University POLITEHNICA of Bucharest
Doctoral School of Materials Science and Engineering Faculty
Splaiul Independenței, Nr. 313, Sector 6, București 060042
Tel/Fax: 021 402 9624; www.sdsim.upb.ro

PhD Thesis Summary

Contributions regarding the evaluation of the secondary resources contained into iron ore tailings, in the circular economy frame

PhD Candidate: Alina-Cristina POPESCU-ARGEŞ

PhD Supervisor: Prof. Ion PENCEA

DOCTORAL COMMISSION

President	Prof. Florin MICULESCU	from	University ”Politehnica” of Bucharest, Romania
PhD Supervisor	Prof. Ion PENCEA	from	University ”Politehnica” of Bucharest, Romania
Referee	Prof. Mihai Ovidiu COJOCARU	from	University ”Politehnica” of Bucharest, Romania
Referee	Prof. Costică BEJINARIU	from	Tehnical University „Gheorghe Asachi” of Iași, Romania
Referee	Senior researcher Ph.D. Roxana Mioara PITICESCU	from	National Research&Development Institute on Non-Ferrous and Rare Metals, Bucharest, Romania

Bucharest

2021

Table of Contents

1-PNT-page number into thesis; 2- page number into thesis summary

Keywords: metallurgical waste, secondary resources, recovery, valorisation, sampling, holistic characterization, critical raw materials, enhanced landfield mining&management, Circular Economy.

Chapter 1. STAGE OF THE APPROACHED FIELD. TOPIC RELEVANCE AND THESIS AIMS.

The increase of the global population, together with technological progress and the increase of the global standard of living has generated a dramatic increase in the consumption of mineral resources, metals, biomass etc. It is considered that in this decade those resources are consumed as if Earth's population would benefit from the resources of three planets the size of the Earth. The effect of a growing appetite for the consumption of processed resources overlapped with the detrimental effect of the economic-industrial model unsustainably practiced until recently which is called linear economics. To counteract the detrimental systemic trends, the European Union announced its goal of becoming the world's most resource efficient economy through the implementation of the concept of Circular Economy launched in 2015. In 2020, the EU published an action plan for circular economy. This plan provides for the closure of the loop of materials used in the manufacture of goods, in order to obtain zero waste.

a) b)

Fig. 1.1. Economic structures: a) linear economy; b) circular economy [4].

Another problem that the EU faces is the supply of critical raw materials (CRM), especially the so called 'rare-earth elements' and special metals (Li, Mg, Ni, Ti, V) which are mentioned in the EU's list of CRM from 2020 and which has 30 CRM, as opposed to 14 raw materials in 2011, 20 raw materials in 2014 and 27 raw materials in 2017. The EU imports over 95% of CRM and it is dependent on major suppliers like China, Russia, Australia, Brazil.

The EC considers that the EU's success regarding the transformation and modernisation of its economy depends on the sustainable provision of both prime and secondary raw materials which are necessary for the expansion of clean and digital technologies in all industrial ecosystems of the EU. The CMs are at the top of the list in 2020, they are absolutely necessary for the strategic development of EU's industry, namely the production of a wide range of products as shown in Table 1.1 which provides a synoptic view of CRM applications. Consequently, the EU has moved towards the recovery of secondary resources in order to obtain CRM and base metals found in in extractive waste or landfills. For this reason, the EU (EC) has initiated the ERA-MIN research program under the auspices of HORIZON 2020 to explore existing secondary resources in the EU as well as to identify the most efficient technologies for capitalizing on secondary resources. Successful projects were NEMO, RE-MINE-with Romanian participation, ENVIREE, with Romanian participation, METGROW + (Metal Recovery from Low Grade Ores and Wastes) (https://metgrowplus.eu/), ProSUM (Prospecting Secondary raw materials in Urban mine and Mining wastes- http s://metgrowplus.eu/), CHROMIC etc. In Romania, 1369 landfills were inventoried in 2007, containing approximately 80 billion tons of metallurgical waste. Of these, there are approximately 93 tailings ponds with a total volume of approximately 324 million m^3 of stored tailings.

Table 1.1 Relevance of critical raw materials for industrial ecosystems.

	Aerospace/ defence	Textiles	Electronics	Mobility/ Automotive	Energy-intensive industries	Renewable energy	Agri-food	Health	Digital	Construction	Retail	Proximity / social economy	Tourism	Creative/ cultural industries
Antimony	✓	✓		✓						✓				
Baryte				✓	✓			✓		✓				
Bauxite	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓				
Beryllium	✓		✓	✓		✓			✓					
Bismuth	✓		✓		✓			✓	✓	✓				
Borate	✓		✓	✓	✓	✓	✓		✓	✓				
Cobalt	✓	✓	✓	✓	✓	✓			✓					
Coking coal				✓	✓	✓								
Fluorspar					✓		✓				✓			
Gallium	✓		✓	✓		✓			✓	✓				
Germanium	✓		✓		✓	✓								
Hafnium	✓		✓		✓	✓			✓					
Indium	✓		✓			✓			✓					
Lithium	✓		✓	✓	✓	✓		✓	✓					
Magnesium	✓		✓	✓	✓				✓	✓				
Natural graphite	✓		✓	✓	✓	✓			✓	✓				
Natural Rubber	✓	✓		✓				✓						
Niobium	✓		✓	✓	✓			✓		✓				
Phosphate rock					✓		✓							
Phosphorus	✓				✓		✓							
Scandium	✓			✓		✓								
Silicon metal	✓	✓	✓	✓	✓	✓		✓		✓				
Strontium	✓		✓		✓			✓		✓				
Tantalum	✓		✓		✓	✓			✓					
Titanium	✓		✓	✓	✓			✓		✓				
Tungsten	✓		✓	✓	✓			✓						
Vanadium	✓			✓	✓	✓		✓		✓				
PGM	✓		✓	✓	✓	✓		✓						
HREE	✓		✓	✓	✓	✓		✓		✓				
LREE	✓		✓	✓	✓	✓		✓		✓				

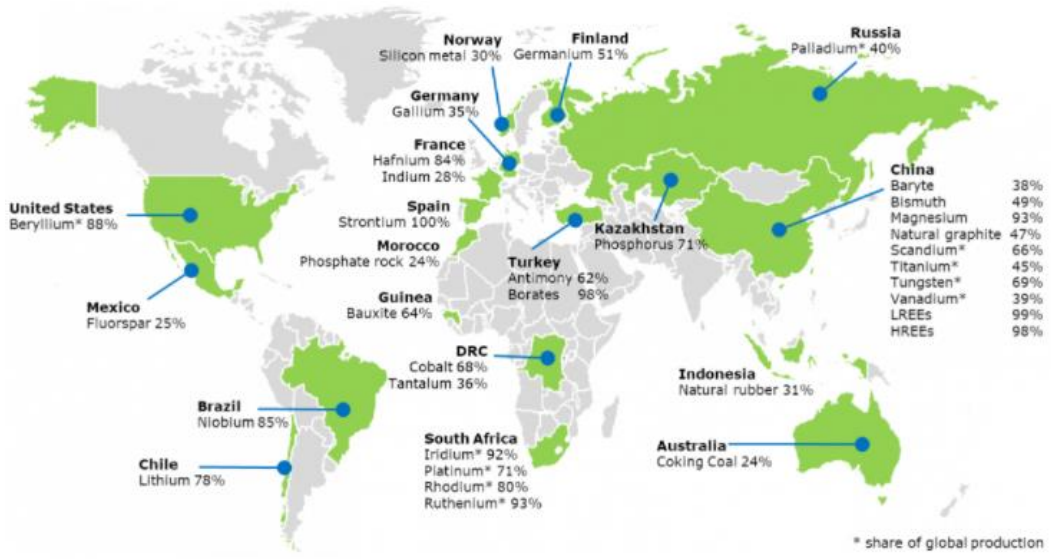


Fig. 1.2 Countries accounting for largest share of EU supply of CRMs **[10]**

The metallurgical extractive waste stored in ponds and dumps (historical landfills) has large volumes, it occupies large areas of land and creates environmental and human health problems that Romania, according to the Waste Directive, has the obligation to solve.

The topic of this thesis is limited to this issue and comes with an innovative idea of great economic value but also with a new technical approach, namely switching the investment perspective in conventional remediation to a new concept called 'Enhanced Landfills Mining' (ELFM). In this context, the thesis addresses the issue of qualifying dumps as secondary resources and, within the capacity of a thesis, it creates competence on ELFM issues (creating the conceptual model of a dump, creating the model of resource distribution in the dump, sampling dumps, laboratory test related to sampling, statistical data processing in order to estimate the investment risk, which will contribute to increasing the circularity of the metallurgical industry in Romania.

The main aim of this thesis is the consolidation from an exploratory and technical point of view in terms of capitalizing the secondary resource of the metallurgical field.

CHAPTER 2. METALLURGICAL WASTE MANAGEMENT IN THE CONTEXT OF CIRCULAR ECONOMY OF THE EUROPEAN UNION

2.1. GENERAL FRAMEWORK OF METALLURGICAL WASTE MANAGEMENT

The metallurgical industry is recognized as a major waste generator. Metallurgical waste is the objective of the thesis, but this approach is from the perspective of capitalization of landfills/ponds of waste metals in which it is likely to find base metals (Fe, Cu, Zn, etc.) in the form of compounds or, in happy cases, CRM in the form of oxides or complex compounds such as monazite, allanite, chalcopyrite, sphalerite, marcasite, pyrrhotite etc.

2.2. SPECIFIC ASPECTS OF THE NATIONAL METALLURGICAL WASTE POLICY

Romania's policy on overall waste management on its territory is subsumed by EU policy and is specified in the document 'Strategia Naţională de Gestionare a Deşeurilor' (SNGD) ('National Waste Management Strategy'), revised in 2013 and approved by GD 870/2013. SNGD is implemented through the National Waste Management Plan (PNGD), the purpose of PNGD is to develop a general framework conducive to waste management at national level with minimal negative effects on the environment. P NGD provides data on the situation of waste in Romania in the period 2010 - 2014, and makes a projection of waste quantities for the period 2015 - 2025. Also, the planned action plan covers the period 2018 - 2025. Already, EU forecasts in the field of waste industrial have different horizons, respectively short-term 2025, medium-term 2030 and long-term 2050. From the analysis of public information on PNGD, it can be stated that there is no clear methodology promoted at country level on landfilled waste with significant volume in the sense of recovery and eradication of this problem which is very large because landfilled waste is not inert as specified by law. The topic of the thesis is in line with the objectives of the PNGD, in that it develops, for the first time at national level, the newest method of holistic investigation of historical landfills. This method leads to identifying the investment needs towards reducing detrimental effects of such deposits in the context of the opportunity offered by the EU is interested to increase its resilience based on secondary resources latent in Europe, namely in Romania.

2.3. INDUSTRIAL WASTE MANAGEMENT FROM THE PERSPECTIVE OF SUSTAINABLE DEVELOPMENT AND THE CIRCULAR ECONOMY

The Circular Economy Paradigm imposes a fundamental change in the approach of the use of secondary resources - of which metallurgical waste is a part -, which includes interdependent approaches in the field of energy, materials management, etc. The new issue of Sustainable Materials Management (SMM) includes two innovative concepts:

1) Enhanced Waste Management (EWM), and
2) "Enhanced Landfill Mining" (ELFM).

Within the EWM, prevention and reuse /recycling are becoming even more comprehensive in the sense that the issue of full recovery of waste is raised so that the idea of waste disposal as a "final solution" is excluded. ELFM management especially addresses the massive metallurgical waste dumps/ponds that are attractive for the waste business and it is intended to answer more pertinently to the questions of business people which generally consist of:

- What are the exploitable / salable materials?
- What are the available quantities ie volumes, masses?
- Are there risks of hazardous or radioactive waste, etc.?

A full and correct application of the algorithm ELFMM (Enhanced Landfill Mining and Management) is the only way to gather data and information pertinent enough to answer the questions of business people who promote business specific to capitalization of metallurgical waste.

The end of this chapter reiterates the opinion of Professor Nicolae Anastasiu, corresponding member of the Romanian Academy: *'Take advantage of European funds to encourage projects that will bring opportunity* to *eradicate some of metallurgical dumps/ponds, giving back the fields to the natural circuit and the elimination of the historical pollution caused by these deposits"*

CHAPTER 3. SECONDARY RESOURCES OF RAW MATERIALS IN THE METALLURGICAL SECTORS

3 .1. General considerations

The production of goods worldwide is largely based on mineral resources extracted from the Earth's crust. Raw materials are the basis of the EU economy today and will continue to be, ensuring jobs and competitiveness. For this reason, the supply of raw materials from domestic resources or from the world market is essential for maintaining and improving the quality of life. Non-energy raw materials are used in all industries that produce consumer goods. For this reason they are considered fundamental as they are irreplaceable. In this context, the EC emphasizes the need to step up research into waste treatment so that technological solutions can be found to help industrial waste to avoid situations where valuable raw materials end up in landfills. The people of EC are also concerned at the significant amounts of resources in the form of waste and residues that have been exported outside the EU. These exported resources could have been recycled into secondary raw materials within the EU. The difficulty of supplying rare metal precursors (REEs), generally oxides, consists both in the shortage of ores with REE concentrations that are conducive to technological exploitation on an industrial scale and in technological costs. Due to the difficulties of extraction, the prices of rare metal precursors are high. In 2018, the cost of Neodymium Oxide (Nd_2O_3) was $ 107,000 / ton. Its price is expected to rise to $ 150,000 / t by 2025. Europium (I), Z = 63, is even more expensive, about $ 712,000 / t.

3. 2 Secondary raw material resources - a significant factor in the circular economy and EU's resilience to supply raw materials

A particular issue that has an impact on the value of the thesis is the EC's decision to facilitate the development of a functioning EU market for secondary raw materials. Furthermore, the EC will implement a series of measures to support this market, such as the introduction of requirements on certain levels / percentages of recycled material incorporated in manufactured products.

3. 3. Metallurgical powder waste - significant secondary resource of MP / MPC

The recovery of metals and the recycling of metallurgical powder waste presented in this subchapter addresses the main secondary resources that are found in international and national practice, namely the powder fraction of landfills related to steel and ferrous ore extraction.

3.3.1. The superior use of metallurgical powders through the synthesis of geopolymers

Commercial geopolymers are used for heat-resistant coatings and adhesives, refractory ceramics, binders for fire-resistant composite fibres, encapsulation of toxic and radioactive waste and special cements for concrete.

3.3.2. Recovery of metals, recycling and reuse of metallurgical slag

The current practice of slag removal from landfills presents environmental challenges, this is why there is a need to increase the recyclability and the potential to reuse these materials. Environmental performance of slag can be improved by binding toxic metal species in stable spinel phases.
The conventional possibilities for the recovery of metallurgical waste which can be found in a waste dump are systematized at the level of the EU in the BAT reports. These reports have another new and valuable possibility added to them, meaning MPC extraction.
A particular problem of metallurgical extractive waste dumps is acid drainage (Acid Mineral Drainage - AMD). Currently, due to the need of resources that contain critical rare metals and the EU legislation which imposes increasingly stringent environmental conditions, the AMD is taken into consideration as a potential source for the recovery of metals as part of an ampler strategy to address the AMD and increase the circularity of the metallurgical industry as a whole.

3.4. Romania's position on the issue of secondary resources as a significant factor of Circular Economy

Romania specifies its position on the new EU tendencies in the document Strategia Națională pentru Dezvoltarea Durabilă a României 2030 (Romania's National Strategy for Sustainable Development 2030), succinctly called SNDDR2030. SNDDR2030, referring to Objective 9, aims at 2030, among others, 'The rehabilitation of industries to become sustainable, with increased efficiency in the use of resources and increased adoption of clean and environmentally friendly technologies and industrial processes, ...'. Surprisingly, the SNDD 2030 does not say anything related to the use of secondary resources which can be found in abundance in Romania.

Romania has taken on tasks resulting from EC/EU documents regarding the eradication of pollution caused by extractive waste dumps which it has not fulfilled. These tasks are also present in the current government's documents: 'Rational use of natural resources, including that of materials which are nowadays considered waste, with the priority of reusing existing resources in local and national economic circuits by reintroducing waste into the circular economy'.

3.5. Conclusions on the importance of the MPC for the EU technological sphere and beyond

The EC considers that EU's success regarding the transformation and modernisation of its economy depends on the sustainable provision of primary and secondary raw materials needed for the expansion of clean and digital technologies in all EU industrial ecosystems.

Romania is seen as a resource for CRM, especially for natural graphite but also for critical metals such as Tl, Tu, V, Q. In Romania, the industry of metallurgical extractions has basically ceased to exist but it has left behind approximatively 340 Gm^3 of specific waste.

The traditional approaches regarding the management of mining and metallurgical waste are unsustainable.

The application of the principles and international practice of capitalization of waste ponds/dumps according to ELFM is the only viable solution for Romania.

In this context, Romania has the historic opportunity to eradicate some of the deposits of waste which create environmental problems and inter-relation problems with the EC/EU, if it can prove that these are secondary resources of CRM with other exploitable conventional resources based on the implementation of an innovative ELFM.

CHAPTER 4 RESEARCH METHOD

4.4. The budget of methods used to characterize landfilled metallurgical waste

The theme addressed in this paper imposes a multidisciplinary character of the research activity, this imposes an interdisciplinary research method.

In this context, the acquisition of information and know-how from available sources and the development of know-how to complete the need to achieve specific objectives of the thesis was used effectively. Thus, the elements of ELFMM management were documented based on the specialized literature and an algorithm was built for its application in the case of landfilled waste in Romania. The construction of the conceptual model of the Teliuc 2 site was carried out according to the mentioned algorithm with the available means. The construction of the secondary resource distribution model in Telic 2 pond was done with the know-how developed in the thesis based on the EURACHEM model of Double Replicated Balanced Sampling Method (BDDSM) [125], and modern methods and techniques for investigating granular/powdery waste. such as optical microscopy (MO) and electron microscopy (SEM-EDS), analytical spectrometry (XRFS, SDAR-OES), X-ray diffraction (XRD), loss on ignition (LOI). In order to know the uncertainty budget and the magnitude of the effects of the uncertainty factors, original theoretical studies were performed which substantiate and guide the ways of approaching the sampling of the ponds. In this sense, the original "top-down" approaches for

estimating the measurement uncertainty developed in the papers [129, 130], corroborated with an efficient algorithm for correlation analysis and data self-correlation, published in [131] , was the basis for adapting and developing the BDDSM method and creating the algorithm for analyzing "ANOVA in two stages" of XRFS data to establish the contents of the Teliuc 2 pond, such as SiO2, Fe2O3, CaCO3, Al2O3, Y, Sr, Ba etc.

The standard practice of RENAR accredited laboratories according to SR EN ISO / IEC 17025: 2018 consists in maximum caution regarding the extension of the application of the result to the batch from which the analyzed sample was taken. The vast majority of analytical reports mention "The result refers only to the tested portion"! The extension of the results obtained on the sampled specimens (10) at the pond level imposed the overcoming of the previous paradigm due to the variability of the samples taken from the same lot. This approach was carried out in a scientific manner by combining theoretical research by modelling and simulating cases of practical interest and, subsequently, by developing an effective and relatively inexpensive engineering method (BDDSM). This approach ensures the consistency and efficiency of research in the field of ELFMM as the modern research methodology is based on the axiom "Theory guides, the experiment decides"

CHAPTER 5. RESULTS

The main objective of the thesis is to investigate the secondary resource of a historical pond resulting from the processing of ferrous extractive waste in a manner compatible with the ELFMM model. To estimate the contents of secondary raw materials in the pond, it was mandatory to use investigative methods such as MO, XRFS, SEM-EDS, DRX and LOI. The particularity of the thesis changes the paradigm of laboratory analysis in the sense that the result does not refer only to the analysed/tested sample but it is used to estimate the content of the target analyte at pond level through the theory of sampling (TOS) of granular materials. The mathematical modelling of unit/granule sampling is based on the TOS theory developed by P. Gy. The theoretical model Gy is not used in the thesis because the discrete sampling (grain-by-grain or lump-by-lump) does not apply to tailings ponds as they mainly contain (> 90%) powdery material with granules of size in the range (200 nm, 1 mm). Since discrete sampling is inapplicable, it was necessary to develop other methods for simulating possible situations in the case of incremental sampling i.e. by taking material at macro level (2 ... 5 kg with common utensils, scaffold, mini-shovel, etc.).

The tests necessary to measure the analyte contents in waste involve a series of sub-sampling with strong detrimental effects on the representativeness of the analytical sample in relation to the pond/dump.

