

RESEARCH RELATED TO THE PAST EXPLOITATION IMPACT OF CALIMANI SULPHUR ORE UPON THE ENVIRONMENT

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Abstract

This paper emphasizes an ascertainment over the pollution level on terrestrial and aquatic ecosystems within the past exploitation region of Calimani mountains sulphur ore. Experimental data are introduced here, concerning the transformation of the sulphur and sulphides into sulphuric acid, chemical changes that exist in the surface waters, on the refuse waste dumps and in the regions limitrophe to areas affected by the past exploitation of Calimani ore. Through the surface exploitation of materials including high quantities of sulphur and metallic sulphides, draining phenomena of the acid waters and solubilization phenomena of the heavy metals have been amplified.

Key words: : heavy metals, ore exploitation, photochemical changes, refuse waste dump, sulphur diggings.

JEL Classification: Q51; Q53; N5

I. INTRODUCTION

Calimani Mountains belong to the volcanic chain that forms the West side of the Eastern Carpathians of Romania, being placed at the 47°07' Nordic latitude, 25° 14' East longitude and 1300-2100 m altitude.

The volcanic intense activity has determined the occurrence of huge storages of lava, evolved on a length of 450km, among which 375 on Romania's territory (Stumbea, D., 2010, Ionce, A., 2010).

Calimani Mountains represent the only place of Romania where exploitable *sulphur diggings* gathered up. The sulphur can be found under the form as impregnations, nests or small veins.

The sulphur diggings have been formed after closing the lava eruptions, from cold gas leakages, and after chemical changes between the volcanic gas leakages (sulphur dioxide and hydrogen sulphide) and the ground waters that circulated through the loosening deposits (Ono et al 2003, Aziz 2008, Sekomo, 2012).



The *sulphur ore* also includes other components, meaning mainly: *iron sulphide* (iron pyrites – cubic FeS₂ and marcasite – diamond shaped FeS₂); *sulphates* – alunite – trigonal KAl₃(SO₄)₂(OH)₆; *gypsum* – CaSO₄.2H₂O; *mica* (silicates): kaolin – Al₄[Si₄O₁₀](OH)₈, calcium feldspar – CaAl₂Si₂O₈, periclins – NaAlSi₃O₈; *limonite* (mixture of iron hydroxides, aluminum hydroxides, sulphates and carbonates); *hematite* (Fe₂O₃), as well as some compounds of zinc, copper, plumbum, nickel or manganese etc.

The *native sulphur* content varies in large limits comprised between 10-43% (*Management Plan of Calimani National Park, 2010*).

The sulphur ore extraction has been carried out in Negoiu Romanesc of Calimani Mountains, placed in the South-East region of Suceava County. The exploitation was accomplished by means of the blasting method with explosives on exteriorly, within heights of 1550 - 1860 m. Simultaneously with the sulphur rock extraction, removing the refuse from marginal regions of the sulphur ore has also been carried out. The refuse achieved after uncovering was deposited in the three waste dumps, meaning: Ilva Dumitreleu, Pinu and Puturosu. The refuse waste dumps include a large variety of rocks, refuse material and soil. From the technological process of achieving the technic sulphur, the wet

refuse resulted after the wet beating, flotation and heat treatment operations, which are specific to the sulphur ore that was deposited in the Dumitreleu mud-setting pond.

Through the surface exploitation of materials including high quantities of sulphur and metallic sulphides, draining phenomena of the acid waters and solubilization phenomena of the heavy metals have been amplified. (Luís 2009, Gonzalez –Fernandez 2011, Prasad 2011, Wazoh Hannatu et al. 2014). The natural sub-serving factors that have amplified the effects of anthropogenic actions within this region are specific to:

- the *orographic* type (long mountainsides, downgrade slopes);
- the *climatic* type (low temperatures: yearly mean temperatures included between 2.4 – 4.0°C); high quantities of rainfall of 1022 mm yearly average);
- the *edaphic* type, where the soils met are represented by *districambosol soils* (the *cambosol* class), the *prepodzols* soils, as well as the *humico-feri-iluvial* soils (the *spodisols* class). The first two classes have an andic feature, meaning acid moderated (pH de 4.5- 5.2) and low-moderated humus content (an average of 26.6%) (*Management Plan of Calimani National Park, 2010*).

