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Ph.D. thesis summary

Mineralogy and geochemical distribution of heavy metals from some mine tailings associated to Volcanic Massive Sulphide deposits in the Tulgheș metamorphic unit (Eastern Carpathians)

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INTRODUCTION

The doctorate thesis entitled “Mineralogy and geochemical distribution of heavy metals from some mine tailings associated to Volcanic Massive Sulphide deposits in the Tulgheş metamorphic unit (Eastern Carpathians)” is divided into 11 chapters and 2 Annexes, including 129 bibliographical references, from which 3 represent the author’s published work in ISI and B+ journals.

The study had as main objective to establish the degree in which mining can influence the quality of soils from the surrounding areas, both through acid mine drainage and the high contents of heavy metals. This was accomplished by investigating the mineralogy of the top stratum (0-20 cm) of the tailings and through establishing the way in which the heavy metals are distributed in specific environments.

For evaluating the environmental risk that the presence of the tailings and tailings ponds resulted from complex sulphide mining pose it is necessary to understand the way in which these elements are associated and distributed depending on the physico-geochemical parameters.

In order to determinate these parameters, the mineralogy and heavy metal contents, 145 samples were taken from various mine tailings which lay within three mining areas where important polymetallic sulphide deposits were exploited: Fundu Moldovei, Leşu Ursului and Bălan.

A major impact on the quality and composition of the soil from certain areas is caused by mining activities, excavations, treatment and processing the ore. These operations generate mine waste dumps (tailings) which usually contain, among other pollutants, significant quantities of heavy metals (Ionce, 2010).

Protecting the soils and keeping its functions unaltered for nature and human society represents one of the major concerns of modern day society.

Chapter I

GEOGRAPHIC AND GEOLOGICAL SETTING OF THE STUDIED AREAS

I.1. GEOGRAPHICAL LOCATIONS

The studied tailings are located in the areas of Fundu Moldovei, Leșu Ursului and Bălan

I.2. GEOLOGICAL CONTEXT OF THE TULGHEȘ LITHOGROUP

Kräutner (1988) divided the Tulgheș lithogroup into 5 formations, from Tg₁ to Tg₅:

- Tg₁ – blastodetrritical-quartzeous formation
- Tg₂ – mainly graphitic formation with black quartzites
 - inferior member
 - superior member
- Tg₃ – rhyolitical metasedimentary formation
 - Isipoaia member
 - Leșu Ursului member
 - Moroșan member
 - Fundu Moldovei member
- Tg₄ – blasto-detrritic-philitic formation
 - Bașca member
 - Pârâul Crucii member
 - Afinet member
 - Botuș member
 - Pângărați member
- Tg₅ – mainly graphitic formation, with green schistis and limestones

The metallic sulphide ore is hosted at the level of the Tg₃ formation, while the manganiferous mineralisations are associated to the black quartzites (Tg₂).

From the geological context point of view, all three studied areas belong to the Putna unit, Tulgheş lithogroup, which is widely spread in the Eastern Carpathians and which has been studied by many geologists because of the economic potential given by the polymetallic sulphide, manganese and barite mineralisations.

Chapter II

BRIEF HISTORY OF THE MINING ACTIVITIES IN THE STUDIED AREAS

The history of mining in the Suceava county, in which the areas of Fundu Moldovei and Leșu Ursului are located, begins way before the founding of the feudal state of Moldavia. For the Bălan area, documents from Sândominic show mining activities dating back to the 14th century A.D..

The Ottoman domination caused a downfall of the mining activities, after a period in which it quickly developed (between the 14th and the 16th centuries), reaching the point when, in the 18th century Moldavia was forced to import iron and copper from Transylvania and Banat (Maghiar and Olteanu, 1970).

In 1777, after the exploration of the underground resources in the Suceava county, the Iacobeni iron ore deposit was discovered, as well as the copper ore from Pojorâta, then the silver and lead from Cârlibaba and the pyrite from Fundu Moldovei. At the end of the 18th century, the Iacobeni mine is passed under Austrian administration.

Towards the end of the 18th century, the Bălan copper ore deposits begin to represent important resources for the Austrian-Hungarian Empire.

In 1805 the manganese, the pyrite deposit from Dealu Negru, village of Fundu Moldovei was discovered, as well as the rich ore from Valea Colbului, north-east of Pojorâta (Maghiar and Olteanu, 1970).