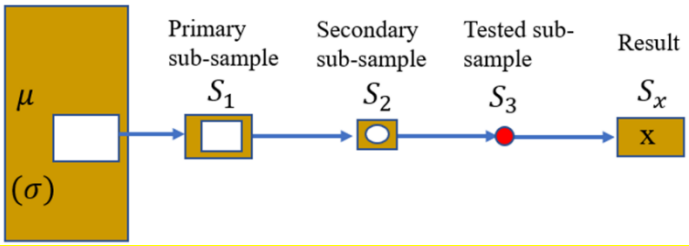


Fig. 5.6. Schematic representation of the sub-sampling imposed by the analytical process

The issue with sampling is the act of obtaining the representative sample or samples that have the same characteristics of those of the dump (contents of elements, minerals, granulation, etc.). The representativeness of the analytical sample is critical because the dump can contain tens of thousands of m^3 of waste and the analytical sample has a volume of the order of a few mm^3! This is why, the correct performance of sampling and the integrated analytical process is essential for the characterization of a heap/pond. Achieving the correct sampling and interpretation of the analytical results requires knowledge of the behaviour of the analytical results depending on the level /

concentration of the target analyte and the non-homogeneity distribution. This is done effectively only by theoretical analysis and simulation. In order to achieve the objectives of the thesis, it was necessary to develop the LOI method and the Double Replicated Balanced Sampling Method (BDDSM) method. In this context, Q n Chapter 5 presents the simulation results on the sampling characteristics of the granulated waste (distribution functions associated with the concentration of the analyte bearing mass, the value and dispersion of the concentration of the analyte bearing mass). Subsequently, the principles and implementation of the marginal recovery method related to LOI are presented. The method BDDSM is taken from the EURACHEM documents, it is adapted and developed to be applied to the sampling processing waste tailings which come from mining iron.

5.1. Modelling and simulating of the characteristics of granular waste materials sampling

The problem of theoretical study through statistical modelling and simulation of the sampling process was mainly aimed to establishing the order of magnitude of the uncertainty of the sampled concentration in relation to the concentration of the lot. In the simplified sense the item of interest is contained in the particles of type A, which are in minority compared to the number of particles of type B, which form the gangue, one can calculate the concentration of a sample relation:

$$c_E = c_o * \frac{Y}{X} = c_o * R \tag{5.1}$$

where Y represents the mass of the sample elements of type A contained in the colleted X mass, c_E is the concentration of the analyte in the sample, c_o is analyte concentration in the Y mass and R is the ratio of random variables associated i.e. R = Y / X.

In this context, the variance (dispersion) of the concentration c_E, $V(c_E)$, could be estimated with increased accuracy if the distribution of the variable R is known, respectively:

$$\sigma^2(c_E) = c_o^2 * \sigma^2(R) \tag{5.2}$$

If the variance of the concentration c_E is noted with $\sigma_{cE}^2$and V (R) with σ_R^2 then the relative standard deviation to the sampling concentration is:

$$\sigma_{RcE} = \frac{\sqrt{\sigma_{cE}^2}}{c_E} - = \frac{\sqrt{c_o^2 \cdot \sigma_R^2}}{c_o * \mu_R} = \frac{\sigma_R}{\mu_R} = \sigma_{RR} \tag{5.3}$$

where μ_R is the mean of R and σ_{RR} is the standard deviation relative to the variant R=Y/X.

Thus, if σ_{RR} is estimated theoretically, it can be stated that the relative standard deviation attributable to the concentration was also estimated due to the variability of the analyte as a proportion as well as a sample distribution. This way is incredibly valuable since it is the only one that allows the efficient attainment of information about sampling performance at low costs. Also, this approach allows the exploration of various sampling scenarios which is equivalent to conducting case studies by simulation.

5.1.2. Modelling the critical concentration distribution with uniform distributions in the case of incremental sampling

This model corresponds to the most unfavourable case when X and Y do not have central tendencies, implicitly they have large dispersions. In this case, the probability distributions of the variables X and Y are given by the relations:

$$f_X(x) = \begin{cases} \frac{1}{2b}, & x \in [x_o - b; x_o - b] \\ 0, & x \notin [x_o - b; x_o - b] \end{cases} \tag{5.8}$$

$$f_Y(y) = \begin{cases} \frac{1}{2a}, & y \in [y_o - a; y_o - a] \\ 0, & y \notin [y_o - a; y_o - a] \end{cases} \tag{5.9}$$

The theoretical value of variable R = Y / X resulted from the calculations given in thesis is:

$$\mu_R = \frac{y_o}{2b} * \ln\left(\frac{x_o+b}{x_o-b}\right) \quad (5.19)$$

The relation (5.19) demonstrates that the value of the average concentration of the analyte, which is proportional to μ_R does not depend on the magnitude of the uncertainty of the realization of yo which is proportional to a, which is the width of the subinterval of yo.
For x = b / xo <0.05, the expression of μ_R can be simplified by neglecting the terms in b/xo with powers greater than unity and by Taylor series development of the logarithm from the previous expression, we obtain:

$$\mu_R \approx \frac{y_o}{x_o}\left(1 + \frac{b^2}{3*x_o^2}\right) \quad (5.21)$$

The previous relationship shows that the average value of R is predicted i.e. yo / xo with a shift ('bias') positively complicated that depends only on the distribution of X.

Estimating the variance of R is of the greatest interest, as it expresses the inaccuracy of the measurement. In the case of the CRM analyte, it is found in ore in the concentrations of << 1%. Estimating such contents on the basis of sampling becomes a problem as small volume samples are most likely to take a small mass of analyte.

The variance of R, denoted V (r) is calculated with the well-known relation:

$$V(r) = \overline{r^2} - \mu_R^2 \quad (5.22)$$

in which $\overline{r^2}$ represents the average of r^2.

Based on Eq. (5.22) it was obtained:

$$V(r) = \frac{1}{6g} * \left(\frac{\mu-gu}{1-u}\right)^3 * \frac{3-u}{1+u} + \frac{1}{6g} * \left[8 * u^2\left(\frac{g-\mu}{1-u^2}\right)^3 + 6 * (g-\mu) * \frac{\mu^2-g^2*u^2}{(1-u^2)^2}\right] + \frac{1}{6g} * \left(\frac{\mu+gu}{1+u}\right)^3 * \frac{3+u}{1-u} - \left[\frac{y_o}{2b} * \ln\left(\frac{x_o+b}{x_o-b}\right)\right]^2 \quad (5.29)$$

where μ = yo/xo, u = b/xo and g = a/b

Rel.(5.29) shows that the variation of the R report depends in a complicated way on the theoretical average μ≡μR, the widths of the uniform distribution of the probability ratio g = 2a / 2b, but in particular the relative uncertainty u = b/xo i.e. the uncertainty with which the sampling of the mass that can be associated with the reproducibility of the sampled mass is performed.

In order to apply the theoretical results obtained based on the use of uniform distributions, computer simulation is required for several scenarios of practical interest. These scenarios are described in the thesis. Only the more special cases are presented in the summary. Thus, the probability distributions of R for relatively large volume samples have trapezoidal profiles for concentrations between 1% and 0.01% as long as the factors b/x and a/y do not change. This is noteworthy and used in practice. If the volume of the sample decreases for ω = constant then the shape of the distribution of R changes and the relative standard deviation increases as shown in Fig. 5.11 a, b, c. (in the inset are given the values of the quantities X, b, Y, a, CV-the coefficient of variation of R, FN-the norming factor that estimates the completeness of the calculations performed during the simulation).

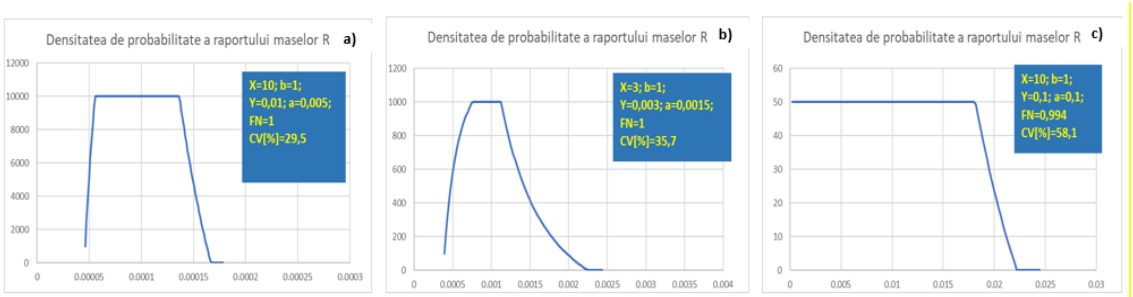


Fig. 5.11. Types of distributions of R derived from the general distribution fR (r): a) asymmetric trapezoidal; b) bearing curvature; c) inverted sigmoid

Conclusions:

i) Modelling the variance of the sample concentration with uniform distribution functions is pertinent because the variance of the mass containing analyte does not have a physical model to indicate a clustering of its values in the extracted sample.
ii) Modelling the variance of the sample concentration with uniform distribution functions is in accordance with the recommendations of the standard ISO/IEC Guide 98-3: 2008 'Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)
iii) The profiles of the distributions associated with R are trapezoidal for C_L >0.1% and acquire curvilinear shapes for C_L <0.1%. For small values of C_L and high distributional heterogeneity, the distribution of R becomes uniform, bounded to the left by zero, which looks like a single sampling has equal chances to provide results between 0 % and 2 C_L which is unacceptable for the decision act.
iv) The RSDs associated with c_E are placed in the range [30%; 60%] which shows that sampling is the critical factor in investigating the potential of a dump as a secondary resource of critical elements.

5.1.4. Modelling sampling with normal truncated distribution of the sampled mass (X) and uniform distribution of the analyte carrier mass (Y)

This modelling targets the most favourable scenario for the case of investigating ponds/dumps in order to estimate the contents of rare earths and other elements specified in the CRM list. In this case the mass of the sample is made with good enough precision σ and the value of X is centred on its average value, denoted in this case by μ. The mass of the sample (X) is distributed:

$$f_X(x) = \begin{cases} C * \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right), & x \geq 0 \\ 0, & x < 0 \end{cases} \quad (5.31)$$

wherein C is the normalization constant, respectively:

$$C = \frac{1}{\sqrt{2\pi}\sigma * \Phi(\frac{\mu}{\sigma})} \quad (5.32)$$

where $\Phi(\frac{\mu}{\sigma})$is the cumulative distribution of the normal distribution N (0,1) given by the relation:

$$\Phi\left(\frac{\mu}{\sigma}\right) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\frac{\mu}{\sigma}} \exp\left(-\frac{t^2}{2}\right)dt \quad (5.33)$$

The analyte carrier mass (Y) incorporated in mass X has a uniform distribution in the range [yo-a; yo + a], respectively:

$$f_Y(y) = \begin{cases} \frac{1}{2a}, & y \in [y_o - a; y_o + a] \\ 0, & y \notin [y_o - a; y_o + a] \end{cases} \quad (5.34)$$

where y_o is the average mass of the analyte carrier substance incorporated in the mass sample X and - is the standard deviation of the values of Y.

Following the calculations, described in the thesis in detail, the distribution $f_R(r)$ results:

$$f_R(r) = \sqrt{2\pi}\sigma\mu * \left[\Phi\left(\frac{\mu}{\sigma}\right) - \Phi(abs\left(\frac{2y_o}{r} - \mu\right))\right] + \sigma^2\left[\exp\left(-\frac{\mu^2}{2\sigma^2}\right) - \exp\left(-\frac{\left(\frac{2y_o}{r}-\mu\right)^2}{2\sigma^2}\right)\right] \quad (5.39)$$

Conclusions. The expression of $f_R(r)$ does not have an accessible analytical form, which means that its exploitation can be done only on the basis of numerical calculation.

The variance of R, $V(r) = \overline{r^2}$-μ_R^2, was estimated by numerical calculation in Excel for each case. Several sampling scenarios for $c_E \leq 10\%$ concentrations were explored. The cases in which the analyte is present in the dump with high values of mass concentrations i.e.> 10% have been ignored because these cases are known and do not pose problems for sampling. To exemplify the special utility of the theoretical simulation, the case C_E = 1% will be presented in comparison, but the case c_E = 0.1%. Thus, if the analyte-bearing mass has a concentration of 1% and a spatial dispersion of 10% of the value of Y then sampling is feasible because the accuracy is very good and the relative standard deviation is about 5% (Table 5.6, in which A- accuracy, AR relative accuracy (%), SD-standard deviation, RSD-relative standard deviation (%)). In this case the distribution of R is quasiuniform but with small width (Fig. 5.16).

Tabelul 5.6. Input and output data for simulating the sampling characteristics in the case μ_{Lot}=0,01 (1%)

Date date intrare		Date de iesire	
μ_X[g]	100	μR	0.01001
σ_X [g]	1	A	0.00001
μ_L	0.01	AR[%]	0.13857
y_o[g]	1	SD	0.00047
a[g]	0.1	RSD(%)	4.73

Fig. 5.16. Distribution graph of $f_R(r)$ for input data in Table 5.6

In the case of the contents of analyte-bearing masses in the dump it is 0.1%, the distributional variability of the analyte-bearing mass is 50% from yo, the sampling performance decreases significantly to the threshold where sampling is compromised (Table 5.5, Fig. 5.15).

Tabelul 5.7 Input and output data for simulating the sampling characteristics in the case μ_E=0,10 (10%)

Date date intrare		Date de iesire	
μ_X[g]	100	μR	0.10006
σ_X [g]	1	A	0.00006
μ_E	0.1	AR[%]	0.05688
y_o[g]	10	SD	0.02884
a[g]	5	RSD(%)	28.83

Fig. 5.15. Distribution graph of $f_R(r)$ for input data in Table 5.7

The cases presented above highlight the influence of the primary parameters of sampling (μ_X, σ_X, μ_L, a) on the sampling performance (A, A_R, RSD) for values that are found in the practice of ore mining. High sampling masses i.e. 1000g and 100g were taken into account and the problem of measuring the contents of analyte-bearing masses was raised at these levels. This is impossible in laboratory practice because the equipment performs measurements on samples that have masses in the range of 0.01-1 g.

The simulation program implemented in Excel can simulate cases with concentrations below 1 ppm but these are irrelevant for the exploitation of extractive waste dumps as secondary resources.

Main conclusion. The analysis of the simulated cases showed that the optimal scenario of a successful sampling is primary sampling with large volumes, followed by the formation of a composite sample that must be homogenized as well as possible by grinding so that the subsamples in the composite sample have a dispersion of analyte-carrying substance as small as possible. Practically, homogenization forces the transition from the uniform distribution of the mass of the analyte-carrying

substance in the sample to a clustered distribution which, naturally, is considered to be of the Gauss-Laplace type.

5.1.5 Modelling truncated sampling with normal truncated distribution of the sample mass and the mass of the analyte incorporated into the sample carrier

This modelling targets the most likely sub-sampling scenario when the sub-sample has been ground and homogenized. In this case, the mass of the sample is made with a better accuracy, σ_X , and the value of X is centred on its average value denoted in this case by μ_x . In this scenario, the mass of the sample, (X) is considered to have the distribution:

$$f_X(x) = \begin{cases} C_X * \exp\left(-\frac{(x-\mu_X)^2}{2\sigma_X{}^2}\right), & x \geq 0 \\ 0, & x < 0 \end{cases} \tag{5.40}$$

in which C_X is the normalization constant

The mass of the analyte incorporated in the sample will be a normally distributed variable, denoted by Y, and it is admitted that it has an average value μ_Y, respectively the probability distribution density function has the expression:

$$f_Y(x) = \begin{cases} C_Y * \exp\left(-\frac{(y-\mu_Y)^2}{2\sigma_Y{}^2}\right), & x \geq 0 \\ 0, & x < 0 \end{cases} \tag{5.43}$$

in which C_Y is the normalization constant.

The thesis shows in detail the deduction of the mathematical expression of the probability density distribution of R, respectively:

$$f_R(r) = \frac{1}{2\pi\sigma_X\sigma_Y\Phi\left(\frac{\mu_X}{\sigma_X}\right)\Phi\left(\frac{\mu_Y}{\sigma_Y}\right)} \exp\left(-\frac{(r\mu_X-\mu_Y)^2}{2(r^2\sigma_X^2+\sigma_Y^2)}\right) * \left[\sqrt{2\pi}\cdot gh\cdot\Phi\left(\frac{g}{h}\right) + h^2\exp\left(-\frac{g^2}{2h^2}\right)\right] \tag{5.48}$$

where:

$$g = g(r) = \frac{r\mu_Y\sigma_X^2+\mu_X\sigma_Y^2}{r^2\sigma_X^2+\sigma_Y^2} \tag{5.49}$$

$$h = h(r) = \frac{\sigma_{X*}\sigma_Y}{\sqrt{r^2\sigma_X^2+\sigma_Y^2}} \tag{5.50}$$

in which all used notations have their meanings previously specified in this summary.

It is observed that the probability density of the analyte carrier mass in the sample has a complicated mathematical expression that does not have an analytical form. However, $f_R(r)$ incorporates the exponential specific to the normal distribution of $N^*(\mu_Y/\mu_X, \sigma(r))$ which shows that R is realized with increased probability around the value of μ_Y/μ_X, respectively R has a tendency of clustering around the real value. On the other hand, $f_R(r)$ has a standard deviation that varies according to r, which shows that it is not a true normal distribution, but a quasi-abnormal distribution. The expression of $f_R(r)$ allows the simulation of the distributions of the probability density of R for all the scenarios that may be encountered in practice and, based on that distribution the standard uncertainty of σ(r) corresponding to $c_E=\mu_Y/\mu_X$ can be calculated. To exemplify, the problem of sampling 1g for an elementary XRFS or XRD analysis is presented. Figure 5.22 shows that the probability density of R for the increments with small masses become large and certifies that the value of them apart from the average R group have higher probabilities of occurrence. (In the insect are presented the values of the input quantities μX, μY, σX, σY and the output values Rmedium, relative accuracy, RSD and the normalization condition CdNorm)

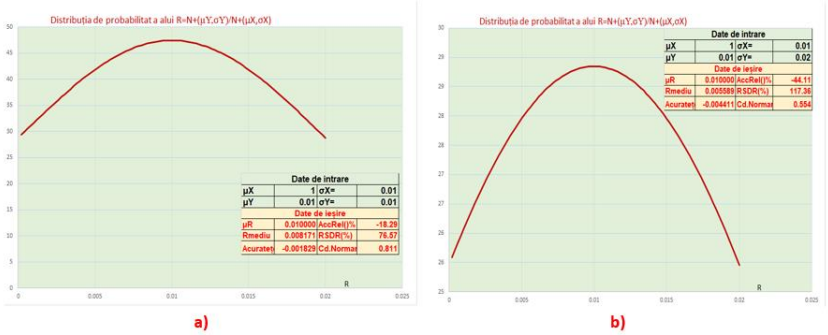


Fig. 5.22. $f_R(r)$ graphs and specific data for the cases: a) μ_X =1g cu a=0,01 g; b) μ_X =1g cu a=0,02 g

A specialist in the recycling of metallurgical extractive waste must be aware that for the evaluation of the analyte content in the landfill based on the instrumental analysis of the respective powdery waste, the total uncertainty u_T associated with the measured samples must be taken into consideration i.e. the sampling uncertainty u_E and the measurement uncertainty u_M respectively must be considered:

$$u_T = \sqrt{u_E^2 + u_A^2} \tag{5.51}$$

Thus, even if the laboratory can ensure an uncertainty u_A = 1%, although often $u_A \geq 5\%$, the sampling of samples for analysis generates an uncertainty of over 50% if no special measures are taken.

Conclusions.

Modelling and simulation of some cases of interest for incremental sampling show that accuracy and precision depend on the concentration of target analyte to the characteristics of sampling i.e. the mass of the primary sample, the precision of the sampling mass, the analyte mass incorporated in the sampling and its precision, which can only be obtained through theoretical research like it was shown in the thesis.

Expressions of probability density functions of the variable R = Y/X were deducted in full in the thesis and they represent valuable original contributions because they have become tools for evaluating the behaviour of samples of various interest analytes according to their concentration in the target warehouse concentration which can be evaluated preliminary by sample measurements or by in situ measurements, as is the case with hXRFS measurements.

5.2. THE BALANCED DESIGN DUPLICATE SAPMPLING METHOD

The mathematical pattern of the Balanced Design Duplicate Sampling Method, (BDDSM) (Fig. 5.25) is published by Eurachem/Eurolab in 2019, ISBN 978-0-948926-35-8, Second Edition http://www.eurachem.org, called 'Measurement uncertainty arising from sampling: A guide to methods and approaches', which is the version of the document with the same title in 2007.

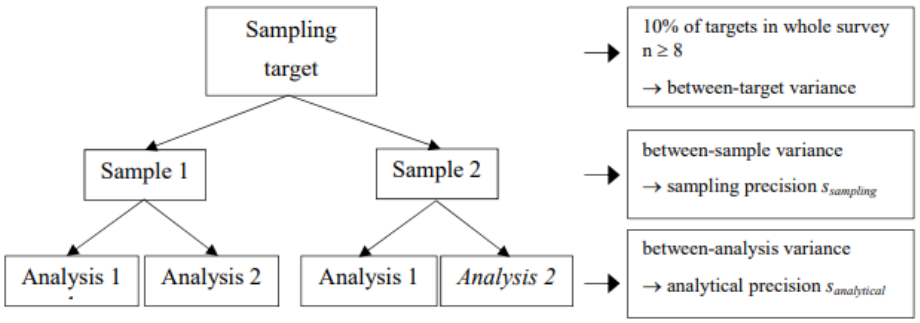


Fig. 5.25. Balanced experimental design for empirical estimation of uncertainty (i.e. two-stage nested design), using the 'duplicate method' [125]

The BDDSM method presented in EURACHEM (2019) is incomplete because it does not take into consideration the uncertainty associated with the variability of the measurand at the level of the landfill (dump, pond).

