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## MINERALOGY AND GEOCHEMICAL DISTRIBUTION OF HEAVY METALS FOR THE FAGUL CETĂȚII TAILINGS, ROMANIA

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### Abstract

This study was conducted on samples taken from the “Fagul Cetății – Iazul nr. 4” tailings pond in the Eastern Carpathians, Romania and is focused on exploring the way in which heavy metals from sulphide rich material are spatially distributed in relation to the geochemical conditions. For comparison, concentrated ore samples from the same area, genetically linked to the Tulgheș lithogroup were also analysed. The mineralogical and chemical composition of the samples was determined along with the main physico-chemical parameters such as pH and Eh values. The results show that the mineralogical composition of the tailings is dominated mainly by quartz, chamosite and muscovite-illite, while in case of the processed ore, the main minerals are, as expected, pyrite and quartz. Some traces of jarosite, ankerite, muscovite, gypsum, albite as well as microcline were identified and linked to the geochemical conditions at the surface of the tailings, which revealed an heterogenic environment that can be divided into an acid, oxidizing area in the E and N, characterised by high contents of As, Fe, Pb, Sn and Co and a neutral area in the south-western slope of the tailings that revealed higher contents of Mn.

*Key words:* Eh, heavy metals, mineralogy, pH, tailings

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### 1. Introduction

In the context of rising awareness regarding the future of the surrounding environment, many contemporary scientists have started looking towards the impact that the presence of various abandoned mining sites or the resulted waste deposits have on the adjacent areas and the soils around them (Balaban et al., 2011, 2013; Nagy-Korodi et al., 2011; Paldyna et al., 2017; Stumbea, 2010). The top stratum is the most dynamic area not only for the tailings but also for their composition, constantly changing as a response to the ongoing climatic conditions. Moreover, the ore preparation processes which the tailings have gone through, the moisture, the vegetation and the human

activities are also factors which catalyse the dispersal of elements through prevailing media, and they may, to some extent, influence the mineralogical and chemical composition of the tailings.

The intensity of the Acid Mine Drainage (AMD) phenomenon which occurs in case of sulphide rich mine tailings is mainly controlled by the actual quantity of sulphides, such as pyrite, which is exposed to oxidizing conditions such as air and humidity (Akcil and Koldas, 2006; Modoi et al., 2014). Observing the mineralogical composition of the material as well as the geochemical distribution pattern of trace elements along the tailings' surface and correlating it with measurements of the physico-chemical parameters and knowledge about the supergene dispersal of elements which occurs

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in these cases can ultimately result in highly useful information about the nature and degree of the contamination, which is crucial to environmental risk assessments as well as the subsequent choice of rehabilitation techniques, where possible (Alpers et al., 1994; Dold, 1999; Jambor, 1994; Jambor and Blowes, 1998; Paiu et al., 2017; Plumlee, 1999).

For comparison reasons and in order to verify if the correlations between the geochemical conditions and the distribution of heavy metals are valid for similar but more concentrated materials, the analysis was performed on both tailings samples and processed ore samples which have resulted from the same ore deposit in the same area, deposited in similar conditions and within a nearby area which is subject to similar climatic factors.

The studied tailings mound at “Fagul Cetății – Iazul nr. 4” are comprised of approximately 11.2 million cubic meters of waste material (MMP, 2012) this volume was accumulated during the active period, between 1975 and 2006 (MMP, 2007) as a result of ore processing through flotation. Presently the site is closed and pending ecological rehabilitation. The position of the pond is in the vicinity of the Sândominic village, an establishment that lies at its base, therefore this may pose a significant environmental and human health risk, due to the fact that some of the surrounding lands are being used as hay fields. One notable incident was recorded on the 31<sup>st</sup> of May 2012 when about 1200 m<sup>3</sup> of mine waste material has, due to the torrential rain, slid to one such hay field, thus affecting about 1.5 hectares of soil (MMP, 2012).

## 2. Context of the study

### 2.1. Geological and geographical context

The Bălan mining sector (Fig. 1) has historically been a highly important source of polymetallic sulphides (mainly, but not exclusively chalcopyrite) for the Romanian industry. The site is located in the central zone of the Eastern Romanian Carpathians, NE part of the County of Harghita. The landscape there is dominated by the Hășmașu Mare Mountain and lies close to the Sândominic village (Fig. 2), 42 km off Miercurea Ciuc. The city of Bălan, located at 46°30' North and 25°44' East, extends on

the banks of the Olt River and has developed as a result of the continuous growth of mining industrial activities in the area. Climatically, this mountainous area is characterized by an annual average temperature of 7°C and average annual precipitations of about 712-730mm.