The surface exploitation of the sulphur ores caused a quality deterioration of all ecosystems surrounding the Calimani region. In this way, during both periods when activities were carried out (started in 1970) and after their stopping in 1997, and because of high toxic residues emitted in the atmosphere, almost 350 ha of field were affected. Starting with 2007, the past ore exploitation of Calimani has been included within the Calimanin National Park. The sulphur and sulphides chemical changes into sulfuric acid, and respectively sulphates, existing in the surface waters within Calimani Ore Exploitation areal, have been underlying upon catalyst chemical changes induced by the microorganisms that grew in such environments. (Dițoiu, 2005, Dold, 2005)

Such microorganisms, also known under the name of oxidant sulphurous bacteria, have used within the synthesis process of organic substances the energy achieved by some inorganic compounds; as regards the hydrogen source used in the view of reducing the carbon-dioxide, they have used the water. (Wang, 1991, Prietzel, 2008)

Concerning the aerobe conditions, such substances were air-blown up to the level of sulphates, which have always persisted in water, as long as the dissolved oxygen was able to prevent the chemical changes of sulphates reduction into hydrogen sulphide (Mohammad Shamsuddoha et al., 2013)

One can also mention that such mountain waters of low depth are well aired and easily to be permeated by the sun rays, ensuring in this way the optimal conditions on such chemical changes.

The soil and water acidity, produced by sulphur and polymetallic sulphur compounds air-blown signifies one of the main factors of metals chemical changes into toxic movable ions. Afterwards, these are easily absorbed by the terrestrial and aquatic flora. (Prietzel, 2008, Aziz 2008)

This paper is dedicated to the impact over the soil and aquatic ecosystems, impact that was produced by the refuse material deposits, coming from sulphur preparation. The measurements have been carried out in 2010, after twelve years from stopping the activities.

II. EXPERIMENTAL DATA CONCERNING THE SOIL POLLUTION LEVEL

Research has been carried out in order to analyze the level of soil alteration surrounding the Calimani Ore Exploitation region. By means of uncovering the sulphur ore and polymetallic sulphides, an area of about 350ha has been altered. The refuse including approximately 8% sulphur covered an area of about 100ha.

This paper emphasizes the measurements results achieved in 2010 for samples collected from the refuse deposits, taking into account the following points:

- Sample **S1** – the refuse average sample, collected from the three actual waste dumps;
- Sample **S2** – the average sample of impure soil, collected from the limitrophe regions surrounding the refuse waste dumps;
- Sample **S3** – polluted soil, collected from the limitrophe region near the mud-setting pond;
- Sample **S4** – the proof sample, collected from the unaffected region, for about 10km distance from the pollution source, where the vegetation is growing naturally.

The soil samples were collected on two depths, meaning: 0-5cm and 5-30cm, by means of a sampling probe.

The soil average samples were achieved by intermixing four samples, collected from each point of harvesting. All these samples have been prepared in the laboratory, in accordance to ISO 11464/2006 Standard.

a. Setting the pH

The pH was set up in accordance to SR 7184-13/2001 Standard: from the sample of air-dried, minced and screen filtered soil, with a stitch diameter of 2mm, a water slurry with the soil-water ratio of 1/2.5 was prepared (the mass-volume ratio). The activity of hydrogen ions was measured in such solution, expressed in pH units. The pH measurements were carried out with the aid of a WTW 526 type pH-meter based on combined electrodes. The specific conductivity of the bi-distilled water was of 2µS/cm.

b. Metals determination

Processing the laboratory samples in order to identify the heavy metals existing in the soil, by means of spectrometry in atomic absorption, has been carried out in accordance to *SR ISO 11466/1999 Standard*: soil and air-dried refuse samples were used, screened by means of sieve on 1.50mm diameter, wherefrom 1g of sample was weighted each time. These have been mineralized on 105°C temperature by the aqua regia (each 2ml of HNO₃ 65% and 6 ml HCl 37%), by means of the MWS3 microwave digestion oven of Berghof type. The extracts achieved by filtering the mineralized samples were transferred into calibrated flasks of 100ml that included HNO₃ 0.5mol/l.

