UNIVERSITY OF PETROSANI
DOCTORAL SCHOOL

PhD field: Mines, Oil and Gas

THESIS

SUMMARY

Critical analysis of contaminated sites resulting from mining activity, with an example in the closed mining perimeters in the Jiu Valley

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CONTENTS OF THE DOCTORAL THESIS

KEYWORDS

Soil contamination, contaminated site inventory, mining, waste dumps, heavy metals, degree of contamination, phytoremediation.

The doctoral thesis entitled "***Critical analysis of contaminated sites resulting from mining activity with an example in the closed mining perimeters of Jiu Valley***" falls within the fundamental field of Engineering Sciences as well as the doctoral field of Oil and Gas Mines, the field of scientific competence of the doctoral supervisor, Mr. Prof. Univ. Dr. Eng. Radu Sorin Mihai.

In Romania, research on the analysis of contaminated sites is a field under development and implementation. So, at the moment, the National Environmental Protection Agency does not provide accurate data on the sites contaminated by mining activities. In the process of harmonizing national policies with those of the European Union and transposing and implementing EU rules and regulations, the problem of surface water, soil, and groundwater pollution is one of the fundamental aspects of environmental protection that must be treated responsibly by all participants in this process.

In the framework of the doctoral thesis, the main purpose of the theoretical and experimental research concerns the realization of a critical analysis of the contaminated sites resulting from the mining activity, exemplified in the closed mining perimeters of the Jiului Valley and their phytoremediation solutions.

The need for the work is consistent with the National Strategy and the National Action Plan for the management of contaminated sites and will address issues related to soil contamination as a result of industrial activities carried out on mining sites to eliminate or limit (potential) risks for human health and the environment.

The data obtained from the analysis of the soil taken from the contaminated sites in the area of the Jiu Valley coal basin will be able to be integrated into a database with the inventory of the contaminated sites at the local and regional level.

The work includes four specific objectives, respectively:

Objective 1: Inventory of contaminated sites at international, national, and regional levels;

Objective 2: Evaluation of the degree of contamination of the soil collected from the inactive tailings dumps in Jiu Valley;

Objective 3: Remedial measures and management of sites contaminated with heavy metals;

Objective 4: Solutions tested in the laboratory regarding the phytoremediation of tailings dumps in the Jiu Valley.

The present paper is structured in six distinct chapters, each addressing essential aspects of the problem of contaminated sites, followed by a series of conclusions, own contributions, suggestions, and recommendations, and at the end, the bibliography used for the documentation and elaboration of the thesis. In what follows, I have made a brief review of the six chapters in the structure of the thesis.

In **CHAPTER I**, entitled **GENERALITIES REGARDING THE CONCEPT OF CONTAMINATED SITES**, we have addressed in detail the definition and classification of contaminated sites, as well as the methodologies used for their assessment and remediation. We started by defining contaminated sites as those locations where the soil, groundwater, or other elements of the environment have been negatively affected by the presence of hazardous substances resulting from various industrial activities. The classification of these sites was made based on the type and degree of contamination, the source of the pollution, and the potential risk to human health and the environment.

Next, we detailed the procedures and criteria used in evaluating contaminated sites, emphasizing the importance of preliminary assessments and detailed investigations. These assessments are essential to determining the extent of contamination and prioritizing the necessary interventions.

In addition to the technical aspects, this chapter also highlighted the international legislative framework governing the management of contaminated sites. We reviewed a number of policies and regulations adopted by international organizations, such as the European Union and the United States Environmental Protection Agency, which set strict standards for the prevention and control of environmental contamination. These regulations not only impose legal obligations on responsible industries but also provide guidelines for implementing best practices in the assessment and remediation of contaminated sites.

Therefore, this chapter provides a comprehensive basis for understanding the complexity and importance of managing contaminated sites, emphasizing both theoretical, practical, and legislative aspects.

In **CHAPTER II**, titled **GENERAL CHARACTERISTICS OF THE CARBONIFEROUS BASIN OF THE JIULUI VALLEY**, I structured the information in such a way as to provide a comprehensive and detailed picture of the area of the studied area. This chapter is dedicated to analyzing the different geographical and climatic aspects of the Jiu Valley in order to better understand the natural context in which the coal basin is located and to substantiate further studies on the impact of industrial activities in the area.

