UNIVERSITY OF PETROȘANI
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# Mineral waste recovery in the Port of Constanta in the context of the circular economy

Doctoral Thesis

Abstract

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# Chapter 1 - Introduction

The sustainable management of mineral resources is becoming increasingly important in a world where the demand for raw materials is growing. In the context of Romania's accession to the European Union, it is essential to comply with strict environmental protection regulations. These regulations are aimed not only at preventing negative impacts on the environment and quality of life, but also at making full use of mineral resources, eliminating waste generation. This requires the adoption of management strategies that ensure responsible and efficient exploitation of mineral resources while reducing the environmental footprint.

## 1.1. The circular economy concept

The circular economy is an innovative economic model that encourages the recycling and reuse of products to minimize waste and conserve natural resources. This model contrasts with the traditional linear economy, which follows the production-consumption-waste cycle. In the circular economy, resources are kept in use for as long as possible and end-of-life materials in products are recycled and reintegrated into production. Implementing this model brings many benefits, including protecting the environment by reducing waste and emissions, reducing dependence on new raw materials and creating economic and social opportunities.

## 1.2 The importance of mineral waste recovery

The recovery of mineral waste is essential in the context of the circular economy and plays an important role in sustainable resource management. Mineral waste, resulting from various industrial activities, can be transformed into valuable resources through recovery and recycling processes. These processes not only reduce the amount of waste going to landfills, but also contribute to saving natural resources by substituting primary materials with recycled materials. The steel, energy and cement industries are just a few examples of sectors that benefit from the recovery of mineral waste.

## 1.3 The usefulness of waste recovery in the context of the circular economy

Waste recovery plays a crucial role in achieving the goals of the circular economy and sustainable development. It helps to conserve natural resources, reduce pollution and save the energy needed to extract and process new raw materials.

### 1.3.1 Economic Advantages

Waste recovery has multiple economic benefits. First of all, it helps to generate income by commercializing recycled materials and creating new industries and jobs. Investments in advanced waste processing technologies can increase economic competitiveness and reduce dependence on external resources.

### 1.3.2 Environmental Advantages

The environmental benefits of waste recovery are significant. By reducing the amount of waste going to landfill and reducing the need to extract raw materials, emissions of greenhouse gases and other pollutants are reduced. Processing mineral waste and transforming it into reusable materials helps to reduce industry's carbon footprint and protect fragile ecosystems. This plays an important role in combating climate change and promoting a healthier and more sustainable environment.

### 1.3.3 Social Benefits

The social impact of waste recovery is also considerable. Creating new jobs in waste recycling and processing industries can help reduce unemployment and stimulate local economic development. In addition, promoting equal opportunities and fair access to economic opportunities ensures a more even distribution of economic benefits and contributes to greater social cohesion. Waste recovery projects can support community development by providing necessary resources and infrastructure.

## 1.4. Mineral waste generation mechanisms

The generation of mineral waste is influenced by various industrial and port activities. This waste is often the result of material handling operations, such as loading and unloading of seagoing and inland waterway vessels. Determining factors include the adhesion of materials to operating equipment and the cleaning process of storage areas. Waste is generated by the contact of raw materials with various surfaces and is influenced by moisture, grain size, temperature, as well as magnetic and electrical properties of the materials. Studies show that material losses are within the permissible limits set by legislation, which indicates that these processes are managed efficiently.

## 1.5. Partial conclusions

The European Union prioritizes the processing of waste to improve quality of life and remove harmful elements from the environment. Specific approaches are necessary due to the diversity of waste.

Romania's accession to the EU requires compliance with strict environmental rules, including the recovery of mineral resources and waste reduction, to manage the planet's limited capacity to meet the demand for non-renewable resources.

The circular economy, as opposed to the linear economic model, minimizes waste by recycling products at the end of their life cycle, bringing benefits such as environmental protection, reduced emissions, and job creation.

The recovery of mineral waste is essential for the rational use of resources and environmental protection, and is applicable to various industries. The generation of mineral waste is influenced by factors such as material adhesion and atmospheric conditions, and losses are within the limits permitted by legislation.

The chapter emphasizes the need for the sustainable management of mineral resources, the implementation of the circular economy and the use of recycling technologies to protect the environment and achieve economic and social benefits.

# Chapter 2 - Characteristics of the waste landfill in the Port of Constanta

The main characteristic of the waste from the Port of Constanta is its mineral composition and the fact that it is a mixture of commodities specific to Romanian industry. It is composed of over 99% iron ore, coal, coke, bauxite and limestone. We can say that this type of waste is unique in the world, as it was obtained from the loss of bulk raw materials that were transported in the Port of Constanța and which are specific to the Eastern European industry, which is served by this terminal. Because of this, both the properties of ores and coal are of interest in this paper.

## 2.1. Location and volume of the waste landfill

The waste is deposited in Constanța municipality, in the port of Constanța, on the land of the operator Comvex SA, in the area called "Halda 5". The volumetry was carried out by Topominiera SRL.

The total volume of waste from both sectors obtained from the volume calculations performed is 196990.8 $m^3$ .

## 2.2. Specific properties of ores

The preparation operations that can be applied to useful mineral substances, depending on the desired results, are dependent on the physical, chemical properties and morphological characteristics of the mineral components.

## 2.3. Specific properties of coal

Knowledge of the physico-chemical properties of coal, together with its structural parameters, is of particular importance in determining the possibilities of valorization and utilization.

The physical and chemical properties of coals are dependent on their chemical composition and structure, or in other words on the genetic material and the conditions of carbonization.

## 2.4. Purpose of mineral and waste processing

Technical progress in the industrial and energy industries is closely linked to increased production of metals, non-metals and coal. The minerals extracted require physical and physico-chemical processing in order to be economically exploited.

Processing processes have become more sophisticated, with zero-waste technologies now utilizing the entire mass of extracted material, including previous waste. These processes include mechanical, physico-chemical and specialty methods.

## 2.5. The importance of processing

The importance of processing lies in:

1. Provide consumers with concentrates and products of appropriate quality for economic use and processing.
2. Ensuring the possibility for consumers to recover economically from deposits or landfills with low useful substance content.
3. Reduction of transportation costs of useful minerals from the supplier (mine, quarry) to the consumer (metallurgy, thermal power plants, etc.).

## 2.6. Processing operations and processes

The main purpose of mechanical processing is to separate the mineral constituents from an ore or coal from the accompanying tailings, the prerequisite being the individualization of the grains of the different mineral species to be separated. To this end, operations are carried out for the preparation of the material - *the shredding and classifying* - and for the separation of the minerals - the actual *concentration* - by various processes.

**Processing technologies** are the combination of all processing operations to produce one or more economically useful products. These techniques can be used at the same time to green industrial areas or processes.

