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A CONTEXT VISION

Characterization of acid drainage in the minerals of esmeralda Quípama-Boyacá

Caracterización del drenaje ácido en la minería de esmeralda Quípama-Boyacá

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ABSTRACT

Acid drainage is derived from the process formation of some minerals Sulphur's to oxygen contact with water and air, that formation involved chemistry processes, biologic and phenomenon's Chemistry – Physicist. With the objective to characterization the acid drained in to emeralds miners in the municipality of Boyacá – Quipama (Colombia), there has been proposed the study and analysis of the parameters chemist – physicist of underground waters for the mine " $Divino ni\tilde{n}o$ ". Taking into account the determination of the characteristics of the acid drainage, captures were carried out in situ inside the mine and downloads. The obtained results determined that water of the drainages to the interior of the mine presented physical, chemical and biological transformations which gave origin to drainage lightly acid of soft class, presenting anions and cations in issolution, there appeared high concentrations of SO4, Faith, To, Ca. This one was the First study developed to the interior of the mine of emerald " $Divine ni\tilde{n}o$ " in Quipama's municipality.

RESUMEN

Los drenajes ácidos son derivados de la formación del proceso de algunos sulfuros minerales al contacto del oxígeno del aire y el agua, esta formación involucra procesos químicos, biológicos y fenómenos físico-químicos. Con el objetivo de caracterizar el drenaje acido en la minería esmeraldífera en el municipio de Quípama-Boyacá (Colombia), se ha propuesto el estudio y análisis de los parámetros físico-químicos de aguas subterráneas para la mina Divino Niño. Para la determinación de las características del drenaje acido, se llevaron a cabo tomas in situ en el interior de la mina y las descargas. Los resultados obtenidos determinaron que; las aguas de los drenajes al interior de la mina presentaron transformaciones físicas, químicas y biológicas las cuales dieron origen a drenaje ligeramente acido de clase blanda, presentando aniones y cationes en disolución, se mostraron elevadas concentraciones de SO₄, Fe, Al, Ca. Este fue un primer estudio desarrollado al interior de la mina de esmeralda Divino Niño en el municipio de Quípama.

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Introduction

Colombia has been a recognized country by its emeralds in the world and the exploitation of this mineral resource has been one of the most important activities for the country; the supply and demand of emeralds is a free and legalized activity.

The exploitation and extraction of this mineral resource produces negative environmental alterations, countless damages and irreversible destructions that have been evidenced due to this kind of activity. The damages that leave mining activity can be reflected on the landscape, the atmosphere, soils, water, flora and fauna, etc. It has been demonstrated that water is one of the natural resources that are most affected since these interactions with the water and environment modifying its characteristics in several degrees, temporarily or permanently.

This topic is amply illustrated in the report presented by Professor Kitula, The environmental and socioeconomic impacts of mining on local livelihoods in Tanzania. Who warns that problems are associated with a mining activity, are reflected in various areas, being the contamination for mines drainage one of the problems with greater environmental affectation.

During exploitation of certain deposits (coal, metal sulfides, iron, uranium and others) large amounts of sulfurous minerals are exposed to the weathering which can form acid drainage. For this to happen, aerobic conditions are necessary, i.e. the existence of enough quantities of water, oxygen and simultaneously the catalytic action of bacteria [1].

Seeing that, the main responsible for the formation of acid water is presented by the oxidation of pyrite, it has been determined that in mining areas the geochemical reactions are accelerated because the air gets in contact more easily with the sulfides through the access work and the porosity created in the waste and sterile piles. In addition, the change in chemical composition and the increase of the contact surface of the particles [2].

These drains are toxic in several ways for human beings, wildlife and vegetation, also contain dissolved metals, soluble and insoluble organic constituents that generally come from mining operations, mineral concentration processes, waste dumps and mine tailings. At present, the mining activity of the country establishes the principle of sustainability as the duty of properly manage for renewable natural resources, integrity and enjoyment of the environment, which is compatible and concurrent with the need to promote the rational use of mining resources as basic components of the national economy and social welfare (Mine code - law 685-2001); under this principle Colombia is one of the countries that doesn't have a regulation control in terms of pollution that legal and illegal mining causes to the environment. The objective of this research is the characterization of the acid drainage associated to the exploitation in emeralds mines in the municipality of Quipama-Boyacá.

