Hydrology, mineralogy and management effects on the hydrochemistry of a sulphide tailings pond (Troya mine, Spain)

Iribar Vicente[1], Izco Felix[2], Tamés Patxi[2], Velasco Francisco[3], Yusta Iñaki[3]

[1]Departamento de Geodinámica, Universidad del País Vasco, Apdo 644, 48080 Bilbao. Spain. E-mail: vicente.iribar@ehu.es
[2]Dep. de Obras Hidraúlicas. Diputación Foral de Gipuzkoa, Plaza de Gipuzkoa s/n, 20004 San Sebastián. Spain. E-mail: ptames@gipuzkoa.net
[3]Departamento de Mineralogía y Petrología, Universidad del País Vasco, Apdo 644, 48080 Bilbao. Spain. E-mail: nppverof@lg.ehu.es
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ABSTRACT

The tailings produced at the Troya mine (Spain) were disposed in an 700,000 m^3 impoundment. The tailings contain 45 wt % of pyrite, and up to 30 wt% of carbonate minerals. After the closure of the mine in 1993, the impoundment was partially filled and a water pond up to 6 m deep covered the tailings to a limited extent and changes up to 1 m were possible in the water level. In 1997 the drainage water of the Troya mine was diverted to the tailings pond completely flooding the tailings and changing the quality of pond water. Between 1993 and 1997 the pond water had a relative high metal concentration. From 1997 the pond water quality has improved and it has a lower metal content than Troya mine drainage water. A fraction of pond water seeps through the tailings; the seepage water has a metal content lower than the pond water. After 10 years of submersion, the minerals appear totally unaltered except in the surface zone that was exposed before 1997, in this zone pyrite exhibits oxidation marks. The present management plan allows a suitable isolation of the tailings.

INTRODUCTION

Mine tailings are typically disposed in sedimentation lagoons called tailings dams. When the tailings are able to produce acid mine drainage, it is a normal practice to limit the oxygen access to sulphides using soil barriers called "dry covers", or disposing them underwater. Underwater disposal presents several considerations related with the hydrologic management of tailings dams.

To maintain the tailings submerged it can be necessary to import external water to compensate the losses for evaporation and seepage. On the other hand it can be interesting to minimize the water outflow from the dam because of submerged tailings can be oxidized if there is dissolved oxygen in water, and the excess water can have dissolved metals when exits the tailings pond

This paper presents an example of how the change in hydrologic management of a tailings dam results in changes in water quality.

THE TROYA MINE TAILINGS DAM

Troya mine is a stratabound lead-zinc deposit hosted by carbonate and terrigenous units of Lower Aptian age (Fernández-Martínez & Velasco, 1996), located in the Basque-Cantabrian basin at the northern Spain. The average grade was about 13% Zn, 1% Pb, 0.2% Cu. The principal mineral ore minerals association include pyrite-marcasite, sphalerite, galena, and minor chalcopyrite. The gangue minerals are quartz, barite, calcite, and iron-bearing carbonates. Mining works using bord-and-pillar method began in 1986 and continued until mid-1993.

Mining left about 700,000 m^3 of tailings that were disposed in a cross valley impoundment covering an area of 75,000 m^2 with a maximum height of 28 m. The mine closed before it was intended, and in 1993 the impoundment was partially filled with tailings, and a water pond with an estimated volume of 350,000 m^3, with an area of 50,000 m^2 and up to 6 m deep was originated covering the tailings to a limited extent. Consequently the sulphides were partly oxidised in the exposed area in contrast to the major part of the tailings, which had remained unaltered. Later, the upper part of the tailings above the water level of the pond was covered with 4 m of soil to prevent the weathering of the wastes (figure 1).