## 2.7. Partial conclusions

The chapter analyzes the wastes from the Port of Constanta, focusing on the mineral composition and physico-chemical properties, including coal characteristics. The waste is composed predominantly of iron ores, coal, coke, bauxite and limestone, reflecting the specificity of the Eastern European industry. Their location is in the "Halda 5" area, with detailed measurements carried out by Topominiera SRL.

The chapter emphasizes the importance of chemical and mineralogical analysis in industrial preparation and beneficiation processes. It also highlights the benefits of mineral processing, such as improving product quality, reducing the consumption of fuel and leaching agents, and minimizing environmental impact. Processing helps to valorize deposits with low content of useful substances and to reduce transportation costs by storing sterile waste close to the mining sites.

In conclusion, the processing of mineral resources is crucial for modern industry, contributing to the quality of end products and protecting the environment. It details mechanical, physico-chemical and special processing processes and emphasizes the importance of integrating environmental considerations into industrial processes.

# Chapter 3 - Characteristics of the mineral waste in the port of Constanța

The mineral waste in the port of Constanța has been formed in about 25 years of operating bulk cargoes destined for industry in South-East Europe. The following waste generation mechanisms were identified:

**- Technological:** Due to the passage of goods through very long conveyor systems, bunkers, transfer points, etc.;

**- Natural:** Quantities lost in the case of pulverized materials, due to strong winds blowing the materials away during operation or storage; heavy or long-lasting rains dislodging quantities of materials from the storage piles, resulting in quantitative losses or even contamination by mixing different types and sorts of materials;

**- Other:** Due to measurements with high margin of error made for quantitative determination when unloading/loading vessels or barges during unfavorable weather (strong wind, waves);

## 3.1. Chemical composition of the material in the deposit

Following the analysis, it can be observed that iron oxides predominate with a concentration higher than 58%, resulting in a total iron content of about 41%, a value that makes it impossible to use it in the steel industry in its present state. However, by enrichment processes, it is possible to use the mineral in the iron and steel industry.

You can see that more than a quarter of the mass of the waste is lost by calcination. Based on the loss on ignition we can estimate that this is largely due to the fossil fuel content of the waste.

In this context, we can assess that the elements of importance in the valorization of the mixture of ores in the existing deposits may be iron in an iron ore concentrate, coal and coke in a mixture and bauxitic ore together with carbonate minerals.

## 3.2. Particle size composition

In order to determine the granulometry of the waste deposited in the Comvex Constanța premises, a representative sample was analyzed, which included the whole range of the component materials. The analysis was carried out on site, and the moisture content of the materials in the samples was approx. 5% .

## 3.3. Physico-chemical and granulometric characteristics of the material below 0.8 mm

The wet granulometric analysis shows that the fine fraction is found in a higher proportion in the material, about 32.58 % being below 0.056 mm, predominantly in this class is bauxite, about 45% of the total and the coarse classes are located in the coarse mass. The iron seems to follow the same distribution by grade, the lower content in the coarse grade being due to the entrainment of the carbonaceous material in this grade.

## 3.4. Preparation of samples for laboratory testing

Grinding was carried out on the one hand to reduce the size of the grains too large for the flotation process, to clean the mineral surfaces and to break up the concretions that remained at this level, and on the other hand to facilitate the access of the flotation reagents to come into contact with the minerals or other elements for their separation.

## 3.5. Determination of levigable parts PL- STAS 1934/3-72

Leachables are particles below 0.02 mm that are found either as dust between sand grains or as clay films around them. They are removed by wet sanding and sedimentation.

For materials with a high content of leachable parts, the washing is repeated until completely clear water is obtained. After washing and siphoning, the sandy part is dried at 105°C to constant mass.

## 3.7. Clearing and sedimentation tests

As the waste also contains a significant amount of material with a grain size below 0.125 mm, we considered it important to carry out a clarification and sedimentation test, as the physical separation processes that can be applied to this waste, such as gravitational separation and flotation, can only be achieved with the help of water.

Cleavage tests with Magnafloc (0.1% concentration) showed that, at a consumption of 0.4 ml/l, the material settled rapidly, but leachables remained present after 24 hours.

At a consumption of flocculating reagent of 1 ml/l, the water loaded with mineral suspensions, concentration 100 g/l, sedimented almost instantaneously, the turbidity of the clarified water being very low and the sedimentation rate very high.

In conclusion, it can be seen that the material behaves very well in the clarification and sedimentation tests. The sedimentation rate increases in direct proportion to the amount of flocculant used.

### 3.8. Partial conclusions

This chapter of the paper focuses on the characteristics of the mineral waste in the port of Constanta, accumulated over some 25 years of bulk cargo operations for industry in South-Eastern Europe.

In order to understand the chemical composition of the material in the deposit, 60 representative samples were taken from two sectors using an excavator. The chemical analysis of these samples was performed by X-ray spectrometry and the loss on ignition was carried out by Romcontrol SA, revealed the predominance of iron oxides, which account for over 58% of the composition.

The particle size composition of the waste was determined by particle size adapted methods i.e. on-site analysis. These analyses have shown that the fine fraction of the material predominates, with bauxite being predominant in this class, while the coarse grades are found in the coarse grades.

In the clarification and sedimentation tests, given the large amount of material with a grain size below 0.125 mm, it was demonstrated that the use of flocculants, in particular Magnafloc, can significantly improve the efficiency of the process. These trials revealed that the material behaves very well during clarification and sedimentation, with the sedimentation rate increasing in direct proportion to the amount of flocculant used.

The contributions made in this chapter relate to the identification and detailed analysis of the chemical and particle size composition of the mineral waste, the proposal of efficient methods for sample preparation and separation, and the evaluation of the use of flocculants in the clarification and sedimentation process. These contributions provide a solid basis for improving the management and valorization of the mineral waste in the port of Constanta, having a significant impact on industrial and environmental practices.

This chapter emphasizes the importance of these analyses and methods to develop effective waste reduction and recovery strategies, thus contributing to a more sustainable resource management in this industrial context.

## Chapter 4 - Procedures for the separation of mineral compounds from port waste

### 4.1. Introduction

By analyzing the large differences in the physical properties of these minerals constituting the waste from port activities, it is concluded that these minerals could be separated by physical processes such as gravity separation and flotation for the separation of fine coal fractions from hematite and bauxite (Nagaraj, 2005).

Iron ore concentrates must fall into two particle size classes for use in the iron and steel industry, have a maximum possible iron content, an alumina content of less than 5% and a loss on ignition of not more than 10%.

Coal and coke concentrates shall have a calorific value greater than 3000 Kcal/kg and an ash content as low as possible, but not more than 45%.

## 4.2. Gravitational concentration processes

The most effective processes for separating useful mineral substances from tailings are gravity separation processes. Of these, those that have applicability to port waste are: zetaizing concentration, helical trough concentration and hydrocycloning concentration.