Table 5.14 Revised algorithm for estimating sampling uncertainty BDDSM

	Rezultate măsurări				Medii pe sub-probe		Abateri analitice	Medii	Dispersii sub-probe	Dispersii probe
Sub-probe	S1A1	S1A2	2A1	S2A2	S1	S2	la nivel	la nivel de	$4 * D_{i1(x)}{}^2$	$4 * (\bar{X}_i - \bar{X})^2$
Probe	x_{i11}	x_{i12}	x_{i21}	x_{i22}	$\bar{x}_{i1}$	$\bar{x}_{i2}$	subprobe	probe	$(\bar{x}_i - \bar{x}_{i1})^2 = (\bar{x}_i - \bar{x}_{i2})^2$	
1	402	325	361	351	363.5	356	3014.5	359.75	56.25	566.44
2	382	319	349	362	350.5	355.5	2069	353	25	106.09
3	332	291	397	348	311.5	372.5	2041	342	3721	136.89
4	280	278	358	321	279	339.5	686.5	309.25	3660.25	5959.84
5	370	409	378	460	389.5	419	4122.5	404.25	870.25	12723.84
6	344	318	381	392	331	386.5	398.5	358.75	3080.25	475.24
7	297	333	341	315	315	328	986	321.5	169	2777.29
8	336	320	292	306	328	299	226	313.5	841	4719.69
9	372	353	332	337	362.5	334.5	193	348.5	784	1.69
10	407	361	322	382	384	352	2858	368	1024	1624.09
X_{mediu}=	347.85						16595		14231	29091.1
	Anazia i.e. incertitudinea analitică standard									
SSE	16595	20	Vanalysis=SSE-analysis/ dfanalysis						829.75	
$df_{analysis}$=i*j*k-	20	SDa=	28.8		RDS(%)=	Sda*100/			8.28	
Sub-eșantionarea										
SSTsp=	14231	V_{sp}=(SSTsp/ $df_{sampling}$ -$SS_{analysis}$/$df_{analysis}$)/n							296.675	
dfsp=i*j-i	10	SDsp=	17.22		RSD(%)=	SDsp*100/			4.95	
Eșantionarea										
SSTp=	29091.	V_p=(SSTp/ df_p -nV_{sp} -V_a)/nb							904.6	
dfsp=i-1	9	SDp=	30.08		RSD(%)=	SDsp*100/			8.65	
Incertitudinea compusa relativa										
u_{CR}=sqrt(RSD_a^2+RSD_{sp}^2+RSD_p^2)				12.96	%					
Incertitudinea extinsa relativa (95%)										
UR(95%)=2*uC				25.91	%					

For this reason, for the correct estimation of the uncertainty associated with measuring X, it is necessary to take into account the measurand variability at the deposit level and to modify the calculation of given algorithm. Thus, the correct approach to calculating the compound uncertainty of X, noted as u_c, has required the development of the model, as shown in Table 5.14, and taking into account the rel. (5.85). To have control on the accuracy of calculations published data was used and the results obtained from the developed model were compared, partially, with data in the publications.

The values of the uncertainty attributed to the analysis and sub-sampling reported in [125,127,142] coincide with the recalculated values expressed in the extended algorithm. The extended algorithm provides a standard uncertainty relative to sampling at lot level that has a significant value close to the analytical uncertainty. The documents [125,127,142] omit taking into account the component attributed to the lot for reasons that I miss for the time being.

Conclusions. The thesis presents the correct version of the BDDSM method. This method is backed up, in the thesis, by explicit statistical evidences that offer the reader all the evidence needed for a correct application of this valuable method of estimating the sampling uncertainty of tailing ponds.
In the thesis, the analysis of the BDDSM results is explicitly presented, this analysis uses the ANOVA method in two stages with the extended statistical model:

$$x = \mu + \varepsilon_s + \varepsilon_a + \varepsilon_t \quad (5.77.)$$

where μ is the true value of the measuring mass, ε_s ($\varepsilon_{sampling}$) is the 'error' due to sampling, ε_a ($\varepsilon_{analyses}$) is the 'error' due to the analysis, ε_t is the error due to the target (wasteland, pond).

5.3. Development and implementation of the loi method (Loss-On-Ignition) for the characterization of powdering waste

The LOI method is based on sequentially heating the samples to 105 °C for 6 hours, to 550 °C for 4 hours, to 950 °C for 3 hours. Before and after each stage the crucibles are weighed with analytical balances and the following measurands are estimated:

- Humidity (H), which is calculated as:

$$H = \frac{m_{fC} - m_{105}}{m_S} * 100 \quad (\%\ wt.) \quad (5.86)$$

where m_{fC} is the crucible's mass which is filled with primary substance; m_{105} is the mass of the substance and of the crucible after drying at 105 ^oC; m_S is the mass of the initial substance (waste, surrogate) introduced into the crucible (g):

- Organic matter content (OM) of the sample:

$$OM = \frac{m_{105} - m_{550}}{m_S} * 100 \quad (\%wt.) \quad (5.88)$$

where m_{550} is the mass of the crucible filled with waste after being heated at 550 ^oC, (g)

CO_2 content, denoted CCO_2 is calculated as:

$$CCO_2 = \frac{m_{550} - m_{950}}{m_S} * 100 \quad (\%wt.) \quad (5.90)$$

where m_{950} is the mass of the crucible that contains calcined at 950 °C.

For a molar mass of 44 g/mol for carbon dioxide and a molar mass of 100 g/mol for carbonate ($CaCO_3$), the weight loss by thermal decomposition at 950 ° C multiplied by 2,27 is the concentration of calcium carbonate (CCC) in the original sample:

$$CCC = 2.27 * CCO_2 \quad (5.91)$$

The study of the literature showed that during heating, not only organic matter and carbonates contribute to weight loss/mara but also the evaporation of OH groups from crystals in mineral particles and carbonate decomposition generates weight loss. Oxidation of certain minerals can cause an adverse phenomenon, i.e. weight gain. For this reason the LOI test must be calibrated internally for each matrix tested. For this purpose, certified reference materials must be used. There is no certified reference material for the waste addressed. To overcome this impediment, an efficient calibration alternative has been developed, i.e. a variant of the marginal recovery method used in analytical chemistry. The marginal recovery method (MRM), (also called the surrogate recovery method), has been adopted to assess the accuracy of the LOI method. The EURACHEM Guide defines the surrogate as 'the pure compound or element added to the test material whose chemical and physical behaviour is considered representative of the native analyte', while the recovery of the surrogate consists in the recovery of a

pure compound or element specifically added in test/analysed material as 'spike' (also called 'marginal recovery').

The theoretical bases of MRM applied in the LOI test were developed in my own conception. Thus, the marginal recovery yield was calculated assuming that the CCC values in the sample and in the surrogate are averages obtained by the LOI method. The theoretical mass (g) in a sample added with a surrogate, denoted m_{TC} is calculated from the relationship:

$$m_{TC} = m_W * c_W + m_S * c_S \quad (5.92)$$

where m_w is the mass of the waste, c_W is CCC in waste (% by weight), m_S is the surrogate mass (g), c_S is the carbonate concentration in the (% by weight).

The theoretical carbonate concentration in a surrogate additive sample is calculated by the relation:

$$C_{TC} = \frac{m_{TC}}{(m_W + m_S)} \quad (5.93)$$

The recovery efficiency R is defined by the relation [155]:

$$R = \frac{c_{obs}}{c_{ref}} \quad (5.94)$$

where c_{obs} is the observed concentration (or quantity) obtained by applying an analytical procedure to a material containing analyte at a reference level c_{ref}.

Alternative XRFS and XRD methods and techniques were used to evaluate the accuracy of MRM-LOI measurements. The results obtained by MRM-LOI, XRD and XRFS are presented in detail in the thesis as well as in an article being published in the Scientific Bulletin series B. The novelties addressed in this article consist in: a) proving that the method of marginal recovery is effective in ensuring the validity of the results; b) the association of LOI, MRM and XRFS for the validation of LOI accuracy for CCC measurement; c) statistical inference applied to inter - comparison it results XRFS LOI and bilateral t test with significance i.e. 0.05 which has proved to values that are equal in terms of statistics; d) the use of a cheap surrogate as a reference material for overcoming the lack of MRCs which is the most significant achievement because it removes a major difficulty, lack of MRC, and avoids a significant expense related to the consumption of MRC.

5.4. Case study. Investigation of secondary resources of a landfill of iron mining

5.4.1. Significance and context of the activity

In Romania, mining and metallurgical waste is one of the biggest challenges for the environment. According to the ,, ('Report on the conclusions resulting from the technical inspections and control at the tailings ponds in the mining industry, carried out between February 19 and June 8, 2007' (Report M.M.D.D. nr. 111509/22.06.2007), out of a total of 93 mineral tailings ponds existing in Romania, a number of 75 ponds are in the patrimony of the state and 18 ponds are in the patrimony of different companies. Of the 75 ponds belonging to the state, 14 ponds stopped storage on 31.12.2006, corresponding to the complete list in the annex to GD no. 349/2005 and the others are ponds where the deposit was stopped in the previous years. Despite efforts to reduce the amount of waste produced by the mining and metallurgical industries, this type of waste is one of the largest sources of waste in the world.

Magnitude as volume, occupied area, pollution generated by them and the latent potential of waste in Romania led me to choose as a subject a pond resulting from iron ore processing by flotation, since the classification of ponds as a significant secondary resource of raw materials, in the context of Romania's expected development, it would bring particularly high economic and environmental benefits.

5.4.2. **The ELFM algorithm for qualifying a metallurgical extractive landfill as a secondary raw material resource**

The ELFM management aims at eradication the deposit and site rehabilitation. In this sense, a holistic investigation of the site is required in order to acquire the information and data that would allow technical and economic decisions with low risk of failure. Thus, in order to minimize the decision-making risk, ELFM recommends an algorithm that allows the systematic investigation of the site and to obtain the necessary information and data in an efficient manner. This algorithm is shown schematically in Figs. 5.34.

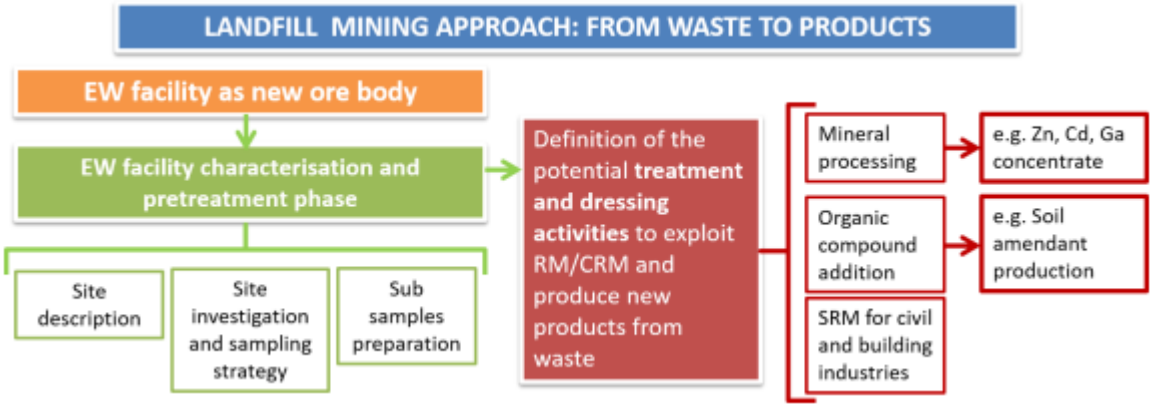


Fig. 5.34. Schematic showing various steps to obtain products from extractive wast [166]

5.4.2.2. The ELFM algorithm for investigating a landfill

According to the investigation practice **the first stage** consists in identifying the site location and its extent both as horizontal and vertical extension. **The second step** is to acquire as much information as possible to avoid consuming resources for the acquisition of information already available. **The third stage** consists of site investigation at the scene and comparing the data available with the facts found on inspection and interviews with people who hold important information and data about the site. **The fourth stage** consists in designing a geophysical investigation plan for obtaining the '***conceptual model'*** of the site as true as possible and for designing the 'targeted' systematic sampling. **The fifth stage** consists in the geophysical investigation of the site in order to build the conceptual model of the site. **The sixth stage** consists in the design and implementation of sampling, respectively sampling for establishing the mineralogical and elemental contents of the site. **The seventh stage** is to analyse the samples in the laboratory and provide analytical results. **The eighth stage** consists in the analysis of the data in order to elaborate the '***model of distribution of resources in the deposit'*** which means their location, estimation of volumes or masses of minerals or recoverable elements as well as uncertainties related to the estimated quantities of minerals. **The ninth stage** consists in the elaboration of the ***integrated feasibility study*** which must contain: 1) establishing the ways of capitalizing the investigated secondary resource, the related costs and the environmental impact due to waste processing and 2) establishing the way of site rehabilitation, the related costs and the source of financial and material resources for this action.

5.4.3. Application of the ELFM algorithm to the IDEMF site

Stages 1 and 2 of the ELMF were performed through documentation. According to the source [159] the wastes from the Teliuc 2 pond (Iron Ore Extractive Waste Tailings Pond-IOEWTP) can be recovered as resources of: silicon minerals, iron (in the form of oxides or carbonates), precious metals (gold 1.13 g/t, silver 0.4 g/t), and additions to construction materials. The IOEWTP pond is considered a secondary resource with a high iron content and is compared to the Lunca Muresului - Deva pond. The data from the specialized literature and from other sources show that the approach of the thesis for the qualification of the IOEWTP pond is opportune and of major economic and ecological importance.

Stage 3 was to visit the site and find the extent of the resource. It was seen the negative impact on the environment of the IOEWTP. A great part of the deposit does not allow grass to grow which would limit pollution with 'flying dust'.

The images in Figs. 5.36, reveal the physical extent of the site as well as the extent of the potential for pollution with 'flying dust'. It is observed that no measures are taken to green the area, i.e. the pond is abandoned without conservation measures.

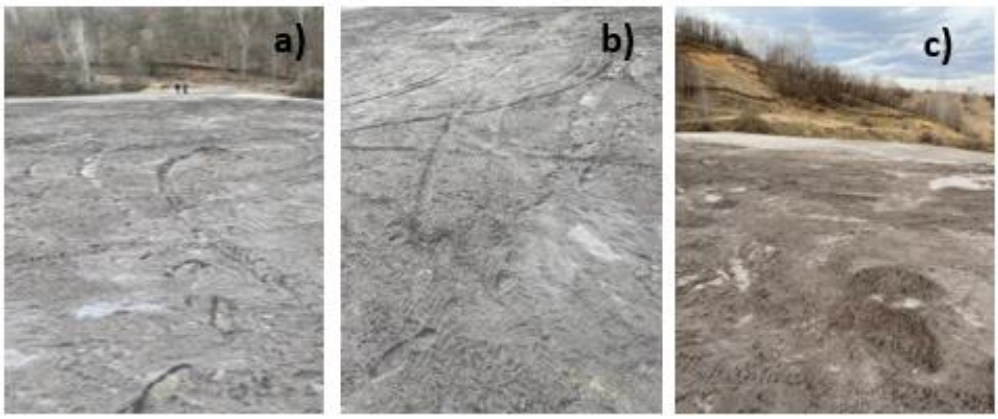


Fig. 5.36. Images collected on the spot 24.04.2020; a) the image of the access to the pond and selenary aspect; b) detailed selenium aspect; c) marginal grassing and lack of vegetation on the pond.

In step 3 a preliminary sampling of samples was carried out to be analysed in order to determine the mineralogical contents and the elements from the targeted areas.

Stages 4-5 are not the subject of the thesis from a scientific point of view, but in order to promote a scientific research project Brantax Ltd. (Bucharest, Romania) was contacted [170] and a geophysical ERT survey was designed to initiate and allow the development of the company's expertise regarding the methods and techniques for characterizing the historical extractive waste ponds in order to capitalize on them, respectively to increase Romania's capacity to align with the new Circular Economy policy. The preliminary investigation performed by Brantax is shown in the images in Fig. 5.40.

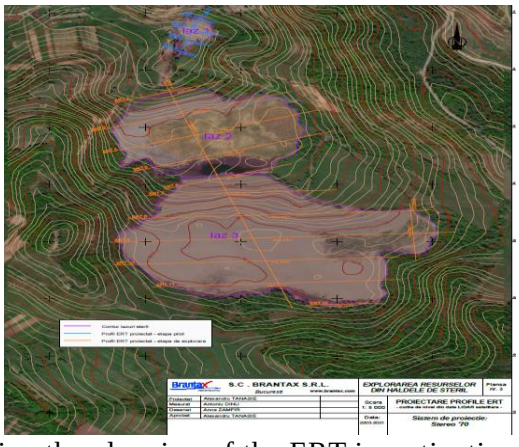


Fig. 5.40. Image regarding the planning of the ERT investigation of the TELIUC pond 2.

The 6th stage provides for the design and implementation of sampling, respectively sampling for establishing the mineralogical and elemental contents of the site. Unfortunately, there was no geophysical exploration of ERT and/or GPR that would allow the design of the targeted sampling. That is why a conventional 'blind' sampling was carried out. A systematic-random sampling was adopted with the taking of a number of 10 increments, each increment having a mass of about 5 kg. The motivation consists in the preliminary exploratory character of the IDEMF pond, but especially in the large number of investigations/tests/measurements (MO, SEM-EDS, XRFS, XRD, LOI) which applies

to each increment that incurs a large volume of work and implicitly costs. However, 10 samples is supported by literature when estimating uncertainty of sampling is done by BDDSM [125, 127, 142-144] . In the matter of sampling, the BDDSM represents the best compromise between the information provided and the costs. From an engineering perspective, BDDSM was considered to be the best approach for estimating sampling uncertainty. As a consequence, 10 samples were collected in the IDEMF pond (Fig. 5.43).

Fig. 5.43. a) the sampling plan; b) sampling method; c) the samples taken.

In the seventh stage the samples were analysed by OM, SEM-EDS, XRD, XRFS, and LOI as it will be showed below. Stages 8 and 9 are not affordable as there is no expertise and infrastructure in Romania for these very important stages. Steps were taken in this regard at the research institutes INCDMRR Bucharest, INCDPM-Bucharest and IGR Bucharest to start the geophysical investigations (ERT, GPR etc.) but their lack of interest was noted due to both outdated ERT and GPR equipment and software and lack of qualified staff regarding the approached topic.
In what's to follow the most representative results obtained for the sample will be presented to exemplify the way of testing the samples and the analysis of the results obtained for each of the 10 samples analysed. The results obtained on all samples are analysed by the BDDSM method in order to draw conclusions regarding the contents of interest associated with the entire pond and their uncertainties.

5.4.4. Results of tests performed on the samples taken P1 ... P10

5.4.4.1. Results of tests performed on sample P1

a. Optical microscopy (OM) observations

The increment extracted from zone 1 (Fig. 5.45) has a complex granular appearance consisting of particles with different morphologies and colours that suggest the presence of a majority of silica-translucent particles, the presence of iron oxides reddish and black particles and fine particles that have unidentifiable mineralogical nature from the analysis of MO images in Figs. 5. 45.

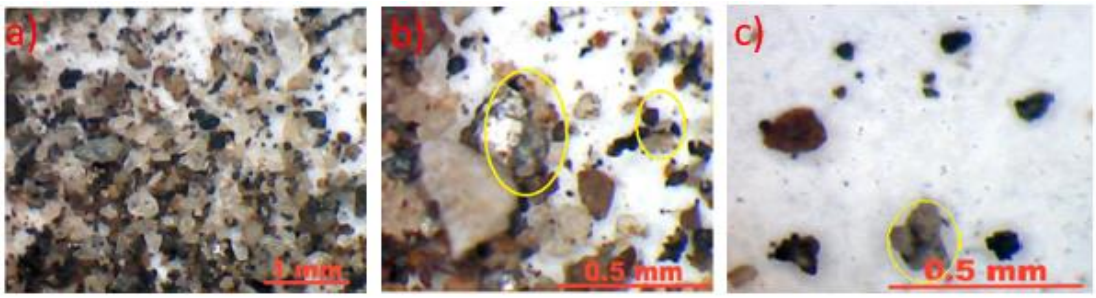


Fig. 5.45. OM images of the granular material taken from area 1, sample P1: a) overview; b) image at intermediate magnification; c) detail image

From the point of view of the TOS theory, P1 waste presents a high constitutional heterogeneity as it contains at least 3 types of particles with different morphologies and granulations both within populations of the same nature and between populations.

b. SEM-EDS investigations

The SEM-EDS investigations were performed with a Zeiss Gemini 500 scanning electron microscope equipped with a field effect Schottky electron emitter. The Zeiss Gemini 500 microscope provides magnifications of 20-1000,000 x and resolutions <0.6 nm at 15 kV. The microscope allows the investigated samples to have a mass of the order of 0.1 g, therefore the primary sample delivered to the laboratory with a mass of about 40 g must be sub-sampled. SEM images highlight both the morphology of the particles and their dimensions.