The tailings contain 45 wt. % of sulphides, mainly as pyrite with minor amounts of sphalerite (1 %) and galena (0.3 %). Gangue minerals in the tailings are mainly composed by carbonates, as calcite, ankerite and siderite in proportions in the order of 30 wt. %; and lesser amounts of quartz (15%), phyllosilicates (muscovite and clay minerals on average 6 wt. %), and barite (1 wt. %). These tailings consist of a fine ground material, with size of silty fine sand, where the sulphides show average sizes of 30µm, whereas the carbonates and quartz of the gangue have grain diameters between 25µm and 60µm. The analysis of four boreholes points out a relative homogeneity in grain size and mineral composition throughout the vertical sections, with only minor gradual changes. Petrographic analysis shows that tailings are little altered, lacking any evidence of oxidation and absence of dissolution of sulphides and carbonates, revealed by the presence of pristine minerals with angular grain boundaries and the lack of secondary minerals. Secondary minerals like goethite were only found in trace amounts in a well-defined level of the former oxidized upper part of the pond, mainly as thin coatings on the pyrite grains or as microscopic pseudomorphs.
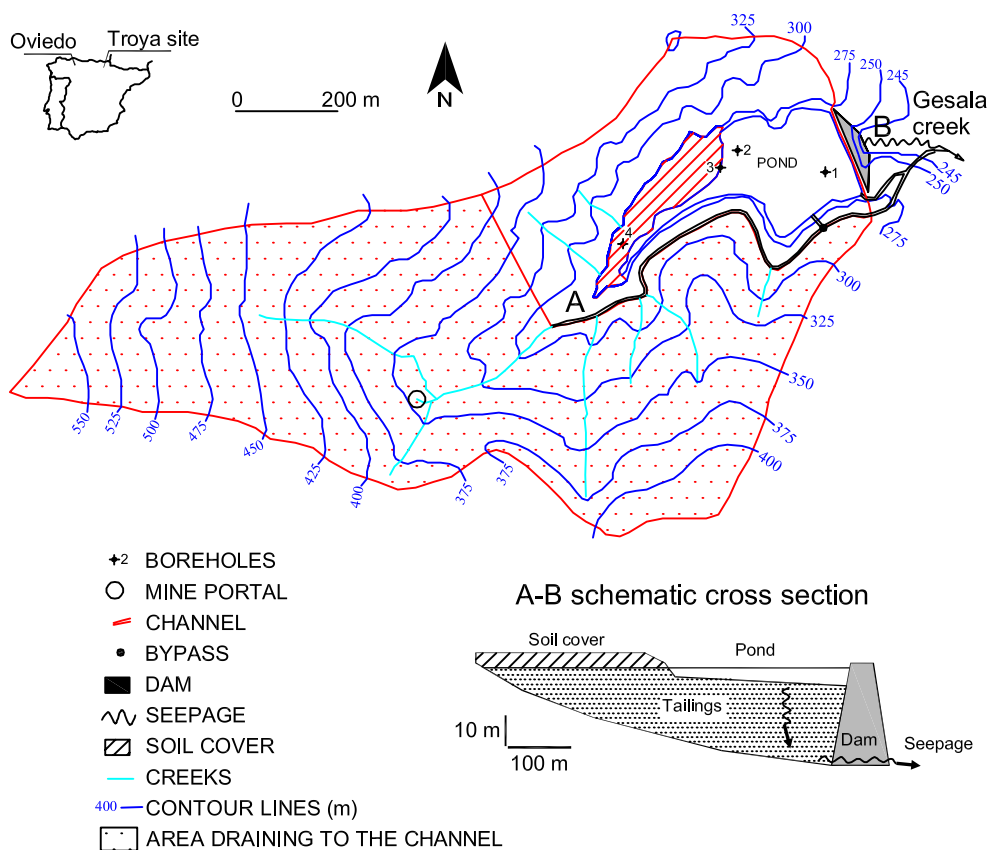
Figure 1. Map of the Troya tailings pond area

Thirty-eight mine tailing samples were analysed by XRF as pressed powder pellets at the facilities of the Servicio de Análisis y Rocas of the Universidad del País Vasco. Troya tailings are very rich in Fe, with an average content of 22% wt. Iron is mainly bounded to pyrite although some minor part is found in ankerite, siderite and goethite. Chemical variation in other relevant elements with respect to their potential toxicity is as follows: Zn (median: 7190ppm; range: [5024–22832]), Pb (median: 2748; [1860–4990]), Cu (median: 493; [22–1702]), and As (median: 439; [236–583]). Downcore distribution of these metals is quite constant, showing an incipient increase with deep in Zn content probably related to inefficient recovery of sphalerite during early times of the mine.

HIDROLOGY OF THE TAILINGS POND

Surface hydrology

The tailings pond is located in a valley with a drainage area of 0.86 km^2. With the purpose of minimize the water inflow to the pond, and also to collect the water that was expected to flow from the mine portal in the future, a diversion channel was built in the left side of the tailings pond. After the channel construction, the drainage area of the tailings pond was 0.24 km^2.

In March 1995, water started to flow from the mine portal (average flow = 34 L/s), this water flowed along the channel reaching the Gesala creek through a water ladder located at the side of the tailings dam, and the creek suffered a severe contamination (Iribar et al, 2000).