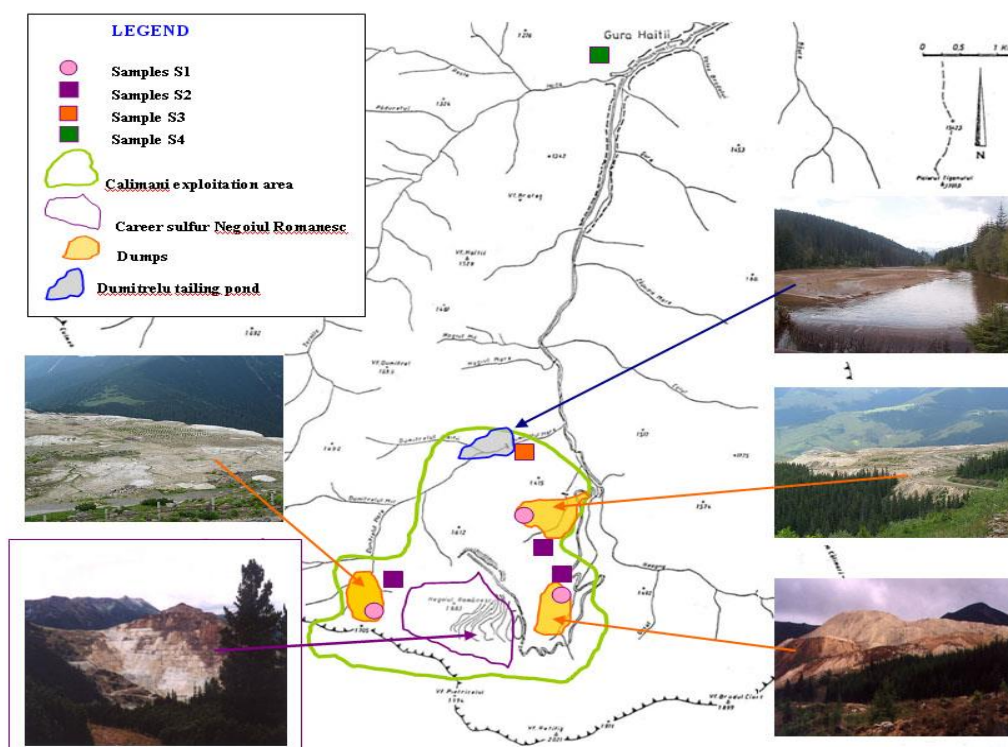


Figure 1. Tracking the past Calimani exploitation ore and the soil sampling points

In order to determine the manganese, each 10ml of LaCl₃ 10% solution was added before reaching the marked line from the calibrated flasks; afterwards, 0.5mol/l of azotic acid was added in order to reach the marked line of the calibrated flask. As regards the air-dried samples, the soil moistures were established, in accordance to SR ISO 11465/1998 standard. The total measurements taken from the soil and refuse metals (iron, manganese, copper, cadmium, nickel) have been carried out by means of a spectrophotometer on flame atomic absorption and graphite oven, on Spectr AA 220 type, and in accordance to SR ISO 8288/2001, SR 13315/1996 and SR 8662-2/1997 standards. The samples results were reported towards the totally dried soil.

c. Identifying the sulphates

Each 1g of air-dried triturable soil was weighted and passed through the sieve of 2mm mesh diameter, in accordance to ISO 11464/2006 Standard. Identifying the sulphates was carried out by means of the turbidimetric method (Standard Methods for the Examination of Water and Wastewater - 19/1995) to a spectrophotometer of molecular absorption on CECIL 8020 type: each 1g of sample was weighted and then mineralized on 500°C, in the presence of 0.25g of aerated salt. Afterwards, these were oxidized with 0.3% peroxide. The total soil sulphates achieved after the filtration can be identified now. The sulphate ion will precipitate into acetic acid-sodium acetate (cushion agent) with barium chloride and will form the barium sulphate crystals.

