

# Evaluation of the quality of water in the ecosystem composed by “El Dollar” mine and “San Francisco” lagoon (Castrovirreyna, Huancavelica, Perú)

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## Abstract

As an advance towards the design of a strategy for bioremediation of the mine “El Dollar”, the study of the quality of water flushing out of the mine and their impact in the Lagoon San Francisco (Huancavelica, Perú) was carried out. Analytic results obtained from field sampling in 2006 indicated that the water of the lagoon has not undergone significant impact due to heavy metal concentration. The concentration of Mg, Na and Ca in water suffered very little transformation during their journey from the mine entrance to the lagoon. The biggest transformation occurred with Zn, Cu, Fe, and Mn which are retained inside the terrestrial ecosystem. On basis of the observed results, Pb and Mn should be considered as elements of importance inside the plan of bioremediation of this ecosystem.

## Resumen

Con el propósito de elaborar la estrategia de bioremediación de la mina “El Dollar”, se desarrolló el estudio de la calidad del agua que sale de la mina y su impacto en la Laguna San Francisco. Los resultados analíticos obtenidos del muestreo de campo en 2006 indicaron que el agua de la laguna no ha sufrido un impacto significativo por la concentración de metales pesados. La concentración de Mg, Na y Ca en agua sufrió una transformación muy pequeña durante su viaje desde la entrada de la mina hasta la laguna. La mayor transformación ocurrió con el Zn, Cu, Fe y Mn, los que son retenidos dentro del ecosistema terrestre. En base a los resultados observados, el plomo y el manganeso deberían ser considerados como elementos de importancia dentro del plan de bioremediación de este ecosistema.

## 1. Introduction

The Peruvian Law N° 28271 that regulates environmental liabilities of the mining activity, considers as environmental passives, those facilities, emissions, remains or deposits of residuals resulting from mining operations, at the present abandoned or inactive, that constitute permanent risk and potential damage for population's health, the surrounding ecosystem and property.

At present, more than 1800 passive environmental liabilities have been identified in Perú as a consequence of the mining activity (tailing deposits, abandoned constructions, plant facilities and mine entrances) (Mendoza et al, 1998) and represent a potential and permanent risk; they can contaminate the courses of water in the ecosystem, public and private property and the population's health, generating a negative perception of the mining.

The risks for exposure of population and the environment to these mining remains reside in the toxicity of the substances contained in those, the powder haulage, and the potential acid drainage. In a smaller extent, they also represent potential danger due to the holes and tunnels that have been open and unprotected, as well as other abandoned facilities, characteristic of the mining task (Redlies, 2005).

It is well known that bioremediation of mines consists of a series of processes guided to remove the present pollutants in the environment and these processes include the bio-sorption, bio-filtration, bio-precipitation and bio-accumulation using native species at low cost; so, natural vegetation surrounding the place of interest and bacteria species, somehow adapted to metal toxicity and extreme conditions of life, would be very useful to reduce the acid water erosion and may mitigate the widespread of contamination to the nearby areas (Conessa *et al.*, 2007; Pandey *et al.*, 2007).

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The Instituto Peruano de Energía Nuclear started in 2005 a technical cooperation project supported by the International Atomic Energy Agency (IAEA) titled "Bioremediation of abandoned mines" (PER/8/014) that has as a main objective to develop a pilot study for bioremediation of abandoned mines taking as a departure point the field studies of an abandoned mine, from physical-chemical characterization to biomass identification (including molecular identification of microbes that had eventually already established some sort of bioremediation process in the selected site (Espinoza, 2003). The area selected for the project's work was the abandoned mine "El Dollar" located in the Andean region of the Province of Castrovirreyna (Huancavelica, Perú) (Figure 1) where the Peruvian government had identified two environmental liabilities of high-priority: the Pacococha Tailing-Factory and its tailings (in front of the Lagoon Pacococha) and the Mine Entrance "El Dollar" (that drains acid water to the San Francisco lagoon) (Bonelli, 2005). Both lagoons are very close and probably they have physical underground connection. From these two lagoons is formed the basin of Pisco river (Ica).

The quality of water of the basin of Pisco River is modified by the quality of the water of the main lagoons of the region, among them the lagoon San Francisco, in a similar way that happens with the neighboring rivers to the lake Tapeng in Taiwan (Liao et al., 2006). On the other hand, the mine "El Dollar", a polymetallic mining unit located at 4950 meters over the sea level, liberates acid water coming from the interior of it to the environment; this water is transported by a channel of natural slope to the San Francisco lagoon, located at about 600 meters far from the mine entrance (Longitude:  $-75.231876^{\circ}$ , Latitude:  $-13.226656^{\circ}$ ).