## 4.4. Flotation concentration

Flotation is a method of concentration based on differences in the surface properties of minerals, widely used in the mining industry for non-ferrous metal ores. In Romania, about 80% of ores processed are concentrated by this process. The process involves grinding the ores to a fine size, mixing them with water to form a pulp and introducing air in the form of bubbles, supported by chemical reagents called frothers. The hydrophobic particles adhere to the air bubbles and form a layer of foam on the surface, constituting the flotation concentrate, while the hydrophobic particles remain in suspension and are discharged as sterile. The buoyancy of particles depends on their wettability, which is determined by their surface free energy: the lower the surface free energy, the better the buoyancy.

## 4.5. Magnetic focusing

Magnetic concentration or magnetic field separation is based on differences in the magnetic properties of the minerals to be separated. This process involves a number of complex phenomena, influenced by the physico-chemical characteristics of the minerals, the nature of the separation medium and the technical specifications of the magnetic equipment used.

The required magnetic field is generated by means of electromagnets or permanent magnets and is characterized by the magnetic field strength, denoted by H. The magnetic field strength at a given point is the force with which the field acts on a unit of magnetic mass. In the International System of Units (SI), the unit of measurement for magnetic intensity is ampere per meter (A/m).

## 4.6. Partial conclusions

Chapter 4 details the various physical concentration processes applicable for the separation of minerals from port waste, with particular emphasis on gravity separation and flotation.

In conclusion, it can be emphasized that the minerals present in port waste can be efficiently separated by physical methods, which allows the production of quality products that can be used in industries such as metallurgy and energy. Gravity separation and flotation are identified as the main applicable methods, each of them presenting both specific advantages and limitations.

Gravity separation is considered to be very effective for separating useful minerals from tailings, and processes such as sieving, helical trough concentration and hydrocycloning are described in this chapter.

Flotation, a process based on the differences in the surface properties of minerals, is widely applied especially for non-ferrous metal ores. The flotation process involves the formation of a slurry in which mineral particles adhere to air bubbles formed by chemical reagents and are subsequently separated in the froth layer.

Flotation reagents play a crucial role in this process and are categorized into collectors, frothers and modifiers, each with a specific role in facilitating mineral separation. Collectors increase the hydrophobicity of mineral particles, frothers stabilize air bubbles, and modifiers adjust the chemical conditions to improve the separation process.

In conclusion, the chapter emphasizes the importance of the correct use of physical concentration methods to valorize mineral waste and obtain high quality products for various industries.

# Chapter 5 - Methods of preparation and valorization of mineral compounds from waste such as those in the port of Constanta

In waste treatment, two main methods can be distinguished: neutralization, which involves taking waste out of the economic cycle, and recovery, which reintroduces waste back into the economy. For port waste, with a high content of useful mineral substances and a lack of sterility, the optimal method is the recovery of the mineral constituents.

In determining the concentration methods, the properties and particle size characteristics of the material are taken into account, tailoring the preparation and processing to the end use. The preparation operations involve determining the particle size characteristics to decide whether the material can be recovered directly or requires particle size separation to avoid similar particle size classes.

## 5.1 Determination and evaluation of particle size

The first step of the investigation is the determination of the particle size characterization, carried out by volumetric or symptometric classification for small particles. Particle size analyses are frequently performed with standardized sieves, using dry or wet methods and arranging the sieves in descending order of mesh size.

The material retained on each sieve and the material passing through the last sieve form the particle size classes, and their sizes are determined by the sieve mesh sizes. The results are plotted graphically and organized in a table, including sieve sizes, grain size ranges and quantities of material, to plot the grain size curves

## 5.5. Methods and technologies for the valorization of mineral compounds from wastes such as those from the port of Constanta.

By analyzing the mineral content, we can conclude that the recovery technology can be based on the technologies used to obtain the concentrates that make up the waste. We will briefly discuss the various methods of obtaining the minerals contained in the waste.

### 5.5.1. Coal preparation methods and technologies

Coal processing aims to obtain the desired grain size and high calorific value by removing inorganic minerals (shales, sandstones, carbonates, sulphides). The slag comes from the rock surrounding the coal bed or in the form of concreting. The processing depends on the physical and chemical properties of the raw coal and the suitability of the machine to the quality of the mineral.

### 5.5.2. Iron ore preparation methods and technologies

Magnetic separation, magnetizing roasting combined with weak-field magnetic separation, gravity methods and flotation are used in iron ore mineralogy. Strong-field magnetic separation is intended for ores below 3 mm, and magnetizing roasting followed by weak-field magnetic separation is used for weakly magnetic ores, although it is expensive. Stream washing is applied for clay ores, and sieving, dense medium separation and table concentration are common methods. Spiral concentrating is effective for fractions of 0.1-1.5 mm, and flotation is preferred for hematite because of lower costs.

### 5.5.3. Raw materials and technologies for cement manufacturing.

Because of the bauxite and limestone content and similar density, separating these compounds is difficult. However, the resulting material can be used in the building materials industry as a raw material for cement.

Cement is used in the preparation of high-strength mortars and concretes, obtained by burning a mixture of limestone and clay, adding siliceous, aluminous and ferrous substances for specific properties.

## 5.6. Partial conclusions

This chapter addresses two main methods for waste management: neutralization and recovery for reintegration into the circular economy. In view of the high content of useful minerals in port waste and the absence of tailings, the optimal method is the recovery of mineral constituents.

Waste concentration methods are based on particle size characteristics evaluated by standardized analysis. These analyses are essential for the choice of appropriate separation and concentration procedures.

The chapter also details the methods of material comminution, emphasizing the importance of this operation in reducing particle size and facilitating subsequent separation. Also presented are the theoretical foundations of separation based on the rate of fall limit velocity, providing an understanding of the physical processes involved.

Also discussed are methods for the valorization of recovered mineral compounds, such as coal preparation, iron ore and cement manufacture. Each method is analyzed in detail, including the technologies used and relevant technological flows such as the use of zeolization, magnetic separation and magnetizing roasting.

In conclusion, it emphasizes the importance of recovering mineral waste from the port of Constanta by efficient methods that reduce environmental impact and contribute to the circular economy by reintegrating it into industry.

# Chapter 6 - Sorting analysis of the waste from the Port of Constanta and the mineral waste processing plant

## 6.1. Waste composition in the Port of Constanta

The wastes in the port of Constanța are mainly mineral raw materials used by port operators and needed by Romanian industries. The complexity of their analysis stems from the mixing of chemical elements between different sorts, which makes it difficult to determine the exact composition by chemical analysis alone.

Analysis of the waste in the port of Constanta shows that it contains a varied mixture of useful minerals, influenced by the types and quantities of goods transported. This mix also reflects local industrial development. The main challenge is to efficiently separate the compounds in the mixture, an essential process to valorize the valuable mineral substances and transform the waste into a useful resource.