In the first subchapter, I detailed the relief and geology of the Ji Valley. The Jiu Valley is characterized by a varied relief, with mountains, hills, and deep valleys that influence the distribution and accessibility of mineral resources. The geological structure is complex, consisting of various types of sedimentary, metamorphic, and igneous rocks, which contribute to the wealth of coal resources in the area. The geological analysis also includes information on the main coal formations and the geological conditions that favored the accumulation of these resources.

The next subchapter is dedicated to climate data, where we present information on temperature, precipitation, evapotranspiration, and the wind regime. The climate in the Jiu Valley is temperate-continental, with significant temperature variations between seasons. We have included statistical data on average annual temperatures, thermal extremes, and the seasonal distribution of precipitation. We also addressed the phenomenon of evapotranspiration, which is essential for understanding the water balance and water availability in the soil.

The wind regime and prevailing wind direction are also analyzed in this chapter. The winds in the Jiu Valley have a significant impact on the dispersion of atmospheric pollutants and on the local microclimate. The data collected indicate prevailing wind directions and average annual speeds, providing a basis for assessing air pollution risks.

The hydrography of the Jiu Valley is another essential component of this chapter, where we have described the main watercourses, rivers, and streams that run through this area.

Finally, we analyzed the soils found in the Jiu Valley, providing information on the types of soils, their structure, and their chemical and physical composition. We included data on soil fertility, water holding capacity, and vulnerability to erosion. These characteristics are essential for land use planning and the implementation of remedial measures in areas affected by mining activities.

Thus, this chapter provides a detailed and integrated description of the natural features of the Jiu Valley Coal Basin, providing a solid context for analyzing the environmental impact of industrial activities and developing remedial and conservation strategies.

In **CHAPTER III**, entitled **THE INVENTORY OF CONTAMINATED SITES AT THE INTERNATIONAL LEVEL**, we carried out a broad and detailed analysis of contaminated sites globally, focusing specifically on the situation within the European Union. This theoretical research was aimed at identifying and quantifying contaminated sites, as well as evaluating their remediation status.

In the first part of the chapter, I presented the methodology used to collect and analyze data on contaminated sites. We used a variety of sources, including official reports from environmental protection agencies, academic studies, and international databases. This approach allowed us to obtain as complete a picture as possible of the number and geographical distribution of contaminated sites.

We have identified an impressive number of 85,000 contaminated sites within the European Union, resulting from various industrial activities such as chemical, metallurgical, ore extraction and processing, waste disposal, and many others. These activities have resulted in the contamination of soil, groundwater, and other environmental components, posing significant risks to human health and ecosystems.

A significant portion of these contaminated sites have already been remediated or are in the process of being remediated, thanks to the sustained efforts of national governments, international organizations, and the private sector. We discussed the various remediation techniques and strategies applied, which include physical, chemical, and biological methods. We also highlighted the importance of risk assessment and prioritization of interventions according to the severity of the contamination and the potential impact on the environment and public health.

Next, we compared the remediation policies and practices adopted in different countries and highlighted examples of success as well as challenges encountered in the process of remediating these affected sites.

The chapter concludes with a discussion of the importance of international cooperation and the exchange of best practices in the management of contaminated sites. We emphasized the need for coherent policies and adequate funding to effectively address the issue of contaminated sites globally. I also mentioned the essential role of education and public awareness in promoting sustainable and environmentally responsible practices.

Thus, this chapter provides a comprehensive perspective on the state of contaminated sites internationally, highlighting both the progress made to date and the remaining challenges in their management and remediation. This analysis constitutes a solid basis for the development of effective strategies to protect the environment and promote sustainability.

In **CHAPTER IV**, entitled **INVENTORY OF CONTAMINATED SITES AT THE NATIONAL AND REGIONAL LEVEL**, we analyzed in detail the current situation of contaminated sites in Romania, both at the national and regional level. At the national level, a total of 210 contaminated sites were inventoried, each with different origins. Hunedoara County was identified as having the largest number of contaminated sites, with a total of 41 affected sites, reflecting a complex industrial history.