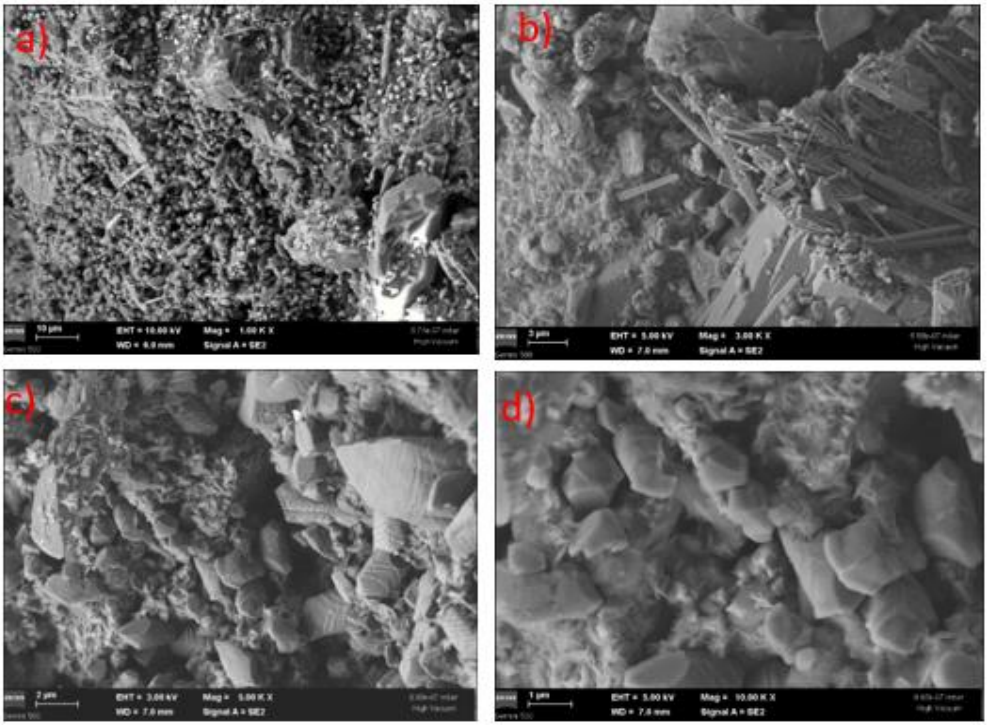
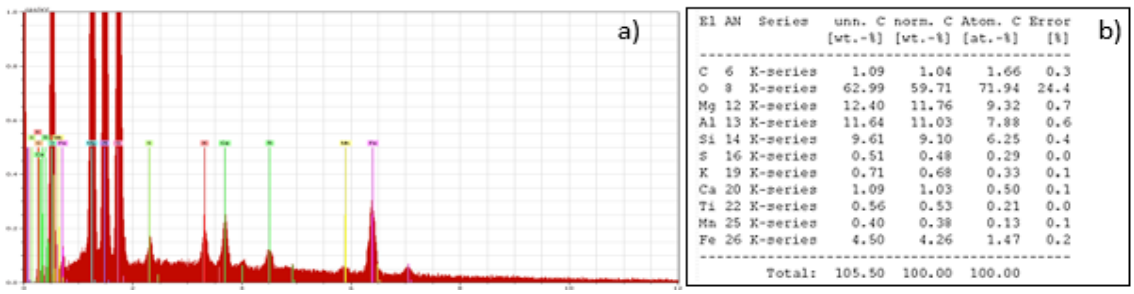


Fig. 5.46. SEM images related to the P1 sample: a) image of the micron fraction; b) detail associated with image a); c) detail associated with image b); d) detail associated with image c).

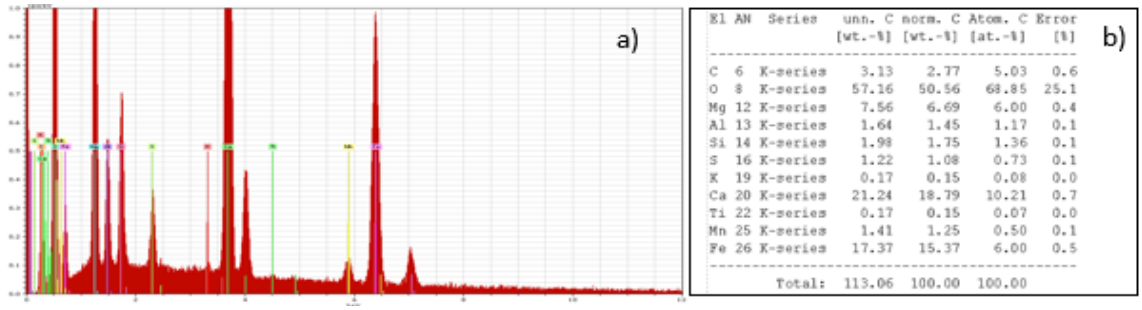
In particular, the SEM investigations highlight the fine/micronic fraction of the sample (Fig. 5.46, a, b) and reveal, in particular, the morphology but especially the dimensional distribution of the waste which has implications for establishing the technology of recovery of that waste. If hydrometallurgical technologies are adopted, then particle size plays an essential role in both flotation and dissolution processes. The fine fraction is the most sensitive in relation to the efficiency of the flotation or dissolution processes.

For each SEM-EDS sample analysed 4-7 EDS analyses were performed on different zones of the analytical sample and in the thesis 4 analysis were presented in the format of Fig. 5.47. All the images and results of the SEM-EDS investigations are analysed in the thesis in order to capture the common details but also the differences that manifest themselves in order to achieve an image of the constitutional and distributional heterogeneity of the analytes in the pond.
EDS analyses were performed on particles with apparent diameters of about 10-15 μm as in the case of EDS analyses on smaller particles it was found that the spectra are affected by background radiation from the support of the samples which significantly affects uncontrollable accuracy of those analyses.



El	AN	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Error [%]
C	6	K-series	1.09	1.04	1.66	0.3
O	8	K-series	62.99	59.71	71.94	24.4
Mg	12	K-series	12.40	11.76	9.32	0.7
Al	13	K-series	11.64	11.03	7.88	0.6
Si	14	K-series	9.61	9.10	6.25	0.4
S	16	K-series	0.51	0.48	0.29	0.0
K	19	K-series	0.71	0.68	0.33	0.1
Ca	20	K-series	1.09	1.03	0.50	0.1
Ti	22	K-series	0.56	0.53	0.21	0.0
Mn	25	K-series	0.40	0.38	0.13	0.1
Fe	26	K-series	4.50	4.26	1.47	0.2
		Total:	105.50	100.00	100.00	

Fig. 5.47. a) EDS spectrum performed on a particle in sample P1; b) the associated elementary analysis to spectrum 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	

Fig. 5.48. a) EDS spectrum performed on a particle in sample P1; b) the associated elementary analysis to spectrum a).

The EDS analyses highlight both major elements such as O, C, Al, K, S, Mg, Si, Ca, Fe and minority elements such as The EDS analyses highlight both major elements such as O, C, Al, K, S, Mg, Si, Ca, Fe and minority elements such as Mn, Ti, Zn, Ba, etc. (Fig. 5.47-5.48). The great advantage of EDS analysis is the measurement of C and O contents that cannot be measured by EDP-XRFS spectrometry as it has the Na-U analytical domain. Mn, Ti, Zn, Ba, etc. (Fig. 5.47-5.48). The great advantage of EDS analysis is the measurement of C and O contents that cannot be measured by EDP-XRFS spectrometry as it has the Na-U analytical domain.
The detailed distribution of Fe in the micron fraction of P1 shows concentrations in certain particles and entanglements in the whole submicron fraction, which attests the presence of Fe analyte in the large mass of the micron fraction.

c. XRFS tests

For the XRFS analysis a first sub-sampling is applied according to [125,142] which consists in dividing (split-area) the primary sample of about 5 kg in 2 subsamples of approximately 2, 5 kg e.g. SPi1 and SPi2, respectively. The procedure for preparing the sample to be analysed is applied in full for each collected sample. Each sub-sample was prepared by sieving with mesh 10 to eliminate the large fraction that has the subsequent origin of the flotation process. After applying the 'quartering' procedure 4 times, a sub-sample of 200 g was retained and processed to perform the analytical sample. Thus, the 200 g subtest was dried at about 110 ^{o}C for 6 hours in a Caloris electric oven, in air. After drying, the waste was re-homogenized and quartered and a quarter of about 50 g was extracted. After primary homogenization, the material was subjected to the three-stage 'coning-quartering' procedure as recommended by EPA USA [117].

Samples for XRFS analysis were prepared in the form of pressed pellets with the special device which is an annex of the XEPOS spectrometer. The sample preparation recipe consists of 6.25 g of waste mixed with 1.4 g of LiB_4O_7 Cereox binder recommended by the XEPOS spectrometer supplier. Two pellets from each type of waste were made to perform the 2 measurements provided by the BDDSM procedure. For the XRFS analysis the analytic Turboquant- Pelette program was used and the Rh radiation emitted at a high voltage of 49 keV applied to the anode. In what's to follow the results obtained on Test P1 are presented, subtests code SP1_1_A1 and SP1_2 analyses SP1_1_A1, SP1_1_A2, SP1_2_A1 and SP1_2_A2.

Table 5.24. XRFS analysis report for sample P1, sub-samples SP1_1 and SP1_2

Metoda TQ Pellet; Data 24-05-2021; Proba SP1_1_A1				Metoda TQ Pellet; Data 24-05-2021; Proba SP1_1_A2				Metoda TQ Pellet; Data 24-05-2021; Proba SP1_2_A1				Metoda TQ Pellet; Data 24-05-2021; Proba SP1_2_A2			
Z	Simbol	c [%]	SD [%]	Z	Simbol	c [%]	SD [%]	Z	Simbol	c [%]	SD [%]	Z	Simbol	c [%]	SD [%]
11	Na_2	0,648	0,024	11	Na_2	0,648	0,022	11	Na_2	0,759	0,022	11	Na_2	0,623	0,02
12	Mg	10,397	0,009	12	Mg	10,332	0,009	12	Mg	9,352	0,008	12	Mg	9,665	0,00
13	Al_2O	2,883	0,011	13	Al_2O	2,583	0,009	13	Al_2O	2,338	0,011	13	Al_2O	2,416	0,00
14	SiO_2	48,811	0,031	14	SiO_2	48,164	0,031	14	SiO_2	49,682	0,031	14	SiO_2	50,05	0,03
15	P_2O	0,581	0,001	15	P_2O	0,684	0,001	15	P_2O	0,681	0,001	15	P_2O	0,677	0,00
16	SO_3	2,402	0,000	16	SO_3	2,326	0,000	16	SO_3	2,429	0,001	16	SO_3	2,390	0,00
17	Cl	0,015	0,000	17	Cl	0,015	0,000	17	Cl	0,012	0,000	17	Cl	0,013	0,00
19	K_2O	1,983	0,006	19	K_2O	1,946	0,005	19	K_2O	1,931	0,006	19	K_2O	1,799	0,00
20	CaO	11,310	0,009	20	CaO	11,699	0,008	20	CaO	11,383	0,009	20	CaO	10,54	0,00
22	TiO_2	0,728	0,004	22	TiO_2	0,818	0,004	22	TiO_2	0,712	0,004	22	TiO_2	0,854	0,00
23	V_2O	0,015	0,001	23	V_2O	0,015	0,001	23	V_2O	0,014	0,001	23	V_2O	0,014	0,00
24	Cr_2	0,026	0,000	24	Cr_2	0,029	0,000	24	Cr_2	0,027	0,000	24	Cr_2	0,030	0,00
25	Mn	0,111	0,000	25	Mn	0,138	0,000	25	Mn	0,115	0,000	25	Mn	0,140	0,00
26	Fe_2	19,605	0,003	26	Fe_2	19,939	0,004	26	Fe_2	20,050	0,004	26	Fe_2	19,35	0,00
27	CoO	0,001	0,000	27	CoO	0,002	0,000	27	CoO	0,002	0,000	27	CoO	0,002	0,00
28	NiO	0,008	0,000	28	NiO	0,008	0,000	28	NiO	0,007	0,000	28	NiO	0,008	0,00
29	CuO	0,027	0,000	29	CuO	0,023	0,000	29	CuO	0,027	0,000	29	CuO	0,026	0,00
30	ZnO	0,124	0,000	30	ZnO	0,126	0,000	30	ZnO	0,128	0,000	30	ZnO	0,106	0,00
31	Ga	0,001	0,000	31	Ga	0,001	0,000	31	Ga	0,001	0,000	31	Ga	0,001	0,00
32	Ge	<	0,000	32	Ge	<	0,000	32	Ge	<	0,000	32	Ge	<	0,00
33	As_2	0,001	0,000	33	As_2	0,001	0,000	33	As_2	0,001	0,000	33	As_2	0,001	0,00
34	Se	0,000	0,000	34	Se	0,000	0,000	34	Se	0,000	0,000	34	Se	0,000	0,00
35	Br	0,001	0,000	35	Br	0,001	0,000	35	Br	0,001	0,000	35	Br	0,001	0,00
37	Rb2	0,008	0,000	37	Rb2	0,007	0,000	37	Rb2	0,008	0,000	37	Rb2	0,009	0,00
38	SrO	0,014	0,000	38	SrO	0,016	0,000	38	SrO	0,016	0,000	38	SrO	0,017	0,00
39	Y	0,002	0,000	39	Y	0,002	0,000	39	Y	0,002	0,000	39	Y	0,002	0,00
40	ZrO_2	0,028	0,000	40	ZrO_2	0,032	0,000	40	ZrO_2	0,026	0,000	40	ZrO_2	0,027	0,00
41	Nb_2	0,001	0,000	41	Nb_2	0,001	0,000	41	Nb_2	0,001	0,000	41	Nb_2	0,001	0,00
42	Mo	0,001	0,000	42	Mo	0,001	0,000	42	Mo	0,001	0,000	42	Mo	0,001	0,00
47	Ag	0,000	0,000	47	Ag	0,001	0,000	47	Ag	0,001	0,000	47	Ag	0,001	0,00
48	Cd	0,000	0,000	48	Cd	0,000	0,000	48	Cd	0,000	0,000	48	Cd	0,000	0,00
50	SnO	0,003	0,000	50	SnO	0,003	0,000	50	SnO	0,003	0,000	50	SnO	0,002	0,00
51	Sb_2	0,001	0,000	51	Sb_2	0,001	0,000	51	Sb_2	0,001	0,000	51	Sb_2	0,001	0,00
52	Te	<	0,000	52	Te	<	0,000	52	Te	<	0,000	52	Te	<	0,00
53	I	<	0,000	53	I	<	0,000	53	I	<	0,000	53	I	<	0,00
55	Cs	0,001	0,000	55	Cs	0,001	0,000	55	Cs	0,001	0,000	55	Cs	0,001	0,00
56	Ba	0,066	0,001	56	Ba	0,075	0,000	56	Ba	0,067	0,001	56	Ba	0,074	0,00
57	La	<	0,000	57	La	<	0,000	57	La	<	0,000	57	La	<	0,00
58	Ce	0,004	0,000	58	Ce	0,004	0,000	58	Ce	0,003	0,000	58	Ce	0,004	0,00
72	Hf	0,000	0,000	72	Hf	0,001	0,000	72	Hf	0,000	0,000	72	Hf	0,001	0,00
73	Ta_2	<	0,000	73	Ta_2	<	0,000	73	Ta_2	<	0,000	73	Ta_2	<	0,00
74	WO	0,002	0,000	74	WO	0,002	0,000	74	WO	0,002	0,000	74	WO	0,002	0,00
79	Au	0,000	0,000	79	Au	0,000	0,000	79	Au	0,000	0,000	79	Au	0,000	0,00
80	Hg	<	0,000	80	Hg	<	0,000	80	Hg	<	0,000	80	Hg	<	0,00
81	Tl	0,000	0,000	81	Tl	0,000	0,000	81	Tl	0,000	0,000	81	Tl	0,000	0,00
82	PbO	0,023	0,000	82	PbO	0,019	0,000	82	PbO	0,021	0,000	82	PbO	0,021	0,00
83	Bi	<	0,000	83	Bi	<	0,000	83	Bi	<	0,000	83	Bi	<	0,00
90	Th	0,001	0,000	90	Th	0,001	0,000	90	Th	0,001	0,000	90	Th	0,001	0,00
92	U	0,648	0,024	92	U	0,648	0,022	92	U	0,759	0,022	92	U	0,623	0,02
		99.8				99.66				99.80				99.88	

According to Table 5.23 the waste contains mainly silica (quartz) (~ 53% by mass) as shown by the OM investigation (Fig. 5.45). Since all the concentrations referred to below are mass concentrations, the nature of the concentrations will no longer be specified. At the intermediate level, the sample contains iron oxides (~ 17%), calcium oxide (~ 11%) and corundum (~ 10%). Magnesium oxide and sulphur tri-oxide (SO_3) are present in the sample at the percentage level, but these results are artefacts

because most likely in the sample there are sulphates and dolomite that provide the Mg and S contents which are taken into account by the software embedded in equipment as oxides.
In the repeated attempt on the sub-sample SP1_2 analytical results similar to those presented in Table 5.24 were obtained.
The XRFS results obtained on sub-sample SP1_2 are similar to those obtained on sub-sample SP1_1 which is normal as the sub-samples are from the same sample. It should be noted that there are differences between results for the same compound or element but these differences are natural in the sense that they come from two sources i.e. the distributional variability of the analyses and the uncertainties of the measurement process.

d. X-ray diffraction test (XRD)

The XRFS results get a much higher value if they are doubled by XRD measurements to highlight the composition of the analysed waste so as to be in conjunction with the phase-composition of the sample elemental composition more relevant in view of detection of the composition of the pond. The XRD test was performed on a sub-sample taken from sample P1. No XRD tests were performed on the 4 sub-samples due to cost and lack of physical resources and access to an adequate diffractometer. XRD tests were performed with the Bruker D8 Advance diffractometer which is equipped with an X-ray tube with copper anode , $\lambda_{CuK\alpha}$ = 1.5415 A, with a linear focus of 12 x 0.1 mm 2 , radiation detector type 1D - LynxEye and Bragg-Brentano protractor θ-θ. A powder holder was used for the test, which was filled with the substance taken from the material prepared for the XRFS test (dried, homogenized and ground by hand) but without any additives.

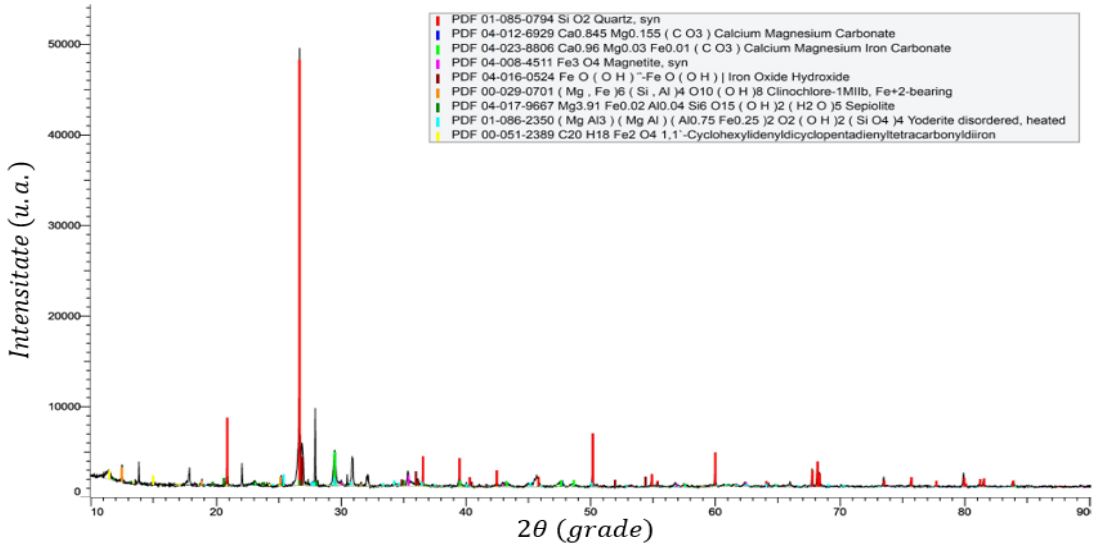


Fig. 5.54. Diffractogram obtained on P1sample

The diffractogram was indexed using ICDD database and the EVA Plus software. The diffractogram in Figs. 5. 54 shows well-defined lines but also lines of low intensity.

Table 5.25 shows the phases identified in sample P1 and the semi-quantitative evaluation related to the diffractogram in Fig. 5.54.

Table 5.25. Crystalline phases identified in sample P1

No..	Symbol	Content	Observations
1	SiO_2	major	Quartz
2	FeO*OH	significant	Caused, mosst probably, by *wathering effect*
3	Fe_3O_4	significant	Overlaped XRD lines
4	$CaCO_3$	significant	With minor substitutions of Ca by Fe and Mg
5	Complex compound (AlMgSiFeO)	significant	Lines with low and overlapping intensities. Naturally such compound exists but its stoichiometry is uncertain

As shown in Table 5.25 the crystalline phase constitution of the waste is predominantly oxidative and the oxides SiO_2, FeO and Fe_3O_4 have the majority incidence. It is found that Al, Mg and Ca are not incorporated in oxides but in calcite and dolomite type compounds and in complex type compound (AlMgSiFeO). Also, the presence of akermanite is possible.

e. Results of LOI measurements

For the LOI measurements, 2 samples of about 25 g were taken from each sub-sample. The sample was placed in ceramic crucibles, which were weighed in advance. After adding the waste to the crucibles, they were re-weighed. All weighing were performed with the Metler ME230 balance which has a standard uncertainty of 1mg. To estimate the standard deviation (SD) related to weighing, 3 weightings were performed under repeatability conditions. Prior to performing the LOI test, the accuracy of the MRM test was verified. The crucibles loaded with the respective waste were dried at 110 ºC for 6 h to measure the humidity (H) in a JP Selecta Dry Term 10 oven. Subsequently, after cooling and weighing the dry samples, they were heated to 550 ºC in the Caloris oven for 4h for measuring the organic mass content. The samples heated to 550 º C were cooled in the oven, weighed and kept in the desiccator until next day, when they were calcined at 950 ºC in the same oven for 4 hours to measure the carbonate content. Samples were cooled down at the same time as the oven and were weighed on the same day. The data obtained from the LOI test are presented in Table 5.26.