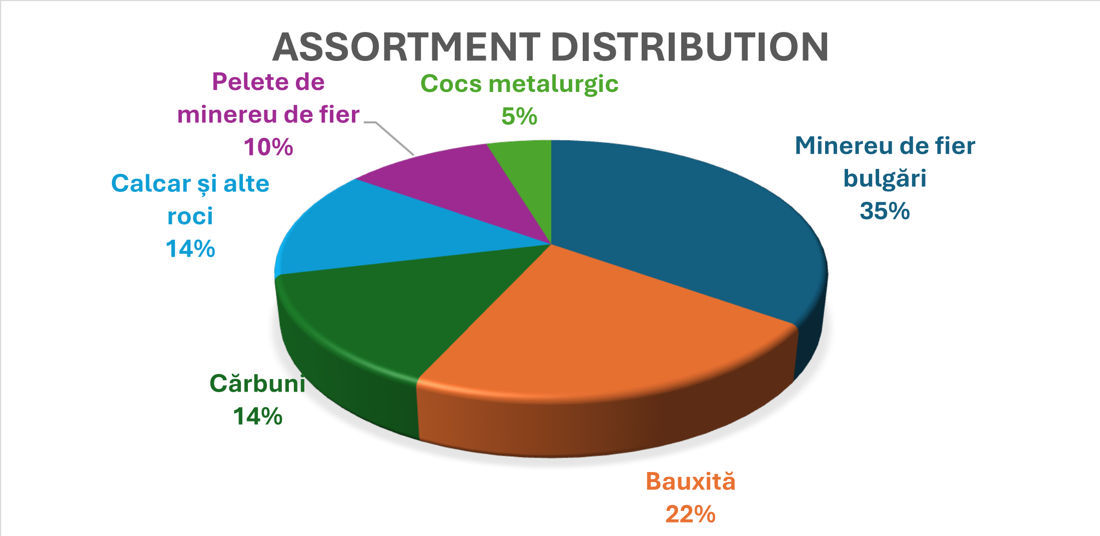


***Fig. 6.1*** *- Graph of the sorting distribution of waste in the Port of Constanta.*

Techniques such as physical sorting, gravity separation, magnetic separation and chemical processes are used to efficiently separate waste, each of which isolates and extracts the mineral components for further use.

Particle size analysis suggests:

- The 50-100 mm fraction can be cleaned of scrap iron and foreign bodies and is used in construction as an aluminous and carbonate material.

- The 6.3-35 mm and 0.5-6.3 mm fractions can be valorized by sieving to obtain iron and coal concentrates, and aluminous-carbonaceous products for the construction or cement industry.

- Material <0.5 mm undergoes flotation for coal extraction, and the remainder can be separated by flotation or concentration spirals for ores and bauxite.

## 6.2 . Mineral waste preparation technology flow

### 6.2.1. Extraction and handling of mineral waste

The mineral waste resulting from the cleaning activity and stored in specially designated areas undergoes the following operations:

- inspection of quantities by visualization, sampling, physical and chemical analysis;
- establishing a collection technology;
- loading waste into cars;
- transportation of waste to the pre-compounding I landfills in Halls 3 and 5;
- unloading waste in strings for pre-combining;
- the consolidation of waste in order to make the best use of landfill sites.

- foreign bodies are transported separately in specially designated areas, e.g.: stone > 100 mm is transported to the stone > 100 mm store;
- Where necessary, waste and transportation routes are wetted;

**6.2.2 Mineral waste preparation**

In order to ensure a stable composition in terms of mineral constituents, the mineral wastes (mixtures) obtained by greening (cleaning) carried out at the discharge front, along the conveyor system, in prestoc, pits and dispatch fronts are transported to the pre-homogenization warehouses (Pre-homogenization Warehouses I) of the workshops 1, and 2. The mineral waste processing plant consists of 2 components:

- *Workshop 1* - The mineral waste sorting and conditioning plant.
- *Workshop 2* - Mineral Waste Processing Plant (MWPP).

In these landfills, the waste undergoes foreign body removal and pre-homogenization operations.

From the pre-homogenization warehouses, materials are taken for processing using Workshop 1.

Figure 6.6 shows the technological scheme of the processing plant.

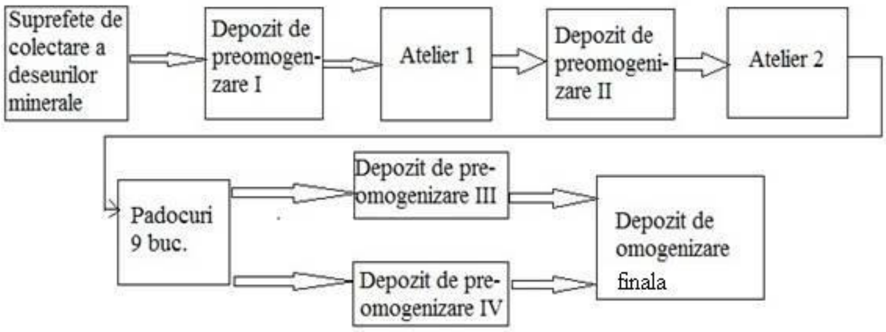


***Fig. 6.6*** *Technological scheme of the processing plant.*

Workshop I is fed by means of vehicles with the waste in the pre-homogenization deposit I, through a feed hopper (2), the flow is regulated by means of a vibrating feeder (3). The waste is taken up by a T1 belt conveyor (5) on top of which is mounted the magnetic extractor (6) which extracts the scrap iron contained in the waste and deposits it in the special paddock (17), the T1 belt conveyor feeds the CV1 vibrating sifter (7) equipped with 2 sieving planes, this separates the waste into 3 granulometric classes, class 0 - 35 mm will be the waste to feed Workshop 2, granulometric class 35 - 80 mm is taken by belt conveyor T3 (9) and feeds the crusher (11) where crushing is done to grain size <35 mm waste to be fed back to the plant. The grain size >80 mm is discharged.