The absorption degree of barium sulphate will be measured with the spectrophotometer, and as regards the sulphate ion concentration, the calibrating plot will be established. Correcting the color degree and turbidity will be carried out by using a control sample, to which no barium chloride or buffer solution are added, and which are subtracted from the sample. From the analysis of data achieved and illustrated in Table 1, the following will result:

Table 1. The soil and refuse composition

Sample code	Depth (cm)	pH	Sulphates (ppm)	Iron (ppm)	Manganese (ppm)	Zinc (ppm)	Copper (ppm)	Cadmium (ppm)	Nickel (ppm)
S1	0-5	2,28	-	43087	268	97,24	30,14	0,545	29,38
S2	0-5	2,42	58000	33658	138,1	22,27	17,21	0,24	20,02
	5-30	2,54	52300	22678	111,5	21,56	16,21	0,19	17,78
S3	0-5	3,47	4530	36101	84	24,78	24,41	0	12,6
	5-30	3,75	3700	48318	113	52,4	31,7	0	15,5
S4	0-5	6,75	320	2579	9,2	4,39	6,79	0,154	10,78

- Sample S1 of refuse, comparing to sample S4 (control sample):
 - for the total heavy metals, the following values could be noticed: values of 17 times higher for iron and 30 times higher for manganese, values of 20 times higher for zinc and 2 up to 5 times higher for the copper, cadmium and nickel, (figure 4) ;
 - the pH highly acid value of 2,28 can be explained by the hydrogen ions presence, produced by means of sulphur oxidation, (figure 2);

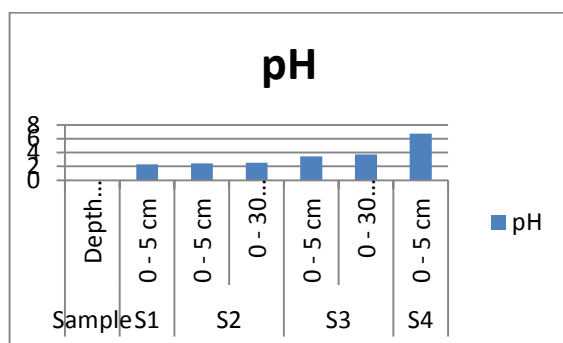


Figure 2. Average values for pH

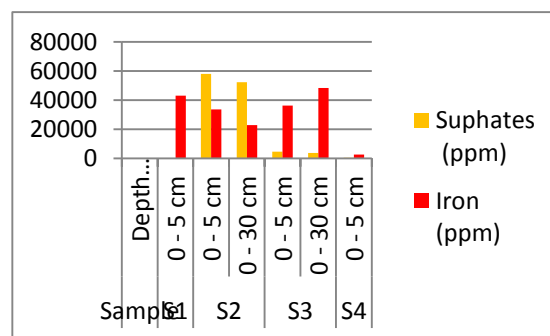


Figure 3. Average values for sulphates and iron

As regards the S2 sample (soil collected from regions near the refuse waste dumps), the following can be mentioned:

- higher values on surface sample metals (0-5cm), as comparing to the samples achieved on depths of 5-30cm. Values that exceed 5 up to 15 times the values measured to S4 sample (control sample) could also be noticed;
 - the strongly acid pH values of 2,42, and respectively 2,54, on the two soil types is emphasized, because of the fall-out that wash the waste dumps and train the solid material on the soil, (figure 2);
 - The total sulphates registered values of 160-180 times higher as comparing to the control sample, (figure.3).
- The S3 sample of polluted soil collected from the region limitrophe to the mud-setting pond:
 - very low values of pH, meaning 3,47 and respectively 3,75, comparing to the soil sample that was not affected (the control sample) and which has the pH of 6,75 value;
 - the metals content is 2-18 times higher towards the metals measured by the help of control sample, (figure 2);
 - The total sulphates on the two soil types have registered values within 100-400 times higher as comparing to the control sample, (figure 3). Maintaining the pH value extremely low on the soil samples from regions limitrophe to refuse deposits and mud-setting pond of refuse is connected to the sulphur presence into the solid and liquid residues, trained on soil by the fall-out.