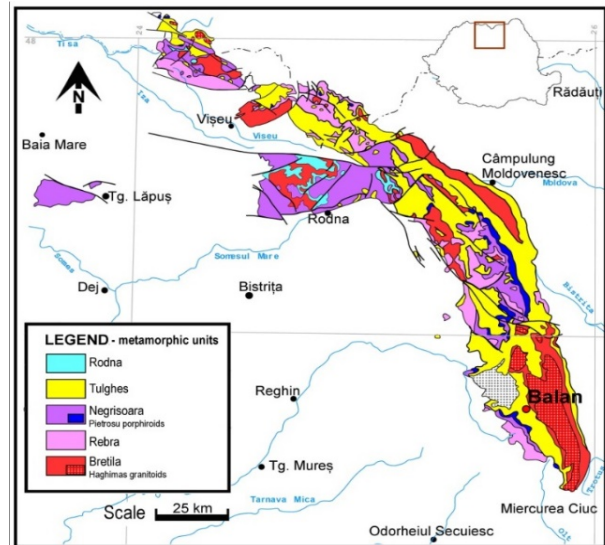


Fig. 1. Location of the Bălan mining perimeter (modified from Balintoni, 2010)

The research area for the present study is the “Fagul Cetății - Iazul nr. 4” tailings pond, which is located just North of Sândominic village and South of the city of Bălan. For the comparison of the geochemical parameters and heavy metal contents, as well as for gaining some insight into the effects of the ore preparation process, concentrated ore samples from the vicinity of the nearby Izvoru Oltului Railway station were also collected (Fig. 2).

A study conducted by Auner and Ciobanu (2009) revealed that the contents of heavy metals in soils from the vicinity of the “Fagul Cetății – Iazul nr. 4” waste deposits were situated around normal values at the time, with the exception of Cu which however did not reach the intervention threshold specified in Romanian Environmental Legislation. The waste material is mostly fine grained, the dominant granulometric fraction being of around 387 μm in diameter, while the sorting degree reaches 1.468 (Balaban, 2012).

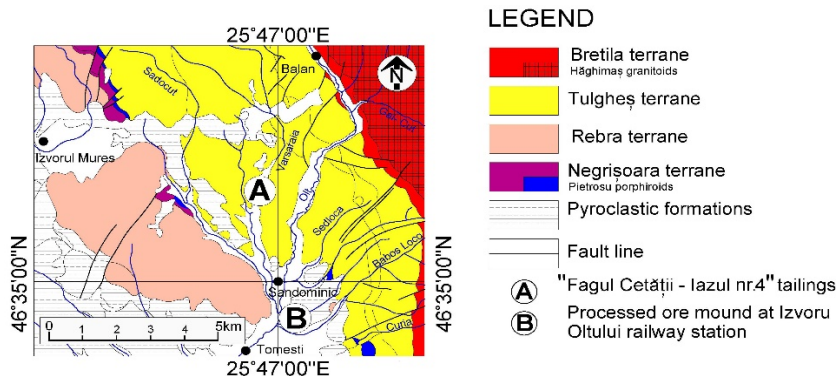


Fig. 2. Location of the studied tailings within the Bălan mining sector (modified from Kräutner and Bindea, 2002)

The Eastern Carpathians in Romania span from the Northern border with Ukraine to the Prahova valley. Geologically they were described by Săndulescu (1984) as being comprised of 3 different chains of formations: Flysch in the East, Volcanic neogene in the West, while in between the two there is the Crystalline-Mesozoic Zone. The tectonic units of this mid-zone are comprised of a pre-alpine basement and its cover, which is of Mesozoic age (Dill et al., 2012). From top to bottom, the Bucovinian, Subbucovinian and Infrabucovinian nappes were identified and described by Ritsema et al. (1981).

The basements of the Subbucovinian and Bucovinian Nappes are composed of the Variscan nappes of Pietrosu Bistriței, Putna, Rarău and Rodna. The Putna Nappe consists of the Tulgheș metamorphic unit, which is a low-grade metamorphic sequence (Balintoni et al., 1983; Krätner, 1988).

The Tulgheș metamorphic unit was thoroughly studied by geologists as it has represented a highly important source of polymetallic sulphide ore, which yielded notable amounts of Pb, Zn and Cu as well as barite (Balintoni, 2010). In 1988, Krätner divided this metamorphic unit from top to bottom into five formations, named from Tg<sub>5</sub> to Tg<sub>1</sub>. Subsequently, in 1994, Vodă and Balintoni elaborated a model which divided the Tulgheș metamorphic unit into 4 sub-units, named from top to bottom: Arșița Rea (Tg<sub>4</sub>, phyllitic-quartzitic in nature), Leșu Ursului (Tg<sub>3</sub>, volcano-sedimentary formation), Holdița (Tg<sub>2</sub>, quartzitic-graphitic nature) and Căboiaia (Tg<sub>1</sub>, quartzitic nature).

The notion of the Tulgheș terrane was later introduced by Liégeois et al. (1996) and Krätner (1996) in relation to the Tulgheș group. Simplifying this model, Balintoni (1997), while discussing the Rodna group separately, described the Tulgheș lithogroup as being a tectono-stratigraphical terrane alongside the other Bretila, Negrișoara and Rebra lithogroups. Pană et al. (2002) attributed to them a peri-Gondwanan origin.

