

## ACID MINE DRAINAGE-RELATED PRODUCTS IN NEGOIUL ROMÂNESC QUARRYING WASTE DEPOSITS (CĂLIMANI MTS., ROMANIA)

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**Abstract:** The purpose of the study is to identify some mineralogical and geochemical features of the weathering products from the waste dumps resulted after the quarrying works of Negoitul Românesc (Călimani) as well as their impact on the environment. The study was carried out on products of limonitization (goethite, hematite), argillic products (beidellite, illite, kaolinite, montmorillonite) and on samples of surface water (puddles developed on the top of the waste deposits). Leachates of argillic products induce in the environment an obviously lower pH (pH = 2.52-4.25), than the solutions emerged through leaching of limonitization aggregates (pH = 5.99-6.17). Chemical features of the small puddles developed onto the upper part of quarry waste deposits suggest that, except for pH, they do not represent a key risk factor to the environment. Argillic wastes act as a barrier that prevents infiltration of contaminated surface water.

**Keywords:** quarrying wastes, weathering, acid mine drainage, acidity, heavy metals

### 1. GEOLOGICAL SETTING

Material of mining wastes in the perimeter of Negoitul Românesc Peak (fragments of rocks and blocks, powdery material with different size of the grain) comes from the surface mining works (quarry) designed and carried out in stages of geological exploration and exploitation of polymetallic mineralization (sphalerite, galena, chalcopryrite, pyrite) and native sulfur of hydrothermal origin associated to Neogene magmatic rocks; mining activity has closed in 1997.

Geotectonically, the perimeter belongs to the Neogene volcano-endogenous megastructure of Eastern Carpathians, developed as a result of a subduction phenomenon followed by collision, from east (Eurasian tectonic plate), to west (Transylvanian tectonic plate) (Mârza, 1999). Calc-alkaline magma (acid, intermediate) formed rocks that belong to andesite (surficial and less deep facies) and to microdiorite, diorite, quartz-diorite types (deeper facies). Volcanic facies ranges from basaltic (basaltic andesites) to rhyolitic.

As Mârza (1999) stated, there are three cycles of magmatic rocks, as follows (from the oldest to the newest): I – acid volcanic rocks (rhyolite,

rhyodacite); II – magmatic rocks of andesite-diorite composition; III – volcanic rocks of andesite composition. Magmatic rocks of Călimani Mountains belong to the latter cycle and were put into place in the upper Pontian – upper Pliocene span of time.

From both petrogenetic and metallogenetic viewpoint, the perimeter belongs to the Neogene Carpathian Province of volcanic-plutonic rocks (Eastern Carpathians Subprovince), where many structural and metallogenetic units of different size and rank stretch-out, as follows (from NE to SW): Oaș District; Baia Mare District, petro- and metallogenetic structures of Țibles and Toroiaga; Rodna-Bârgău District; Călimani-Gurghiu-Harghita District (Stumbea, 2007).

The perimeter of Negoitul Românesc quarry is placed in Călimani-Gurghiu-Harghita District which is composed of Călimani, Gurghiu and Harghita petro- and metallogenetic fields. Călimani petro- and metallogenetic field is a young volcanic-plutonic structure (Pontian-Pliocene), represented by strato-volcanoes with subcrustal structures (dacite, andesites, basaltic andesites and pyroclastic flows), diorites and monzodiorites (affected by propylitic and argillic hydrothermal alteration and partly by

silicification), sporadically mineralized during Pontian. Călimani caldera has a diameter of about 10 km and an EW orientation; associated to satellite volcanic structures, hydrothermal mineralizations as hydrothermal veins and polymetallic disseminated sulfide ore (Pb-Zn ± Au-Ag) were reported. At Negoiu Românesc and Iezerul Mic, buried porphyry copper structures and hypogene mineralized breccias, as well as S mineralizations were described (Mârza, 1999). Hydrothermal alterations are controlled by fractures and by the presence of porphyry copper structures.