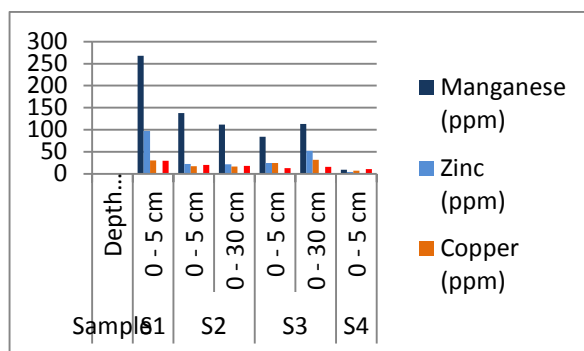


Figure 4. Average values for manganese, zinc, copper, cadmium and nichel

III. EXPERIMENTAL DATA CONCERNING THE SURFACE WATERS QUALITY

3.1. Experimental data of Neagra river pollution level

The sources of surface water pollution from the past exploitation region of Calimani mountains sulphur ore are the following:

- **the refuse waste dumps**, traversed by Neagra River flows, are washed by the rainfall that train significant quantities of suspensions, of high content of sulphur and metals into the surface waters;
- **the uncovered surfaces of ore**, from where the rainfall will train significant quantities of sulphur and metals into the Neagra River;
- **the research galleries**, from where strongly acid mine waters come out and pollute the quality of Neagra River;
- **Dumitreleu mud-setting pond**, from where the polluted waters of highly acid level will fall out directly or by exfiltration into Dumitreleu stream, affluent of Neagra River.

Neagra River, having a total length of 33km and a basin of 302 km², will traverse Calimani mine region to the base of refuse deposits and mud-setting pond. From the hydrological data, it results that at the junction of Neagra and Bistrita rivers, the water volume that flows annually is included within the interval of 84 million m³/year (for a rainless year with 95% insurance) and 177 million m³/year (for a rainy year with 5% insurance). The average volume has the 130 million m³/year value. Its flow will be formed by the junction of Rețițiș, Pinului and Dumitreleu streams.

The water quality evolution of Neagra River was analyzed upstream and downstream, as related to the Calimani ore exploitation and in accordance to the chemical point of view (for the heavy metals, sulphates and pH), and is emphasized in table 2.

This paper carries out an analysis over the results of measurements taken in 2010, for the samples collected from the following points:

- a. Sample W1 – Neagra River, upstream to Calimani ore exploitation
- b. Sample W2 – Neagra, downstream to Calimani ore exploitation.

In the months July, August and September of 2010, momentary samples of water were collected, and these were preserved and manipulated in order to be measured and in accordance to *SR EN ISO 5667-3/2004* standard, as regards the *Water Quality, Sampling, Part 3: Guide on water samples preservation and manipulation*.

a. Identifying the pH. The pH identification was carried out in accordance to *SR ISO10523/2009* standard: by measuring the hydrogen ions activity, expressed in pH units, with a pH-meter of WTW 526 type on combined electrode.

b. Establishing the metals. The determinations of metals dissolved in water were carried out by means of spectrophotometer method with flame atomic absorption, in the following way: iron, manganese and plumbum determinations were performed in accordance to *SR ISO 8288/2001* standard, determination of the iron content was done in accordance to *SR 13315/1996* standard, and determination of manganese content was carried out in accordance to *SR 8662-2/1997* standard. The measurements were performed by a spectrophotometer with flame atomic absorption and graphite oven, of Spectr AA 220.

c. Identifying the sulphates. Identifying the sulphates from water was carried out by means of turbidimetric method (Standard Methods For the Examination of Water and Wastewater- ed. 19/1995), with a spectrophotometer of molecular absorption of CECIL 8020 type, meaning:

The samples of filtered water, in the environment of acetic acid-sodium acetate (buffer solution), were treated by barium chloride and by forming the barium sulphate (crystals of uniform dimension. The absorbance of barium sulphate

suspension was measured to the spectrophotometer and the sulphate ion concentration was determined on the calibrating plot. Correcting the color degree and turbidity was carried out by using a control sample, to which no barium chloride or buffer solution are added, and which are subtracted from the sample.