## 2.2. The primary mineralogy

The Kuroko type Cambrian aged mineralization of Bălan are economically notable

mainly for their Cu and pyrite content (Krätner et al., 1983), but they were also found to contain chalcopyrite, sphalerite, galena, bournonite, galenobismutite, gold, silver, magnetite and hematite, ankerite, microcline, chlorite, microcline and barite. The overall heavy metal concentration of the deposit includes Cu, Fe, S, Zn, Pb, Mn, Ti, Bu, Co, Ni, Cr and As. The polymetallic sulphides are distributed in five main horizons (Stumbea, 2007): Arama Oltului (with disseminated pyrite and chalcopyrite), Sedloca (with pyrite and chalcopyrite disseminations), Fagul Cetății (massive lens and disseminated pyrite and chalcopyrite), Valea Băilor (disseminated pyrite and chalcopyrite) and Bălan (compact and disseminated ore).

## 3. Material and methods

### 3.1. Sampling

For the present study, a total of 54 samples were taken from:

- “Fagul Cetății – Iazul nr. 4” tailings: 50 samples (samples A1 to A50) (Fig. 3)

- Concentrated ore mound at Izvoru Oltului Railway Station – 4 samples (samples B1 to B4). These samples have been taken for comparison reasons and the material represents processed ore that was dumped in the vicinity of the Izvoru Oltului Railway Station to be further transported to Deva.

The sampling depth range was 0-20 cm and the operation was done with a manual, drill-type soil sampler, according to the methods described by Borlan and Răuță (1981), Clichici and Stoici, (1986) and Florea et al., (1987).

### 3.2. Sample preparation

The samples were left to dry under normal conditions, at room temperature for 3 days and they were afterwards dehumidified in the oven for 8 hours at a temperature of 40-50°C. The coarser fragments ( $\phi > 2$  mm) were separated through sieving, together with the vegetation traces.

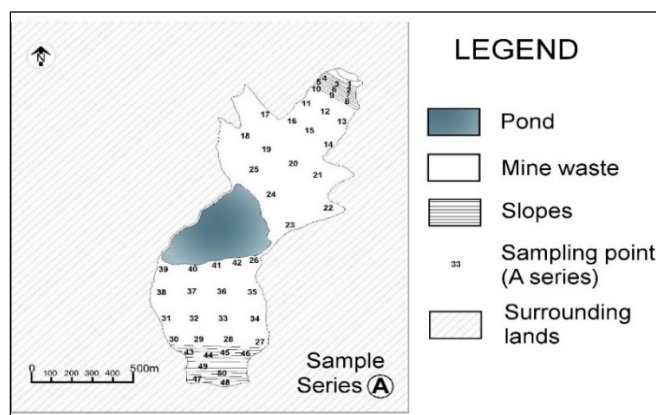


Fig. 3. The sampling points (A series: A1 to A50) within the “Fagul Cetății – Iazul nr. 4” tailings perimeter (top view)

The finer fraction ( $\phi < 2\text{mm}$ ) was then submitted to grinding and milling operations which were performed by using a “Fritsch” planetary mill for 60 minutes at 200 rotations/minute, as described by Clichici and Stoici (1986). The final sample that was subsequently submitted to analysis had a granulometric diameter under 0.01 mm. The representativeness of the final samples was assured through mixing and quartering.

### 3.3. pH and Eh determination

For determining the physicochemical parameters such as pH and Eh, the potentiometric method was used. For both pH and Eh measurements, 10 g of sample were mixed at room temperature with 25 mL of twice-distilled water, contact time of 30 minutes. pH determinations were made by using a pH-meter model “Basic 20+” with a calomel electrode as reference. For the Eh, a “pH-100” potentiometer was used with a calomel-platinum electrode-couple (calomel was used for reference), according to the methods described by Bloom (2000) and Florea et al. (1987). The determinations were done in the “Al. I. Cuza” University’s Geochemistry laboratories.

### 3.4. Major and trace elements contents

The contents of major and trace elements were determined by WD-XRF (Wavelength Dispersive X-Ray Fluorescence spectrometry) on powdered samples by using a PANalytical Axios and a PW2400 spectrometer at the Federal Institute of Geosciences and Natural Resources in Hannover, Germany.

The samples were mixed with flux material and then melted into glass beads. The loss on ignition (L.O.I.) was determined by heating 1 g of sample material to 1030°C for 10 minutes. The residue was mixed with 25 mg lithium bromide and 5 g lithium metaborate and was afterwards fused at 1200°C for 20 minutes. For calibrations and correction procedures a total of 130 Certified Reference Materials (CRM’s) were analyzed as well as monitor samples.

### 3.5. Data processing

The 3D terrain model approximations as well as the geochemical distribution maps were computer-generated in Surfer 9 by using the kriging method, the linear variogram model described by Warrick et al. (1986). The necessary calculations for the correlation matrices were done using Statistica 8.