In the perimeter of quarrying wastes of Negoiu Românesc Peak, there is a monzodioritic body that undergone phenomena of two-stage hydrothermal alteration: stage I (involving alkaline to weak acid solutions) – albitization, biotitization, argillization; stage II (spatially superposed over the products of the first stage and characterized by metasomatic processes with hydrogen and boron) – mineralogical associations of quartz - sericite - tourmaline.

## 2. PETROGRAPHY AND MINERALOGY OF QUARRYING WASTES

The quarrying waste dump is broadly controlled by the presence of andesites; subordinately quartz-andesites and diorites were identified. The fresh rock is often affected by hydrothermal alteration, generally of argillic type; propylitic type appears especially in Ilva perimeter while silicification is rather casual. Hydrothermal alteration is variable in intensity, so that the rocks present different stages of alteration, from an incipient – to an almost complete transformation. Occasionally, andesites present small pits in their mass as a result of a complete leaching of feldspar grains.

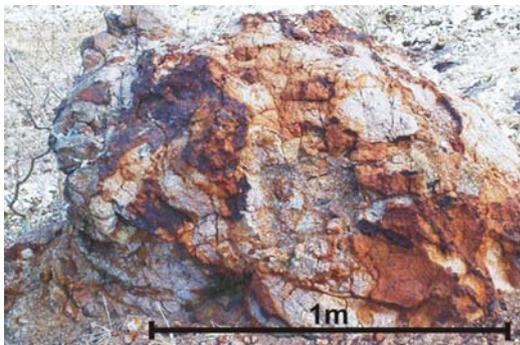


Figure 1. Blocks of andesite with limonitized cracks (Ilva wastes deposit).

Quarrying wastes are disposed in four locations (Puturosul, Dumitreleu, Ilva, Pinul) that

surround the quarry of Negoiu Românesc peak on its north-eastern, northern and western side. The waste material occurs mainly in three forms:

- fragments and blocks of rock, with sizes ranging from centimeters, to decimeters and sometimes even meters (Fig. 1);

- accumulations of a brown-reddish material (ochre) produced by the weathering processes of limonite-bearing rock debris: the grain size ranges from millimeters, to centimeters.

- accumulations of clay minerals; the size of clay mineral debris ranges from centimeter, to millimeter and it represent storage areas of material extracted from the hydrothermally altered zones (Fig. 2);



Figure 2. Accumulations of clay minerals extracted from the hydrothermally altered zones (Ilva wastes deposit).

*Fragments and blocks of rocks* identified within the quarrying wastes belong to the following types: andesites, quartz andesites, basaltic andesites, diorites, basalts (only rarely and almost exclusively in Dumitreleu quarrying wastes site).

Andesites and diorites often appear hydrothermally altered (incipient to advanced argillization) and have a whitish color; the specific gravity is clearly lower than the same type of rocks unaffected by hydrothermal alteration processes.

Quarrying wastes also consist of blocks of andesites slightly affected by argillic alteration and crossed by various systems of cracks. Along these cracks products of limonitization developed; in some cases limonitization affects almost the whole mass of rock debris (Fig. 1). The blocks and fragments of andesites affected by argillization and/or by limonitization often have a rounded shape as a result of physical and chemical weathering. These phenomena have important effects as a result of a previous weakening of rock cohesion throughout hydrothermal alteration processes (argillic and propylitic types).

Another feature of all four quarrying waste deposits is the angular-shaped fragments of dark-colored rocks. In the most cases these fragments

consist of quartz-andesites slightly affected by limonitization. The crack-planes that crisscross the mass of the rock are filled by black ochre (Fig. 3); on these planes black ochre has not undergone processes of oxidation in order to convert it into the brown-reddish variety. The surfaces covered by black ochre shows blue-reddish iridescences.



Figure 3. Black deposits on limonitized andesite (Ilva waste deposit).

In all four waste deposits common fragments of rocks almost entirely affected by limonitization were identified, having a brown-reddish to an intense red color (Fig. 4); their cohesion is weak and some are largely friable proving a severe limonitization. Sometimes, along the cracks and fissures that crisscross the block of rocks, crust of silica aggregates occur; onto these aggregates limonite developed. The silica-limonite mineralogical association is the result of both hydrothermal silicification and weathering processes, the latter being responsible for the thin film of ochre developed onto the surface of silica aggregates.