After 1918, the manganese from Iacobeni began to be exported in Czechoslovakia, Germany, Poland and Italy. During the Second World War, on the basis of the growing war industry, the mining of manganese, chalcopyrite and pyrite intensifies at Iacobeni and Fundu Moldovei (Maghiar and Olteanu, 1970). Fundu Moldovei is now among the 18 mining areas which have been declared as disfavoured zones, the lack of profit leading to a restructuring program in two stages: 1997-1999 and 1999-2007 (Vasilcu, 2004).

Chapter III
POLYMETALLIC SULPHIDE DEPOSITS ASSOCIATED TO THE
TULGHEȘ LITHOGROUP

The polymetallic sulphides mineralizations of the Tulgheș lithogroup are, according to Balintoni (1997) of Kuroko type, which has been described by Dimitrescu (1983) as stratiform deposits of massive sulphides, associated to the Miocene vulcanites and pyroclastites, from acid to intermediary, stacked in a shallow marine environment.

The main polymetallic sulphide deposits associated to the Tulgheș lithogroup (after Balintoni, 2010) are: Novăț-Novicior, Baia Borșa – Gura Băii, Baia Borșa – Burloaia, Baia Borșa – Dealul Bucății, Arșița-Botoșel, Fundu Moldovei, Valea Putnei – Prașca, Pârâul Colbului – Giumalău, Bașca – Izvorul Giumalău, Fagu, Leșu Ursului, Hărlăgia, Bălan and Fagul Cetății.

Chapter IV
LOCATIONS OF THE STUDIED TAILINGS

From the Fundu Moldovei area, the tailings of Dealu Negru, Prașca I and Prașca II were studied.

From the Leșu Ursului area, the tailings of Isipoaia, Pârâul Ursului – Puțul 7 and Pârâul Leșului were studied.

From the Bălan area, the tailings of Fagul Cetății – Iazul 4 and a concentrated ore mound close to the Izvoru Oltului Railway Station were studied.

Chapter V

SAMPLES AND ANALYTICAL METHODS

V.1. SAMPLING

For the present study, from the Fundu Moldovei, Leșu Ursului and Bălan areas, 145 samples were taken: 22 samples from Dealu Negru (series DNST), 4 samples from Prașca I (series P1ST), 5 samples from Prașca II (series P2ST), 20 samples from Isipoaia (series ISST), 20 samples from Pârâul Ursului – Puțul 7 (series PUST), 20 samples from Pârâul Leșului (series PLST), 50 samples from Fagul Cetății – Iazul 4 (series FCST) and 4 samples from the concentrated ore mound near the Izvoru Oltului Railway Station (series IOST)

The samples were taken by using a manual drill-type soil sampler, from a depth range of 0 – 20 cm, according to the methods described in literature (Borlan and Răuță, 1981; Clichici and Stoici, 1986; Florea et al., 1986).

V.2. PREGĂTIREA PROBELOR PENTRU ANALIZĂ

The tailings samples were dried in normal conditions for 3 days and then in the oven at 40-50°C. From the dry samples the vegetation was removed, then the samples were manually grinded in an agate grinder, afterwards in a Fritsch Pulverisette planetary mill, until a granulometric diameter of <0.01mm was reached. From the grinded and homogenized material, samples were taken for chemical and physic-chemical analysis.

V.3. METODE ANALITICE

For the study, a total of 145 samples were analysed through various methods. The heavy metals analysed by XRF were Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn, together with As and Fe.

The pH in aqueous and saline suspension as well as the redox potential were determined through the potentiometric method on all 145 samples. The heavy metal contents were determined by XRF on all 145 samples. The mineralogy was determined through XRD on 56 selected samples and the granulometry was studied through Camsizer on 5 selected samples.

Chapter VI

MINERALOGY OF THE STUDIED TAILINGS

The tailings generally had as main mineralogical components quartz, muscovite-illite, chamosite and albite, to which accessory minerals such as albite (in case where the material did not undergo preparation processes and the material was deposited in dry state), kaolinite and ankerite (at Pârâul Câinelui), chamosite – as main newly-formed mineral (in case of all the tailings, except Pârâul Câinelui) and sometimes pyrite (at the concentrated ore mount from Izvoru Oltului).

Through XRD in the studied samples, traces of feldspar, talc, calcite, chabasite, gypsum, hematite, microcline and possibly stilpnomelane, rectorite and anatase (only in few samples).

It was observed that jarosite is only present up to a pH of 5.25, and it is a major mineral component only up to pH 2.43. Similarly, gypsum appears at a pH of less than 6.48. Generally, jarosite and gypsum positively correlate, appearing in acid environments.