### 3.6. Mineralogical analysis

For determining the mineralogical composition of the samples, the XRD method was used on a series of 12 samples which were selected from the total. The samples were selected based on their macroscopic aspect in order to improve the diversity of the analyzed material. For this operation, a Philips X’Pert PW371-

diffractometer was used, with Cu-K $\alpha$  radiations at 40mA and 40kV, 1° divergence slit. The device was also equipped with a point detector, sample changer and a secondary monochromator. The sample diameter was of 28 mm. The investigation was done was from 2° to 80° 2 $\Theta$ , at each 0.02° step for 3 seconds/step.

## 4. Results and discussion

### 4.1 pH and Eh values

As it can be seen from Table 1, the pH and Eh values for the studied samples reveal a moderately acid, moderately oxidizing environment for the mine tailings of “Fagul Cetății – Iazul nr. 4” (Fig. 4), with an average pH of 5.88 and an average Eh of 0.367 V and a strong acid and strong oxidizing environment for the processed ore samples, with an average pH of 2.63 and an average Eh of 0.408 V (Table 1).

This difference is mainly linked to Fe, especially pyrite, which is clearly most abundant in case of the processed ore (Table 4). The environment at the “Fagul Cetății – Iazul nr. 4” can be divided into two areas: one in the eastern and northern sides, which is more acidic, and another in the south, which is close to the neutral domain. The Eh-Ph diagram of the Fe–water system in the physico-chemical conditions of the studied samples (Fig. 5) shows a clear difference between the dominant speciation forms of Fe in the tailings, which is Fe<sub>2</sub>O<sub>3</sub> (the most oxidized form) and the Fe[2+] form in the processed ore.

### 4.2. Major elements

When looking at the major chemical components for the tailings and for the concentrated ore, as expected, the percentage of Fe is higher in the processed material (from 9.84% to 31.6%), on the basis of a decrease in Si (from 29.3% to 8.25%), due to the fact that miners separate ore minerals from silica-rich gangue.

Also, the loss on ignition is higher in case of the processed ore, probably due to the massive amount of iron sulphide, as S content was of 0.34% in the tailings and 0.09 in the processed ore. Al contents were much higher (5.18%) in the tailings than in the processed ore (1.69%).

### 4.3. Trace elements

Determining the contents of potentially toxic trace elements is especially important when significant quantities of sulphide is exposed to oxidation, as this results in Acid Mine Drainage, which can remobilize some of these contaminants (such as As, Pb or Hg), ultimately having an impact on human health as the last link of the food chain (Akcil and Koldas, 2006; Oelofse et al., 2007). When comparing the average content of trace elements in the studied samples (Table 2) it can be seen that there is a significantly higher content of As, Bi, Co, Cu, Ni, Pb and Sn in the processed ore than in the tailings.