Table 5.26. Data obtained in the LOI test applied to sample P1

Cod	m_i	m_{110^oC}	H	m_{550^oC}	OM	m_{950^oC}	CCC	**Measurands**	Values	SD
SP11a	21.231	20.771	2.17	20.541	1.12	19.509	11.29	H [%]	2.182	0.170
	21.232	20.803	2.02	20.601	0.98	19.551	11.47	MO [%]	1.056	0.070
	21.232	20.731	2.36	20.512	1.07	19.462	11.51	CCC [%]	11.42	0.12
SP11b	23.561	23.082	2.03	22.743	1.49	21.617	11.09	H [%]	2.099	0.057
	23.563	23.06	2.13	22.715	1.52	21.581	11.18	MO [%]	1.626	0.211
	23.565	23.063	2.13	22.640	1.87	21.522	11.02	CCC [%]	11.09	0.08
SP12a	22.848	22.353	2.17	22.113	1.09	20.979	11.53	H [%]	2.197	0.106
	22.901	22.418	2.11	22.211	0.93	21.124	11.02	MO [%]	1.189	0.322
	22.986	22.454	2.31	22.111	1.55	21.016	11.08	CCC [%]	11.21	0.28
SP12b	24.172	23.598	2.37	23.332	1.14	22.182	11.08	H [%]	2.284	0.154
	24.257	23.682	2.37	23.415	1.14	22.251	11.17	MO [%]	1.125	0.027
	24.17	23.661	2.11	23.405	1.09	22.236	11.23	CCC [%]	11.16	0.08

where: mi -initial mass, m_ (110 ^ 0 C) -mass at 110 0C, m_ (550 ^ 0 C) - mass at 550 0C; m (950 ° C); mass at 950 ° C; Um-moisture; OM- organic mass; CCC-Calcium carbonate content

The data in Table 5.26 show that the waste is approximately dry, with a humidity of around ~2%. Also, the content of organic matter is tolerable from a technological point of view at level1~3%. The carbonate content is around 11% for all sub - samples taken from P 1. The detailed intercomparison analysis of the LOI, XRFS and XRD results obtained on the SP1_1 and SP1_2 subtests will be performed in the subsequent stage of the pond qualification algorithm as a secondary raw material resource.

The investigation structure of sample P1 was applied identically to samples P2…P10 and the processing and analysis of data related to samples P 1 ... P10 was performed in subchapter 5.4.5.

5.4.5. Processing and analysis of the results obtained from the samples taken

The ANOVA analysis of the BDDSM results is applied to the XRFS results obtained on the sub- samples taken at laboratory level. The XRD results are not quantitative but semi-quantitative in the sense that they identify the mineralogical phases and provide information on the relative quantity depending on the intensity of the diffraction lines. The EDS analyses are punctual i.e. at the particle or particle group level and provide information on the heterogeneity of the elemental particle compositions in the samples but do not provide a credible average composition. Unfortunately, XRFS data are related to oxide contents because this is the current stage of XRFS analysis on metallurgical extractive waste, in general, and on metallurgical waste from iron ore processing in particular. For example, the XRFS analysis posted in [171] is presented in Table 5.56.

Table 5.56 Chemical composition of iron ore tailings [171]

Oxides	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	Na_2O	K_2O	LOI
Concentrations (wt%)	47.39	24.82	8.85	7.42	0.097	0.32	0.70	10.40

From the Table. 5.56 results that the posted analysis presents only the major elements as well as the LOI value. Also, the results in Table 5.56 are similar to some of the results presented in the thesis. The data in Table 5.56 are accompanied by a representative diffractogram Fig. 5.119. It can be seen that the phases indexed in diffractograms in Figs. 5.119 are quartz and magnetite while the waste analysed in the thesis also shows calcite and dolomite. Aspects taken from the literature have the role of emphasizing that the thesis approached the analysis of waste according to the current stage of the analysis of extractive waste (tailings).

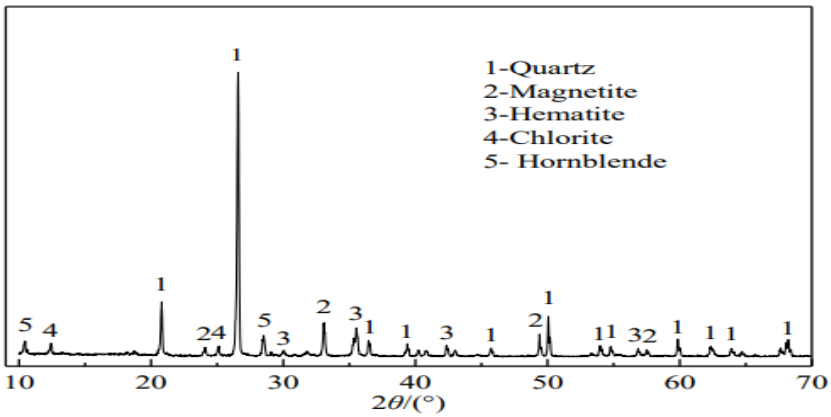
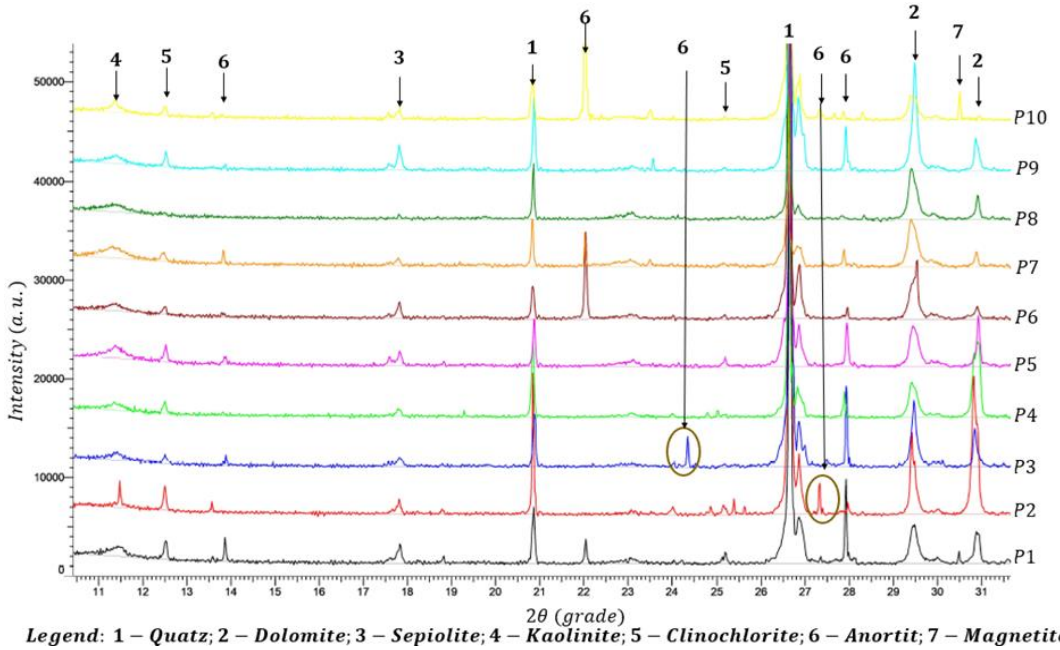


Fig. 5.119. Diffractogram obtained on an extractive waste from the processing of Fe ore [171]

The diffractograms obtained on the 10 investigated samples (fig. 5.121) have a structure of lines similar to the diffractogram in Fig. 5.119. The global mineralogical analysis of the chosen samples P1…P10 shows that there is a similarity of the contents of major phases i.e. quartz, dolomite, calcite but also certain incidences of phases difficult to index (Fig. 5.121). The diffractograms related to samples 1, 6 and 10 show diffraction lines with significant intensities at 2θ = 22.1° which can be attributed to the $BaSiO_3$ phase but also to the anorthite ($CaOAl_2O_3$ * $2SiO_3$). In [172] this line is attributed to kaolinite.



Legend*: 1 – *Quatz*; 2 – *Dolomite*; 3 – *Sepiolite*; 4 – *Kaolinite*; 5 – *Clinochlorite*; 6 – *Anortit*; 7 – *Magnetite

Fig. 5.121. Details of the diffractograms of samples P1..P10 in the angular range 2θ=10-31°

The presence of the elements Na, K, Mg, Mn etc., can be attributed to the presence of complex minerals such as: clinochlorite, sepiolite, yoderite, anthophyllite, hornblende, phyllosilicates.

Establishing exactly the existence and concentrations of these phases is extremely difficult because they have polymorphic structures, they can also exist in an amorphous state. Therefore, in this case the data will be analyzed as provided by the XRFS analyses and the contents of major phases identified with certainty from the diffraction data corroborated with the EDS and XRFS and the average values of the respective measurements will be established, the uncertainty of measurement (analytical uncertainty) the uncertainty of sub-sampling, the uncertainty of sampling at pond level and the confidence interval related to the measurands. The data processing was performed in Excel with an algorithm developed based on the theoretical model presented in subchapter 5.3.

5. 4.5. 1. Processing and analysis of SiO_2 concentration values at deposit level

The XRFS results obtained on the 20 sub-samples and the analysis repeated 2 times i.e. 40 values of SiO_2 concentration are presented in Table 5.57, area of cells marked in green. All calculations are explicitly presented in Table 5.57 according to the procedure described in subchapter 5.3.

Table 5.57. Primary data and their processing for the majority phase SiO_2

	Measured values (% wt)				Sub-sample mean		Analytical SD	Means	Sub-sample SD	Sample SD
	S1A1	S1A2	S2A1	S2A2	S1	S2	at sub-sample level	at sample level	$4 * D_{i1(x)}{}^2$	$4 * (\bar{X}_i - \bar{X})^2$
	x_{i11}	x_{i12}	x_{i21}	x_{i22}	$\bar{x}_{i1}$	$\bar{x}_{i2}$			$(\bar{x}_i - \bar{x}_{i1})^2 = (\bar{x}_i - \bar{x}_{i2})^2$	
1	48,811	48,164	49,682	50,058	48,487	49,87	0,280	49,1788	1,9113	45,6606
2	52,680	55,751	53,8865	53,0094	54,216	53,45	5,102	53,8320	0,5901	6,4989
3	53,415	53,140	51,7811	50,8103	53,278	51,30	0,509	52,2869	3,9291	0,2927
4	55,166	56,392	53,7811	53,1381	55,779	53,46	0,959	54,6196	5,3818	17,0102
5	49,572	49,406	50,9240	51,1683	49,489	51,05	0,044	50,2679	2,4228	20,9662
6	51,383	50,932	52,1562	52,8339	51,157	52,50	0,331	51,8265	1,7883	2,1369
7	52,050	52,450	51,7476	51,4692	52,250	51,61	0,119	51,9293	0,4118	1,5780
8	55,455	55,645	54,6354	54,1009	55,550	54,37	0,161	54,9594	1,3983	23,0796
9	52,784	51,979	53,5296	53,2311	52,381	53,38	0,369	52,8812	0,9969	0,4193
10	53,907	54,477	53,0191	53,7652	54,192	53,39	0,440	53,7923	0,6404	6,1002
X=	**52.6**						8,314351		19,471	123,743

Analysis i.e. standard analytical uncertainty						
SSE	8,31435	20	Vanalysis=SSE-analysis/ $df_{analysis}$			0,415
$df_{analysis}$=i*j*k -i*j	20	SD_A=	0.6	RSD(%) =	SD_A*100/ X	1.23
Sub-sampling						
SSTsp=	19,4708	V_{sp}=(SSTsp/ $df_{sampling}$ -$SS_{analysis}$/$df_{analysis}$)/n				0,76
dfsp=i*j-i	10	SDsp=	0.88	RSD(%) =	SDsp*100/X	3.53
Sampling						
SSTp=	123,743	V_p=(SSTp/ df_p -nV_{sp} -V_a)/nb				5.9
dfsp=i-1	9	SDsp=	2.43	RSD(%) =	SDsp*100/X	4.62
Relative compound uncertainty						
u_{CR}=sqrt($RSD_a{}^{\wedge 2}$+$RSD_{sp}{}^{\wedge 2}$+$RSD_p{}^{\wedge 2}$)			5.06	%		
Relative expanded uncertainty with 95% confidence level i.e. k=2						
UR(95%)=2*uCR=			**10.13**	%	U(95%)	**5.3 %**
Confidence interval with 95% confidence level			**[47.2------57.9] %**			

Table 5.57 shows that at the pond level a concentration of SiO_2 can be considered, c_{SiO2} = 53.6%, which has a relative standard uncertainty due to the analytical process u_{RA} = 6.16%. The uncertainty relative to sub-sampling is s U_{SER} = 3.53%. The uncertainty due to sampling is u_{RE} = 6.90%. Thus, the relative compound uncertainty associated with c_{SiO2} is u u_{cR} = 8.63%. This uncertainty generates a confidence interval associated with the value c_{SiO2} = 53.6%, I = [44; 63]. Based on these data, the technologist who offers the recovery solution must take into account the minimum value of c_{SiO2} if he wants to avoid technological risks if he has a limit value of the minimum SiO_2 content. Otherwise it must take into account the value c_{SiO2} = 63%.

To decrease the overall uncertainty associated c_{SiO2} can increase the number of samples, we can increase the sample size and can lower the analytical uncertainty by increasing the number of repeated attempts, but costs increase exponentially. Just by increasing by three the XRFS scans would increase the number of scans from 40 to 60.

5.4.5. 2. Processing and analysis of Fe_2O_3 concentration values at the pond level

Method of processing and analysis of the values of the Fe_2O_3 concentration measurements is the same as in the case of the SiO_2 concentration measurement (Table 5.58.).

Tabelul 5.58. Primary data and their processing for the majority phase Fe_2O_3

	Measured values (% wt)				Sub-sample mean		Analytical SD	Means	Sub-sample SD	Sample SD
	S1A1	S1A2	S2A1	S2A2	S1	S2	at sub-sample level	at sample level	$4 * D_{i1(x)}{}^2$	$4 * (\bar{X}_i - \bar{X})^2$
	x_{i11}	x_{i12}	x_{i21}	x_{i22}	$\bar{x}_{i1}$	$\bar{x}_{i2}$			$(\bar{x}_i - \bar{x}_{i1})^2 = (\bar{x}_i - \bar{x}_{i2})^2$	
1	19.604	19.939	20.050	19.352	19.77	19.70	0.2995	19.73661	0.00505	44,87734
2	15.621	15.055	15.995	15.522	15.33	15.75	0.2717	15.54884	0.17729	2,81056
3	13.505	13.366	14.455	15.915	13.43	15.18	1.0752	14.31092	3.06211	17,24178
4	13.057	13.173	14.455	15.058	13.11	14.75	0.1880	13.93628	2.69468	24,02573
5	14.899	14.813	15.355	14.901	14.85	15.12	0.1067	14.99263	0.07392	7,777961
6	14.857	15.829	15.495	15.619	15.34	15.55	0.4799	15.45042	0.04592	3,509332
7	16.032	16.323	16.981	16.611	16.17	16.79	0.1108	16.48719	0.38258	0,040089
8	17.924	18.559	17.011	18.078	18.24	17.54	0.7721	17.89344	0.48591	9,07651
9	17,877	17,017	16,965	17,035	17.44	17.00	0.3728	17,22402	0,199566	2,80185
10	19,224	19,780	17,312	16,843	19.50	17.08	0.2643	18,29045	5,87773	14,49131
X	16.39 %						3.9414		13.0047	126.652
Analysis i.e. standard analytical uncertainty										
SSE		3,9414	20		Vanalysis=SSE-analysis/ dfanalysis				0,197072297	
$df_{analysis}$=i*j*		20	Sda=		0.4		RDS(%	Sda*100/	2.71	
Sub-sampling										
SSTsp=		13,004	V_{sp}=(SSTsp/ $df_{sampling}$ -$SS_{analysis}$/$df_{analysis}$)/n						0,551701118	
dfsp=i*j-i		10	SDsp=		0.74		RSD(%	SDsp*10	4.53	
Sampling										
SSTp=		126,65	V_p=(SSTp/ df_p -n$V_{sp\ -Va}$)/nb						6.4	
dfsp=i-1		9	SDsp=		2.53		RSD(%	SDsp*10	15.42	
Relative compound uncertainty										
u_{CR}=sqrt($RSD_a{}^{\wedge 2}$+$RSD_{sp}{}^{\wedge 2}$+$RSD_p{}^{\wedge 2}$)					16.30		%			
Relative expanded uncertainty with 95% confidence level i.e. k=2										
				UR(95%)=2*u	32.60		%		U(95	5.24%
Confidence interval with 95% confidence level					**[11.1; 21.7] %**					

The Fe content in the pond can be considered the most important because it can be capitalized in the current technological conditions. Therefore, establishing the average content and the extensive uncertainty related to this content are two very important targets. At storage level, it can be considered that the concentration of Fe_2O_3, c_{Fe2O3} = 16.4% which has a standard relative uncertainty due to the analytical process u_{RA}= 2, 9%. The extended relative uncertainty with a confidence level of 95% associated with c_{Fe2O3} is U_R(95%)=33.0 %. This uncertainty generates a confidence interval associated with the value c_{SiO2} = 16.4%, relative to i.e. I = [11; 22]. The uncertainty associated with c_{Fe2O3} is high, but this is normal in the case of sampling as shown in Subchapter 5.1 which showed that as the value of the analyte concentration decreases, the value of the uncertainty associated with this analyte increases.

5. 4.5. 3. Processing and analysis of CCC concentration values at the pond level

The CCC content is important for the recovery of waste as an additive for cement or geopolymers. But the maximum level of 12% is reasonable in these cases as well.

Table 5.60. CCC primary data obtained by the LOI method and the results of their processing

	Measured values (% wt)				Sub-sample mean		Analytical al SD	Means	Sub-sample SD	Sample SD
	S1A1	S1A2	S2A1	S2A2	S1	S2	at sub-sample level	at sample level	$4 * D_{i1(x)}{}^2$	$4 * (\bar{X}_i - \bar{X})^2$
	x_{i11}	x_{i12}	x_{i21}	x_{i22}	$\bar{x}_{i1}$	$\bar{x}_{i2}$			$(\bar{x}_i - \bar{x}_{i1})^2 = (\bar{x}_i - \bar{x}_{i2})^2$	
1	11.4	11.09	11.2	11.16	11.25	11.185	0.0557	11.22	0.0049	19.687
2	10.0	9.65	9.34	8.89	9.835	9.115	0.1697	9.475	0.5184	0.89681
3	9.11	8.39	9.27	9.65	8.75	9.46	0.3314	9.105	0.5041	0.04285
4	7.7	7.26	7.38	7.41	7.48	7.395	0.09725	7.4375	0.00723	9.78438
5	9.78	9.99	9.04	9.54	9.885	9.29	0.14705	9.5875	0.35403	1.37358
6	9.18	8.97	8.73	8.85	9.075	8.79	0.02925	8.9325	0.08123	0.01904
7	8.77	8.41	8.84	8.86	8.59	8.85	0.065	8.72	0.0676	0.31697
8	8.3	8.55	8.42	8.59	8.425	8.505	0.0457	8.465	0.0064	1.15133
9	8.45	8.75	8.56	8.38	8.6	8.47	0.0612	8.535	0.0169	0.87049
10	8.29	8.79	8.65	8.42	8.54	8.535	0.15145	8.5375	2.5E-05	0.86118
X=	**9.0 %**						1.1537		1.5608	35.0036

Analysis i.e. standard analytical uncertainty						
SSE	1.1537	20	Vanalysis=SSE-analysis/ dfanalysis			0.057
$df_{analysis}$=i*j*	20	Sda=	0.2	RDS(%)	Sda*10	2.67
Sub-sampling						
SSTsp=	1.5608	V_{sp}=(SSTsp/ $df_{sampling}$ -$SS_{analysis}$/$df_{analysis}$)/n				0.049
dfsp=i*j-i	10	SDsp=	0.22	RSD(%)	SDsp*1	2.46
Sampling						
SSTp=	35.003	V_p=(SSTp/ df_p -nV_{sp} -V_a)/nb				1.9
dfsp=i-1	9	SDsp=	1.37	RSD(%)	SDsp*1	15.18
Relative compound uncertainty						
u_{CR}=sqrt(RSD_a^2+RSD_{sp}^2+RSD_p^2)			15.61	%		
Relative expanded uncertainty with 95% confidence level i.e. k=2						
UR(95%)=2*u		**31.21**	%	U(95%%)	**2.8%**	
Confidence interval with 95% confidence level			**[6.2; 11.8] %**			

5. 4.5. 4. Processing and analysis of MgO concentration values at the storage level

The incidence of magnesium in the investigated waste, estimated by means of MgO, is relatively high if we compare it with other data from the literature [171,172]. Analytical evidence (XRFS, EDA and XRD) shows that Mg is present in samples in significant quantities but not "bound" in MgO but in dolomite, modified calcite, anorthite and probably in complex compounds such as hornblende, phyllosilicates, etc.