Table 2 and figures 2, 3 and 4 illustrate the average values of the three series of physical – chemical indicators that were measured, and which are compared with the limit values imposed by means of the Ministry order no. 161/2006 (in order to approve the standard as regards the classification of surface water quality, and in the view of establishing the ecological state of the elements existing in water), standard issued by transposing the European Directives on national level.

From the analysis of data achieved in table 2, the following can be noticed:

○ **Neagra River – upstream to Calimani ore exploitation**

On origins, the Neagra River represents an unpolluted mountain river that offers good life conditions for the aquatic biocenosis:

- low acid pH of 6.14;
- dissolved iron of 0.111 mg/l;
- dissolved zinc of 25.4 µg/l;
- dissolved copper of 5.3 µg/l;
- dissolved manganese 0.032 µg/l;
- dissolved plumbum 0.9 µg/l;
- sulphates 33 mg/l.

With the exception of pH, which has a low acid feature (due to the substrate composition, specific to the region), all parameters will be framed within the first class of quality.

○ **Neagra River – downstream to Calimani ore exploitation**

After crossing the ore exploitation region, even after ten years from stopping the activity, the quality of Neagra stream got worse:

- high acid pH of 3.01;
- dissolved iron 60.54 mg/l;
- dissolved copper 238 µg/l;
- dissolved manganese 2.05 µg/l;
- sulphates 719 mg/l.

For these values, the river will be framed in the Vth class of quality (the water is lowered). As regards the dissolved zinc of 467µg/l and the dissolved plumbum of 8.39µg/l, the river water will be framed in the IIIrd class of quality. Considering this point of taking-off, the water is lowered and has the aspect determined by refuse mudding action, with brown-grey color and opalescent aspect.

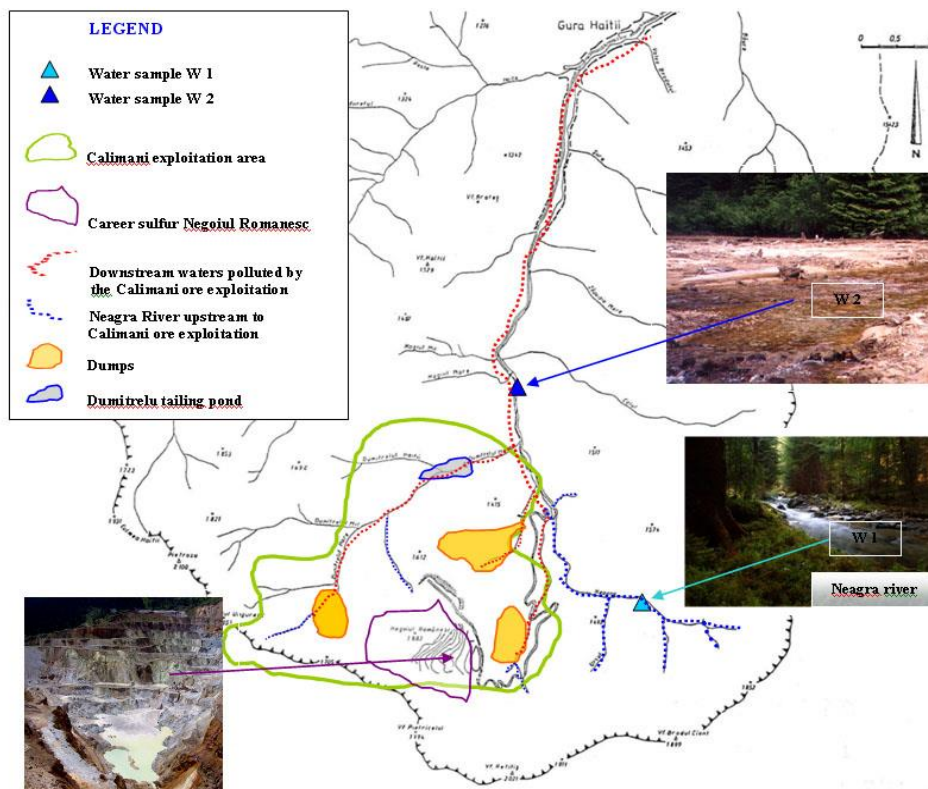


Figure. 5. The hydrographic network of Neagra River

Table 2. Physical-chemical characteristics of Neagra River (average values)