Figure 4. Limonitization (Ilva waste deposit).

Accumulations of brown-reddish powdery material (ochre) (Fig. 5) consist of millimeter-sized grains that were produced throughout the weathering of rocks affected by intense limonitization processes; hematite-bearing mineralogical

associations can be assumed as well. These aggregates are washed out by meteoric water and resettled down in the form of small alluvial cones at 2-3 m distance from the block of source rock.



Figure 5. Accumulations of brown-reddish powdery material (Dumitreul waste deposit).

*Clay minerals aggregates* (Fig. 2) occur as areas of white, white-yellowish or white-greenish color, alternating with brown-reddish or blackish occurrences of limonite-rich mineralogical associations. Clay minerals were formed through the hydrothermal alteration processes of Neogene volcanic rocks, mainly andesites, quartz-andesites and diorites.

Clay minerals occur as mineral aggregates of powdery appearance (during the dry periods of time) or as pasta-like aggregates (during the wet periods of time). Into the mass of these aggregates, there are scattered fragments of more or less hydrothermally altered rock; the size of rock fragments is about a couple of centimeters (1-2.5 cm). Similar accumulations with almost no pre-existing fragments of rock or with millimeter-sized grains of rocks were found as well (Fig. 6).

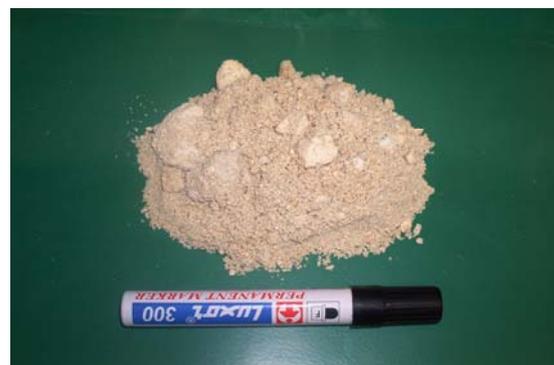


Figure 6. Argillic accumulations – argillization of almost entire mass of the pre-existing rock (Pinul waste deposit).

Field studies had also outlined transitional stages towards an exclusively clayey material,

characterized by the presence of a less altered core material, along with millimeter-sized fragments of feldspar, present in a powdery mass consisting exclusively of clay minerals (Fig. 7).



Figure 7. Argillic accumulations – transitional stage of argillization (Pinul waste deposit).

The main features of quarrying waste deposits are as following:

*Pinul waste deposit* develops at its top a plateau on which there are only rare deposits of blocks and fragments of black colored rocks affected by limonitization. Most of the rock material is powdery, it has a clayey composition, alternating here and there with powdery limonite and hematite material; the mass of waste material contains scattered centimeter and millimeter-sized fragments of andesites, quartz-andesites, diorites and basaltic andesites.

The upper plateau of the waste deposit forms a large exposed to the wind area. Therefore and as a consequence of the predominant powdery-shaped material, the latter undergoes wind erosion as well as erosion caused by flood in heavy rain periods.

*Ilva waste deposit* has also developed a plateau at its upper part, smaller yet than that developed in the upper part of Pinul deposit. The plateau is relatively safe from the wind by a mountain slope and its material consists predominantly of andesites which have undergone hydrothermal alteration processes (argillic type) and, in patches, limonitization processes.

Waste deposit material is represented by agglomerations of rock fragments consisting of andesites affected by limonitization; at the top of the waste deposit, clayey material (whether fragments or dust) are in a quite small quantity. When occurs, clayey material proves its origin from areas less affected by argillization.

*Dumitreleul deposit* is the most expanded quarrying waste accumulation. The upper plateau is almost entirely covered by agglomerations of fragments and blocks of rocks both affected by limonitization and argillization. Clayey material or

the powdery limonite and hematite are mainly located on the slopes of the deposit, which makes it extremely susceptible to leaching processes of meteoric water. Therefore slopes of the deposit often present the specific morphological features of pluvial floods.

Starting from the location of the waste deposit and the nature of deposited material (mainly decimeter-sized grains), wind erosion appears to be a process with only a reduced impact on the dynamics of powdery material dumps.