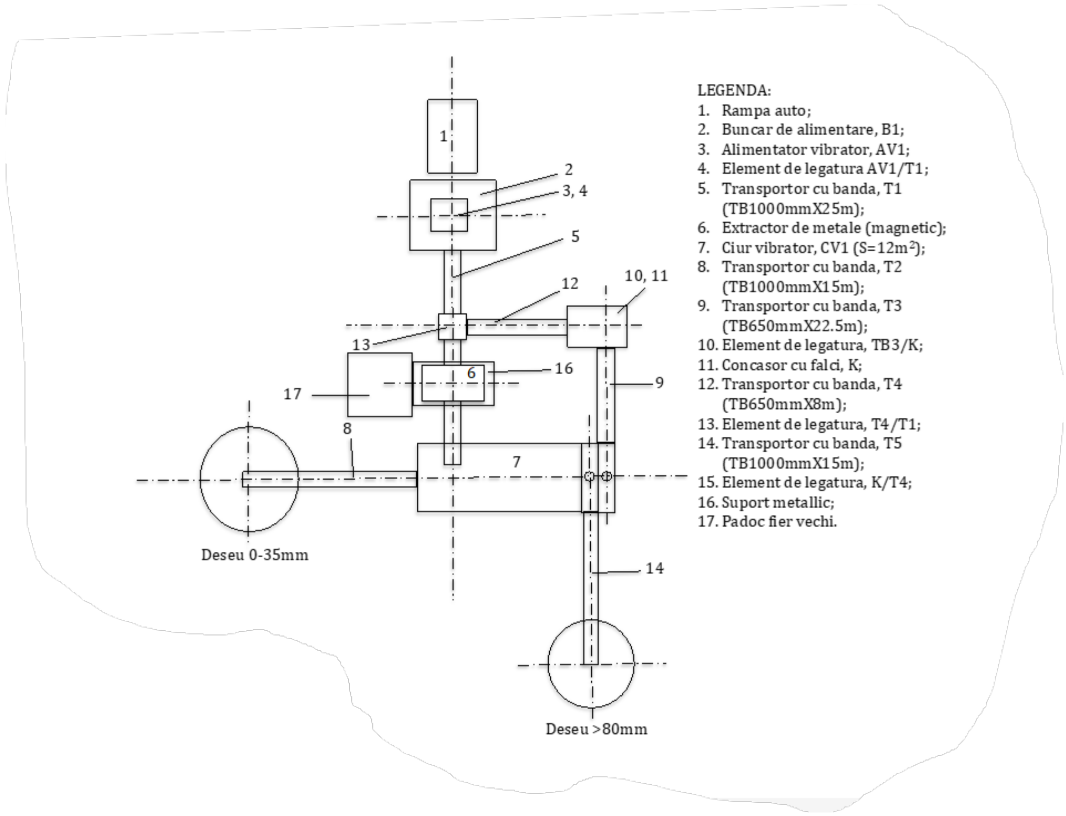


***Fig. 6.7*** *Technological scheme of the mineral waste sorting and conditioning plant*

The mobile sorting and crushing plant (Workshop 1) consists of: feed hopper, electro-magnetic scrap extractor, vibrating screen with 3 sieving planes, jaw crusher and belt conveyor

The following processes take place in Workshop 1:

- disposal of ferrous scrap metal;
- disposal of plastic, rubber, textile and vegetable waste;
- disposal of mineral waste with a grain size larger than 80 mm;
- crushing of mineral waste with a grain size between 35 mm and 80 mm;
- classification of materials into 2 - 3 particle size classes.

The obtained products are temporarily stored in another pre-homogenization warehouse (Pre-homogenization Warehouse II), where they undergo further homogenization operations.

All the work and equipment used in this first cleaning and crushing process make up Workshop 1.

## 6.3. Mineral waste processing plant

From the pre-homogenization deposit II, where there is a mixture of minerals, sort 0 ÷ 35 mm, the materials (the mixture of minerals) are fed into Workshop 2 - Mineral Waste Processing Plant (MWPP). Figure 6.8 shows the schematic of the technological flow of the Mineral Waste Processing Plant. The IPDM component equipment is presented in Table 6.2

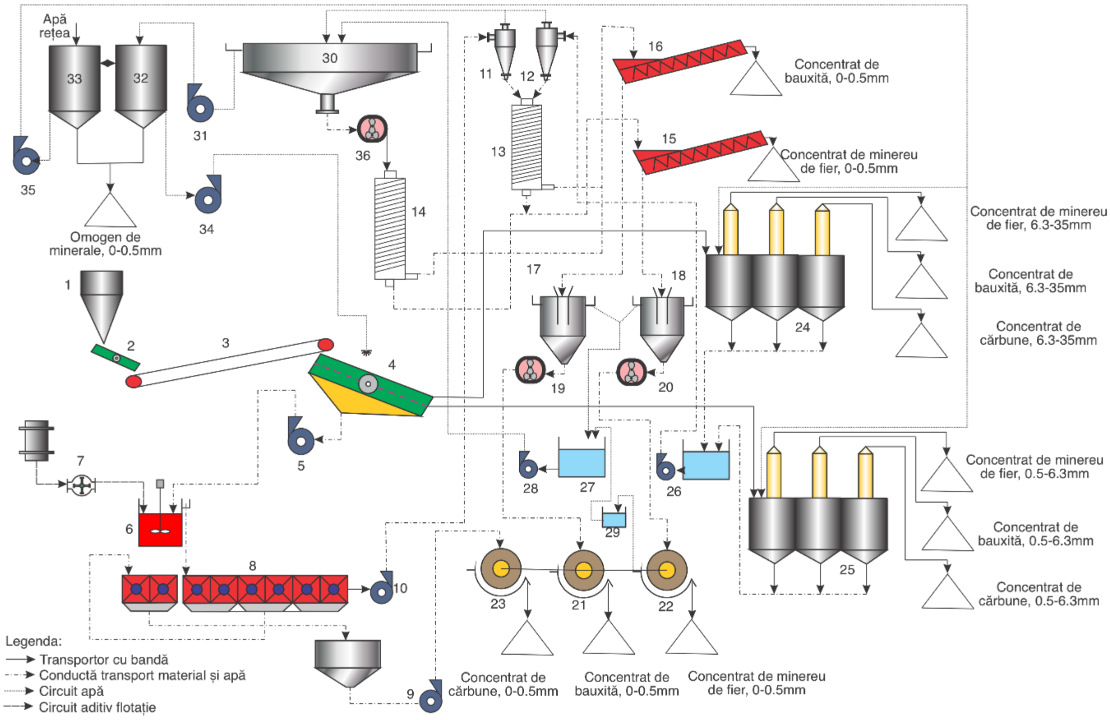


***Fig. 6.8*** *IPDM technology flow*

### 6.3.1 Description of the technological flow

The plant is fed by auto means through the hopper (1), the dosing of the waste stream is done by the vibrating feeder (2), the material flow is conveyed to the vibrating screen (4) by means of a conveyor belt (3). The vibrating sifter makes a particle size sorting and divides the waste into 3 particle size classes to be treated separately, the separation is a wet process and here the necessary process water is added to the tank (32) by means of a centrifugal pump (34). The separation of constituents from the waste mass is done by particle size classes due to the different behavior of the granules depending on their size. The particle size classes are:

**a. Particle size class 0-0.5mm.**

The fraction below 0.5mm together with the added water is picked up by the pump (5) and transferred to the agitator (6) to be conditioned with the flotation additive introduced via a dosing pump (7). From the agitator it enters the flotation machine (8) where the coal mixture is separated and transferred via centrifugal pump (9) to the filtration system (23) which extracts the water and discharges the "*Coal concentrate, 0 - 0.5mm*", the water resulting from the filtration process is collected in the collection basin (29).

The flotation machine reject is transferred by means of a centrifugal pump (10) to the hydrocyclone assembly (11) where a first separation of the water from the material is made to ensure dilution for processing on the concentration spiral (13). The water is transferred to the thickener (30) and the material is transferred to the concentration spiral (13).