In June 1997 the water of the channel was diverted to the tailings pond trough a bypass. The objective of that action was to use the pond like a purifying element for the mine water (Iribar et al, 1999). The pond's overflow is spilled to the Gesala creek through the water ladder.

Hydrogeology

Groundwater flows trough the tailings. On the one hand the tailings pond is located over a saline spring (flow <0.1 L/s) that gives the name to the Gesala creek (*gesala* is brine in Basque language), on the other, some water of the tailings pond flows downward throughout the tailings. The pond seepage (average flow = 4.7 L/s) comes out at the dam toe and runs into Gesala creek.

Water Balances

Before June 1997				
Input	(L/s)	**Output**	(L/s)	
Precipitation	1.6	Evaporation	1	
Surface runoff	2.6 - 4.3	Pond seepage	4.7	
		Pond overflow	0.0 - 0.2	
Total	4.2 - 5.9	Total	5.7 - 5.9	

After June 1997				
Input	(L/s)	**Output**	(L/s)	
Precipitation	1.6	Evaporation	1	
Surface runoff	11.1 - 18.6	Pond seepage	4.7	
Mine drainage	34	Pond overflow	41.0 - 48.5	
Total	46.7 - 54.2	Total	46.7 - 54.2	

Table 1. Average annual water balances of the tailings pond

A water budget of the tailings pond has been evaluated for an average hydrologic year; the water budget has been developed for 1993-1997, and post 1997 hydrologic states (table 1). Precipitation, mine drainage flow and seepage flow have been measured. Surface runoff has been estimated from data of nearby catchments, and from Thornthwaite type monthly water-balance calculations. Evaporation from the pond has been estimated from evaporation pan data of a nearby reservoir. Pond overflow has been computed in the balance.

Taking into account the volume of dammed water and the flow calculated with the balances, the residence time of water in the pond before June 1997 was about 2 to 3 years, and after June 1997 the residence time is about 2 to 3 months.

HIDROCHEMISTRY

From 1995 Diputación Foral de Gipuzkoa has monitored the water chemistry at several points. In this paper the chemical analyses of (1) the channel water, (2) the pond water in the overflowing zone, and (3) the seepage water are used. Table 2 summarizes the water quality in these points, and time series of Ca^{2+}, HCO_3^-, SO_4^{2-}, Cl^- and Zn are shown in figures 2 and 3. The metal concentrations (Fe, Zn and Mn) shown in table 2 are from unfiltered samples. The pond water is saturated in O_2. The PHREEQC programme (Parkhurst & Appelo, 1999) has been used to help the interpretation of hydrochemical data.
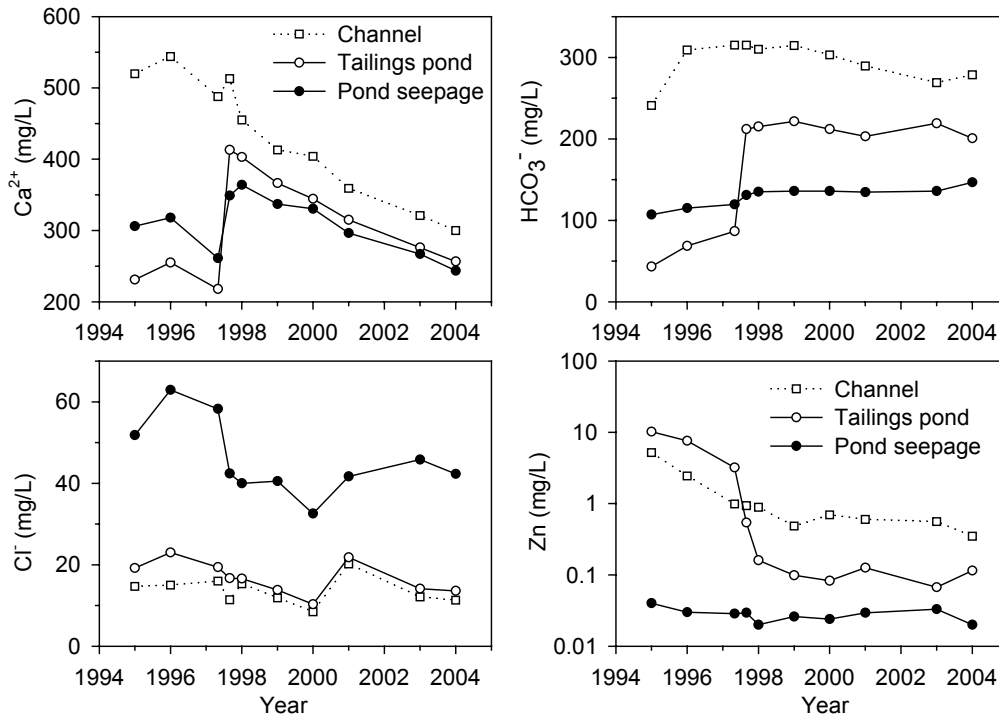
(mg/l)	1995 - June 1997			June 1997 - 2004		
	channel	pond	seepage	channel	pond	seepage
pH	7.8	7.6	7.7	8.1	8.1	7.7
HCO_3^-	296	62	111	306	214	136
Cl^-	16	20	56	12	15	41
SO_4^{2-}	1355	632	749	870	835	751
Ca^{2+}	525	237	306	419	368	328
Mg^{2+}	64	25	21	35	34	30
Fe	23.5	0.40	0.03	8.2	0.44	<0.02
Mn	0.81	0.78	<0.02	0.38	0.20	<0.02
Zn	2.7	7.7	0.04	0.7	0.18	0.025
P_{CO2}	$10^{-2.56}$	$10^{-2.95}$	$10^{-2.74}$	$10^{-2.64}$	$10^{-2.91}$	$10^{-2.63}$
$SI_{calcite}$	1.14	-0.18	0.35	1.24	1.13	0.39
$SI_{ankerite}$	1.57	-1.90	-1.73	1.46	0.55	-1.49