Materials and methods

To carry out the research work, initially, it was proceeded to the compilation of existing geological information in the study area (Quipama - Boyacá) based on the data provided by El Instituto Geografico Agustín Codazzi IGAC. The tracing was done on the western emerald belt; evaluating the mining district of Quipama, which has presented deposits of emeralds, quartz, white calcite and calcium amongst carbon minerals with high contents of calcite, pyrite and codazzite.

2.1. Study area:

The study area belongs to the western foothills of the Eastern mountain range; located between the sub-basin of Minero River, placed in the southern part of the municipality, the Itoco Ravine micro-basin, located in the eastern part of the municipality, and the Sorquecito stream or Cristalina, (Figure 1)

Figure 1: Study area.



Source: own.

A previous analysis was carried out, identifying the main rivers that could be affected by the emerald

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production in the study area of the project, the points were chosen considering: accessibility to the site, existence of communication riverbeds and the uses of soil around sampling sites.

The selected points for the study are found in three lotic ecosystems: Minero River, Serquecito Ravine or Cristalina, Llano Grande Ravine or Itoco Ravine, the Divino Niño mines and Puerto Arturo, as listed below:

2.2. Minero River

Sampling points: 200 m. before the outh of the Itoco Ravine, at the intersection of Minero River and Itoco Ravine, 200 m. after the mouth of the Itoco Ravine.

Type of sampling: Physicochemical in situ conductivity, pH, dissolved oxygen and water temperature.

2.3. Itoco Ravine

Sampling points: 200 m. before the drainage of Puerto Arturo mine, at the drainage point Mina Puerto Arturo, 200 m. after the drainage of Puerto Arturo Mine.

Type of sampling: Physicochemical in situ conductivity, pH, dissolved oxygen and water temperature.

2.4. Sorquecito Ravine or Cristalina

Sampling points: 200 m. before the mouth of the Itoco Ravine, 100 m. before the mouth of the Itoco Ravine, at the intersection of Sorquecito-Itoco.

Type of sampling: Physicochemical in situ conductivity, pH, dissolved oxygen and water temperature.

2.5. Divino Niño Mine

Sampling points: Infiltration water.

Type of sampling: Physico-chemical laboratory parameters: sulfates, calcium, chlorine, zinc, manganese, magnesium, potassium and bromine.

2.6. Puerto Arturo Mine

Sampling points: Drainage or discharge

Type of sampling: Physico-chemical laboratory parameters: sulfates, calcium, chlorine, zinc, manganese, magnesium, potassium and bromine.

2.7. Sorquecito Ravine or Cristalina

Sampling points: White or Reference Point.

Type of sampling: Physico-chemical laboratory parameters: sulfates, calcium, chlorine, zinc, manganese, magnesium, potassium and bromine.

Sampling: Sampling took place in September 2015, during high rainfall. Measurements were made in field at Minero River, Serquecito Ravine or Cristalina and Llano Grande Ravine or Itoco sites.

For the physicochemical analysis of water, measurements were made in situ through portable equipment with the following parameters: pH (YSI pH), temperature °C (YSI Oximeter), conductivity meter YSI, dissolved oxygen mg/L (YSI Oximeter) and oxygen saturation percentage % (YSI Oximeter).

Samples taken were punctual, the flasks used were rinsed thrice with the sample to analyze, the sample was stored in an icebox to maintain its chemical characteristics (NTC-ISO 5667- 1), later it was taken to "Ingeniería Medio Ambiental Ltda Análisis y tratamiento de aguas y suelos" where analytical methodologies were applied according to the examination of water and wastewater.