The present work has the purpose of evaluating the concentration of elements present in the discharge of the mine that could have significant impact in the water of the Lagoon San Francisco identifying, in this way, the high-priority pollutants to be considered in the elaboration of bioremediation strategies for the area.

## 2. Material and Methods

In June 2006, samples of superficial water of the mine entrance "Dollar" and the Lagoon San Francisco, were collected according to the recommendations of the Instituto Nacional de Recursos Naturales for the surveillance of quality of waters (INRENA, 2006).

For the surveillance of the quality of water, physical-chemical and biological methods (Fall et al, 2007) were used, however, these last ones should be properly integrated to the program of general surveillance (Rendon et al, 2006; Ruiz et al, 2006; Benet-Monico et al, 2006). We used validated physical-chemical methods because the biological indicators of the Andean Region are not standardized.

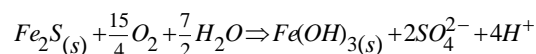
Collected samples were sent to ALS Environmental Co. (ALS Perú), for the determination of physical and chemical parameters, inorganic, and organic. For the determination of heavy metals (total and dissolved) the analysis is carried out using procedures adapted Standard from Methods for the Examination of Water and Wastewater 20th Edition 1998 published by the American Public Health Association, and with procedures adapted from Test Methods for Evaluating Solid Waste SW-846 published by the United States Environmental Protection Agency (EPA). The procedures involved preliminary sample treatment by acid digestion, using either hotplate or microwave oven, or filtration (EPA Method 3005A). Instrumental analysis is by atomic absorption/emission spectrophotometry (EPA Method 7000 series), inductively coupled captures-optical emission spectrophotometry (EPA Method 6010B), and/or inductively coupled captures -mass spectrometry (EPA Method 6020). The activity concentration of K-40 and U-238, expressed in bequerelios/L (Bq/L), was determinate for its isotopic abundance from the concentrations of potassium and total uranium in the samples. The results are presented as mean values with an uncertainty of 95% (Eurachem, 2000).

As standard of reference for the effluents of the mine entrance, the values settled down by the R.M. N° 011-96/EM/VMM "Niveles Máximos Permisibles de Emisión de Efluentes Líquidos para la Actividad Minero-Metalúrgica" (MEM, 1996) was used. For samples of water of San Francisco lagoon, the standard values settled down in the D.L. 17752

“Ley general de Aguas” (Peru, 1993) were used.

### 3. Results and Discussion

The water drained out of the “El Dollar” mine presents physical and chemical characteristics markedly different to the water of the San Francisco lagoon (Tables 1 and 2). These characteristics are determined by the process of sulfide oxidation, being observed to high concentration of sulfate (566 mg/L), however, the determinations of sulfur in water gave values below the detection limit for what is probable that the sulphur’s like the FeS<sub>2</sub> and FeS are oxidized quickly in contact with the oxygen and the water, ending up being acidified the means due to the drop present alkalinity (<1mg CaCO<sub>3</sub>/L) according to the equation:



Given their strongly acid character, the water of the mine entrance will be characterized for high concentrations of Fe (12.5 mg/L), sulfates and H<sup>+</sup>, derived of the oxidation of the FeS<sub>2</sub>: Si (8.04 mg/L), Al (3.17 mg/L) and some derived basic ions of the mineral hydrolysis carried under these conditions. The conductivity in the water of the mine entrance is high (1126 μS/cm) and the concentration of ions dissolved in the means is considerable regarding the water of the San Francisco lagoon.

Monterroso and Masias (1998) have classified drainage of mines in three types according to the degree of influence of the process of sulfur’s oxidation and the degree of neutralization of the generated acidity. In this way, the waters of the mine entrance “El Dollar” is classified in the Group IIIa, not considered as waters neutralized, moderately affected by the sulfur’s oxidation, where the acidity generated during the oxidation of the FeS<sub>2</sub> is barely neutralized, presenting values pH means in the range 3.1 at 3.5. The characteristics of this water are oxidizers, and they maintain in breakup relatively high quantities of Fe, (generally valued means between 20 and 200 mg /L with ends of 4 and 340 mg/L). The relationships molars of SO<sub>4</sub>: Fe (45:1 for the mine entrance) in breakup they it plows always very superior to the theoretical one derived of the oxidation of

the pyrite; this shows an important precipitation of iron components in the channels of circulation of water.