Ankerite only appears at pH higher than 4.02. A clear basophile behaviour is attributed to kaolinite, which only appears at $\text{pH} > 7.88$ in few samples of the Pârâul Câinelui tailings. Pyrite is associated to the acid domain, appearing only at $\text{pH} < 7.56$.

Chapter VII

GEOCHEMICAL DISTRIBUTION OF HEAVY METALS AT THE TAILINGS' SURFACE

As is distributed in high areas of the tailings, with very high average contents in case of the Isipoaia tailings (577.42 mg/kg). The high As contents were mainly associated to acid areas of the tailings and relatively high contents of Fe and Cu.

Co has low average contents in all tailings, up to 55.22 mg/kg and a relatively uniform distribution. Because of the low contents it cannot be stated whether it correlates with acid or neutral environments.

Cr has low contents, sometimes below detection limit and was mainly distributed uniformly, and on the slopes (Pârâul Ursului tailings). No association to any type of geochemical environment could be made, as it only correlates to Mn and Ni.

Cu has high average contents in all cases, up to 1285 mg/kg (Fagul Cetății tailings). It is distributed mainly in the high areas of the tailings, in acid and oxidating environments and is associated especially to Fe, Pb, As and Sn.

Fe has high average contents in all tailings, reaching 994466 mg/kg in case of the Isipoaia tailings. It was associated to the high areas of the tailings, to acid and oxidating environments and it had significant correlations with Cu, As, Pb and Sn.

Mn has average contents of up to 893.28 mg/kg (Fagul Cetății tailings) and is associated to Ni and Cr, as it is distributed mainly towards the slopes and base of the tailings, in slightly acid to neutral environments.

Ni has very low average contents, sometimes below detection limit, reaching a peak of 25.95 mg/kg in case of the Pârâul Ursului – Puțul 7 tailings. Where a distinct preferential distribution could be observed (Isipoaia and Pârâul Ursului tailings), Ni is distributed on the slopes and towards the base of the tailings, along with Cr and Mn, in less acid areas, close to the reductive domain.

Pb has very high average contents in case of the Isipoaia tailings, reaching almost 1000 mg/kg. Geochemically it is associated to Fe, Cu, Sn, As and is distributed towards the top of the tailings, in acid environments.

Sn correlates with Pb, occupying similar regions that are acid and oxidating. The Sn contents were rather low, reaching a maximum average of 32.68 mg/kg in case of the Isipoaia tailings.

Zn has average contents of up to 511 mg/kg in case of the Fagul Cetății tailings and is geochemically associated to Co.

Chapter VIII

pH AND REDOX POTENTIAL

The pH and Eh values for the studied samples show conditions that vary from highly acidic and oxidant (Isipoaia tailings) to neutral, slightly alkaline and reductive (Pârâul Câinelui tailings).

For the Dealu Negru tailings, the pH gradually decreases from the tailing's top towards the base. This could be observed also in case of the Isipoaia and Pârâul Ursului. For the Fagul Cetății tailings, the acid regions did not occupy certain positions in relation to the altitude or the tailing's morphology.

The only tailings where a neutral to slightly alkaline, reductive environment was present, was Pârâul Câinelui. This is explained through the fact that it is much older than the others.

The good correlation between the redox potential values and the results obtained through the two methods of pH determination confirms that the analysis were done correctly.

A clear correlation between acidic and oxidating environments and the presence of high quantities of sulphides was established through pH and Eh determinations.

Chapter IX
GRANULOMETRY

It was observed that the samples taken from the Leșu Ursului area belong to a much coarser granulometric fraction. This is explained through the fact that, unlike the Dealu Negru and Fagul Cetății, the material at Leșu Ursului did not undergo preparation processes.

Chapter X

DISCUSSIONS

X.1. THE FUNDU MOLDOVEI AREA

From the pH and Eh point of view, at the surface of the **Dealu Negru** tailings, there are two clearly distinct geochemical environments:

- A highly acidic and strong oxidating environment, located in the upper region of the tailings, towards the top, where the contents of Fe, Cu, As, Ni, Pb, Sn and Zn progressively increase.
- A less acid and less oxidating environment, located on the slopes of the tailings, towards the base, where the contents of Mn, Cr and Ni slightly increase.

The main environmental problem here are the high contents of As.

The **Praşca I** mine tailings represents a moderately acid and moderately oxidating environment, with a mineralogical composition dominated, like in case of Dealu Negru, by quartz, illite, muscovite and chamosite.