The physicochemical parameters measured were: sulfates, calcium, chlorine, zinc, manganese, magnesium, potassium and bromine, these samples were taken at three (3) points within the influence area, described below and mentioned in Table 1, where it can be observed the analyzes performed on the samples.

3. Results

• Study Area. The municipality of Quipama is between 600 and 1800 m.a.s.l, its temperature ranges between 20 ° and 21 °C and the mean precipitation values range are from a minimum of 572 mm a year to a maximum of 2,905.3 mm at year.

This area includes a topography in which the mountain landscape predominates, the most representative orographic accidents have place between 1000 and 1600 m.a.s.l.

In relation to the municipal hydrography, it is watered by the waters of some Rivers and Ravins, of all protude: Minero, Desaguadero, Llano Grande or Itoco, Caco, Moray or Chirche, Batán, Sonadora, Guaquimay, Piñuela, Amarilla, Ramal, Pavas, Cormal, Sacán, Serquecito or Cristalina among others minor.

Table 1: Analytical method of measurement in laboratory.

PHYSICO-CHEMICAL					
Parameter	Analytical Method	Unit			
Alkanility	SM 2320 B	CaCO3 mg/L			
Sulfide	SM 4500 SO4 E	$\mathrm{mg/L}$			
Calcium	SM 3500 Ca D	$\mathrm{mg/L}$			
Chlorine	Hach 8021	$\mathrm{mg/L}$			
Bromine	Hach 8016	$\mathrm{mg/L}$			
Dissolvem oxygem	SM 4500 O G	$\mathrm{mg/L}$			
Physical Properties					
рН	SM 4500 H B	Und pH			
Conductivity	SM 2510 B	Microsiemens / cm			
Metals					
Aluminium	SM 3111 B	$\mathrm{mg/L}$			
Magnesium	$\mathrm{SM}\ 3500\ \mathrm{Mg}\ \mathrm{E}$	$\mathrm{mg/L}$			
Ferrous iron	Hach 8146	$\mathrm{mg/L}$			
Total iron	SM 3111 Fe B	$\mathrm{mg/L}$			
Manganese	SM 3500 Mn B	$\mathrm{mg/L}$			
Potassium	SM 3500 K D	$\mathrm{mg/L}$			
Zinc	Hach 8009	$\mathrm{mg/L}$			

Source: own.

- Weather. Weather. The precipitation behavior is of a bimodal nature, and the periods of greatest intensity belong to the months of April and October, with mean values of 315.2 and 422.9 mm respectively. The water balance remains above potential evapotranspiration throughout the year. The damp regime is super damp, with two (2) bioclimatic floors: equatorial and sub Andean where life zone is classified in very damp tropical forest (bmh-T).
- Geology. The geology of the municipality is part of the Western Emerald Belt that includes the mining districts of Muzo, Quípama, Coscuez, Peñas Blancas, within the National Reserve Zone. The mining district of Quípama is embedded in the Stalk Formation (lower Cretaceous) constituted by a thick package of black shales or finely laminar carbonaceous lutitas, with intercalations of more siliceous lutitas.

According to [3], the country's type of emerald deposit is unique in the world in accordance

- to mesothermal deposits (300 °C) developed through thermochemical reduction of sulfates rich in hydrogen and sulfides by interaction with organic strata. Na, Ca, Fe and alkalis induced by albitization halos and carbonation are around mineralized structures during metasomatic alterations in the rock wall of black shales.
- Geomorphology. Owing to the interrelationships to tectonics and hydrological events originated by the raising of the oriental mountain range, geological formations are presented of shape principally structurally, with the deep cannons and the shape of "V", with earrings strongly inclined to straighten. Its topography is very broken with deep dissection tied to the nature of the rocks that compose it, to the structure and to the regime of dampness, facilitating a major degradation and transport of meteoric material to the riverbeds.
- Hydrography. The hydrographic network from the municipality of Quipama, is formed by two (2) sub-basins, those are the Chirche River and the Minero River, both drain in a direction towards the northeast. The drainages present a tectonic model with strong slopes, therefore, water bodies present a torrential character, and this associated to improper practices in the use of soils, for both mining and agriculture, which accelerate unstable process of slippage. To the oriental slope of the subbasin of the Chirche river, the following microbasins compose it: Carróz, Torrás or Cortadera, Sacán, Nucuamás and turutuní; the western slope of the Mining Rio the microbasins compose: Fulling mill, Itoco and The Caco.