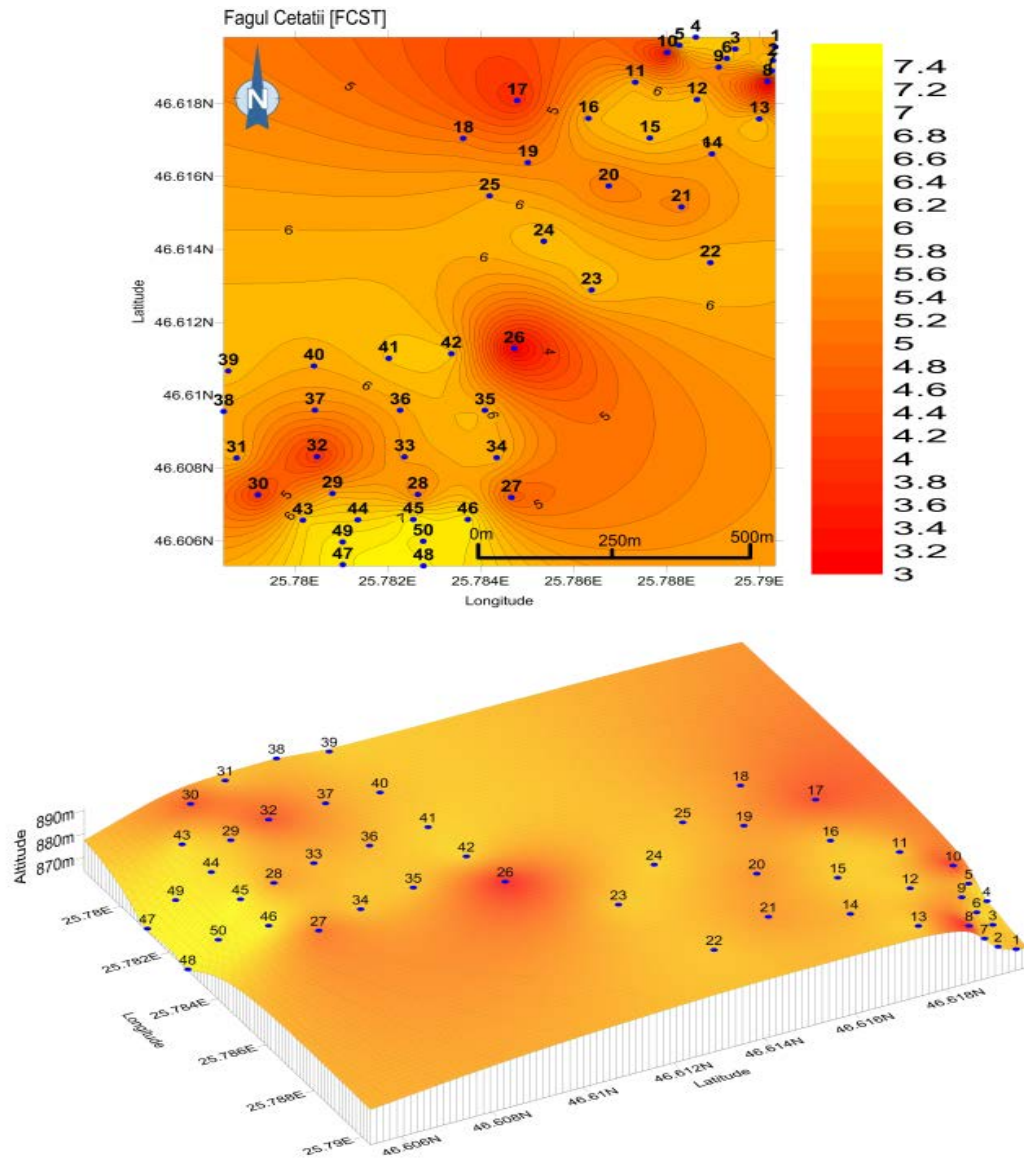


Fig. 4. The pH at the surface of the “Fagul Cetății – Iazul nr. 4” tailings

Table 1. pH and Eh for the analyzed tailings samples, determined in aqueous suspensions

Sample	Eh [V]	pH	Sample	Eh [V]	pH	Sample	Eh [V]	pH
A1	0.419	5.73	A19	0.381	5.35	A37	0.359	5.45
A2	0.410	6.53	A20	0.384	5.17	A38	0.346	5.94
A3	0.396	6.32	A21	0.376	5.32	A39	0.334	6.36
A4	0.433	6.58	A22	0.360	6.20	A40	0.337	6.01
A5	0.395	6.67	A23	0.353	6.33	A41	0.329	6.43
A6	0.36	6.67	A24	0.350	6.44	A42	0.330	6.48
A7	0.349	6.82	A25	0.355	5.99	A43	0.320	6.72
A8	0.477	2.65	A26	0.439	2.94	A44	0.320	6.77
A9	0.400	5.43	A27	0.403	4.63	A45	0.316	7.33
A10	0.449	3.35	A28	0.385	5.40	A46	0.318	7.21
A11	0.397	6.14	A29	0.370	6.05	A47	0.318	7.16
A12	0.381	6.36	A30	0.368	4.02	A48	0.314	7.24
A13	0.374	6.39	A31	0.334	6.08	A49	0.319	7.11
A14	0.386	5.79	A32	0.395	3.92	A50	0.318	7.07
A15	0.375	6.32	A33	0.357	5.87	B1	0.404	2.47
A16	0.372	6.15	A34	0.345	6.15	B2	0.401	2.36
A17	0.397	3.78	A35	0.344	6.17	B3	0.398	2.33
A18	0.378	5.14	A36	0.348	5.91	B4	0.431	2.29

Also, there is a much higher content of Ba, Ce, Cr, V, Zn and Zr in the tailings than in the processed ore, which confirms that the flotation process has been efficient. The contents of Cs, Hf, Mo, Sb, Sm, Ta, Sr and W were under or close to the detection limit of the analytical apparatus.

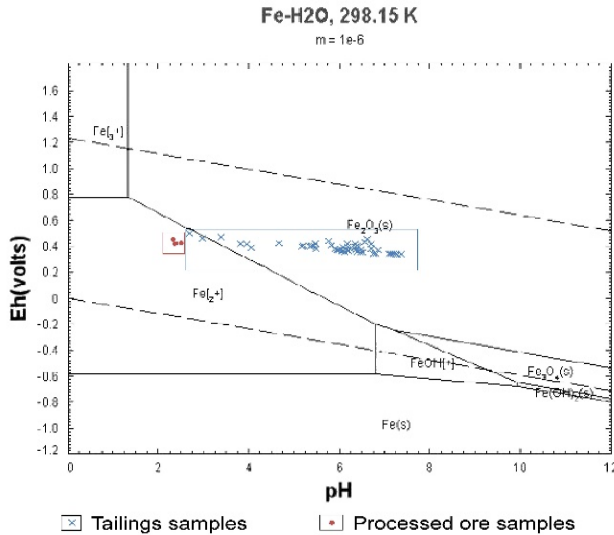


Fig. 5. The Eh-pH diagram for the Fe-water system with the most probable speciation forms of Fe (from Sherik and Davis, 2009 with modifications)

The other studied elements, such as Ga, La, Nb, Nd, Rb, Sc, Th, U and Y had similar contents in case of both sample patches, as the preparation process did not have a significant influence on them, the main focus being on Cu and pyrite, which also explains the increased content of Fe, Cu, Pb in the concentrated ore.