Table 2. Chemical analyses and selected equilibrium modelling results of the tailings pond system (SI = saturation index). Median values

Before 1997 the chemical composition of channel water and pond water was quite different. From June 1997 the concentration in SO_4^{2-}, Cl^-, Mg^{2+}, Ca^{2+} and HCO_3^- in the channel and the pond is similar and have a parallel time

trend, although the concentration in HCO_3^- and Ca^{2+} is lower in the pond than in the channel. After the channel diversion to the pond, the concentration in Fe, Zn and Mn is lower in the pond than in the channel.

The time trend of Mg^{2+}, Ca^{2+} and SO_4^{2-} of the seepage water is similar to the pond water. The most important differences between both waters are in the content in Cl^-, HCO_3^- and in Fe, Mn and Zn.

Figure 2. Time series of water chemistry (mean annual concentrations). Note that concentration scale for Zn is logarithmic

Hydrochemical processes in the tailings pond

Origin of pond water before 1997

Before 1997, the pond water was practically stagnant; the origin of the hydrochemistry can be explained by the sulphide dissolution in the tailings banks and beaches that were emerged when the water level lowered in the pond.
A mass balance has been developed considering that Ca^{2+}, Mg^{2+}, Fe, SO_4^{2-} and HCO_3^- dissolved in water come from sphalerite, pyrite, ankerite and calcite dissolution, $Fe(OH)_3$ precipitation and from of CO_2 degassing. Considering that the pond water renewed two times in the 1993-97 period, the balance shows that about 900 tons of tailings were dissolved.

	Sphalerite (dis.)	Pyrite (dis.)	Ankerite (dis.)	Calcite (dis.)	Fe(OH)₃ (prec.)	CO₂ (degas.)
mg/L	11	387	522	335	509	329
tons (1993-97)	8	271	366	235	356	

Table 3. Mass balance of tailings pond water before June 1997

Origin of pond water after 1997

Once the channel water is diverted to the pond, the tailings are completely submerged. Channel and pond water chemistry is similar, although pond water has usually lower concentrations than channel water. The following processes can explain the changes of water quality between the channel and the pond:
(1) Dilution of channel water with precipitation and surface runoff water.
(2) Calcite precipitation and CO_2 degassing as is suggested by the calculated saturation indexes.
(3) Fe hydroxide sedimentation, and possible adsorption of Zn and Mn on the precipitated hydroxides.