*Puturosul* is the closest waste deposit relative to the main sulfur quarry and it is located on its north-eastern side. From the viewpoint of the deposited rock material, the deposit is different from the other three, being dominated by large amounts of fragments and blocks of andesites and quartz-andesites with nests and centimeter-sized lenses of sulfur, as well as centimeter-sized – to powdery aggregates of clayey material. Fragments of rocks affected by limonitization could be observed in some areas of the eastern slopes of the deposit, represented especially by brown-reddish blocks of andesites.

### 3. METHODS OF INVESTIGATION

*Sampling.* There are two types of samples collected from the four waste deposits: solid samples (rocks and products of weathering) and liquid samples (water samples from the seasonal puddles developed onto the plateaus of Ilva and Dumitreleul waste deposits). Solid samples were collected using a geological hammer and a chisel (for rock samples), while samples of secondary products (either powdery or pasta) were collected using a small shovel and a masonry trowel.

*Samples processing.* Samples collected in the field were processed according to the type of determination supposed to be performed. Thus, thin sections have been made through representative samples of transparent mineral-forming rocks as well as polished sections on samples of metallic mineral-bearing fragment of rocks.

In order to make pH and Eh determinations, powdery samples were immersed in distilled water (pH = 6.11), in a 3:1 volume ratio (3 parts distilled water: 1 part solid sample); the samples were homogenized for 5 minutes, and left for 1 hour before making determinations of pH and Eh.

*Determinative methods* used in order to get information on the factors, processes and products of weathering as well as on the acid mine drainage were: description of a macroscopic solid samples (rocks and products of weathering and of acid drainage); detailed description of solid samples

using an optical stereomicroscope (SZM-45T2); mineral identification by means of a light transmitted microscope (ML microscope Meiji 9400); metallic mineral identification using a reflected light microscope (ML microscope Meiji 9400); XRD analyses (Philips PW 1730); pH and Eh determination of powdery products of weathering and of the leachates emerged from the quarrying waste deposits (pH ion-meter Corning M555); determination of some cation amount (Na, K, Ca, Pb, Zn, Cu, Cd) in leachates (pH ion-meter Corning M555).

## 4. RESULTS

### 4.1 Petrographic aspects

As stressed above, the rock blocks and fragments of the waste deposits belong to the following petrographical types: andesites, quartz-andesites, basaltic andesites, diorites and basalts (rarely only).

In the quarrying waste deposits fragments of andesites largely prevail; they are light to dark grayish and consist of mineral grains of less than a millimeter size. In this grayish mass of minerals white or yellowish-white feldspars were identified; the size of feldspar grains ranges between less than a millimeter to a millimeter and the mineral appears either hydrothermally altered or weathered. Under the microscope, the following minerals were identified: feldspars (plagioclases), pyroxenes (clino- and/or orthopyroxenes), more rarely amphiboles and only accidentally olivine.

Some samples of andesite present either slight disseminations of pyrite and/or chalcopyrite (hydrothermal impregnation) or millimeter-sized veins (hydrothermal s.s. process). The andesites fragments of Puturosul waste deposit contain also native sulfur that occurs as small nests and lenses in the andesite mass or as impregnations which give a quite intense yellowish color to andesite.

The andesites are often hydrothermally altered (broadly argillic type, rarely propylitic or silicic) having thus a whitish color and a reduced specific gravity.

Quartz-andesites have an important participation of silica, as quartz; they are characterized by a high hardness and are less susceptible to weathering. Basaltic andesites are also varieties of andesites characterized by a larger amount of mafic minerals (especially amphiboles and subordinately pyroxenes); they have a dark grayish to blackish color. Diorites have a grainy texture; the microscopic study revealed the presence

of following minerals: quartz, a large participation of feldspar (plagioclases especially), amphiboles and biotite.

### 4.2 Weathering products

Solid weathering products identified in the quarrying waste deposits of Negoiiul Românesc Peak belong to the following categories:

- products of limonitization, from less intense limonitization process (on the planes of minimum strength of rocks fragments) to processes affecting the whole mass of rock fragments;

- products of argillization, from a partly argillic process to a total argillization of rocks that leads to powdery clayey masses.