3.4. Correlation factors

The correlation matrix for the most important heavy metals contents as well as for the pH and Eh for the samples taken from the “Fagul Cetății – Iazul nr. 4” tailings (Table 3) clearly shows that the acidic environment was associated with an increase of Fe, As, Pb and Sn contents, while neutral environments were statistically associated with an increase in Mn contents. The statistically significant correlations found between certain elements can divide them into two antagonistic groups: Fe, As, Co, Cu, Ni, Pb and Sn on the one side and Mn, Cr and Ni on the other.

3.5. Distribution maps

The distribution map made for Fe in case of the “Fagul Cetății – Iazul nr. 4” tailings (Fig. 6) shows higher contents of Fe in the northern, more acidic part, correlated with Pb, Cu and Zn, which tend to occupy roughly the same areas.

Table 2. The average contents of trace elements for the studied samples

	Fagul Cetății [ppm]	Processed ore [ppm]		Fagul Cetății [ppm]	Processed ore [ppm]		Fagul Cetății [ppm]	Processed ore [ppm]
As	148.60	852.00	La	40.50	30.00	Sn	28.22	111.00
Ba	579.90	223.00	Mo	<b>3.64</b>	<b>3.00</b>	Sr	34.72	12.75
Bi	26.54	174.00	Nb	15.02	13.00	Ta	<b>5.08</b>	<b>7.50</b>
Ce	79.94	20.00	Nd	23.88	19.25	Th	19.78	19.50
Co	55.22	324.00	Ni	18.28	49.25	U	4.38	5.75
Cr	36.22	9.50	Pb	336.4	2065	V	44.46	17.50
Cs	<b>23.76</b>	<b>23.75</b>	Rb	57.72	31.25	W	<b>6.00</b>	<b>6.25</b>
Cu	1285.00	4154.00	Sb	<b>31.98</b>	<b>72.25</b>	Y	29.66	24.50
Ga	15.04	3.25	Sc	9.62	8.00	Zn	511.00	240.00
Hf	<b>7.76</b>	<b>9.00</b>	Sm	<b>19.68</b>	<b>22.00</b>	Zr	226.90	143.70

\*The values marked in bold were under or close to the limit of detection of the device

Table 3. Correlation matrix for the “Fagul Cetății – Iazul nr. 4” tailings

	Eh	pH <sub>aq</sub>	Fe	Mn	As	Co	Cr	Cu	Ni	Pb	Sn	Zn
Eh	1.00	<b>-0.73</b>	0.17	<b>-0.44</b>	<b>0.30</b>	0.11	-0.08	0.09	<b>-0.34</b>	<b>0.30</b>	0.12	-0.02
pH <sub>aq</sub>	<b>-0.73</b>	1.00	<b>-0.36</b>	<b>0.49</b>	<b>-0.39</b>	-0.13	-0.10	-0.09	0.28	<b>-0.43</b>	<b>-0.36</b>	-0.04
Fe	0.17	<b>-0.36</b>	1.00	0.06	<b>0.89</b>	<b>0.84</b>	0.10	<b>0.79</b>	<b>0.29</b>	<b>0.84</b>	<b>0.73</b>	<b>0.84</b>
Mn	<b>-0.44</b>	<b>0.49</b>	0.06	1.00	-0.26	-0.12	<b>0.62</b>	0.08	<b>0.65</b>	0.03	0.09	<b>0.30</b>
As	<b>0.30</b>	<b>-0.39</b>	<b>0.89</b>	-0.26	1.00	<b>0.88</b>	-0.24	<b>0.67</b>	-0.02	<b>0.82</b>	<b>0.58</b>	<b>0.67</b>
Co	0.11	-0.13	<b>0.84</b>	-0.12	<b>0.88</b>	1.00	<b>-0.37</b>	<b>0.75</b>	0.12	<b>0.59</b>	<b>0.48</b>	<b>0.75</b>
Cr	-0.08	-0.10	0.10	<b>0.62</b>	-0.24	<b>-0.37</b>	1.00	-0.05	<b>0.54</b>	0.20	<b>0.34</b>	0.08
Cu	0.09	-0.09	<b>0.79</b>	0.08	<b>0.67</b>	<b>0.75</b>	-0.05	1.00	<b>0.32</b>	<b>0.72</b>	<b>0.51</b>	<b>0.93</b>
Ni	<b>-0.34</b>	0.28	<b>0.29</b>	<b>0.65</b>	-0.02	0.12	<b>0.54</b>	<b>0.32</b>	1.00	0.14	<b>0.30</b>	<b>0.40</b>
Pb	<b>0.30</b>	<b>-0.43</b>	<b>0.84</b>	0.03	<b>0.82</b>	<b>0.59</b>	0.20	<b>0.72</b>	0.14	1.00	<b>0.65</b>	<b>0.74</b>
Sn	0.12	<b>-0.36</b>	<b>0.73</b>	0.09	<b>0.58</b>	<b>0.48</b>	<b>0.34</b>	<b>0.51</b>	<b>0.30</b>	<b>0.65</b>	1.00	<b>0.60</b>
Zn	-0.02	-0.04	<b>0.84</b>	<b>0.30</b>	<b>0.67</b>	<b>0.75</b>	0.08	<b>0.93</b>	<b>0.40</b>	<b>0.74</b>	<b>0.60</b>	1.00