Regarding the research carried out at the regional level, I focused on the area of Jiu Valley, which has a long tradition in the exploitation of mineral resources. The current study of the mining activities in Jiu Valley has revealed the existence of 14 mining operations over time, of which, currently, only two mining operations still extract the useful mineral substance, respectively Vulcan and Livezeni, and the other two mining operations, Lupeni and Lonea, are in the process of closing, reflecting an industrial transition and a change in the economic dynamics of the region.

A significant part of my research focused on the inventory of tailings generated by these mining operations. From the 14 mining operations, we identified a total of 49 tailings dumps. The analysis of the status of these dumps showed that 51.03% were greened, 18.36% are still active, and 30.61% are inactive.

In my PhD thesis, I focused specifically on inactive tailings dumps. These dumps can pose a significant long-term hazard to the environment and human health if not properly managed and remediated.

Therefore, this chapter provides a detailed perspective on the state of contaminated sites in Romania, with an emphasis on sites resulting from the mining activity carried out in the Jiu Valley. This chapter emphasizes the importance of proactive management and well-planned interventions to protect the environment and public health, contributing to a safer and more sustainable future for communities affected by mining activities.

In **CHAPTER V**, entitled **ASSESSMENT OF THE DEGREE OF SOIL CONTAMINATION COLLECTED FROM INACTIVE STERILE LANDFILLS IN**

THE JIU VALLEY, research was carried out on the 14 inactive waste dumps, resulting from mining activity, located from west to east in the Jiu Valley.

One step was to create a map of the surfaces to be analyzed. According to Ministerial Order No. 184/1997 (for the approval of the Environmental Assessment Procedure), 17 sampling points were established.

The first campaign to take soil samples from the tailings dumps was carried out in June 2022, and the second in 2023 in the same month.

Soil samples were taken in accordance with the requirements and provisions of the standard (STAS 7184/1:1984). The soil samples were subjected to chemical analyses in the Environmental Laboratory of the University of Petrosani, resulting in excesses in all analyzed samples of the normal concentrations allowed in the soil (Order 756/1997) of several heavy metals. It was found that heavy metals such as (Cr (total), Cu, and Ni) were identified in the tailings dumps from the western part of the Jiu Valley, and heavy metals were identified in the eastern part (Cr (total), Cu, Ni, Zn, Co, and Pb);

In order to capture this contamination as faithfully as possible, the degree of contamination of the soil taken from these tailings dumps was determined by five dedicated methods, as follows:

I. The geoaccumulation index (I_{geo}) method for heavy metals consisted of using the values determined at the 17 sampling points from the inactive tailings dumps in the period 2022–2023. The calculations showed that the level of pollution caused by the tailings falls within the range of 0-1, which indicates to me an unpolluted to moderately polluted soil. The highest values of the geoaccumulation index were identified for Ni on the waste heaps Old Funicular-Uricani, Block 0 - Lupeni, and Defor - Petrila, which exceeded 0.80, thus falling into the level 0-1 class.

II. Contamination factor (FC) method: by means of this method, the contamination index (IC) was initially calculated for each heavy metal present in the soil samples. From the studies carried out in the 2022-2023 period, the highest values were at: Cr (total) on the tailings dump Well 7 Vest (old dump) - Vulcan, with the highest value recorded on the tailings dump Old Funicular - Uricani, and for Ni, Zn, and Co, the highest values were recorded on the tailings dump Branch 1, 2, 3, and 4 - Petrila;

III. The total contamination factor method (FCT) was a method that allowed the normalization of the contamination index values for each heavy metal. The calculations showed that the waste dump Old Funicular - Uricani has a total contamination factor of 2.69 in the study year 2022 and slightly higher than 2.82 in the study year 2023.

IV. The Pearson correlation coefficient method is a method that allows us to determine if there is an association between the concentrations of heavy metals in tailings samples from various sampling points of the dump. It was found that, during the two-year study period, when the concentrations of Zn, Co, and Pb are high in the sterile material, the concentrations of heavy metals Cu and Cr decrease, which indicates that there are interactions between them that can lead to the formation of compounds that are insoluble or to their absorption on soil particles, which reduces the availability of other elements.