The concentration spiral (13) separates the material into 2 sorts - "heavy" and "light", these 2 sorts enter the spiral classifiers (15) respectively (16) with the help of which 2 products with high sedimentation rate are extracted, namely "*Iron ore concentrate, 0-0.5mm*" and "*Bauxite concentrate, 0-0.5mm*".

The mixture of water and material with medium settling velocity is pumped into the 2 thickeners (18) and (17) where it settles, the overflow water, clarified, is transferred to the constant level basin (27). The 2 thickeners (18) and (17) provide the necessary dilution for the feed to be transferred via peristaltic pumps (20) and (19) to the filter assemblies (22) and (21) where the products "*Iron Ore Concentrate, 0-0.5mm*" and "*Bauxite Concentrate, 0-0.5mm*" are extracted. The water extracted from the filtration is collected in the collector basin (29) and pumped to the constant level basin (27).

The constant level basin (27) collects water and particles with high sedimentation velocity (leachables), the collected slurry is pumped by centrifugal pump (28) to the thickener (30). In the thickener (30) sedimentation of the leachable fractions takes place, this sediment is transported by the peristaltic pump (36) and reprocessed by the concentration spiral (14) which separates the sediment into 2 sorts - "heavy" and "light", these 2 sorts enter the spiral binders (15) respectively (16) where reprocessing takes place.

The clarified water in the thickener (30) is transferred by centrifugal pump (31) to the water tanks (32) and (33). The sediment from these tanks is extracted and is the product "*Mineral Homogen, 0-0.5mm*".

**b. Particle size class 0.5 - 6.3mm**

The waste separated granulometrically by the 0.5-6.3mm vibrating sieve (4) is transferred via a belt conveyor to the sieving machine (25). Sieving is the process by which gravity separation based on density occurs in a pulsating stream of water. The water required for the process comes from the reservoir (33) and is pumped by the centrifugal pump (35).

The sieving machine (25) separates the waste into 3 sorts " *Iron ore concentrate, 0.5-6.3mm*", " *Bauxite concentrate. 0.5-6.3mm*" and " *Coal concentrate, 0.5-6.3mm*". The recovered process water which may contain material particles smaller than 0.5mm is pumped by centrifugal pump (26) into the hydrocyclone assembly (12) where conditioning is performed to enter the 0 - 0.5mm fraction processing circuit.

**c. Particle size class 6.3 - 35mm**

The waste separated granulometrically by the vibrating screen (4) of grain size 6.3 - 35mm is transferred by a belt conveyor to the sieving machine (24). The water required for the process comes from the reservoir (33) pumped by the centrifugal pump (35).

The sieving machine (24) separates the waste into 3 sorts " *Iron ore concentrate, 6.3 - 35mm*", " *Bauxite concentrate, 6.3 - 35mm*" and " *Coal concentrate, 6.3 - 35mm*". The recovered process water that may contain material particles smaller than 0.5mm is pumped by centrifugal pump (26) into the hydrocyclone assembly (12) where conditioning is performed to enter the 0 - 0.5mm fraction processing circuit.

### 6.3.2. Components of the mineral waste processing plant

The construction data of the components of the mineral waste processing plant were established following research carried out and offered by various manufacturers on the basis of specific requirements.

The products obtained from waste processing have the physical and chemical qualities necessary to be reintroduced into the economic circuit. In Annex 1 are presented certificates of analysis for product sorts carried out by accredited surveyors.

The projected "processing" capacity of Workshop no.1 is 100 t/h, respectively 1400 t/day taking into account two shifts of 8 h/day of which 7 hours of operation on each shift, the rest of the time being allocated to the starting, stopping and maintenance of the machines.

Mineral waste processing plants do not all work at the same time, they are used depending on the processing needs of the waste.

## 6.4. Mass balance

The products obtained after treatment of mineral waste are:

*Iron ore concentrate*, *grain size 0÷6.3 mm*, moisture content approx. 10%, iron content min. 55%, used in the iron and steel industry, representing approx. 20% of scrap mass;

*Iron ore concentrate, grain size 6.3÷35 mm*, moisture approx. 8%, iron content min. 55%, used in the iron and steel industry, approx. 13% of scrap mass.

*Coal concentrate, grain size 0÷35 mm*, moisture approx. 10 %, calorific value approx. 5000 kcal/kg, ash approx. 20 %, representing approx. 30% of waste mass;

*Bauxite concentrate, grain size 0÷35 mm*, moisture approx. 10 %, Al2O3 content ca. 35%, used in the cement industry and in construction as an additive for fillers, approx. 30% of the waste mass.

*Mineral homogeneous, grain size 0÷0,5 mm*, moisture approx. 10%, representing approx. 5% of the waste mass, for this product further research is needed to determine its usefulness.

*Mineral wastes* (cod.19 12 12 09), rubber and plastic *wastes* (cod.19 12 12 04), ferrous waste (cod.19 12 12 02) etc. resulting from treatment, representing ca. 2% of the mass of waste.

The annual production is dependent on the working hours of the plant, meteorological factors (the plant cannot operate in negative temperatures, heavy rain, strong winds, etc.), market factors, amount of mineral waste, etc.

## 6.5. Environmental impact of the processing plant

Although significant amounts of water are used in the technological process, about 10% of the water used in processing is absorbed by the material and the remaining approx. 90% is recovered. Water is pumped through the process plant equipment.

There are no direct sources of soil pollution during the operation of the plant. There will be a positive impact during the operation of the mineral waste processing plant due to the greening of the area within the Ore Terminal belonging to COMVEX and the freeing up of significant areas of port territory that can be used for other purposes, areas or free spaces in the terminal area that are currently used for waste storage.

During the period of operation, there are no sources of air quality pollution, as the activity is sorting mineral waste in a process that does not result in emissions into the atmosphere above the permitted limit.

In Workshop 1, where sorting and crushing is carried out, the processes carried out do not produce emissions above the permissible limit as the mineral waste is wet. During dry periods, they will be wetted by mobile means.

The operation of the mineral waste processing plant generates noise and vibration sources that fall within the limits set by STAS 10009 / 1988.

The noise level from the operation of equipment (e.g. engines, crushers) is below the limits set in STAS 10009/1988 and this is constantly monitored.

## 6.6. Partial conclusions

In this chapter, a detailed analysis of the waste in the Port of Constanta was carried out, identifying the main materials such as iron ore, bauxite, coal and limestone. The sortational analysis was crucial for optimizing the use of resources and efficient waste management, facilitating informed decisions in the separation and recovery processes.

For the separation of mineral components, techniques such as physical sorting, gravity separation, magnetic separation and flotation have been proposed, each applicable for different particle size classes. Processing facilities are essential in this context: Workshop 1 utilizes a mobile sorting and crushing plant, while Workshop 2 has advanced processing equipment including hoppers, conveyors, flotation machines and concentration spirals.