\*The statistically important correlation coefficients were marked in bold

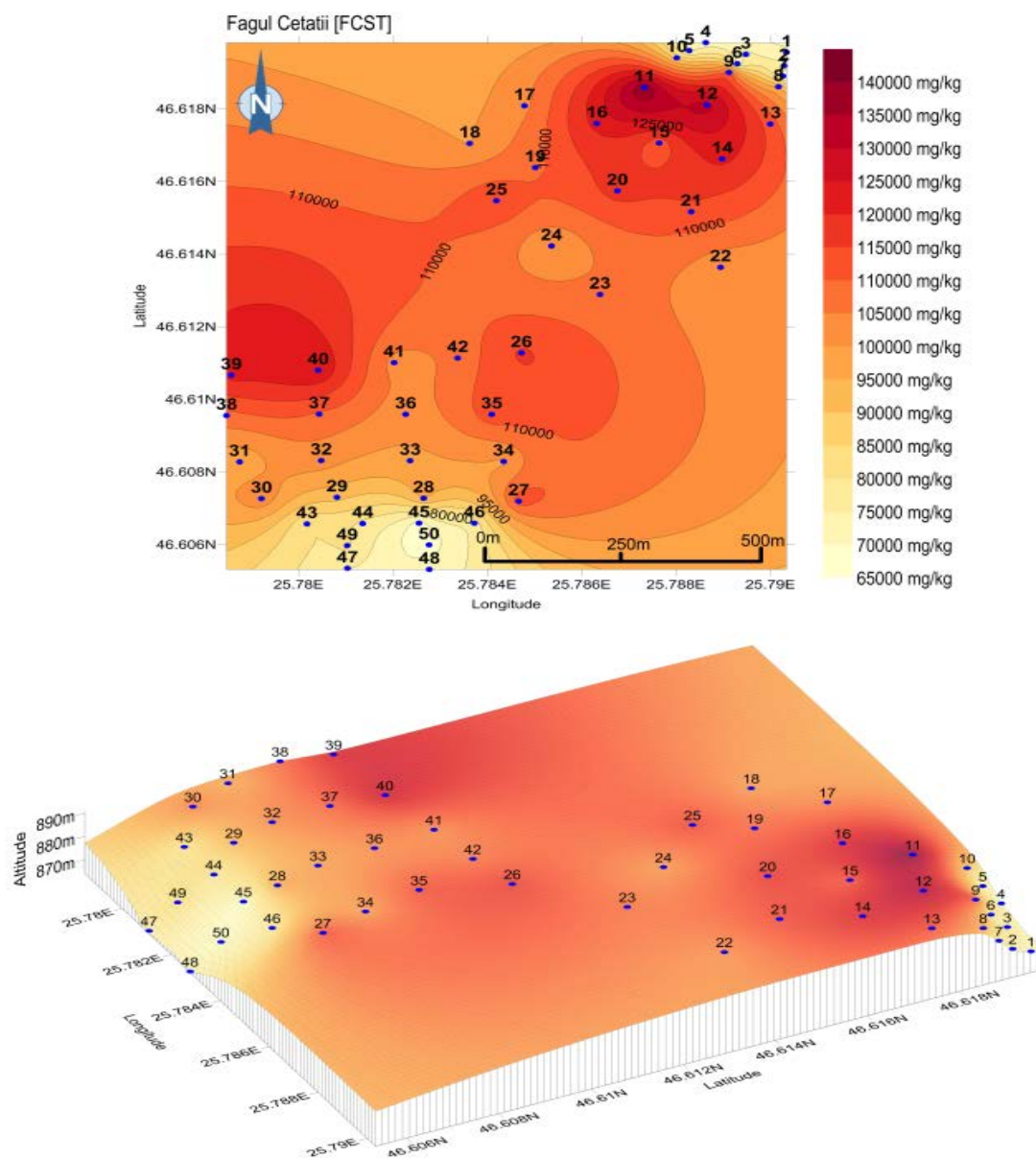


Fig. 6. The distribution of Fe at the surface of the “Fagul Cetății – Iazul nr. 4” tailings

### 3.6. Mineralogy

The main mineralogical constituents (Table 4) for the tailings at “Fagul Cetății – Iazul nr. 4” are quartz and Fe-rich chlorite, in some cases joined by muscovite-illite. The trace minerals often included pyrite, ankerite, and in some cases albite, microcline, calcite, gypsum and jarosite.

