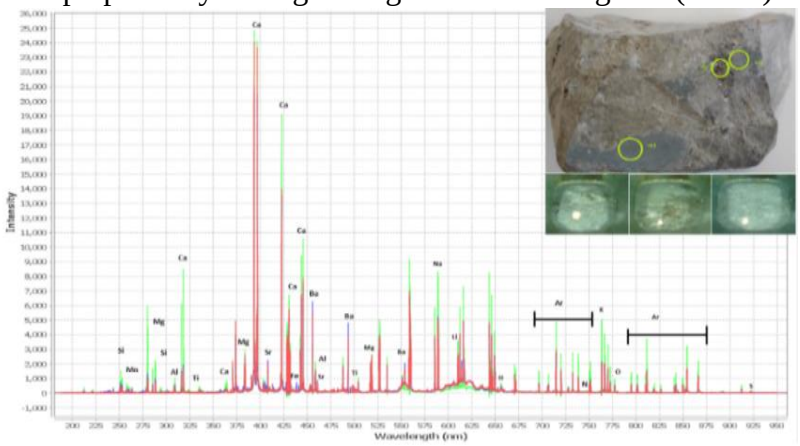


Fig. 5.3. LIBS spectrum obtained from sample S1. Laser irradiation sites (top left) and the patterns of the irradiated spots

5.3.3. Discussions and Conclusions Regarding the LIBS Analysis of Blast Furnace Slag from the Călan slag dump

LIBS analyses are point-by-point. This aspect is both an advantage and a disadvantage! Characterizing the composition on a macro scale requires many point-by-point laser irradiations. Fortunately, LIBS performs thousands of point-by-point analyses in a matter of minutes, which it stores, statistically processes, and averages, thereby facilitating chemical analysis on a macro scale. Due to the inhomogeneity of the samples, multiple locations on each sample were analyzed. Each sample exhibits distinct differences between specific target areas. The morphological and textural heterogeneity of the analyzed samples is reflected in the variety of spectral line structures. If the goal is to accurately measure Li, there is a dedicated LIBS instrument, namely the LIBS Z-901 Li Lithium Analyzer (www.kimet.ro, accessed on May 21, 2024) which can reveal more better the CRM contents of the sampled specimens.

5. 3.4. Conclusions

The purpose of this study was to develop a reliable method for measuring major, minor, and trace elements contained in old ACBFS and EAF slag deposits using the ED-XRFS technique and appropriate statistical analysis of the data. The performance characteristics of the XRFS procedure we used to measure the chemical composition of ferrous slag (ACBFS, EAF) are suited for preliminary screening to investigate the recycling potential of these slags.

Particular attention was paid to the analysis of CRMs to ensure compliance with Regulation (EU) 2024/1252, which recommends that Member States, among other things, "*promote the recovery of critical raw materials from extractive waste, in particular from closed extractive waste facilities*."

The LIBS results represent relevant novel findings, as, corroborated with other results of the investigations carried out on ACBFS and EAF slags, they facilitated the publication of a notable article, namely: Timiș, A.L.; et al., The New Paradigm Caused by Regulation (EU) 2024/1252 on the Upcycling of Landfilled Ferrous Slags - Case Study: Iron and Steel Slag Dumps in Romania. Minerals, 2025, 15, 260. Q2

Chapter 6. GENERAL CONCLUSIONS AND ORIGINAL CONTRIBUTIONS

6.1. General Conclusions

As highlighted in the thesis, raw materials are essential to the EU economy. They form the foundation of horizontal and vertical industries for a wide range of products and equipment used in everyday life, as well as for the implementation of modern, environmentally friendly technologies, also known as green technologies. The requirements of the circular economy and current technological trends toward the development of green energy sources (wind turbines, photovoltaic panels, electric batteries, etc.). Critical materials are often used in defense systems, military equipment, and other technologies that are vital to national security. Strategic materials are a subset of critical raw materials, particularly those considered vital for key sectors such as green technologies, digital industries, defense, and the aerospace industry. At the EU level, the following are considered strategic materials: Cu, W, Co, Ni, and Mg in the form of metals and alloys; platinum group metals; natural graphite; germanium; boron; and rare earth elements for magnets (Nb, Yb, Eu, etc.) [228].

The thesis demonstrated that ***secondary resources in Romania are part of the solution for increasing the EU's resilience to disruptions in the raw materials supply chain*** [229].