3.1. Places to sampling

• Minero River. In the watershed of the Minero River the majority of its watercourses are born in the tops that enclose it. This River is born in boundaries of Boyacá and Cundinamarca, crosses the province of Boyacá's west from south to north, gathering the waters of the rivers as the Batán, the Guazo formed by the union of the Villamizar and the Cantino, and it also joins it to the Itoco Ravine. This Minero River, has this name in Boyacá because it runs near to the Emeralds mines, it is also really torrential; its waters are black due to the quantity of minerals that it washes along its tour, its geographical coordinates correspond to latitude 53°48 ' 24 "N, length 74°06 ' 26, 39 "W, altitude 496 m.a.s.l; it happens by means of the hills called "Fura-tena", which used to be adored by the aborigines.

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• Llano Grande and Itoco Ravine. The Itoco Ravine is located to the west of the Minero River and the anticlinal forms Itoco's in which axis are found the mines of Emeralds (Bûrgl, 1854), this system lotus has an altitude of 589 m.a.s.l. Its coordinates are 5°31 ' 42 "N and 74°7 ' 58 "W, this is also known as Gully Big Plain, Itaca and Itoco River (Figure 2).

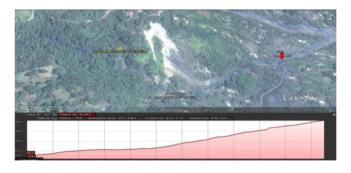
Figure 2: Itoco River and stream, Location and profile of earring of the riverbed.



Source: own.

• Serquecito Ravine or Cristalina. This ravine is originated in the municipality of Quipama, its waters run in a southerly direction and it ends on the Quebrada Itoco (see Figure 3) in the geographical coordinates latitude 5 ° 32'09,19"N, length 74 ° 09'16,72 "W, altitude 642 m.a.s.l.

Figure 3: Serquecito Ravine or Cristalina, location and slope profile of the riverbed.



Source: own.

3.2. Physico-chemical analysis

For the characterization of acid drainage in the study area, three sampling points were made:

- a) Divino Niño Mine. The drainage water from this mine flows into the Itoco Ravine and Minero River. The drilling depth of the mine is 30 meters.
- b) Puerto Arturo Mine. The drainage water from this mine flows into the Itoco Ravine and Minero River. The drilling depth of the mine is 200 meters.
- c) Sorquecito Ravine or Cristalina. At the sampling point, there were no changes of contamination.

Table 2 presents the report of physical-chemical results obtained from the sampling.

Table 2: Results of physicochemical analysis.

STATIONS					
PARAMETER	UNITY	Mina Divino Niño	Mina Puerto Arturo	Quebrada Cristalina	
Alcalinidad	$\mathrm{mg/L}$	340	276	21	
Hierro ferroso	$\mathrm{mg/L}$	0,47	1,01	0,97	
Hierro Total	$\mathrm{mg/L}$	3,9	3,9	3,9	
Aluminio	$\mathrm{mg/L}$	3,06	4,02	1,97	
Sulfato	$\mathrm{mg/L}$	1483	1614	2176	
Cobre	$\mathrm{mg/L}$	0,12	0,14	0,15	
Cromo	$\mathrm{mg/L}$	0,05	0,01	0,02	
Magnesio	$\mathrm{mg/L}$	357	1136	357	
Manganesio	$\mathrm{mg/L}$	0,01	0,05	0,01	
Potasio	$\mathrm{mg/L}$	0,1	0,35	0,01	
Bromo	$\mathrm{mg/L}$	0,05	0,01	0,01	
рН	Und	6,8	7,01	7,15	
Conductividad	$\mu\mathrm{S/cm}$	2300	2470	123	
Oxigeno Disuelto	$\mathrm{mg/L}$	3,7	3,2	5,5	
Zinc	$\mathrm{mg/L}$	0,29	0,33	0,91	