The **Praşca II** tailings represents an approximately identic environment to the one at Praşca II, with a mineralogical composition mainly dominated by quartz, illite, muscovite and chamosite, to which jarosite and gypsum are added.

X.2. THE LEŞU URSULUI AREA

The surface of the **Isipoaia** tailings represent a highly acidic and oxidating environment. The toxicity of As and its high contents makes it a major threat for the environment, especially through its position on the bank of the Bistriţa river. Here, there are two environments:

- A highly acidic and oxidating environment in the high areas of the tailings, where the contents of Fe, Cu, Pb, Sn and As increase

- A slightly acid, almost neutral environment, close to the reductive domain on the slopes, represented by Mn, Ni and Zn, which are negatively correlated with Fe, Cu, Pb, Sn and As
- At Isipoaia, there are dangerously high contents of As, Pb and Cu also.

For the **Pârâul Ursului – Puțul 7** tailings, two environments were identified:

- a highly acid and oxidating environment in the high regions of the tailings, in which Fe, Pb, Cu, As and Sn are abundant
- a slightly acidic, close to neutral environment on the slopes towards the base, with slightly oxidating conditions, close to the reductive domain, in which Cr, Ni, Mn, Zn and Co are abundant.

In case of this tailings, a high content of As was determined.

The neutral to slightly alkaline environment at **Pârâul Câinelui** is not generally characteristic to the tailings associated to polymetallic sulphide mining and can be caused by both the fact that this tailings is much older and the fact that here, a lesser quantity of sulphide might have been exposed to oxidation processes.

The heavy metal contents from Pârâul Câinelui are within normal limits.

X.3. THE BĂLAN AREA

From the general characteristics of the **Fagul Cetății – Iazul 4** tailings, it can be seen that the conditions are mainly slightly acid and oxidating. Generally, on the north-eastern and south-western slopes there is a slightly lower content in heavy metals than on the top, where the geochemical environment can be divided into two areas:

- an acid an oxidating area, located in the E and NE of the tailings, which is rich in Fe, As, Co, Cu, Pb, Sn And Zn
- a less acid area in the west, close to the pond, in which there are higher contents of Cr, Ni and Mn

In case of the Fagul Cetății tailings, the main environmental problem is posed by the rather high contents of As.

The average contents of heavy metals in the concentrated ore mound near the **Izvoru Oltului** railway station and the average pH and Eh values suggest a highly acid, highly oxidating environment. The Fe contents of more than 30% confirms the fact that the material represents concentrated ore.

Chapter XI

CONCLUSIONS

The original contributions of the author to the thesis' domain of study can be summarized in the following conclusions, drawn from the interpretations of the analytical data obtained for the samples taken from the Fundu Moldovei, Leșu Ursului and Bălan areas:

1. All of the studied tailings, except the ones at Pârâul Câinelui represent highly acid and oxidating environments.
2. The relative small differences between the pH values determined in saline suspension and the ones determined in aqueous suspension suggest a relatively low participation of amorphous matter in the mineralogical composition of the studied material.
3. The main mineralogical constituents of the analysed material were quartz, chamosite, muscovite and illite, sometimes albite; traces of jarosite, albite, ankerite, gypsum, talc, pyrite, hematite, kaolinite, stilpnomelane and microcline were also identified.
4. There are two groups of elements that correlate negatively:
 - i. Group I (Fe, Pb, Cu, As, Sn) – mainly concentrated in the most acid and oxidating areas, where new minerals such as jarosite and gypsum had formed
 - ii. Group II (Mn, Cr, Ni) – mainly concentrated in less acid areas of the tailings, which has a pH close to the neutral domain and a redox potential close to the reducing domain, where ankerite was identified and some kaolinite had formed, most probably through the weathering of albite.

Zn and Co in highly acid, oxidating conditions associate to Group II and in slightly acid towards neutral conditions, associate to Group I.
5. The granulometric analisys confirms the fact that the material from the tailings ponds belong to a much finer granulometric fraction than the one deposited in dry conditions.

6. From the environment protection point of view, the analysis carried out on the mine tailings showed dangerously high As contents, especially in the case of the Isipoaia mine tailings (577,42 mg/kg).
7. The Pârâul Căinelui mine tailings have the lowest contents of heavy metals, which are close to normal values.
8. The analysis confirms the fact that the material from Izvoru Oltului represents concentrated ore.

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