In contrast to the tailings samples, as expected, the main minerals from the processed ore were pyrite and quartz, followed by trace minerals such as jarosite, Fe-rich chlorite, muscovite-illite and gypsum.

Both in the tailings and in the concentrated ore, quartz is a main mineral, most probably due to its high resistance to chemical and mechanical alteration to which the ore was submitted during the preparation process. The effectiveness of this process is also demonstrated by the fact that the quantity of pyrite is much higher in the processed ore, while the more fragile minerals, such as albite and muscovite are

either absent or have a less notable overall presence, as trace minerals.

The most likely sources for the quartz as well as for the Fe-rich chlorite and muscovite are the initial rock formations that hosted the Cu and pyrite ore. As Riezebos (1979) demonstrated through XRD analysis, the initial quartz and albite-rich material generates alteration products such as kaolinite and illite and therefore, it is possible that illite could have formed through the supergene alteration of muscovite (Deer et al., 1975).

The albite, which has only been present in the tailings samples as a trace mineral, has also been identified in the initial rock formations that hosted the ore. In spite of its hardness of 6 to 6.5 on the Mohs scale, albite easily weathers in aqueous environments and therefore it probably was affected by the supergene alteration processes (in case of the tailings) or the ore processing stage (in case of the processed ore).

**Table 4.** The main, accessory and trace minerals from the studied samples

Sample	Main and accessory minerals	Trace minerals
A3	Quartz, Fe-rich Chlorite, Muscovite-Illite	Dolomite/Ankerite, Albite, Pyrite, Microcline
A6	Quartz, Fe-rich Chlorite, Muscovite-Illite	Dolomite/Ankerite, Albite, Pyrite, Microcline
A12	Quartz, Fe-rich Chlorite, Pyrite	Muscovite-Illite, Dolomite, Calcite, Albite
A15	Quartz, Fe-rich Chlorite	Pyrite, Muscovite-Illite, Albite, Microcline
A17	Quartz, Fe-rich Chlorite, Muscovite-Illite	Gypsum, Pyrite, Albite, Microcline
A26	Quartz, Fe-rich Chlorite, Muscovite-Illite	Jarosite, Gypsum, Albite
A30	Quartz, Fe-rich Chlorite	Pyrite, Muscovite-Illite, Ankerite, Albite, Calcite
A36	Quartz, Fe-rich Chlorite	Pyrite, Muscovite-Illite, Ankerite, Gypsum, Albite
A39	Quartz, Fe-rich Chlorite, Muscovite-Illite	Pyrite, Gypsum, Ankerite, Albite, Microcline
A42	Quartz, Fe-rich Chlorite	Pyrite, Muscovite-Illite, Ankerite, Albite, Gypsum
A45	Quartz, Fe-rich Chlorite	Muscovite-Illite, Ankerite, Pyrite, Albite
A48	Quartz, Fe-rich Chlorite, Muscovite-Illite	Ankerite, Albite, Pyrite, Microcline
B1	Pyrite, Quartz	Gypsum, Hydro-Jarosite
B3	Quartz, Pyrite	Fe-rich Chlorite, Jarosite, Muscovite-Illite, Gypsum

Albite has been commonly identified in similar sulphide rich mine waste material deposited in dry conditions, while it has been found to be much less present in case of wet conditions such as tailing ponds (Balaban, 2012). The ankerite was also mentioned by Krättner et al. (1983) as present in the parental material, which represents its most likely source.

The forming of gypsum is can be linked to the presence of calcite, which has neutralized the acidity of the environment leading to the precipitation of Fe, while the calcium and sulfate ions formed gypsum (Ritsema and Groenenberg, 1993; Kashir and Yanful, 2000; Simon et al., 2002) which is commonly encountered in weathered pyrite rich tailings (Smolders et al., 2004). The presence of the jarosite in some of the samples surely has to do with the strong acidic and oxidizing conditions which lead to the alteration of pyrite, as this mineral appears only in 3 samples, A26, B1 and B3, all of them revealing pH values lower than 3 (Table 1).

#### 4. Conclusions

The tailings have a mineralogy dominated by quartz, Fe-rich chlorite and muscovite-illite. For the processed ore, the main minerals are pyrite and quartz. The ore processing has altered the frailer minerals, especially albite, while not significantly affecting quartz. Jarosite was associated to strong acidic and oxidizing conditions, with  $\text{pH} < 3$ , while the formation of gypsum on the basis of calcite pointed to a wet environment.

Two antagonistically distributed groups of elements could be distinguished: Fe, As, Co, Cu, Ni, Pb and Sn on the one hand and Mn, Cr and Ni on the other.

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