*The products of limonitization* can be recognized by the brown-reddish to reddish color they give to the rock debris; the main mineral of the mineralogical association is goethite (Table 1). In the waste deposits of Negoiiul Românesc Peak limonite was identified either as thin films on the crack surfaces of rocks fragments (mainly andesites) (Fig. 1) or as earthy aggregates (in the case of almost total limonitization of rocks) (Figs 4 and 5); sometimes limonite coats or limonite stains developed on andesites and diorites were found. When limonite occurs on cracks of the rocks, its color is reddish (hematite) while the earthy aggregates are brown.

Limonite formed as a result of weathering of hydrothermal iron sulfides (pyrite, rarely chalcopyrite) scattered in the mass of rock fragments (Audry et al., 2005; Todd et al., 2003; Bonnissel-Gissingner et al., 1998). It occurs frequently accompanied by hematite, kaolinite and quartz (Table 1); the presence of Mn hydroxides may be assumed (Stumbea, 2006). Moreover, as was stated before, some blocks and fragments of rocks from the waste deposits develop on their surface a black film with reddish and bluish iridescences; these can be associated to the development of so-called black limonite or to a more important accumulation of Mn oxides and hydroxides.

Initially, limonitization affects the in situ Neogene volcanic rocks of the perimeter; once brought to the surface through mining works and deposited as quarry wastes, rocks undergo an intensified limonitization induced by weathering processes. Weathering products are composed of powdery Fe oxyhydroxides and clay minerals, resulting from the physical and chemical alteration of Fe-rich mineral associations; the primary source of Fe in the perimeter of waste deposits is the hydrothermal sulfides (especially pyrite) genetically associated to andesites and diorites.

Table 1. XRD analyses of solid products of limonitization

No.	Angle	D space	Rel. int.	Mineral phase
1	27.99	3.68	41	Hematite
2	38.15	2.70	100	Hematite + Goethite
3	41.77	2.53	52	Hematite + Goethite
4	48.01	2.21	37	Hematite + Goethite + Kaolinite
5	57.99	1.85	32	Hematite + Goethite + Quartz + Kaolinite
6	63.51	1.67	39	Hematite + Goethite + Quartz + Kaolinite
7	74.66	1.51	15	Hematite + Goethite
8	76.02	1.46	21	Hematite + Goethite + Quartz

The powdery products of limonitization identified in the waste deposits contain also clayey components (kaolinite, Table 1) and aggregates of millimeter-sized grains (<1-3 mm) representing fragments of andesites, quartz-andesites and diorites.

In order to determine the influence of powdery aggregates on pH and Eh values of surface waters from the perimeter, samples were immersed in distilled water in a solid/liquid volumetric ration of 1/3, followed by a 5 minutes stirring; then the samples were left to settle for 60 minutes. The insoluble products were deposited at the bottom of the beaker; the bottom-layer of this precipitate has a dark-brown color and consist of less than a millimeter sized grains while its top-layer is brown-yellowish and consists of micrometer-sized grains. pH and Eh measurements were performed at the upper part of the leachates; values of measured pH and Eh are presented in table 2.

Data of table 2 and figure 8 show that powdery products of limonitization generate an obviously less acidic environment (pH = 5.99-6.17)

than the samples of argillization products (pH = 2.52-4.25). Despite a very weak increase within the first 12 hours after the immersion of the solid sample, the pH variation in respect of time (Fig. 8) shows a quite constant behavior with a discrete drop of values. Plot of pH and Eh data on Pourbaix diagram of iron shows that solutions where powdery limonite is involved are characterized by the solid hydroxide compound of iron –  $\text{Fe}(\text{OH})_{3(s)}$ , as Eneroth & Koch (2003) stressed as well. Otherwise, the appearance of the leachate remained murky even after 72 hours from the beginning of the experiment and kept a yellowish to ochre color.

Determination of Na and K of the resulting solution (leachate) following immersion of powdery limonitization material indicates values of 189 mg/l Na and 36.9 mg/l K (Table 3), which - in relation to the participation of these cations in distilled water where the sample was dipped in - is an apparent input of approximately 66 mg/l Na and 36 mg/l K, from the pulverulent limonitization material.