The presence of radioactive elements in water was not significant; mine entrance presented concentrations of 0.0235 Bq/L of U-238 and < 0,0620 Bq/L of K-40; on the other hand, the lagoon San Francisco presented concentrations of 0.0002 Bq/L of U-238 and 0.0774 Bq/L of K-40.

The total heavy metals of environmental importance were Zn (52 mg/L), Mn (34.5 mg/L) and Fe (12.5 mg/L). Other elements of smaller abundance were Ca (75.9 mg/L), Na (24.9 mg/L) and Mg (15.4 mg/L) (Table 3).

Concentrations of zinc and iron surpass the permissible maximum levels settled down in Peru for effluents miner-metallurgist (Zn:3 mg/L and Fe:2 mg/L), this way, as consequence of the characteristics of oxidation that plows carried out in the water of the it mines entrance the levels of zinc and iron were 17 and 6 times more respectively.

The lagoon San Francisco is to body of water located at a distance of 600 meters of the mine entrance “Dollar” approximately; it receives his effluents in continuous form. During the travel, acid waters coming from the mine entrance will suffer to series of interactions with the components that form the environment, this way, the waters will suffer in first instance to dilution process (hydrological component) for then interaction with the geologic components for sedimentation of solids in suspension, adsorption of elements with the colloidal particles of the floor, infiltration to different levels and geochemical processes by means of the formation of compound and throws that cannot be transported by the course of water.

The biological components also contribute in the retention process or decrease of fractions of pollutants during the journey; for example, microbial activity, geochemical processes, root retention and bioaccumulation constitute factors of importance for this process. As a consequence of these interactions, the strongly acid of the waters of the Mine entrance (pH=3.2) it is neutralized, arriving at acceptable levels for the waters of to lagoon (pH =7.8).

The elements that suffer little or any transformation during the transfer of the water of the mine entrance to the Lagoon are Mg, Na, and Ca, arriving at the lagoon relative

fractions from 0.1 to 1.0, regarding the initial concentration in the mine entrance. The elements that suffer intermediates transformations in the ecosystem are Pb and As, with relative fractions among 0,1 and 0,01 and the elements that suffer the biggest transformations it plows the Zn, Cu, Fe and Mn.

Based on these observations, it is appreciated that the elements of importance for the environment are Pb, As, Zn, Cu, Fe and Mn that which means that these elements will be incorporates to the terrestrial ecosystem producing different impact degrees.

The analytic results indicates that the concentrations of heavy metals and other elements were below the established levels in the Ley General de Aguas, Clase III, presenting better quality in comparison with other bodies of water as the rivers Mantaro, Yauli and Andaychagua in the region of La Oroya [UNES, 2000].

When evaluating the temporary variation of the concentrations of heavy metals, taking like bases the studies made in the years 2000, 2002 (BGR, 2002), we can appreciate that the Cu, Zn, Mn and Pb levels have been increased in function of the time, presenting to positive tendency.

Hakanson and Bryhn (2007) discusses the remediation strategies for the sustainable handling in lakes of Denmark, using indicators easy to measure, understand and to predict, as well as the uses of predictive models validated. In our study, we don't have predictive models validated for the Andean area of study, however, when carrying out estimates of curved of concentration in function of the time, it was found that Pb, Mn, Zn and Cu present to positive tendency and they present the following model:

$$Y = (A * c) - m$$

Where:

Y: Concentration of the element (mg/L)

A: Year calendar

c: slope of the curve

m: intersection factor

Under certain general conditions, estimates of the temporary variations allow to estimate the year in that the concentrations will surpass the permissible maximum

levels settled down by the Ley general de Aguas del Perú if the discharge level continues and don't vary the conditions of the means.

It is important to mention that although we did not identified any extractive activity in the place of interest for this study, however, registration of trout culturing in Pacococha Lagoon financed by the Peruvian Government exists, reason for which it is important to maintain the quality of this water in such a way that peoples living close to this areas can carry out their economic activities without risk to the health of anybody.

#### 4. Conclusions

Considering exclusively the physical and chemical analysis of the hydrological component of the ecosystem "Mine-Lagoon San Francisco", we can affirm that in spite of the high acidity level due to the process of oxidation that they carried out in the mining unit, the waters of the Mines entrance don't have any significant impact in the waters of the Lagoon San Francisco.

If the rate of discharge of water through the mine entrance into the lagoon is constant, then it is being considered that to medium term the manganese and lead concentrations in the waters of the lagoon will end up surpassing the levels settled down by Ley General de Aguas, by the years 2016 and 2044 respectively, for what is convenient to consider these two elements inside the strategies of integral bioremediation that it will be carried out in this ecosystem.