The study not only details the composition of waste in the port, but also provides solutions for its efficient management, promoting recycling and reuse of mineral resources, thus contributing to the economic sustainability of the steel, energy and construction industries.

# Chapter 7 - Research on the use and valorization of mineral homogenates

The only product from mineral waste processing that has no clear use is "Mineral Homogenate". Two directions of use can be identified: separation of mineral compounds by more advanced methods or its use in its current form

## 7.1. Research for the separation of mineral compounds by selective flocculation

A promising method for processing fine-grained iron ores is selective flocculation, which has been intensively studied in recent decades. It involves the use of a mixed slurry of iron ore and other materials (bauxite, coal, etc.) with particles smaller than 0.5 mm. Selective flocculation not only reduces the environmental impact, but can also contribute to the circular economy through waste recovery (Tammishetti, 2017). The aim of the research is to evaluate the efficiency of this method in separating iron ores from impurities, with the intention to implement it in waste processing plants.

### 7.1.1. Materials and methods

The residues from the Mineral Waste Processing Plant in the Port of Constanta were sampled manually, using 100 kg from a total of 100 increments. After mixing and homogenization, a representative sample of 5 kg was selected, referred to as "sample K". The sample was sieved to obtain three particle size fractions (K1, K2 and K3) and then subjected to magnet treatment to separate the magnetic and non-magnetic fractions.

Six samples were obtained for SEM-EDS and X-ray diffraction analysis: K1, K1M, K2, K2M, K3 and K3M. The reagents used were anionic polyacrylamide (PAM A100 0.1%) as flocculant, NaOH 0.1M as pH modifier, and SHMP 0.02 M as dispersant, with consumptions of 250 g/t and 80 g/t, respectively.

### 7.1.2. Sedimentation and flocculation studies

Natural and flocculant (polyacrylamide) sedimentation experiments were performed at a pulp density of 8% solids. Tests were carried out in a 500 ml beaker with 40 g dry sample in 500 ml distilled water, using 250 g/t PAM and 80 g/t SHMP dispersant, at pH=4, 6 and 10.5.

In order to determine the effect of reagents on decantation, initially tests were performed without reagents. Subsequently, all tests were performed at pH = 10.5, adjusted with 5% NaOH for visible dispersion.

The density of the raw sample was also determined: 2,279 g/cm3.

### 7.1.3. SEM-EDS and XRPD analysis

The SEM-EDS analysis of the unpolished polymineral aggregate - sample K, revealed the presence of grains with a maximum size up to about 400 micrometers. On the surface of most of the grains, agglomeration of small-sized powders of

There are mostly granules that represent some kind of composite composed of at least two phases, as well as granules that contain fine-grained particles of other phases on their surface. This is present in all fractions investigated, especially in K1. Such examples are significantly less represented in the smallest fraction, the grains are more homogeneous, which facilitated the identification of mineral phases.

In the light of the above observations, it is clear that the results of the mineralogical determination obtained by X-ray analysis of the tested material differ from the phases that could be determined by EDS analysis carried out as a point analysis.

X-ray diffraction analysis revealed the presence of magnetite in all magnetic fractions, while this phase was absent in the non-magnetic fractions, which was expected. Hematite, gibbsite and quartz are present in both fractions.

EDS analysis showed high and elevated carbon concentrations in all analyzed samples. Individual grains consisting mainly of carbon and oxygen were also observed. X-ray analysis determined that the phase corresponding most to amorphous matter is present only in sample K1.

In general, the mineralogical composition of coal mainly includes phases such as quartz, muscovite, kaolinite, carbonates (calcite, dolomite, siderite), oxides (magnetite, hematite) and pyrite, unless calcined. (Ritz, 2010)

The presence of quartz, hematite, magnetite, calcite, dolomite, dolomite, goethite and layered silicates as main phases that may correspond to the coal composition are confirmed by X-ray analysis, with the fact that sulfur-containing phases (e.g. sulfides) are missing in our samples. Gibbsite was also identified by this analysis, but its presence is unrelated to the coal composition described above.

The heterogeneous nature of the material is more visible after elemental EDS mapping.

### 7.1.4. Selective flocculation tests

In solid-liquid systems, the settling rate of solids is influenced by grain size and shape, fluid and solids density. Decreasing particle size reduces sedimentation velocity, which requires flocculation technique to accelerate the process, especially for fine particles.

The research aimed to use selective flocculation to maximize the percentage of iron oxide in the precipitate and to separate impurities in the preaplin. The reagents (dispersant and flocculant) that have performed well in previous studies for iron oxides were chosen.

At the same time, there is an increase in the content of other elements in the suspension (and hence a decrease in those in the sediment), this was one of the objectives of this research and which indicates the possibility of selective flocculation of iron ore from other impurities in such complex systems. Theoretically, the selective flocculation depends on many parameters, such as: particle surface chemistry, particle size distribution, degree of particle dispersion, polymer functional groups, etc.

## 7.2. Research on valorization of mineral homogenates in agriculture

The study of the mineral homogenate provides the basis for its rational use as fertilizer and amendment, with the aim of obtaining higher yields both quantitatively and qualitatively, in terms of increasing soil fertility, but also protecting the environment.

### 7.2.1. Metodology

In order to assess the applicability of the product as a fertilizer on agricultural soils, macro (N, P, K), meso (Mg, S, Na) and micro (Cu, Zn, Fe, Mn) elements as well as heavy metals were analyzed to determine the risks of accumulation in the soil.

The product has a low fertilizing potential in macroelements, with 0.32% nitrogen and below detection limit values for phosphorus, potassium and sulphur. The mesoelement concentration is 0.288% Mg and 0.026% Na. The organic carbon is 8.9% and the loss on ignition is 28.40%. Experiments on tailings pits, where there were coal residues, showed that in 2-3 years of cultivation, wheat and maize yields can increase due to the activation of coal by soil microorganisms.

Testing with HCl revealed that the micronutrients are low, allowing the application of high doses with low risk of accumulation in the soil. It is recommended to conduct further studies in vegetated pots and subsequently in experimental fields to assess product efficacy and environmental impact.

At ICPA, experiments were carried out in vegetative pots with 1.5 kg substrate/pot, varying the proportion of mineral homogenate (100%, 50%, 25%, 12.5%, 0%) and using NPK 15:15:15 mineral fertilizers (1 g/pot: 0.15 g N, 0.15 g P, 0.15 g K).

### 7.2.2. R esults obtained

A crop of wheat (*Triticum aestivum L.)* was sown on January 23, 2020 and sprouted on January 27, 2020. The crop was harvested on March 2, 2020. After oven-drying the harvested plant samples at 70°C, they were weighed, ground and analyzed for nitrogen, phosphorus and potassium content using the Kjeldhal method, colorimetric ammonium metavanadate assay and photometric flame assay, respectively. The methods of analysis used were SR EN ISO 20483/2007, PTL 20 and SR EN ISO 6869:2002, PTL 24, respectively.