Table 2. pH and Eh data of powdery weathering products from the quarrying waste deposits of Negoiiul Româneșc peak

Sample	Measurement 1		Measurement 2		Measurement 3		Measurement 4	
	pH	Eh (meV)						
A1	4.25	165.4	4.87	122.4	4.62	142.9	4.32	162.3
A2	3.44	220.1	3.69	208.7	3.23	229.7	3.15	233.3
A3	2.95	242.4	3.22	230.1	3.01	239.7	2.78	250.1
A4	2.65	256.1	2.56	260.2	2.56	262.4	2.52	264.2
A5	3.53	216.0	3.67	209.6	3.41	221.5	3.25	228.8
<b>Am</b>	<b>3.36</b>	<b>220.0</b>	<b>3.60</b>	<b>206.2</b>	<b>3.37</b>	<b>219.2</b>	<b>3.20</b>	<b>227.7</b>
L1	5.99	67.2	6.17	52.6	5.72	74.1	5.58	85.7
L2	5.64	82.2	5.70	78.5	5.51	89.6	5.43	94.2
L3	5.49	90.7	5.81	72.1	5.56	86.7	5.47	91.9
L4	5.85	69.8	5.72	77.4	5.87	68.6	5.65	81.4
<b>Lm</b>	<b>5.74</b>	<b>77.5</b>	<b>5.85</b>	<b>70.1</b>	<b>5.66</b>	<b>79.7</b>	<b>5.53</b>	<b>88.3</b>

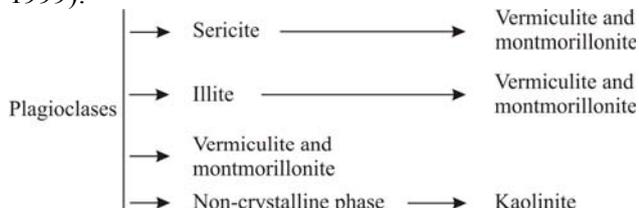
A1-A5 – powdery products of argillization; L1-L4-powdery products of limonitization; Am, Lm – mean values of pH and Eh; measurement 1-immediately after the settlement of powder particles; measurement 2-after 12 hours; measurement 3-after 24 hours; measurement 4-after 36 hours.

Previous studies concerning solid waste materials in quite similar areas and contexts of Baia Mare perimeter (Romania) (Damian & Damian, 2006; Damian et al., 2008) compel the necessity of further studies carried out on the quarrying waste dumps of Negoitul Românesc in order to evaluate the amount of heavy metals in the solid waste materials and their impact on the environment (surface waters, soils, vegetation).

*Argillic products* of alteration can be identified in the quarrying waste perimeter by the whitish, white-greenish or white-yellowish color they give to the surface of rock fragments; they appear as well as masses of powdery material having the same colors.

This argillic material mainly consists of clay minerals, such as beidellite, illite, kaolinite, montmorillonite, vermiculite and nontronite. In the mass of powdery products, fragments of pre-existing rocks can be found (andesite and diorite, especially), having dimensions of centimeters (in the case of partially argillized material) or millimeters (if argillization is quasi-total).

Clay minerals originated by hydrothermal alteration and/or weathering processes of feldspars from the volcanic rocks (andesites, diorites); the most susceptible to alteration are plagioclases which present the widest participation in these rocks. Some of the mechanisms of rocks altering are (Stumbea, 1999):



In order to determine the pH and Eh induced by the powdery material of clay minerals in the hydrographic environment the same procedures as in the case of powdery limonite products were

performed. Analytical data are presented in table 2 and figure 8 which emphasize almost constant pH values of leachates; however, a slight tendency towards decreasing values of this parameter in time can be observed, similar to that it was described for the sample of powdery limonite. pH and Eh data plotted on Pourbaix diagram of iron revealed that iron of solutions generated by leaching of argillic solid products belong to the  $Fe^{2+}_{(aq)}$  type.