Source: own

4. Discussion

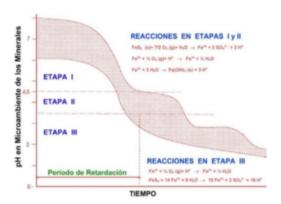
The results obtained for the study of acid water were evaluated from the drainage pH and the metal contents or mineral species present in the same one; each sampling point presented the following classification, according to the parameters established in [4].

4.1. Divino Niño Mine - Puerto Arturo Mine.

The residual water of the mines as a function of PH is presented as a soft, slightly acidic class; they presented anions and cations in solution, there are high concentrations of SO4, Fe, Al, Ca and to a lesser proportion other elements (Table 2). The values of dissolved oxygen in the intakes were very low, presenting a hypoxia condition for sensitive organisms and species. The oxidation of the sulfide minerals contributed acidity

to the medium. The acidic water formation stage for these intakes (Figure 4), were oxidized due to air and existing bacteria. In general the availability of alkalinity (Table 2) in the medium is enough to achieve the partial equilibrium of the acidity produced. [5–7].

Figure 4: Water forming stage for Divino Niño mines – Puerto Arturo. (Drenaje Acido de Mina, Osvaldo Aduviere).



Source: own.

The color present in the acid drainage found is reddish brown (Figure 5), this color is attributed to the Fe (III) ion, which tends to be dark by oxidation, as it is exposed to oxygen in the air [8–11].

Figure 5: Drainage color for Divino Niño mine.



Source: own.

The research presented in the excavation area, sulphurous minerals that are found between the rocks, this type of rocks are under the layer of the ground, in some cases can be found under the water table. At some points, it was observed that under normal conditions the soil that covers this type of rock and the groundwater surrounding it minimize contact with oxygen, significantly reducing acid generation. Some

critical points were found inside the excavation of the El Divino Niño mine where a high acidity condition due to the exposure of sulfurous rock ratios with air and water (Figure 6 and Figure 7), in the presence of this type of rock accelerates the rate of acid generation causing significant environmental impacts as follows:

Figure 6: Color of the rock in Divino Niño mine.



Source: own.

Figure 7: Acid Drainage Stream from Divino Niño Mine to Minero River.



Source: own.

4.2. Cristalina Ravine.

Sampling in the ravine is of a hard class, neutral to alkaline; the levels of some metals are considered low (Table 2), this type of water is presented with these characteristics when there are leaks from a surface or aquifers circulating above the current where limestone and dolomitic materials circulate. The filtration of

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this type of material occurs in rocky systems recently excavated, where its contribution of pollutants is high. The concentration of ferrous iron (Table 2) present in the sample may change from alkaline class to acidic class; because is observed an underground filtration to the ravine.

Although it was possible to estimate the quality of the drainage within the drillings in the study mines, it is important to consider shots with greater frequency and greater rigidity about the sulfurous mineral of the rock, as well as the distribution of the same velocities of oxygen flow, water and chemical concentrations [12–15].

In the future, studies on the geodisponibility of materials in reservoirs, particularly sulfur ores, they should be developed for a specific analysis as sources of possible environmental contamination. It is convenient to make an inventory of the points of discharge of water drainage by the mining at Minero River, as well as to determine the environmental damage caused by these discharges to that zone.

5. Conclusions

Generally, this investigation determined that the captures and water analysis of the drainages of the mining industry in the points of interest were physical, chemical and biological transformations which gave origin to drainages lightly acid of soft class, presenting anions and cations in dissolution, they presented high concentrations of SO4, Fe, Al, Ca. Clearly, it presents the degradation quality of superficial and underground water of the zone.

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7. Conflict of interests

The authors declare that they don't have any conflict of interest.

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