Mg is part of the CRM list and at the evaluated contents, the investigated deposit can be qualified as a secondary source of Mg. On the other hand, if Mg is 'strongly bound' in compounds (covalent and ionic bonds) then there is, for now, the problem of obtaining metallic Mg from this secondary resource. However, Mg compounds can be used in agriculture as fertilizers. Also, bound Mg does not affect the use of waste in road construction**.**

Table 5.61. Primary data and their processing results for the majority phase MgO

	Measured values (% wt)				Sub-sample mean		Analytical SD	Means	Sub-sample SD	Sample SD
	S1A1	S1A2	S2A1	S2A2	S1	S2	at sub-sample level	at sample level	$4 * D_{i1(x)}{}^2$	$4 * (\bar{X}_i - \bar{X})^2$
	x_{i11}	x_{i12}	x_{i21}	x_{i22}	$\bar{x}_{i1}$	$\bar{x}_{i2}$			$(\bar{x}_i - \bar{x}_{i1})^2 = (\bar{x}_i - \bar{x}_{i2})^2$	
1	10,39	10,33	9,352	9,664	10,36	9,508	0,0510	9,936456	0,732968	0,292211
2	7,134	10,27	9,283	9,355	8,706	9,320	4,9435	9,012747	0,376411	1,707861
3	12,09	12,17	12,65	11,97	12,13	12,31	0,2319	12,22624	0,031301	26,21589
4	5,317	11,59	11,35	11,17	8,454	11,26	19,6959	9,859582	7,89749	0,149629
5	12,82	12,80	12,37	12,44	12,81	12,40	0,0023	12,61032	0,166133	34,67204
6	4,925	11,90	11,61	11,69	8,415	11,65	24,3576	10,03385	10,48785	0,540762
7	9,377	9,251	9,512	9,481	9,315	9,497	0,0085	9,405806	0,033346	0,271163
8	6,364	6,566	6,288	6,487	6,465	6,388	0,0403	6,426629	0,005942	41,97859
9	9,369	9,456	9,269	9,385	9,413	9,328	0,0105	9,370280	0,007199	0,350211
10	7,247	7,354	8,284	8,232	7,301	8,259	0,0071	7,779807	0,917725	14,23351
X=	**9.67 %**						49,348		20,6564	120,412

Analysis i.e. standard analytical uncertainty						
SSE	24.99	20	Vanalysis=SSE-analysis/		2,47	
$df_{analysis}$=i*j*k	20	Sda=	1.6	Sda*100/	16.25	
Sub-sampling						
SSTsp=	20.66	V_{sp}=(SSTsp/ $df_{sampling}$ -$SS_{analysis}/df_{analysis}$)/n			0,20	
dfsp=i*j-i	10	SDsp=	0.4	RSD(%)=	SDsp*10	4.64
Sampling						
SSTp=	120.41	V_p=(SSTp/ df_p -n$V_{sp\ -Va}$)/nb			5.3	
dfsp=i-1	9	SDsp=	2.6	RSD(%)=	SDsp*10	23.72
Relative compound uncertainty						
u_{CR}=sqrt($RSD_a{}^{\wedge 2}$+$RSD_{sp}{}^{\wedge 2}$+$RSD_p{}^{\wedge 2}$)			29.12	%		
Relative expanded uncertainty with 95% confidence level i.e. k=2						
	UR(95%)=2*u_{CR}=		58.24	%	U(95%)	5.6 %
Confidence interval with 95% confidence level			**[4.0; 15.3] %**			

The extended relative uncertainty UR (95%) = 58% regarding the content of MgO in the pond shows that it is heavily in the pond. For a technological decision to capitalize on the Mg resource, an additional research is required.

5.4.5.7. Conclusions

The BDDSM method reveals the existence of SiO_2 as the majority phase with a concentration of 53.6% and U_R (95%) = 17% mainly due to the variability at pond level. The Fe_2O_3 content, which estimates the Fe content, is C_{Fe2O3} = 16.9% and U_R (95%) = 33% caused by variability at the pond level. Calcium content is estimated by CaO in XRFS analyses and by calcite content in LOI analysis. The XRFS and LOI data are compatible and attest to a calcite content of about 9% with an extended relative uncertainty of about 30% which is reasonable at the pond scale.

The Mg content in the dump is high in relation to the data from the specialized literature i.e. 9.8% vs 0.1%. Also, the Al_2O_3 content is about 2 times lower compared to the value reported in the same publication i.e. 3.1 vs 7.42%. These aspects attest to the specificity of this waste.

Many elements from the CRM list are present at trace level in the investigated waste, elements such as: Mg, V, Ni, Co, Ga, Nb, P, Sc, Ti, Ta, W, Sr etc. The data regarding the elements Sr and Y from the CRM list are analysed in the thesis. Also, the data related to Ba were analysed. It is found that at low concentrations the BDDSM method appropriately discriminates the real artefact data by estimating the uncertainty.

For the concentration of the analyte from the investigated pond on the order 10-20%, the BDDSM method generates uncertainties of 10-25% which is normal at level 10 of sampling points. For the improvement of the accuracy of data analytes of interest the number of samples can be increased, the sample size can be increased and the analytical uncertainty can be lowered by increasing the number of repeated attempts. On the other hand, decision-makers must take into account that the improvement of the sampling procedure involved an exponential increase in the costs of sampling. In this regard, I mention the motto of the US EPA agency: '***Sampling is one of those endeavors that you get what you pay for***' [117].

5.5. Complex characterization of concentrates obtained from waste from the processing of iron ore

5.5.1. Introduction

Any technology 4R (reduce, reuse, recycle, recuperate) depends on the characteristics of the waste. The aluminothermic technology for metallurgical waste treatment depends on the accuracy of the analytical results that determine correct dosage of the reagents (oxidizing, reducing, inhibiting, pre-alloys). In this sense, I have performed the characterization of the aluminothermic precursors using XRFF, XRD, LOI, SEM, OM methods and techniques.

5.5.2. Materials and methods

Three types of metallurgical waste were selected for their complex characterization of which two types are sampled primarily from two huge historical dumps in Romania whose identities are kept anonymous for legal reasons and the third is a dust resulting from obtaining steel in an electric arc furnace. The samples obtained from the sampling were ground and sorted in a granulometric manner using a magnetic drum separator in order to obtain a fraction of waste enriched with iron. The samples dried at 105-110 ^oC for 6 hours were investigated by spectrometry ED(P)-XRFS, XRD and SEM.

5.5.3. Results and discussions

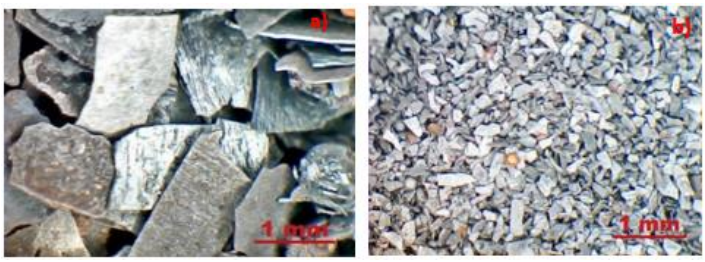


Fig. 5.122 Microscopic optical images of the iron waste

The studied wastes were named as follows: IOW1; IOW2 and IOW3. The products of aluminothermic reactions denoted as follows were also investigated: P-IOW1; P-IOW2 and P-IOW3. The calculated oxide composition of the samples is given in Table 5.66.

Table 5.66 Oxidic compositions of wastes

Element	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	Fe_2O_3	ZnO	As_2O_3	PbO
IOW_1	-	0.23	0.57	2.97	0.01	0.03	-	1.23	91.62	0.02	0.002	-
IOW_2	1.92	0.45	2.69	3.45	0.10	0.09	0.18	0.67	84.86	0.06	0.006	0.006
IOW_3	1.96	4.98	0.76	0.15	2.61	2.16	1.91	5.38	51.27	19.33	0.003	1.830
U(95%)*	0,04	0,08	0,06	0,04	0,04	0,08	0,10	0,60	0,08	0,12	0,002	0,006

It can be seen in Table 5.66 that there is a small difference in the oxide compositions of IOW_1 and IOW_2 waste if Na_2O, Al_2O_3, CaO, CuO are considered as main oxides, i.e. with less than 3% by weight, but there is a much larger difference when analysing the oxides of Fe_2O_3 and ZnO, i.e. greater than 10% by weight. Thus, IOW_1 and IOW_2 wastes are very well suited for aluminothermic recovery, as they have over 84% Fe_2O_3 , do not contain many amounts of inhibitors Al_2O_3 , SiO_2 and CaO <3% by weight and the content of detrimental elements (Cl, As, Cd, Cs, Hg, Pb, U) are insignificant.

The composition measured with the XRFS technique is questionable from the point of view of oxides quantification, this is why the XRD analyses of the precursors are necessary to highlight phase conntents of samples. In the figure 5.123, the diffraction patterns obtained from waste IOW_1 are presented.

It can be seen in Figure 5.123 that IOW_1 waste contains not only hematite but also magnetite as a major phase (75%), while the hematite content is only 19%. Also, the elements Ca and Si are not found in the form of compounds i.e. CaO and SiO_2 as they were identified after the XRFS analysis but in the form of $CaSi_2$ (6%) as it can be seen in the diffractogram obtained (figure 5.123).

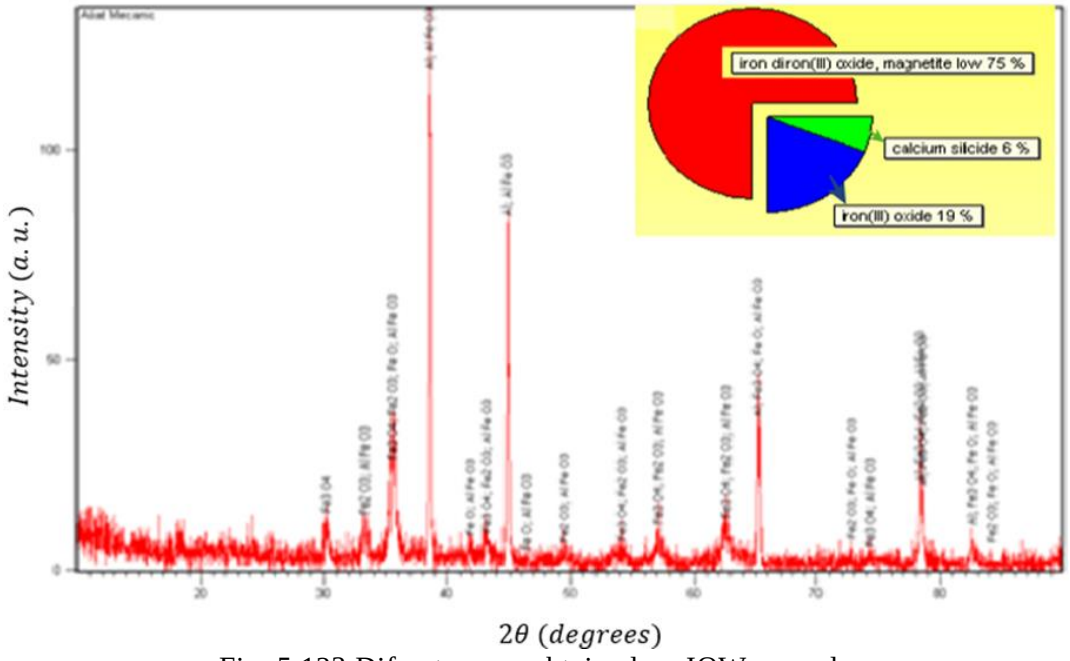


Fig. 5.123 Difractogram obtained on IOW_1 sample

The ratio of Fe oxides identified in different allotropic forms in the IOW_2 specimen is completely different compared to IOW_1, because hematite predominates (68%) compared to magnetite (16%) and wüstite (6%), as shown in the diffractogram representative of FIG. 5.124.

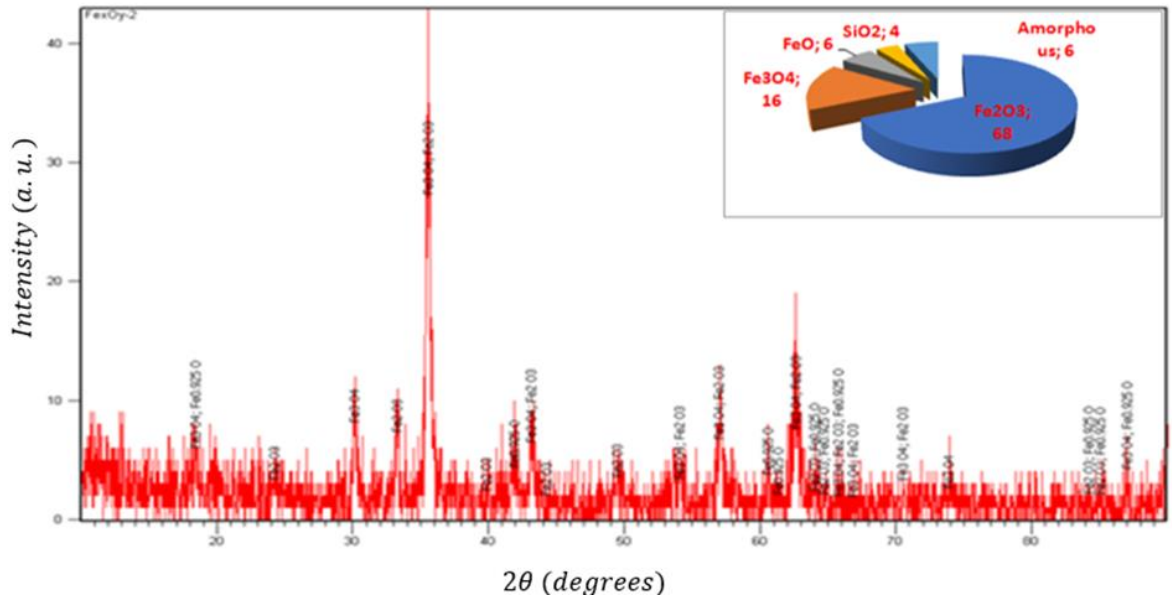


Fig. 5.124 Difractogram obtained on IOW_2 sample

The chemical composition of IOW_3 powder obtained from the XRFS test required a thorough XRD investigation, namely the use of MoKα radiation to avoid the parasitic effect caused by iron fluorescence and to extend the range of interplanetary distances. The diffractogram obtained on the IOW_3 specimen is shown in Figure 5.125.

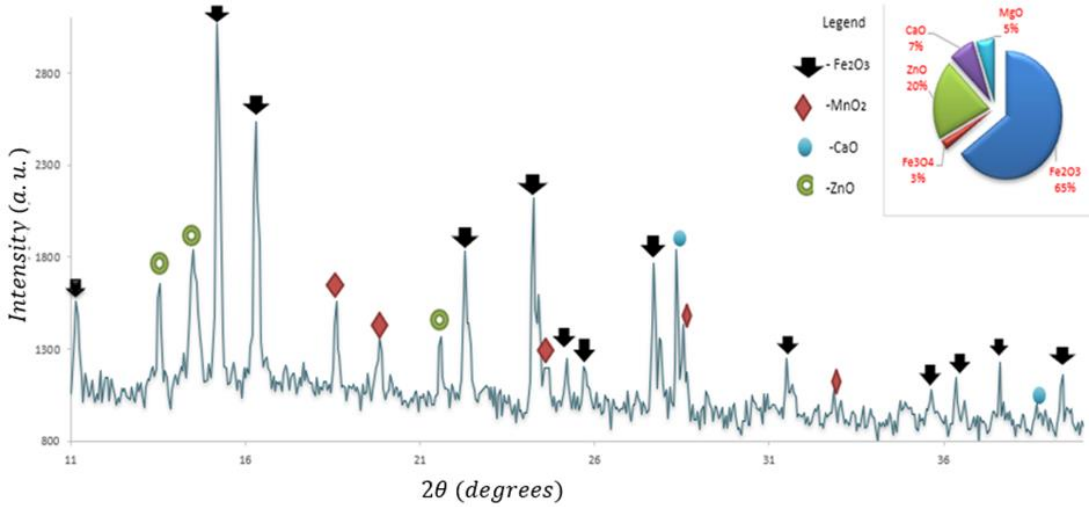


Fig. 5.125. Difractogram obtained on IOW_3 sample

The diffractometric investigations on the IOW_3 sample show a ZnO (20%) and CaO (7%) content compared to IOW_1 and IOW_2. The MgO content (4%) appears only in IOW_3, while SiO_2 and $CaSi_2$ were not identified in this specimen. Also, the EAF powder (IOW_3) contains mainly hematite and a small fraction of magnetite (3%) which indicates a lower thermal efficiency compared to the IOW_1 precursor.

The F QUANTA INSPECT electronic microscope was used to identify the morphology and particle size of three types of waste. Figure 5.126 shows the morphological aspects of the waste particles related to the three samples, at different magnifications.

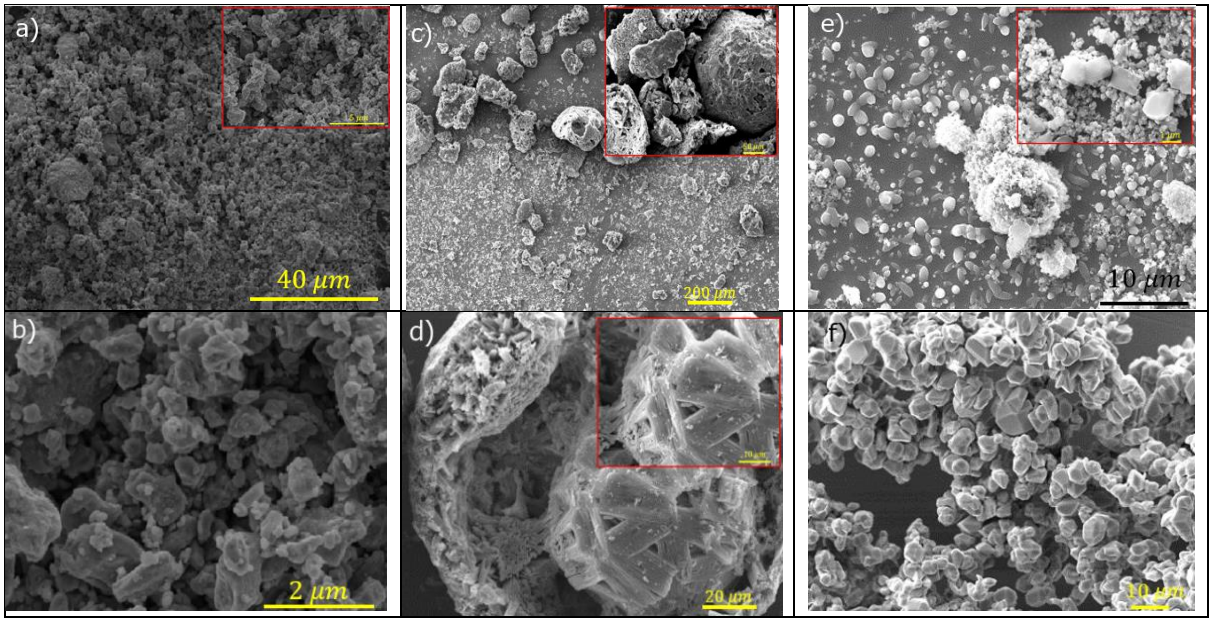


Fig. 5.126 SEM images of the particules: a,b) IOW_1 waste; c,d)IOW_2 waste ; e,f) IOW_3 waste.

The SEM images in Figs. 5126 show that the waste have various morphologies and dimensions which influence in a specific way the recovery yield and the quality of reaction products as shown below.

The images in Figs. 5.127 a, b, c clearly describe the slag and the piece of iron resulting from each aluminothermic process performed on the studied waste. Optical microscopy images (Fig. 5.127 d, e, f) show iron specimens subjected to microstructural investigations using a Reichert UnivaR metallographic microscope.

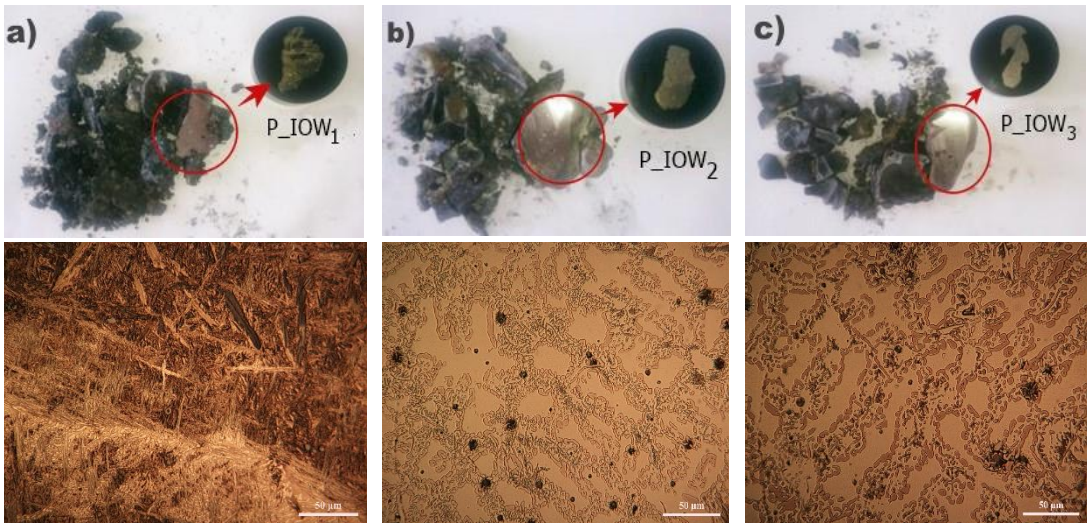


Fig. 5.127. Products of aluminothermic reactions performed with precursors IOW_1,IOW_2 and IOW_3: a) P_ IOW1; b) P_ IOW2; c) P_IOW3 and related steel microstructure recovered: d) P_ IOW1; e) P_ IOW2; f) P_IOW3

The microstructures of the recovered steels differ, as can be seen in Fig. 5.127 d, e, f. This finding was expected because the microstructure of the recovered steel depends on the composition of the waste, the thermodynamics of the aluminothermic process, which is controlled by the contents of the kit, and the size and shape of the crucible [183,186, 197].