Table 7.11 presents the results showing the influence of different rates of mineral homogenate with and without chemical fertilizers on dry matter yield in wheat. The data show the following.

**Table 7.11** - Influence of soil to mineral homogenate ratio with and without mineral fertilizer on dry matter yield of wheat.

| Sample No. | Composition | Dry mass (g/vas) | % | Mass difference |
|---|---|---|---|---|
| 1. | OM 100% | 0.352 | 74.26 | -0.122 |
| 2. | OM 50% + Sol 50% | 0.561 | 118.35 | 0.087 |
| 3. | OM 25% + Sol 75% | 0.491 | 103.59 | 0.017 |
| 4. | OM 12.5% + Sol 87.5% | 0.571 | 120.46 | 0.097 |
| 5. | Sun 100% | 0.474 | 100.00 | 0,000 |
| 6. | OM 100%+NPK | 0.530 | 111.81 | 0.056 |
| 7. | OM 50% + Soil 50% + NPK | 0.684 | 144.30 | 0.210 |
| 8. | OM 25% + Soil 75% + NPK | 0.803 | 169.41 | 0.329 |
| 9. | OM 12.5% + Soil 87.5% + NPK | 0.635 | 133.97 | 0.161 |
| 10. | Soil 100% + NPK | 0.706 | 148.95 | 0.232 |

- Dry matter production increases with increasing soil weight in the mixture.
- The mineral homogenate did not cause toxicity to the plants, the plants emerged and developed normally, with no visible toxic effects due to the product. The lower yields are due to the low organic matter and nutrient content of the mineral homogenate, but at least in the first growing cycle it shows no toxicity.
- The introduction of the mineral homogenate into the growing medium did not lead to phytotoxic effects.
- Fertilization has led to yield increases, which have increased with the share of soil in the mix.
- The obtained data allow us to assess that the application of homogeneous doses of 10-30 t/ha of minerals on agricultural land does not lead to the deterioration of the agricultural crop and is a method of integration of this product into the environment.
- Future research could lead to improved product characteristics and better product recovery, based on the idea that in nature nothing is useless and only the lack of knowledge at a given moment does not lead to the product's valorization.

The presented data show the influence of the homogeneous mixture of minerals with the soil, with or without fertilizers, on the nitrogen content of wheat leaves. The nitrogen values fall within the normal range of nitrogen content in wheat leaves in both fertilized and unfertilized versions.

Mineral fertilization increased the nitrogen values in wheat leaves in all variants of the homogeneous mineral and soil mixture. In both the fertilized and unfertilized variants, nitrogen levels were higher in the substrate consisting of 25% mineral homogeneous with 75% soil.

## 7.3. Partial conclusions

The mineral phases in the mineral homogenate, obtained from the port waste (sample K) in the settling pond in Constanta, are predominantly iron ore, coal and bauxite (gypsum).

EDS and XRPD analyses showed that the main granules contain up to 80% carbon and oxygen, while the smaller granules contain iron and oxygen. X-ray analysis confirmed the presence of quartz, hematite, magnetite, calcite, dolomite and goethite, but did not find sulfides. The gypsite identified is not associated with the coal composition.

Selective flocculation, using a commercial anionic polyacrylamide-based flocculant, was effective at pH 10.5, with an improvement in iron content after flocculation (34.18% overall and 41.38% for the -25+0 μm class), and Fe recovery of 90.43-94.24%. Extending the sedimentation time to 5 min was beneficial.

Impact assessment on wheat yield showed promising results with no phytotoxic effects. Yield increase was proportional to the amount of mineral homogenate and nitrogen values were normal. The highest phosphorus values were obtained with a participation of 12.5-25% of the mineral homogenate fertilized with NPK. However, the potassium content was low and variable. It is suggested to use the product together with NPK mineral fertilizers at 10-30 t/ha.

Future research will explore optimizing conditions for improving potassium content and will continue to evaluate long-term effects. Preliminary studies indicate that mineral homogenate can be a valuable addition to the crop substrate and can contribute to increased crop production and environmental protection. In the field of mineral processing, selective flocculation has demonstrated that the separation of iron from impurities is possible, promoting circular economy and reducing environmental impact.

# Chapter 8 - Contributions and conclusions

## 8.1. Final conclusions

The paper analyzes the mineral composition and physico-chemical properties of waste from the Port of Constanta, essential for industrial processing and valorization. It details the chemical and mineralogical analysis, including density, moisture, color, color, luster, magnetism and electrical conductivity of the waste, relevant for classification and concentration. It also examines cohesive properties such as hardness, cleavage and grain size, and emphasizes the importance of the petrographic composition and degree of incarbonization of the coals, including optical, electrical and magnetic properties.

The paper highlights the optimization of processing methods, the shift from simple technologies to complex technological flows and the importance of greening affected areas. It details mechanical, physico-chemical and special processing procedures, and presents chemical analyses showing the predominance of iron oxides and fossil fuels. The particle size composition of the waste and the effectiveness of flocculants, such as Magnafloc, are discussed for the development of effective waste minimization and recovery strategies.

The rigorous methodology used includes mechanized sample collection, homogenization, and physical and chemical separation, emphasizing the importance of assortment analysis for resource optimization. Separation techniques are proposed and the necessary processing facilities are presented, promoting recycling and reuse of mineral resources. In conclusion, the paper provides efficient and sustainable solutions for the management and valorization of mineral wastes, supporting industrial and environmental practices...

## 8.2. Personal contributions

Mineral waste processing methods have been proposed that reduce the consumption of fuel and leaching agents while minimizing environmental impact. Transportation costs are also reduced by storing sterile waste close to the mining sites.

Significant contributions from some 25 years of operation in the Port of Constanța are presented, including waste generation mechanisms and a strategic approach to waste management. An original process for the recovery of reusable mineral materials and the importance of shredding for further separation is described.

The recovery methods examined include coal preparation, iron ore and cement manufacture, emphasizing the contribution to the circular economy and the reduction of environmental impacts. Detailed sortal analysis identifies and quantifies the main constituents of waste.

It was also studied the possibility of economic valorization of deposits with low content of useful substances, their processing allowing to obtain quality mineral products. The theoretical results have been validated through publications and conferences, and their applicability has been demonstrated at the processing plant in the Port of Constanta, which has been operating in optimal parameters since 2019. The research included the optimization of the plant to meet the required quality standards.

## 8.3. Future research directions

Research on the mineral homogenate of port waste showed the presence of a mixture of iron ore, coal and bauxite. Selective flocculation has proved effective for mineral separation, but further research is needed to produce industrially usable materials.

The impact of the mineral homogenate on crop production has been evaluated, indicating that it has no phytotoxic effects on wheat plants and may even increase crop yield. This suggests directions for further research to optimize its use.

The overall contributions highlight the importance of selective flocculation and the use of mineral homogenates in agriculture, promoting circular economy and reducing environmental impacts.

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