V. The method of isolines of concentrations of heavy metals in the soil is a method used to draw contour lines in order to join the points of the same concentration of a heavy metal, which led to the creation of maps that show us the geographical distribution of pollutants. After drawing the isolines, the percentage of variation was calculated, which is essential for the analysis of the concentration isolines. This method provides a clear and quantifiable determination of changes in heavy metal concentrations in soil. Using this method, I found that the values of heavy metal concentrations in the study year 2023 change on the influence surface at the level of the plateau, which indicates to me a high mobility of these heavy metals, which can be caused by: pH, vegetation, microbial activity, processes of oxidation of the sterile material, precipitation, and infiltration of water into the body of the dump. All these factors contribute to the dissolution of chemical compounds, favoring the mobility of heavy metals;

The use of the five methods for evaluating the ***degree of contamination (GC)*** of the soil with heavy metals led to the identification of waste dumps that affect the soil as a result of the storage of the waste material. Thus, the Old Funicular - Uricani Tailings Dump and the Branch1, 2, 3, and 4 -Perila Tailings Dump were identified in the western part; they have a much higher degree of soil contamination compared to the other tailings dumps that are inactive.

Within **CHAPTER VI**, entitled **MEASURES FOR REMEDY AND MANAGEMENT OF SITES CONTAMINATED WITH HEAVY METALS**, the fastest phytoremediation methods, namely phytostabilization, phytoextraction, and phytodegradation, were analyzed among the multitude of measures for remediation and management of sites contaminated with heavy metals and phytovolatilization. These techniques involve the use of plant species capable of remediating soils contaminated with heavy metals through different mechanisms.

To test the effectiveness of these methods, plant species with specific phytoremediation capabilities were selected. Two main methods were applied in the laboratory: phytostabilization and phytoextraction. Three species of plants with different soil decontamination capacities were chosen: hyperaccumulating plants, phytostabilizing plants, and phytoextracting plants.

Thus, 27 pots of vegetation were prepared, in which soil taken from the Old Funicular - Uricani Tailings Dump , soil taken from the Branch 1, 2, 3, and 4 tailings dump - Petrila and control sample soil were placed. These two tailings dumps were selected due to the differences in heavy metal content between the western and eastern parts of the Jiu Valley mining basin.

Native plants were chosen to be able to grow near these mine tailings deposits, taking into account the limiting, ecological, and vegetation factors. The selected hyperaccumulating plants were calendula (*Calendula officinalis*), marigold (*Alyssum spp.*), and violet (*Viola calaminaris*). The phytoextracting plants chosen were: lupine (*Lupinus spp.*), St. John's wort (*Hypericum perforatum*), mustard (*Brassica spp.*), and the phytostabilizing plants chosen were: clover (*Trifolium spp.*), millet (*Panicum miliacum*), and wheat (*Triticum aestivum*).

The results of the experiment showed that, in the soil of the Old Funicular - Uricani Tailings Dump, the mustard phytoextractor plant (*Brassica spp*.) developed optimally. In the soil on the tailings dump Branch 1, 2, 3, and 4 - Petrila, the plant had good development, and in the control soil, a single specimen emerged. The same behavior was observed for the phytostabilizing plant wheat (*Triticum aestivum*). The millet plant species (*Panicum miliacum*) did not emerge in any of the pots. The other plants sprouted but did not develop as well as those previously mentioned.

The critical analysis of the results indicated that the phytoremediation method can be adapted according to the specifics of each landfill body, taking into account the concentration of heavy metals and the vegetation and limiting factors of the plant species used.

Thus, the phytoremediation of tailings dumps from the Jiu Valley mining basin proves to be an effective and economical method, especially in the context of the lack of an ecological rehabilitation strategy after the cessation of mining activities. This can lead, over time, to the stabilization and removal of heavy metals from the environment, thus contributing to the reduction of risks to human health and the environment.

Following the research activities carried out as part of the doctoral thesis with the title "*Critical analysis of contaminated sites resulting from mining activity, exemplified in the closed mining perimeters of Jiu Valley*" **the final conclusion** was drawn according to which the waste heaps resulting from the mining activity carried out in the Jiu Valley constitute a significant danger to human health and the environment. Although the concentrations of heavy metals in the analyzed soil samples do not directly reach the alert thresholds established by the regulations in force, the age of the dumps and their specific conditions contribute to the increase in the mobility of these metals.