The elementary compositions of the recovered pieces of iron (Fig. 5.127) were measured with the optical emission spectrometer with electric discharge in an argon atmosphere, SpectromaxX, AMETEK and the results are published in table 5.67.

Table 5.67. Elemental composition of recovered iron products

Element	C	Si	Mn	Mg	S	P	Cr	Ni	Ti	Al	Zn	Pb	As	Fe
IOW1	0.50	0.30	1.10	0.04	0.018	0.026	0.18	0.30	0.09	0.06	0.007	0.02	0.001	97.15
IOW2	0.65	0.40	1.30	0.03	0.021	0.025	0.16	0.10	0.09	0.09	0.005	0.03	0.02	97.08
IOW3	0.07	0.54	0.10	0.21	0.032	0.045	0.12	0.21	0.07	0.12	0.020	0.08	0.005	98.38
U(95%)	0.04	0.08	0.06	0.02	0.040	0.040	0.08	0.10	0.02	0.03	0.004	0.02	0.002	0.12

The elemental composition of the iron pieces recovered from IOW_1 and IOW_2 are similar, while that resulting from the IOW_3 test differs, as the concentrations of Zn, Pb, Mg and As are significantly higher compared to those of IOW_1 and IOW_2.

5.5.5. Conclusions

Aluminothermy is an emerging technology for the recovery of solid metallurgical waste, but the most important aspect is that it seems to be the most suitable solution for the eradication of historic landfills in Romania.

Aluminothermic technology for the material and energy recovery of waste critically depends on the holistic characterization of waste. In this sense, both the related text of the thesis and the published paper [141] underline the critical information provided by XRFS, XRD, SEM and metallographic methods aimed at controlling the effectiveness of this technology.

CHAPTER 6 CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND PERSPECTIVES FOR THE DEVELOPMENT OF THE THESIS TOPIC

6 .1 General conclusions

In order to improve the security of raw material resources at EU level, it is planned to widen access to both primary and secondary sources. This approach applies to all raw materials, including base metals, industrial minerals, aggregates and biotic materials, but it is needed to a greater extent for raw materials that are critical for the EU [7]. Taking into account the above considerations, it was decided that the theme of the thesis addresses the ways in which we can evaluate the potential of the extractive metallurgical waste as a secondary resource of significant economic interest. It should be noted that the scale of the problem of the secondary resource is reinforced by the Waste Directive [11] which provides in Art. (30): 'The Member States need to ensure the inventory of closed waste facilities, located on their territory in order to identify those which cause serious negative environmental impacts or likely to become in the short or medium term, a serious threat to human health or the environment 's. These inventories must provide an appropriate basis for an appropriate program of measures'.
The problem of secondary resources in Romania was also addressed by Prof. Nicolae Anastasiu, Corresponding Member of the Romanian Academy, in 2015 when I started my doctoral internship in the paper '*Mining waste and critical minerals - a residue? No - a neglected alternative'* (2015, https://www.researchgate.net/publication/280947001). This paper states '*The EU is facing a great challenge: in line with all these goals, a detailed knowledge of the waste in the extractive industry, respectively of the tailings ponds, which have been built near the old mining operations or to the former preparation plants, appears, today, as a necessity and represents a future alternative likely to stimulate investments in the Carpathians and to launch Romania as a valuable partner in the delivery of new types of raw materials. Let's take advantage of European funds that encourage projects that will pave the way for the alternatives we need now and in the near future. Let's access them and enjoy the expected results.* In this context, this thesis is limited to an important issue that raises concerns at EU level, namely addresses the issue of secondary resource represented by ponds/industrial waste dumps in Romania from the perspective of their modern management practiced at European level, known as the name ELFMM (Enhanced Landfills Mining & Management).

Romania, as a member of the UN and the EU, has adhered to the 17 sustainable development objectives of Agenda 2030, adopted by UN General Assembly Resolution A/RES/70/2/. For the implementation of the 2030 Agenda in Romania, the Government of Romania, by GD no. 877/2018, adopted the National Strategy for Sustainable Development of Romania 2030 , SNDDR2030 [28]. The Department for Sustainable Development of the Romanian government (http://dezvoltaredurabila.gov.ro) is entitled to implement SNDDR2030. Previous data shows that Romania does not meet many of the commitments made to the EU/EC on the waste management, including the goal of closing the abandoned landfills. Surprisingly, SNDD 2030 does not provide anything related to the use of secondary resources that are found in more than significant quantities in Romania.

Bibliographic research, of which a significant number of papers are cited in the thesis, shows that many EU countries (Germany, France, Belgium, Norway, Poland, etc.) pay more attention to secondary resources, apply and receive funding for such projects in which they develop technologies and capitalize on the secondary resource through the exclusive implementation of an ELFMM management dedicated to each deposit of waste. I mention that ELFMM has as main elements the 'conceptual model of the site' studied and the 'resource distribution model in the target site'. The same bibliographic research shows that there is no published information demonstrating that there is an organization in Romania (research institute, university, private organization, NGO, etc.) that has the expertise in the ELFMM management (knowledge, technical expertise, incipient or consolidated infrastructure, etc.). Thus, besides the fact that SNDD 2030 does not provide anything related to the use of secondary resources, it is even worse that Romania does not have, at least at the level of publications, the competence or the will to take advantage of the opportunity offered by the CRM crisis. In this context, the topic of the thesis is in the direction of correcting an unfortunate attitude i.e. ignoring the capitalization of secondary resources in Romania!

It can be considered a major contribution of this thesis, the fact that the issue of exploring the secondary resource in Romania was initiated by applying the ELFMM management for the holistic capitalization of a secondary resource. This fact is proved by the content of the thesis as well as by the inclusion of research centre ECOMET of UPB in the HOVARED-2021 consortium that applied in the ERAMIN3-2021 competition. (To see site www.eramin.eu)

Note. In the most concise way, the problem of the thesis is the following: a dump/pond contains tens of thousands of m^3 of waste and a sample measured with an equipment (XRFS, XRD etc.) has a mass of the order of grams. The problem to be solved is the representativeness of the analysed sample and the composition of the analysed sample must reflect the real average composition of the dump! This problem is addressed in many ways by the theory and practice of sampling.

Practically, obtaining the information on the total content of exploitable/recoverable substance in economic conditions, having associated a reasonable uncertainty, is the key element of the investigation of a extractive pond. This fact is obvious because the decision to capitalize or postpone the capitalization until a future term when conditions conducive to the recovery/treatment of the respective landfill will be created depends on the value of the target resource (quantity and price per tonne). In this context, the thesis mainly addresses the issue of obtaining primary information on the total content of exploitable substance and estimating the uncertainties associated with the measurements through efficient sampling and subsampling. As previously shown, this topic is of actuality, it has a pro-active character for Romania in several directions i.e.

a) scientific: development and implementation of the most important component necessary for the capitalization of a secondary resource, respectively the efficient method to evaluate the contents of analytes and the associated uncertainties;

b) economic: implementation of the EU's circular economy policy in Romania;

c) environment: reduction of multiple pollution caused by metallurgical extractive waste (dust, acid drainage, underground leaching) by eradicating metallurgical extractive waste deposits;

d) agricultural: rendering in the natural circuit of the land occupied by the historical waste landfills.

From a scientific and technological point of view, to obtain reliable results, the thesis approached a rigorous research methodology at the level of means it had, respectively the problem of its location at the actual level of the domain i.e. its place at the level of the front knowledge concerning the qualification of waste landfills as secondary raw material resources, with the CRM corollary. This route requires theoretical knowledge first and technical/engineering knowledge second. Thus, modelling and simulation of sampling is an approach of utmost importance for the researcher to know the related phenomenology and not to perform/ orce experiments destined from the start of failure. Subsequently, the identification of efficient and accessible waste characterization methods and techniques is the second essential factor. Once the know-how is consolidated, the programming of the exercise becomes rational, which was done accordingly in the thesis.

The modelling of sampling with functions of uniform distribution, normal and combined, founded the phenomenology and effects of constitutional heterogeneity and spatial distribution of the target analyte in waste. Thus, in the case of a concentration of 1% of the analyte carrier mass in the pond, sampling becomes critical when the sample volume decreases and the distributional variability of the analyte carrier mass is comparable to the average incidence of analyte in the pond, which generates a relative standard uncertainty ~ 100% which is unacceptable.

If the actual analyte concentration is << 1% the sampling accuracy is negatively polarized (bias) which is an inconvenience as laboratory measurements underestimate the value of the analyte in the pond. In these cases, the relative expanded uncertainty exceeds 100% which show that in such cases sampling is prone to failure in the sense that it cannot provide reliable data unless you are running a special sampling.

The measurement of the humidity, of the organic mass content and of the equivalent calcite content of the metallurgical extractive waste is a necessity for establishing the technological parameters for their pyro metallurgical recovery. In the thesis it is shown that the LOI method is effective for measuring humidity, and the content of the organic mass equivalent of calcite.

The Marginal Recovery Method (MRM) is effective in ensuring the validity of the results. The results presented in the thesis demonstrate that LOI calibrated with MRM provides results with sufficient accuracy. Also, the calibration of LOI by MRM can be performed as a routine procedure in geotechnical and waste characterization laboratories.

During the researches for the realization of the thesis, it was not possible to build the model of the deposit resource due to easy to understand reasons, the lack of geophysical infrastructure, the necessary expertise as well as the lack of the necessary financial resource. For this reason, a ‘low-cost’ sampling method was developed. The fact that EURACHEM recommends BDDSM was a guarantee regarding the chosen option. But EURACHEM does not provide the theoretical basis of the method but ‘fragments’. For this reason, a study elaborated for the development of the theoretical basis of the BDDSM method using the EURACHEM model (ed. 2019) was necessary. The study was performed in detail to justify the accuracy of each calculation step. Subsequently, the calculation algorithm in Excel related to BDDSM was implemented and its accuracy was validated by intercomparison with the data published by EURACHEM and NORDTEST. The thesis provides data attesting that the BDDSM method and the algorithm were correctly implemented.

The core of the thesis is subchapter 5.4 where the application of the BDDSM method to a metallurgical extractive landfill resulting from the flotation processing of iron ore for incremental sampling is presented.

BDDSM applies directly to the results of XRFS and LOI tests. But in order to have a complete picture of the state of the waste (granulation, morphology, spatial dispersion of the analytes, granular and mineralogical entanglement, etc.), MO, SEM-EDS, and XRD investigations were performed.

The research related to subchapter 5.4 allows the formulation of the following conclusions:

a) The BDDSM method developed in this thesis is effective, relatively inexpensive and can be used efficiently for the primary phase of analysing the potential of a landfill to be qualified as a secondary raw material resource;

b) For the subsequent stage of refining the accuracy of the data obtained in the primary phase, an improvement of this method is required, possibly with the widening of the analytical range, respectively using AAS analytical methods, ICP, XRD Rietveld analyses, RAMAN, combined mineralogical analyses MO (LP) -XRFS-XRD etc.

Regarding the qualification of the investigated pond, it is found that it contains SiO_2 as the majority phase with a concentration of 54% and U_R (95%) = 17% due mainly to the variability at the pond/deposit level. The Fe_2O_3 content, which estimates the Fe content, is C_{Fe2O3} = 17% and U_R (95%) = 33%, caused by the distributional variability at pond/storage level. Calcium content is estimated by CaO in XRFS analyses and by calcite content in LOI measurements. The XRFS and LOI data are compatible and attest to a calcite content of about 9% with an extended relative uncertainty of about 30% which is reasonable at the pond scale. The Mg content in the dump is high in relation to the data from the specialized literature i.e. 9.8% vs 0.1%. Also, the Al_2O_3 content is about two times lower compared to the value reported in the same publication i.e. 3.1 vs 7.42%. These aspects attest to the specificity of this waste. In the investigated waste are present at trace level many elements from the list of CRM 2020 such as: Mg, V, Ni, Co, Ga, Nb, P, Sc, Ti, Ta, W, Sr etc. The paper analyses the data regarding the elements Sr and Y. Also, the data related to Ba were analysed.

At the level of the issue of capitalization of secondary resources in Romania, the following general conclusions can be formulated:

Romania has a historic opportunity, offered by the issue of EU resilience to ensure the supply of CRM, to promote projects to explore the existence of CRM in ponds and dumps, which also serve to solve environmental problems by eradicating some of the metallurgical extractive dumps / ponds through the use of European funds.

Unfortunately at the decisional level of Romania, the problem of a secondary resource in Romania does not get the attention needed with the corollary eradication historical pollution.

The integral and correct application of the ELFMM algorithm, as described in the thesis, is the only way to obtain the relevant data and information to substantiate the answers to the questions of businessmen who promote specific businesses for the recovery of metallurgical waste.

6. 2. PERSONAL CONTRIBUTIONS

Choosing a challenging theme i.e. to establish a modern way of capitalizing the secondary resource of Romania in the context of specific requirements of circular economy is a contribution, whereas it comes to cover a niche with significant economic, environmental and social potential. At the time of establishing the topic of the thesis, no other thesis with a similar topic was published in Romania, at least at the level of the bibliographic research performed.

Laying the foundations for the comprehensive management of historical extractive landfills (ELFMM), which cause pollution of all environmental factors and discomfort of the population in the area, is an important contribution both as a tool to address the waste and from a scientific point of view. The capitalization of this acquisition is made both by substantiating some research-development projects and by publishing, in the nearest future, a specialized work (book, manual).

The documentation of the thesis for arguing the scientific and experimental options is original in the sense that it uses and combines scientific aspects with legislative aspects and aspects of governmental policy regarding secondary resources in Romania. Highlighting the importance of this resource, including by highlighting the views of other Romanian specialists, in contrast with the official tendencies represent an act of professional integrity revealed in the thesis.

The studies and experiments related to the thesis are original, in the sense that the author designed, under the guidance of the doctoral coordinator, the necessary measurements and analysed the results in terms of the goals pursued by the thesis.

The theoretical aspects of modelling and simulation with functions of uniform and normal truncated probability distribution densities are original, not published due to lack of time, as their validation has been done recently. Thus, three modelling and simulation variants were made:

Modelling the distribution of critical concentration with uniform distributions in case of incremental sampling;
Sampling modelling with normal truncated distribution of the sampled mass and uniform distribution of the analyte-bearing mass;
Modelling of sampling with normal truncated distributions of the sampled mass and the analyte-bearing mass incorporated in the sample.
In each case, the theoretical expressions of the expectancy and their dispositions (variance) were established and simulations were performed for analyte concentrations from 10% to ppm values.
By modelling and simulation, the effects of analyte concentrations and spatial dispersions of the target analyte on the values obtainable by sampling were established exactly. All mathematical expressions are integrally deducted i.e. so there is no doubt regarding their accuracy but also for the profound understanding of sampling artefacts that can be revealed by the simulation.
It has been shown that at concentrations of the order of tens of ppm the relative dispersion or the coefficient of variation of the measured mass easily exceeds 50% and reaches values of over 100% in case of a significant spatial heterogeneity.
As a result of the simulation it is particularly noted that a pre-sampling according to &5.4 from the thesis must always be applied and if a concentration under 1% of the targeted analyte is noted, then a special projection of the sampling is required subsequent to determine the resource of the analyte from the pond/dump with adequate uncertainty.
The results of the modelling and simulations presented in the thesis represent only a part (approximately 40%) of the modelling and simulations performed in the field of sampling. Since all the mathematical expressions used were deducted in integrum I consider that they can be integrated, also, in a paper that will be published in the near future because in there is no such a work in Romania's literature.
The MRM method, from EURACHEM documents, is intended especially for AAS, ICP, GDS, etc. spectrometric methods. Translating it to the LOI test is a very important contribution revealed in the thesis [200]. The special importance of MRM-LOI consists in:

- Ensure efficient and accurate calibration of the LOI attempt
- Avoid major expenses by using a cheap surrogate as reference material
- Replaces the lack of CRMs that are not commercially available

The method was disseminated at the conference ROMAT 2020 and is being published in the journal University Politehnica of Bucharest Scientific Bulletin, Series B.
The adequacy of the BDDSM method for sampling metallurgical extractive waste landfills is the major achievement of the thesis in the sense that the methods developed by the sampling coryphaeus, such as P. Guy, P. Minkinen and S. Ebensen, were not applied to intricate powdery wastes with higher constitutional heterogeneities which cannot be quantified. In this context, the theoretical development of BDDSM is a completely original lifesaving solution as it has never been applied to such waste. Also, the development of the calculation algorithm in Excel, manageable and robust, represents a major contribution to the operationalization of this method. Implementation of the BDDSM at the Teliuc 2 extractive metallurgical landfill and obtaining its relevant characterization using a budget of judicious methods built is a great achievement, such a 'breakthrough' in the field but especially in Romania, where, through this, they lay the foundations for characterizing the potential of abandoned historic landfills for their temporary transformation into a secondary resource, followed by the rehabilitation of sites and the return of the land occupied by them in their natural circuit.
The concept of thesis and the accumulation from the research period related to the thesis contributed to the UPB initiative of starting an attempt to set up a consortium to implement ELFMM with EU funds project grants within HOVARED, respectively:

ERA·MIN 2
RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

PROJECT: HoVaReD

Date: **31.03.2021** **PREPROPOSAL** ID: 160

PROJECT TITLE

Holistic Approach for Valorisation and Rehabilitation of the Metallurgical and Extractive Waste Deposits

TOPIC

Topic 1: Supply of raw materials from exploration to mining

SUBTOPICS

Sub-Topic 1.1: Exploration, Sub-Topic 3.2: Increase resource efficiency through recycling of residues or remanufacturing of used products and components, Sub-Topic 5.1: New business models (implementing circular economy aspects), Sub-Topic 5.2: Improvement of methods or data for environmental impact assessment, Sub-Topic 5.4: Health safety issues

PROJECT DURATION	TOTAL REQUESTED FUNDING	TOTAL COSTS
24 Months (05 / 2022 to 04 / 2024)	1546850 €	1815438 €

The ERAMIN-3 project proposal brought together 13 partners from 6 countries who joined the theme of capitalizing on secondary resources in their countries using ELFM management and agreeing to share their know-how at the consortium level. Thus, this single proposal can be considered as both the subject itself and the results obtained during the doctoral stage were validated internationally, although the project has not qualified for financing.

Own contribution and requested funding

Organisation name	Personnel	Travel	Consumables / Equipment	Subcontracts	Other	Overhead	Requested Funding	Total Own Contribution	Total Costs
SPAQUE	294000	8000	6040	87200	35000	30804	322731	138313	461044
University Politehnica of Bucharest	72000	6000	4500	16800	3500	17200	120000	0	120000
Geological Institute of Romania	48000	6000	9000	0	4500	12500	80000	0	80000
University of Bielsko-Biala	35166	44077	128926	7713	0	52042	267924	0	267924
ICAMCYL	67050	2000	500	15000	0	10432	94982	0	94982
Faculty of Science, Charles University	17000	10000	6000	10000	4000	9240	47803	8437	56240
GEOMIN s.r.o.	28000	5000	5000	10000	0	9495	35933	21562	57495
G IMPULS Praha spol. s r.o.	22000	4000	2000	0	0	7000	24500	10500	35000
Miroslav Karas - Destro	8000	2000	0	0	27000	4625	26014	15611	41625
ISTANBUL TECHNICAL UNIVERSITY	40252	8334	10250	2000	1866	21000	83702	0	83702
Central Mining Institute	156517	5510	1102	0	0	40782	203911	0	203911
Centro Tecnológico del Mármol, Piedra y Materiales	46830	3000	110050	0	0	16958	130008	46830	176838
Biomatex	39699	8264	61379	0	0	27335	109342	27335	136677
TOTAL	874514	112185	344747	148713	75866	259413	1546850	268588	1815438

The thesis produced know-how for the capitalization of the secondary resource in Romania in the context of the circular economy and validated it through pertinent experiments. The thesis achievements must be evaluated also in terms of material resources and infrastructure related to the thesis.

6.3. PERSPECTIVES FOR FURTHER DEVELOPMENT

The BDDSM method can be used for various other applications in the field of materials science. Thus, if it produces a new or improved material, a coating, a new product, etc., the BDDSM can be used to validate the quality of the material, of the product especially the stability of the process in the sense that at least 100 test tubes (demonstrative pieces) must be produced out of each 10 of them will be sampled and out of these 2 will be sub-sampled. Each sub-sample was measured two times in repeatability conditions or strict reproducibility and the result are subjected to the ANOVA analysis. The average values obtained will be judged from the prism of uncertainty associated at level of intern homogeneity (u_{RSP}) i.e. in the subsamples level which reflect the intrinsic homogeneity of the material (pieces) and

at the level of stability of the technological process estimated by the uncertainty of the sampling $U_{RE}(95\%)$. If u_{RSP} or $U_{RE}(95\%)$ exceed the minimum accepted values, e.g. u_{RSP} = 3%, U_{RE} (95%) = 10% then the quality of the material, product, etc. is not compliant. In any case one cannot talk about a new product (material) or process technologically or improved, without being validated using a procedure statistics at least minimal as BDDSM which is based on ANOVA analysis in two steps.