Hydrochemical processes between tailings pond and seepage water

The hydrochemical differences between the pond and seepage water that are caused when pond water moves throughout the tailings can be explained by the following processes:
1) Precipitation and/or adsorption processes that take out Fe, Zn and Mn from water; metal concentrations in seepage water are very low, even below the detection limit.
2) Depletion of O_2 dissolved in pond water; pyrite and/or organic matter can be the reducing substances.
3) Mixing of pond water with the saline spring that is under the tailings pond.
4) Processes that keep the HCO_3^- concentration of seepage water rather steady and unrelated with the HCO_3^- concentration observed in the pond water.
Forward geochemical modelling is used to test these hypotheses. The water of the pond is used as starting solution, and we have tried to obtain the composition of the seepage water before and after June of 1997 throughout a set of reactions. The best results have been obtained by mixing the pond water with 30% of saline water (Table 4), and reacting the water with calcite and goethite at $P_{CO_2} = 10^{-2.3}$. The results hardly change whether initial water is anoxic or dissolved O_2 of starting solution is used to oxidize pyrite.

mg/L	(A)	(B)
HCO_3^-	110 - 130	120
SO_4^{2-}	755 - 897	850
Cl^-	> 56	100
Ca^{2+}	307 - 360	330
Mg^{2+}	< 21	18
Na^+	> 45	100

Table 4. Theoretical composition of the overall underground contributions. (A) Limits imposed by observations. (B) Composition used in the model with better results

Hydrochemistry as a tracer test

The change of the chemistry of the pond water carried out in 1997 is also reflected in the seepage water; it demonstrates clearly that the main component of seepage water is pond water. The hydrochemical information obtained during that change can be used as a tracer test to obtain hydrodynamic information of the system (fig. 3).
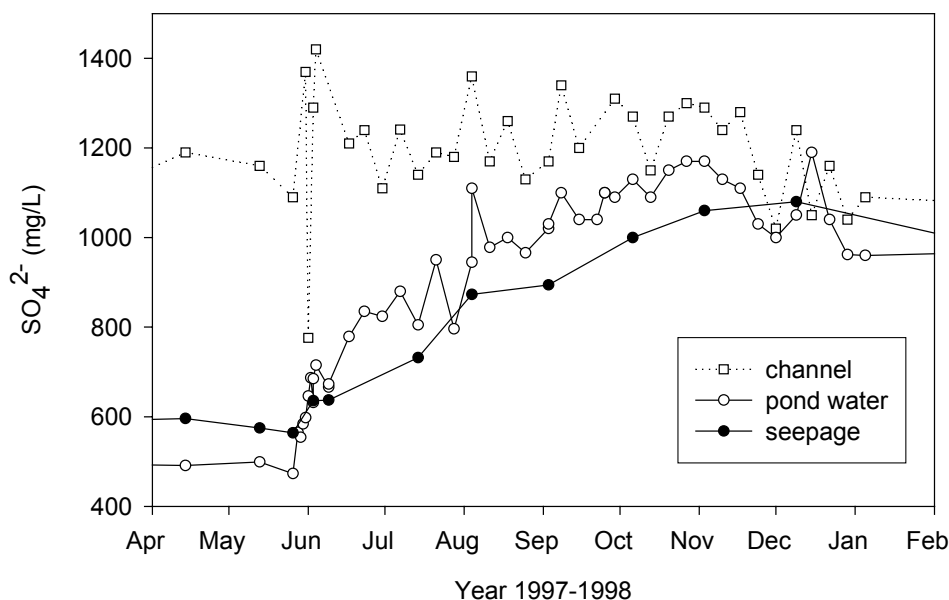

Figure 3. SO_4^{2-} concentration in the tailings pond system (1997-98)

In that system, the observed residence time of water in the pond is in the order of 5 months, similar to the residence time calculated using the water balances. The residence time of water circulating throughout the tailings is of 1.5 month. Considering that 70 % of seepage water comes from pond, the volume of mobile water in the tailings is about 13×10^3 m^3, and therefore the effective porosity of tailings is 0.02. Since total porosity of tailings is in the order of 0.3, most of the water that is in tailings pores is stagnant.

CONCLUSIONS

Different effects were observed on the hydrochemistry and the mineralogy of the tailings pond whether they were maintained partially or totally submerged.

When the tailings were partially submerged there was sulphide oxidation, and the pond water had a relatively important concentration in Zn and Mn.

When extra water was added to the pond, the tailings were completely submerged, and there are not signs of sulphide oxidation although the water is saturated in O_2. The pond also serves to settle the iron hydroxides present in the extra water.

In both situations, with the tailings partially and fully submerged; when the pond water saturated in O_2 crosses the tailings there is not significant sulphide oxidation. It is possible that the O_2 dissolved in water is depleted oxidizing the organic matter that gradually deposits in the pond's bottom.

ACKNOWLEDGEMENTS

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