On the other hand, unlike the case of brown-reddish material (ochre), leachates of powdery argillic products became clear either immediately (in less than 0.5 hours) or within the first 36 hours; the insoluble products deposited at the bottom of the beaker have yellow-brown or yellow-greenish color.

Analyses performed using a Corning M 555 pH ion-meter provided with Na and K electrodes are presented in table 3 and refer to determinations on solutions obtained by the immersion tests of powdery argillic samples in distilled water.

Data of table 3 suggest inputs of 4355 mg/l to 1.96 weight % Na and between 7.33 and 45.4 mg/l K, from the solid argillic samples into the distilled water.

*Liquid products (surface water).* Water samples were taken from the small accumulations (puddles) developed onto the upper part of quarry waste deposits; only water accumulations which have no obvious connection with inputs from other parts of the waste perimeter (small streams, melting snow) were sampled. Liquid samples (surface water) were subjected to determinations of pH and Eh, as well as determinations of the amount of some cations such as Na, K, Ca, Pb, Zn, Cu and Cd.

Samples of water collected from puddles from the top of the quarry waste deposits are colorless and odorless; their pH values (Table 4) are typical to the high-end range of pH values recorded for the mine waters affected by acid rock drainage (acid mine drainage) processes (Jambor et al., 2000).

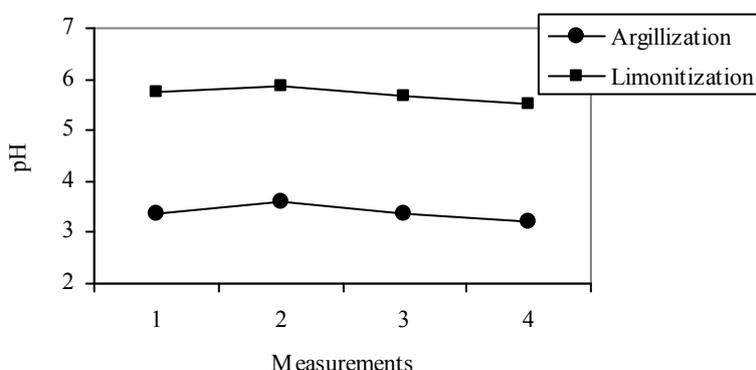


Figure 8. pH data of leachates (average data) vs. time. Measurements 1-4 as in table 2

Table 3 Contents of Na and K (mg/l) in immersion solutions of powdery argillic material and powdery products of limonitization

Sample	Na	K	Na <sub>H2O<sub>d</sub></sub> = 123mg/l K <sub>H2O<sub>d</sub></sub> = 0.812mg/l
A1	4355	45.4	
A2	8020	37.0	
A3	11064	7.33	
A4	19652	8.29	
A5	7467	29.1	
L1	102	8.8	
L2	189	36.9	
L3	76	25.1	
L4	121	14.0	

A1-A5, L1-L4 as in table 1

Table 4 Values of pH, Eh and cation contents (mg/l) of surface waters from the top plateaus of quarry waste deposits

Measurement	Sample					
	W1	W2	W3	W4	W5	W6
pH	4.89	5.15	4.97	5.21	5.01	5.10
Eh (meV)	122.4	112.1	119.2	109.7	117.6	114.1
Na	135.0	73.0	101.6	87.2	64.8	91.5
K	14.2	8.7	11.5	5.2	12.0	6.6
Ca	19.5	23.2	44.1	71.8	37.9	54.4
Pb	0.29	0.27	0.29	0.22	0.22	0.26
Zn	0.8	0.8	0.9	0.9	0.8	0.8
Cu	0.1	0.2	0.1	0.3	0.3	0.1
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

The plot of pH and Eh data in Pourbaix diagrams of iron reveals the presence of Fe<sup>2+</sup><sub>(aq)</sub> as in the case of solutions emerged from immersion tests of powdery argillic samples in distilled water.

Quantitative determinations of Na amount appear to be close to that of rainwater or of water from melting snow, while K shows a obviously higher concentration that suggests an input from the reaction of the rainfall water with underlying clay minerals of quarry waste deposits. The comparison between Na and K amounts of water collected from puddles developed on the top plateaus of the quarry waste deposits and those specific to some drinking mineral water extracted from quite geologically similar areas shows that while Na amounts are obviously higher in puddles water from the waste deposits, K content is rather similar.