The theoretical and experimental acquisitions related to the thesis represent a germinal nucleus that needs further developments in the following directions:

- Integration of methods and techniques for geophysical investigation of landfills to provide the data needed to build the conceptual model of the site
- Completing the necessary expertise for projecting for the 'target' sample in situ
- Deep procurement of the deposits through consecrated geophysical means
- Development of an advanced theory for the BDDSM method with a larger number of samples taken that is adaptable to the volume of the site i.e. depending on the variability of the measurement to be able to estimate the relevant size of the sampling grid unit

It is necessary to obtain the financing of a project on this topic that would allow the establishment of a consolidated infrastructure that could allow the geophysical and analytical investigation of a site with reasonable costs. The defining task of the project would be the creation of a competent and the necessary infrastructure for resource distribution model in the site investigated the content values to have uncertainties as small as possible.
One way to strengthen the topic is the establishment at national level of a group of specialists who, depending on the model of the in situ resources, can create the ways (technologies, integrated processes etc.) to capitalize the resources and rehabilitate the site. Also, this team should develop the feasibility study so as to provide potential investors with relevant information of an economic and environmental nature.
The development of the thesis topic will be followed by publications derived from the 'thesis material' so as to create a visibility of the working group on this topic that was set up at UPB and to promote access to European projects such as the one mentioned above.
Another way of development is the establishment of a consortium at national level in order to exploit the niche 'secondary resources' in Romania through national and European research projects. In this direction, a first nucleus formed by UPB and Romanian Geological Institute was constituted according to the collaboration agreement no. 14020 din 04.08. 2021.
Practice shows that in some areas the estimation of heterogeneity is performed (for example, the reception of the grains in bulk cargo ships, the control of the contents of active substances in pills, the control of the analytes from the bulk ores etc.). Also, the Directorates of Public Health and the Sanitary Veterinary and Food Safety Directorates face the problem of sampling and need well-trained specialists. All of these arguments support the need to address sampling in technical higher education.
I consider that the field of capitalization of secondary resources with its main corollary-sampling will develop in Romania due to its necessities, regardless of social and political conditions, which may delay the development of the field but not block it in the long run!

Articles Published in Web of Science Journals in the Doctoral Thesis Field

1. ***A.C. Popescu-Argeș****, R.N. Turcu, C. Ungureanu, A. Priceputu, I. Pencea, F. Niculescu, A.-L. Timiș*, Validation of the LOI results obtained on particulate waste through Marginal Recovery and XRFS methods, UPB Scientific Bulletin-*in press*, **2021**
2. ***A.C. Popescu-Arges****, M. Mihaly, I. Pencea, R.N. Turcu, M. Branzei, M.O. Cojocaru, A.C. Berbecaru, T.A. Coman, S.R. Milasan, C. Predescu*, Complex characterization of the metallurgical solid wastes for aluminothermic 4R approach, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, Vol. 83, Issue 2, Pages 291 – 302, **2021**, , WOS:000661663200025
3. Pencea Ion; Branzei Mihai; Cojocaru Mihai Ovidiu; Turcu Ramona Nicoleta; Predescu Cristian; Berbecaru Andrei; **Arges Alina Popescu**; Comanescu, Brindus, A New Robust Top-Down Method for Measurement Uncertainty Estimation of the ED(P)-XRFS Outcomes Carried on a Fluorescence Glass, REVISTA DE CHIMIE Vol:69, Issue: 9, Pages 2487-2493, Sept. 2018, Factor Impact: 1.412, WOS:000449628400038, ISSN: 0034-7752, Q3.

ROMAT, November 26-27, 2020, Bucharest, Romania

P25. I. Pencea, C. Ungureanu, A. Priceputu, R. N. Turcu, A. Berbecaru, C. Predescu, **A. C. Popescu-Argeș**, **COMPARATIVE STUDY REGARDING THE EXACTNESS OF THE LOI, XRD AND XRFS METHODS FOR THE MEASUREMENT OF THE SOIL-CARBONATE CONTENT**

P31. M. Branzei, M. Mihaly, S. Niculescu, T. A. Coman, **A. C. Popescu Arges**, R. N. Turcu, M. O. Cojocaru, I. Pencea, M. Ion, **A NEW APPROACH FOR HEAT YIELD MEASUREMENT OF THE ALUMINOTHERMIC TESTS CARRIED ON IRON BEARING POWDERED WASTES**

11.00-11.10 Oral Presentation O.IV.5.

M. Mihaly, R.N. Turcu, I. Pencea, M.O. Cojocaru, M. Branzei2, T.A. Coman, C. Predescu, A. Berbecaru, **A.C. Popescu-Arges**, A.D. Stoian, **COMPLEX CHARACTERISATION OF THE METALLURGICAL SOLID WASTES FOR ALUMINOTHERMIC RECOVERING TECHNOLOGY**

Selective references

[1] ***, Brussels, 2.12.2015 COM(2015) 614 final Communication From The Commission To The European Parliament, the Council, The European Economic and Social Committee and the Committee Of The Regions Closing the loop – an EU action plan for the Circular Economy,
[2] ***, https://www.eurofer.eu/assets/Uploads/circular-econ-white.png 09.11.2020/18,48h
[3] ***, https://www.interregeurope.eu/plasteco/news/news-article/8056/new-circular-economy-action-plan/ accessed on 14.11.202/ 10.00h
[4] ***, https://e-circular.org/info-mediu/2143/] 25.04.2021, 10.15AP
[5] *A. Berbecaru, A. Predescu, G. Coman, C. Pantelimon, C. Dragan, C. Gradinaru, C. Predescu, A. Nicolae*, Ramuri Stiintifice de Dezvoltare Durabilo-Sustenabila în Metalurgie, Ed. Printech, 2018, ASBN 973-606-23-0847-6, pp. 9-18
[7] ***, Comunicarea COM (2020) 474 final
[10] *G.A. Blengini; F. Mathieux; L. Mancini; M. Nyberg; H.M. Viegas (Editors); J. Salminen; E. Garbarino; G. Orveillon; H. Saveyn; V. Mateos Aquilino; T. Llorens González; F. García Polonio; L. Horckmans; P. D'Hugues; E. Balomenos; G. Dino; M. de la Feld; F. Mádai; J. Földessy; G. Mucsi; I. Gombkötő, I. Calleja*, Recovery of critical and other raw materials from mining waste and landfills: State of play on existing practices Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-76-08568-3, doi:10.2760/600775, JRC116131
[13] M.M.D.D. , Report on the results of technical inspections and control at tailings ponds in the mining industry, nr. 111509/22.06.2007
[16] *D. Vollprecht, L. Machiels, P.T. Jones*, The EU Training Network for Resource Recovery through Enhanced Landfill Mining—A Review, in Processes **Vol.9**, 2021, 394.
[17] *G. A. Dino, R. L. Perotti, W. Alberto, H. Sarkka, F. Coulon, S Wagland, Z. Griffiths, F. Rodeghiero*, "Landfill mining from extractive waste facilities: the importance of a correct site characterization and evaluation of the potentialities. A case study from Italy", Resources Policy, Elsevier 2018, **vol. 59**(C), pages 50-61;
[18] *P.T. Jones, D. Geysen, Y. Tielemans, S. Van Passel, Y. Pontikes, B. Blanpain, M. Quaghebeur, N. Hoekstra*, "Enhanced Landfill Mining in view of multiple resource recovery: a critical review", in Journal of Cleaner Production, **Vol. 55**, 2013, pp.45-55
[20] *S. Celac, A. Vlădineanu*, Strategia națională pentru dezvoltarea durabilă a României 2030, Ed. Paideia, București, 2018, pp. 77-83.
[28]***, REGULAMENTUL (UE) NR. 333/2011 AL CONSILIULUI din 31 martie 2011 de stabilire a criteriilor de determinare a condițiilor în care anumite tipuri de deșeuri metalice nu mai constituie deșeuri în temeiul Directivei 2008/98/CE a Parlamentului European și a Consiliului, https://eur-lex.europa.eu/legal-content/RO/TXT/PDF/?uri=CELEX:32011R0333&rid=1, accesta la data de 12,02,2021 h21,36
[39] *M. Zlagnean, I. Vasile, C. Vasile, N. Tomus, D. Georgescu*,1994b, "Extraction of the concentrates of molybdenite and monazite from Jolotca ore" ICPMRR. Bucuresti. Romania, in Proceedings of the XXI International Mineral Processing Congress, Rome, Italy, July, 23-27, 2000, pp C10-5-10
[40] *R. Fechet , M. Zlagnean , A. Moanta , L. Ciobanu*, Mining wastes - sampling, processing and using in manufacture portland cement, 2010, https://www.researchgate.net/publication/282185479
[41] *M. Zlagnean, N. Cristea, R. Fechet*, Processing eco-technologies of materials from dumps and tailing ponds ("Ecotehnologii de procesare a materialelor din halde si iazuri de decantare"), Editura Focus – Petrosani, acreditata CNCSIS, 2010.
[42] ***, Hotărârea nr. 870/2013 privind aprobarea Strategiei naţionale de gestionare a deşeurilor 2014-2020, Publicat in Monitorul Oficial, Partea I nr. 750 din 04/12/2013 Intrare in vigoare: 01/01/2014.
[43]***, Planul National de Gestionare a Deseurilor, aprobat prin HG nr. 942/20.12.2017, Monitorul Oficial al Romaniei, Partea I, nr. 11 bis, http://www.mmediu.ro/app/webroot/uploads/files/2018-01-10_MO_11_bis.pdf , accesat in data 19.06.2021 10.40 AM.
[47] *P. T. Jones, D. Geysen, A. Rossy, K. Bienge*, „Enhanced Landfill Mining (ELFM) and Enhanced WasteManagement (EWM): essential components for the transition to Sustainable Materials Management (SMM)" , in proceedings of the 5th EWM-ELFM , Bruxeles, 26feb, 2020, https://www.academia.edu/26754335/ accesed on 03,03,2021, 8,23 AM
[48] *D. Geysen, P.T. Jones, K. Van Acker, S. Van Passel, M. Craps, J. Eyckmans, K. Vrancken, B. Laenen, P. Laever*, "Enhanced landfill mining - A future perspective for landfilling" , available at at: https://www.researchgate.net/publication/254434664, accesed on 23Mrch 2021, 20,56h
[49] ***, Best Available Techniques (BAT) Reference Document for the Management of Waste from Extractive Industries, in accordance with Directive 2006/21/EC; EUR 28963 EN; Publications Office of the European Union, Luxembourg, 2018

[50] ***, EUROPA 2020, O strategie europeană pentru o creștere inteligentă, ecologică și favorabilă incluziunii, COM(2010) 2020 final, https://www.mae.ro/sites/default/files/file/Europa2021/Strategia_Europa_2020.pdf
[52] ***, "European Commission, Critical materials for strategic technologies and sectors in the EU - a foresight study, 2020", The reuse policy of European Commission documents is regulated by Decision 2011/833/EU (OJ L 330, 14.12.2011, p. 39), https://ec.europa.eu/docsroom/documents/42881
[56] ***, *https://www.nato.int/docu/review/Topics/RO/Rare-Earth.htm*, accessed ob 23.01.2021, h 21.36
[59] ***, https://www.consilium.europa.eu/en/press/press-releases/2020/07/21/european-council-conclusions-17-21-july-2020/ , European Council conclusions, 17-21 July 2020, On 21 July 2020, the European Council adopted conclusions on the recovery plan and multiannual financial framework for 2021-2027, accessed on 17.01.2021, h 22.13
[70] E. Matinde ; G.S. Simate ; S. Ndlovu , "Mining and metallurgical wastes: a review of recycling and re-use practices", in J. S. Afr. Inst. Min. Metall., vol. 118, n.8, 2018, Johannesburg Aug., http://dx.doi.org/10.17159/2411-9717/2018/v118n8a5
[74] *D.K. Nordstrom, R.J. Bowell, K.M. Campbell, C.N. Alpers*, ''Challenges in recovering resources from acid mine drainage", in Proceeding"IMWA 2017 – Mine Water & Circular Economy", **Vol.2**, Lappeenranta, Finland 2017, pag. 1138-1146
[75] Bian, Z., Miao, X., Lei, S., Chen, S., Wang, W., S. Struthers „The challenges of recycling mining and mineral processing wastes", in *Science*, **vol. 337**, no. 6095, 2012, pp. 702-703.
[78] ***, https://rmis.jrc.ec.europa.eu/?page=crm-list-2020-e294f6, acc 04,04,2021 69,11 AM
[104] *D.Ş. Vereş*, " A comparative study between loss on ignition and total carbon analysis in minerogenic sediments", in Studia Universitatis Babeș-Bolyai, Geologia, **XLVII**, 1, 2002, pp. 171-182.
[114] *S.Yang*, "Influence of heating on the weight loss and mineral phase in MSWI ash: LOI of incineration", in IOP Conf. Series: Earth and Environmental Science, **Vol. 61**, Iss.1, 2017, pp.012079.
[117] ***, "Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples", Environmental Protection Agency, (EPA), USA, EPA/600/R-03/027 November 2003, p.65.
[125] *M.H. Ramsey, S.L.R Ellison, P.Roston*, Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches. Second Edition, Eurachem (2019).
[127] *M. H. Ramsey, S. L. R. Ellison* (eds.) Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches, Eurachem (2007).
[129] Pencea Ion; Branzei Mihai; Cojocaru Mihai Ovidiu; Turcu Ramona Nicoleta; Predescu Cristian; Berbecaru Andrei; Arges Alina Popescu; Comanescu, Brindus, A New Robust Top-Down Method for Measurement Uncertainty Estimation of the ED (P) - XRFS Outcomes Carried on a Fluorescence Glass, REVISTA DE CHIMIE Vol:69, Issue: 9, Pages 2487-2493, Sept. 2018, Factor Impact : 1.412, WOS:000449628400038, ISSN: 0034-7752, Q3
[130] *C. Ungureanu, A. Priceputu, G. Nguyen, I. Pencea, R.N. Turcu, A. C. Popescu-Arges*, Hybrid OLS for uncertainties estimation in direct shear testing, Measurement, In Press, Journal Pre-proof, 19 August 2021, 110018 available at : https://doi.org/10.1016/j.measurement.2021.110018
[131] *R.N. Turcu, I. Pencea, G. Chisiu, V. Manoliu, M. Botan, M. Branzei, F. Niculescu, ,* ***A.C. Popescu-Arges,*** *M. Ioan, C.E. Sfat,* Roughness and wear resistance modifications induced by cyclic high temperature shocks upon a micro-composite refractory enamel, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, Vol. 82, Iss. 4, pp. 223 – 234, **2020**
[141] I. Pencea* 1 , C. Ungureanu 2 , A. Priceputu 3 , Ramona Nicoleta Turcu 1 , A. Berbecaru 1 , C.Predescu 1 , Alina-Cristina Popescu-Argeș, Comparative study regarding the exactness of the LOI, XRD and XRFS methods for the measurement of the soil-carbonate content, RoMat, 2020
[142] *C. Grøn, J. B. Hansen, B. Magnusson, A Nordbotten, M. Krysell, K. J. Andersen, U. Lund*, Uncertainty from sampling. A Nordtest Handbook for Sampling Planners on Sampling Quality Assurance and Uncertainty Estimation, 2007.
[143] *M. Thompson, R. J. Howarth*, Duplicate analysis in geochemical practice. Part I. Theoretical approach and estimation of analytical reproducibility, The Analyst 101, 2006.
[144] *J.A. Lyn, M.H.Ramsey, D.S.Coad, A.P.Damant, R. Wood, K.A.Boon*,, The duplicate method of uncertainty estimation: Are eight targets enough?, The Analyst 132 (11):1147-52, 2007.
[154] *M. Thompson, S. L. R. Ellison, A. Fajgelj, P. Willetts, R. Wood*, Harmonized guidelines for the use of recovery information in analytical measurement, (Technical Report), EURACHEM Guide, 1998, www.Eurachem.com accessed on 01.05.2021, 18.03h

[155] *M. Thompson, Stephen L. R. Ellison, A. Fajgelj , P. Willetts, R. Wood*, Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement, IUPAC, Pure Appl. Chem. 71, 337–348, 1999
[159]***, Project 31-011/2007 (CNMP) – Romania, Eco-Tehnologii De Reabilitare Si Reconstructie Ecologica A Perimetrelor Miniere Afectate De Poluarea Iazurilor De Decantare, Contractor: Institutul National De Cercetare-Dezvoltare Pentru Metale Si Resurse Radioactive – Bucuresti, https://sites.google.com/site/ecotailing/ accessed on 12.06.2021, 8.36PM
[163] *C. Flanagan, B.M. Grail, D.B. Johnson*, New approaches for extracting and recovering metals from mine tailings, Minerals Engineering, **vol. 106**, 2017, pp. 71-78.
[164] *M. Nicolae, I. Melinte, E. Matei, M. Sohaciu, A. Nicolae*, Proceduri de analiză în managementul ecometalurgic, Ed. Fair. Partners, București, pp.23, 2002.
[165] ***, ziarul Adevărul din 19.09.2017
[166] *N. Mehta, G. Antonella Dino, I. Passarella, F. Ajmone-Marsan, P. Rossetti, D. Antonio De Luca*, Assessment of the Possible Reuse of Extractive Waste Coming from Abandoned Mine Sites: Case Study in Gorno, Italy, Sustainability, **Vol. 12**, Iss.6, 2471, 2020, pp.1-22.
[167] *Pedro Martínez-Pagán, Ángel Faz Cano, Enrique Aracil and Joselito M. Arocena*, Electrical Resistivity Imaging Revealed the Spatial Properties of Mine, Tailing Ponds in the Sierra Minera of Southeast Spain, June 2009, Volume 14, Issue 2, 2009, p.63.
[168] *T. Magiera, B. Żogała, M. Szuszkiewicz, J. Pierwoła, M.M. Szuszkiewicz*, Combination of different geophysical techniques for the location of historical waste in the Izery Mountains (SW Poland), Sci. Total Environ., **Vol 682**, 2019,pp. 226–238.
[170] Brantax SRL, e-mail:office@brantax.com, Telefon: +4021 456 00 17 Intrarea Aniversarii, nr. 41, Et. 3, Cam. 504, Sector 3, Cod postal 031463, Bucuresti, Romania, www.brantax.ro.
[171] *Chao Li, Henghu Suna, Jing Baic, Longtu Li*, Innovative methodology for comprehensive utilization of iron ore tailings, Part 1. The recovery of iron from iron ore tailings using magnetic separation after magnetizing roasting, Journal of Hazardous Materials, **174**, 2010,pp. 71–77.
[172] *Chang Tang, Keqing Li, Wen Ni, Duncheng Fan* , Technical Note Recovering Iron from Iron Ore Tailings and Preparing Concrete Composite Admixtures Minerals 2019, **9**, 232.
[183] *C. Perrine, R. Jerome, B. Valerie, O. Luca, H. Jean-Louis, P. Olivier, D. Jeremie, B. Jean-Yves* (2006), "Environmental impacts of steel slag reused in road construction: A crystallographic and molecular (XANES) approach", Journal of Hazardous Materials, pp.1-6.
[184] M. *Branzei, I. Pencea, C. E. Sfat, A. A. Matei, R.N. Turcu , M.O. Cojocaru*, Combined ED(P)-XRFS and WAXD analyses of the metallurgical wastes (2015), in Proceedings of the 7th Black Sea Basin Conference on Analytical Chemistry, 10-15 May 2015, Gold Sand, Bulgaria.
[186] *M. O. Cojocaru, M. Branzei, T. Coman*, Thermodynamics of iron metallothermy, Advanced Materials Research, **Vol. 1114**, pp 112-117 Trans Tech Publications, Switzerland, 2015
[194] *D. A. Iluţiu - Varvara, C.M. Mârza, F.V. Domniţa, I.M. Sas-Boca, M.,Tintelecan*, "An assessment of the Metallic Iron Content from Metallurgical Wastes - Essential Factor for Sustainable Development in the Steelmaking Industry". Procedia Engineering, **vol. 181**, 2017, p. 357-362.
[195] *D. A. Iluţiu - Varvara, C. Aciu, E.M. Pică, C. Sava*, Research on Chemical Characterization of the Oily Mill Scale for Natural Resources Conservation. Procedia Engineering, **vol. 181**, 2017, p. 439-443.
[197] *Branzei M, Cojocaru M.O., Coman T.A., Vascan O.*, A Model of Optimization and Control the Thermite Kit for Aluminothermic Welding, Solid State Phenomena, **254**, 2016, pp. 83-90.
[198] ***A.C. Popescu-Arges**, M. Mihaly, I. Pencea, R.N. Turcu, M. Branzei, M.O. Cojocaru, A.C. Berbecaru, T.A. Coman, S.R. Milasan, C. Predescu*, Complex characterization of the metallurgical solid wastes for aluminothermic 4R approach, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, Vol. 83, Issue 2, Pages 291 – 302, **2021**
[201] ***A.-C. Popescu-Argeş**, R.-N. Turcu, C. Ungureanu, A. Priceputu, I. Pencea, F. Niculescu, A.-L. Timiș*, Validation of the LOI results obtained on particulate waste through Marginal Recovery and XRFS methods, UPB Scientific Bulletin-in press, **2021**