6.2. Personal Contributions

1. The approach to the higher-value utilization of waste and byproducts from the Romanian steel industry can be considered a remarkable contribution, both conceptually and in practical/economic terms, in that it ensures the value of secondary resources is not wasted through lower-value utilization. Furthermore, the recovery of secondary resources as precursors for CRM ***can pave the way for a new specialization in the field of Materials Engineering***, viewed as an integrative discipline within the circular economy framework, that is, a holistic approach to the product lifecycle starting from precursors (ore, ore concentrate, concentration waste, primary product (primary cast iron), steel, waste/byproducts associated with cast iron and steel production, and the utilization of byproducts within the zero-waste approach). The concept of upcycling slag and tailings was disseminated in 4 articles published between 2023 and 2025, of which I am a co-author, and in 2 presentations at the ROMAT 2022 conference.

2. The results obtained through the collaboration with Brantax, to the extent that they could be obtained, demonstrate the feasibility of establishing a UNSTPB - UB - Brantax consortium to carry out exploratory projects at national level, in order to meet the requirements of Regulation (EU) 2024/1252 regarding the screening of secondary sources of CRMs, among others..

3. I contributed to the design and application of an efficient technology for the mechanical processing and de-ironization of crushed and ground slag, known as the DESTRO technology. The technology was applied to the Calan slag dump, with the results published in [127]

4. I demonstrated how to implement a technology for the recovery of air-cooled blast furnace slag from a slag dump as part of a zero-waste approach. A description of this approach is provided in the previously mentioned paper, i.e., [127].

5. A conservative (prudent) approach was designed for the statistical analysis of data resulting from the investigation of trace-level elements in residue/waste deposits, such as CRMs and heavy metals. The conservative approach was applied to the analysis of residues deposited in the Teliuc pond for the

preliminary screening of CRM abundances, using incremental sampling followed by XRFS analyses. The results were published in the prestigious journal Applied Sciences J [15].

6. A procedure was developed and implemented to evaluate the performance characteristics of the XRFS method for its use in screening secondary resources from blast furnace slag (ACBFS) tailings, and specifically for screening critical elements in these tailings. The results were published in the prestigious journal Minerals J [14].

7. Ensuring the validity of the XRFS results allowed me to conclude that the utilization of ACBFS slag from the Călan slag dump as a clinker precursor is not incompatible with the requirements of the Regulation, since the concentrations of CRMs in this slag are close to their concentrations in the Earth's crust. These results were published in Minerals J. [14].

8. Based on laboratory research, I have demonstrated that recycling blast furnace slag from the Călan slag dump as an additive in the clinker recipe yields major environmental and economic benefits,

such as: savings in limestone, a raw material that is becoming depleted; elimination of slag from the stockpile and, subsequently, of associated waste; and a reduction in the carbon footprint by lowering the energy consumption of grinding and by reducing the clinkerization temperature by 50 oC. These findings were published in the journal UPB Sci. Bull series B [143]

9. The results presented, both those previously published and those described in this thesis, can serve as a solid scientific basis for the national institutions responsible for implementing Regulation (EU) 2024/1252.

10. The thesis presents an extensive and relevant bibliography on the advanced utilization of ferrous slags, which includes specific regulatory documents as well as the findings of international experts, and particularly Romanian experts, in this field, notably the research groups at Galați and CEPROCIM S.A. in Bucharest.

Other contributions could also be listed, but I will limit myself to these.

6.3. Research directions derived from the thesis's research questions

1. Establishing a system for investigating ponds and tailings piles based on geophysical exploration (ERT, GPR, EM, LIDAR), followed by directional drilling and XRFS, LIBS, and XRD analyses, and possibly screening with radioactive sources in the drilled borehole. This system requires significant material resources and specialized expertise.

2. Integration of XRD, XRFS, and LIBS methods for elemental and mineralogical characterization.

3. Development of a specialized methodology for estimating resources in slag dumps, given that ACBFS slag is extremely heterogeneous in terms of both grain size and mineralogical texture.

4. Development of a reliable methodology for characterizing ACBFS slag grades intended for the cement industry. In this regard, it was found that to promote fair business practices in this field, the issue of synthetic composition at the delivered batch level must be resolved.

5. The use of fractal theory to characterize the morphology of the fine fraction in tailings ponds. The morphology and, in particular, the roughness of the particles can determine a specific recycling route for the tailings, such as the hydrometallurgical extraction of certain critical materials.

In conclusion, I can state that this thesis proves that Academician Nicolae Anastasiu was absolutely correct, i.e., "Mining waste and critical minerals - a residue? No - an neglected alternative," 2015, https://www.researchgate.net/publication/280947001, accessed on December 1, 2021, at 10:25 AM. To paraphrase Academician N. Anastasiu, I can say that Romania possesses a "treasure trove of recoverable residues" and is still not taking concrete steps toward capitalizing on this asset.