The elements of lives environmental importance are retained in the itinerary of the waters by the terrestrial ecosystem for what becomes necessary to carry out the impact study in the geologic and biological components of the ecosystem.

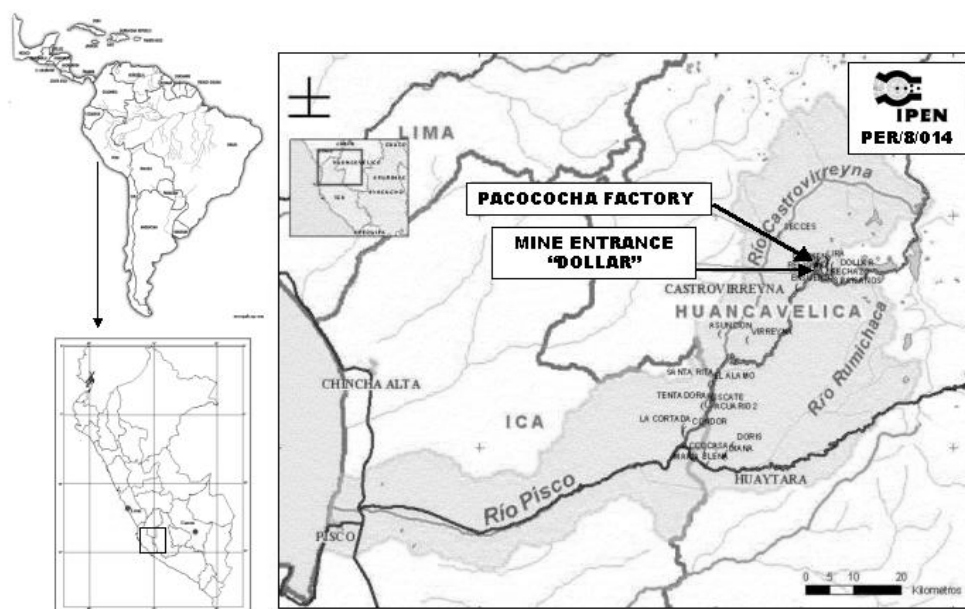
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**Figure 1:** Location of the Study Area.

**Table 1:** Physical-chemical parameters.

N°	Parameters	Units	Entrance to the mine “El Dollar”	San Francisco Lagoon
01	Total alkalinity	mg CaCO <sub>3</sub> /L	< 1	48 ± 2
02	Conductivity	µS/cm	1126 ± 56	249 ± 12
03	Total hardness	mg CaCO <sub>3</sub> /L	300 ± 17	74 ± 4
04	PH	PH	3.17 ± 0.5	7.79 ± 0.5
05	Dissolved total solids	mg/L	818 ± 40	136 ± 5
06	Suspend total solids	mg/L	11 ± 0.8	5 ± 0.4

**Table 2:** Inorganic and organic components in waters.

N°	Component	Units	Mine Entrance	San Francisco Lagoon
01	Chloride	mg/L	< 0.5	19.9 ± 0.5
02	Fluoride	mg/L	0.96 ± 0.1	0.08 ± 0.01
03	Sulfate	mg/L	566 ± 25	37 ± 2
04	Sulfite	mg/L	< 0.002	< 0.002
05	Cyanide	mg/L	< 0.005	< 0.005
06	Total Phosphorous	mg/L	< 0.03	< 0.03
07	Nitrogen - Ammonia	mg/L	< 0.04	< 0.04
08	Nitrogen – Nitrate	mg/L	0.009 ± 0.001	0.012 ± 0.001
09	Nitrogen – Nitrite	mg/L	< 0.01	< 0.01
10	Demands Chemistry of Oxygen	mg O <sub>2</sub> /L	< 20	< 20

**Table 3:** Major macro-element concentrations in waters (mg/L).

No.	Element	Mine entrance				San Francisco Lagoon			
		Total		Dissolved		Total		Dissolved	
01	Fe	12.50	± 0.53	7.98	± 0.38	0.06	± 0.01	< 0.03	
02	Mn	34.50	± 1.26	35.5	± 1.24	0.24	± 0.13	0.22	± 0.11
03	Na	24.90	± 0.81	24.3	± 0.92	19.60	± 0.28	18.9	± 0.25
04	Ca	75.90	± 3.45	74.1	± 3.51	23.70	± 0.72	22.9	± 0.66
05	K	2.00	± 0.11	2.0	± 0.10	2.50	± 0.10	2.4	± 0.10
06	Mg	15.40	± 0.53	14.9	± 0.49	3.86	± 0.11	3.72	± 0.09