Sample code	pH	Dissolved iron mg/l	Dissolved zinc µg/l	Dissolved copper µg/l	Dissolved manganese mg/l	Dissolved plumbum µg/l	Sulphate mg/l
W1	6,14	0,111	25,4	5,3	0,032	0,9	33,12
W2	3,01	60,54	467	238	2,05	18,39	719,2
Quality classes for water surface and on establishing the ecological state (according to – Ministry no. 161/2006)	I	0,3	100	20	0,05	5	60
	II	0,5	200	30	0,1	10	120
	III	1,0	500	50	0,3	25	250
	IV	2,0	1000	100	1,0	50	300
	V	>2,0	>1000	>100	>1,0	>50	>300

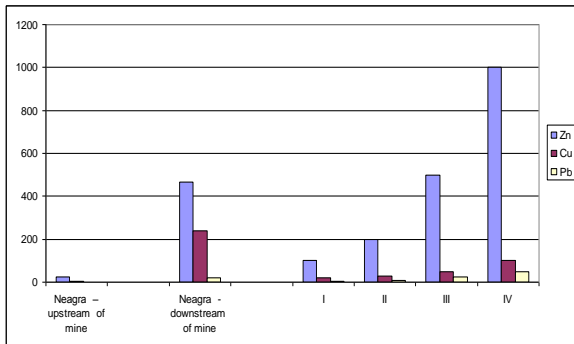


Figure 6. Average values for zinc, copper and plumbum, comparing to the values acknowledged

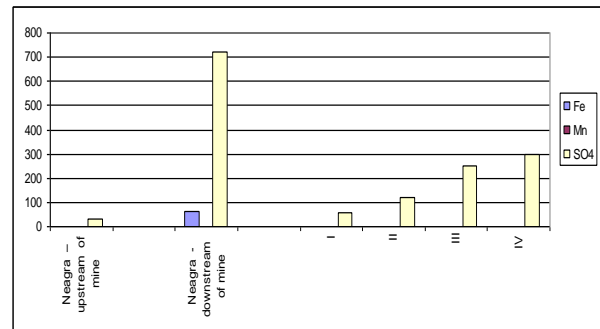


Figure 7. Average values for iron, manganese and sulphates, comparing to values acknowledge

Table 3. Values of metals existing in the water, after the calcium hydroxide treatment (P1) and sodium hydroxide (P2)

Sample type	Iron (mg/l)	Zinc (µg/l)	Copper (µg/l)	Manganese (mg/l)	Lead (µg/l)
Sample P2	15,2	9,28	7,07	0,45	0,2
Sample P3	0,016	0,014	0,01	0,001	0

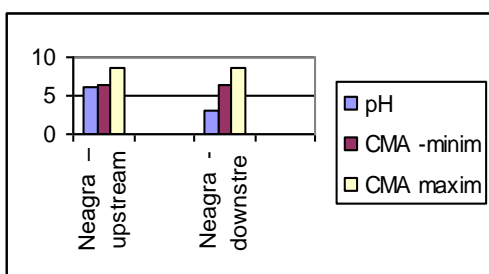


Figure 8. Average values for pH

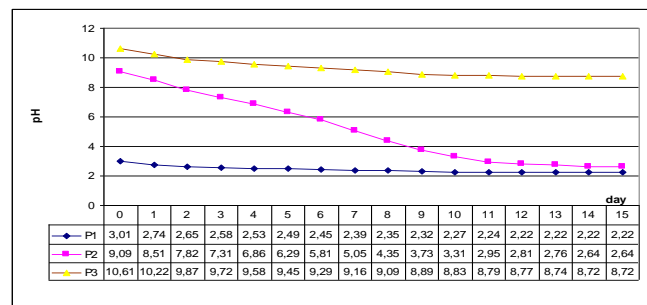


Figure 9. pH dynamics on P1, P2 and P3 water samples

3.2. Experimental research concerning the modifications dynamics of surface water quality, by means of photochemical changes

The presence of photochemical and biochemical changes in the polluted receptor waters of refuse surrounding the Calimani region, which include a high percentage of sulphides, sulphur and metallic ions, was confirmed by a series of laboratory research. Such research aimed towards the pH dynamics analysis, as regards the water (the surface water, soil and refuse affected near Calimani), initially alkalinized with a weak base, calcium hydroxide-Ca(OH)₂, as well as high base, meaning sodium hydroxide - (NaOH). The experiment was

carried out in order to find some optimal solutions of removing these impurities out of waters. In this way, the water samples of Neagra

– downstream of Calimani ore exploitation were collected and processed in the laboratory.