Heavy metals amounts in water puddles of the quarry wastes fall within the specific values of these elements, determined in inland waters of continents, which lead to the assumption that the surface waters accumulated on the top of waste deposits do not generate alarming inputs into the surrounding hydrographic network of Negoitul Românesc Peak area. On the other hand, obviously higher amounts of heavy metals are expected to be found in the drainage waters that pass through the quarrying

waste dump, as Andráš et al. (2008a, b, 2009) and stated for a dump-field in Slovakia.

## 5. CONCLUSIONS

Pinul, Ilva, Dumitreleul and Puturosul quarry waste deposits consist of fragments and blocks of rocks, especially andesites, quartz-andesites and basaltic andesites; along with these debris, in the perimeter of quarry wastes dumps large accumulations of powdery material were found as well.

The solid products of limonitization (ochre) are the result of oxidation processes affecting the veinlets and disseminations of Fe±Cu sulfides (pyrite, rarely chalcopyrite) developed in the rock mass; argillic material represents the consequence of hydrothermal alteration of primary minerals of rocks, especially plagioclases. The main minerals that occur are goethite, hematite and Fe oxyhydroxides (products of limonitization) and kaolinite, montmorillonite, illite and vermiculite (argillic products). Both solid products formed endogenously but once brought to the surface through quarrying works they undergone weathering processes.

The pH determinations performed on limonitization and argillic powdery materials suggest that they represent the main source of acidity in the perimeter of all four quarry waste deposits. pH values range between 2.5 and 6 and place the leachates emerged from the waste materials in the domain of acid rock drainage (acid mine drainage). Leachates of argillic products induce in the environment an obviously lower pH (pH = 2.52-4.25), than the solutions emerged through leaching of limonitization aggregates (pH = 5.99-6.17). Although they have quite higher pH values (maximum of 5.21), water accumulated onto the upper surfaces of waste deposits (puddles) have the features of acid mine drainage products as well.

As far as we are concerned, the process that triggers the acid mining drainage is the oxidation of metallic minerals (Fe and/or Fe±Cu sulfides) scattered in the mass of rocks, which leads to the formation of ochre products and/or the formation of H<sub>2</sub>SO<sub>4</sub>. Then, as a result of quarrying works, rocks affected by limonitization are brought to the surface where they undergo weathering processes and generate quite acid discharges (pH of around 5).

Clay mineral associations of argillic material have a high susceptibility to wind and water transport at distance from their original location; the interaction between argillic material and rainfall waters produces highly acidic leachates (pH of 2.5 to 5). The environmental effect of these mineral associations is increased by the weathering processes which transform minerals of hydrothermal genesis (remnant plagioclase grains, sericite, illite, gibbsite), in other terms of clay minerals group (vermiculite, montmorillonite and kaolinite).

The iron of leachates generated by limonitization products is of Fe<sup>3+</sup> type; the low pH of the environment and the alleged presence of H<sub>2</sub>SO<sub>4</sub> create prerequisites for Fe<sup>3+</sup> to act as an oxidizing agent. On the contrary, iron from the solutions produced by leaching of argillic products belongs to Fe<sup>2+</sup><sub>(aq)</sub> type, so oxidation occurs only in the presence of oxygen. At the pH of the latter solutions (2.52-4.25) and in the absence of Fe<sup>3+</sup>, sulfuric acid dissolves a part of carbonates and heavy metal oxides, but has a minimal effect on heavy metal from sulfide structure. By its presence, Fe<sup>3+</sup> cause the solubilization of heavy metals-bearing sulfides.

Chemical features of waters from the small accumulations (puddles) developed onto the upper part of quarry waste deposits suggest that, except for pH, they do not represent a key risk factor to the environment, especially in the waste areas where argillic materials were deposited; in the latter areas, argillic wastes act as a barrier that prevents

infiltration of surface water. However, it is assumed that the risk arising from the waters that pass through the entire mass of the waste deposits (infiltration) is very high.

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