Over time, the processes of oxidation, erosion, and other natural mechanisms can facilitate the migration of heavy metals, thus increasing the risk of contamination of soils and waters in adjacent areas. This potential migration of contaminants underscores the need to implement rigorous monitoring and management measures at these sites to prevent long-term negative effects on the environment and human health.

As a result of the research carried out during the doctoral studies, ***the following personal contributions were made***:

- ✓ identification of tailings dumps in Jiu Valley;
- ✓ mapping inactive tailings dumps;
- ✓ taking soil samples from the 14 inactive tailings dumps;
- ✓ determination of heavy metals in soil samples in the Environmental Laboratory of the University of Petrosani;
- ✓ determination of the degree of heavy metal contamination of the soil using five established methods, namely: the geoaccumulation index method (I_{geo}), the contamination factor method (FC), the total contamination factor method (FCT), the Pearson correlation coefficient method, and the concentration isolines for heavy metals in the soil;

- ✓ analysis of the variation in the degree of contamination for two years of study (2022-2023);
- ✓ identification of the ecological, limiting, and vegetation factors of the plants that will be used in the phytoremediation techniques, namely: phytostabilizing, phytoextracting, and hyperaccumulating plants;
- ✓ identification and laboratory testing of plant species suitable for use in the phytoremediation method;
- ✓ proposed methods of phytoremediation of tailings dumps studied in order to reduce the concentrations of heavy metals in the soil.

Proposals and recommendations were formulated:

1. ***Systematic monitoring and mitigation:*** Considering the concentrations of heavy metals (total Cr, Cu, Ni, Zn, Co, and Pb) that exceed the permitted limits in the soils of the tailings dumps studied, the ecological status of these areas is potentially endangered. Since the environmental risks associated with mining activities do not disappear with their termination, but on the contrary, they can increase in the absence of systematic control and monitoring, it is recommended to constantly monitor and remediate these tailings dumps.
2. ***Use of phytoremediation technology:*** For the isolation of heavy metals from tailings dumps, it is recommended to use the phytoextraction method with mustard (*Brassica spp.*). It has proven effective in laboratory experiments and has a high potential for extracting heavy metals from soil. Also, the wheat species (*Triticum aestivum*) could be suitable for the immobilization of heavy metals due to its phytostabilizing properties.
3. ***Experimental implementation in field conditions:*** To validate the effectiveness of the experimental phytoremediation model, it is essential to implement these methods in real field conditions. Application of mustard and/or wheat phytoremediation should be followed by appropriate treatment of the plant biomass, including compaction, combustion, and gasification, processes that could generate electricity and heat.
4. ***Combined phytoremediation methods:*** Due to the fact that the heavy metal values in the studied soils do not exceed the intervention thresholds, a combined phytoremediation method can be used. Plants should be used in different proportions, depending on the level of contamination specific to each waste dump, its surface area, and the mobility of heavy metals.
5. ***Testing the suitability of plants for other sterile materials:*** It is recommended to test the suitability of the plants chosen for phytoremediation and for other types of sterile materials resulting from various industrial activities. This will allow the applicability of phytoremediation technology to be extended to other contexts.
6. ***Continuous monitoring of phytoremediation work:*** Continuous monitoring of phytoremediation work and the phytoextraction potential of the chosen plants is essential. Constant monitoring will ensure the efficiency of the process and allow the methods used to be adjusted according to the results obtained**.**

7. ***Further utilization of tailings dumps:*** After stabilization and remediation of tailings dumps, they could be further utilized in various ways, such as conversion to recreational areas, use in biomass production, agriculture, or animal husbandry. This would not only contribute to improving the environment but could also bring economic benefits to the local community.

The implementation of these proposals and recommendations will contribute significantly to the reduction of ecological risks and to the protection of human health, while ensuring a sustainable and beneficial use of the lands affected by mining activities in the Jiu Valley.

The bibliography is the final part of this scientific work, comprising an exhaustive list of authors and titles of cited books and articles published in specialized journals, as well as national and international reference standards and reports. These sources were cited throughout the text and formed the basis of the documentation carried out during the research. The bibliography provides a detailed picture of the specialized literature consulted and ensures the credibility and academic rigor of the work, while at the same time facilitating the verification and deepening of the information presented.