Work mode: the water collected from Neagra river was divided in three samples, of one liter each, samples were placed in three glass recipients (crystallizing apparatus of 30cm diameter), in the following way:

- sample P1 was maintained as such (not treated);
- sample P2 was treated with agaric mineral, up to pH-9.09;
- Sample P3 was brought up to pH-10.61 with sodium hydroxide.

The recipients that contain the three samples were exposed into a light room, where the sunrays got in during the day, for 15 days. In all this period, the samples were daily homogenized, on the same hour, before measuring the pH value. The chemical composition of sample P1 is given in table 2, and, as regards the P2 and P3 samples, these are illustrated in table 3. The dynamics of pH variation to P1, P2 and P3 samples is emphasized in figure 5.

The conclusions drawn after the measurements taken can be thus emphasized:

- As regards the untreated sample P1, with an initial pH of 3.01, the oxidation chemical changes of sulphur and the formation of sulphuric acid take place until the pH value of 2.22 is reached in laboratory conditions. This aspect will prove that the photo-oxidation chemical changes will continue during the following 15 days from the experiment.
- As regards the sample P2 with an initial pH of 9.09, the oxidation chemical changes of the sulphur and the formation of sulphuric acid take place until the pH value of 2.64 is reached in laboratory conditions. In this way, it is proven that the agaric mineral (weak base) will not fully stop the sulphur oxidation and the formation of sulphuric acid (only the hydrogen protons already existing in the water will be dis-acidified in the moment of treatment, by some metals parts fall-out). The photo-oxidation chemical changes will continue for the following 10 days interval.

Analyzing sample P3, with an initially alkaline pH of 10.61, one can deduct that the oxidation chemical changes and formation of sulphuric acid until the pH value of 8.72 is reached in laboratory conditions. This issue will prove that on water samples alkalization on high base (NAOH), the full fall-out of metals existing in the water will be achieved. The low reduction of pH value in the following 15 days is given only by the photo-chemical oxidation changes on sulphur compounds that exist in the water.

IV. CONCLUSIONS

The surface exploitation of Calimani sulphur ore has determined the quality deterioration of all ecosystems surrounding the region. The release of solid residues on refuse waste dumps and of the wet refuse into the mud-setting ponds have generated various forms of impact over the environment, among which the most important can be emphasized here:

- Degradation of large field areas, which cannot be used anymore in other aims for very long intervals of time. Soil and water pollution, by means of various toxic compounds that infiltrate from liquid shape profile, and which can be solubilized by the action of meteoric water.
- Soil samples measurements that indicate a significant pollution of heavy metals and hydrogen ions.
- After crossing the sulphur ore exploitation region, even after 10 years from stopping the activity, the quality of Neagra River will be significantly getting worse; this can be explained by the high content of heavy metals, sulphates and hydrogen ions. This river can be classified into the Vth quality class, in accordance to regulations in force. As regards the waters polluted by residual compounds coming from preparation of sulphur from the sulphur ore, oxidation-reduction reactions of the component elements will take place, chemical changes that are photo-chemically catalyzed, resulting in the formation of sulphuric acid (formation of hydrogen ions). The sulphur existing in the waters might bring to a continuation of such chemical changes, even after their alkalization.

Emphasizing these research experiments carried out in the laboratory, it will result that water purifying coming from ore exploitations on polymetallic sulphides, by means of agaric metal (Dold 2005, Montana 1998), is actually not enough. Concerning the return waters falling out from the sulphur ore exploitation, other chemical methods should be employed, in the view of removing the sulphur and its compounds.

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