

THE AZNALCÓLLAR PIT LAKE – WATER QUALITY AND OPTIONS OF CONTROL¹

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Abstract: The Aznalcóllar mine is well known since the disaster in 1998. A dam of the tailings impoundment broke and about 4 million m³ of acidic water and 2 million m³ of sludge contaminated the river system Rio Agrio-Rio Guadiamar-Rio Guadalquivir with heavy metals. A lot of research has been done to quantify the consequences of the disaster for the river system and to prove the success of the remediation measures. But little is known about the state and the perspectives of the rising lake in the former mine pit.

Parts of the Aznalcóllar pit have been used to dump waste rock from the neighboring pit Los Frailes. Additionally, tailings material and contaminated soil from the river system were deposited in the former mine pit. Consequently, the pit lake sediments are very heterogeneous and highly enriched in heavy metals reaching ore-grade concentrations for some elements. Actually, the pit lake water level is regulated by pumping to stay at least 6 m below the natural groundwater level. The water is acidic (pH 3.6) and has high concentrations of metals (e.g. 800 mg/L Zn, 200 mg/L Mn, 100 mg/L Al, 2000 µg/L Cd). The major concern is that the contaminated lake water may enter the river system and the top aquifer when the lake reaches its natural water level.

Based on recent knowledge, options of future remediation of the lake water quality are discussed.

Additional Key Words: acidification, heavy metals, remediation

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Introduction

The Aznalcóllar mine site is known worldwide because of the failure of a tailings dam in April 1998. Highly contaminated water (about $4 \times 10^6 \text{ m}^3$) and sludge ($2 \times 10^6 \text{ m}^3$) were released from the tailings pond, resulting in a large scale contamination of the Guadiamar river and its flood plains (Grimalt 1999). A lot of research has been done on the consequences of the dam failure for the contaminated river and flood plain areas (e.g. Alastuey et al. 1999, Prat et al. 1999, Madejon et al. 2003, Hudson-Edwards et al. 2003, Sola et al. 2004, Olias 2005, 2006). But little is known about the pit lake in the former Aznalcóllar mine. It is used as disposal site for contaminated materials which were removed during the rehabilitation of the contaminated areas along the Guadiamar river (Hudson-Edwards et al. 2003) and around the former ore processing facilities. The purpose of this paper is to present an overview on the results of recent research. Water and sediment samples were taken during four field surveys (November 2002, December 2003, November 2004, and April 2005). In this paper, only results for the lake water quality will be presented. Based on recent knowledge, options of future remediation of the lake water quality are discussed.

Recent state of the Aznalcóllar pit lake

The Aznalcóllar pit lake is situated about 30 km north-west to Sevilla (Spain) in the eastern part of the Iberian Pyrite Belt (Fig. 1). From historical climatic records obtained from the series 1975-2004 (Junta de Andalucía, *unpublished data*), it is concluded that the average annual precipitation of the Aznalcóllar area is around 600 mm, with a marked seasonal variation (70% of the rainfall is commonly concentrated in the months from November to March). The evaporation is also strongly variable throughout the year, from 250 mm/day during the summer, to almost zero during the winter months. The water table fluctuates due to periodic pumping carried out to keep it far below the local groundwater table. The maximum lake water depth varied around 35 m, the surface area around 0.3 km^2 and the volume around $9 \times 10^6 \text{ m}^3$. The pit wall composition includes several detrital and volcanic lithologies such as felsic epiclastites, dacite porphyries, purple tuffites, black shales and vitric to crystalline tuffs, in addition to the massive sulphide lenses (Almodóvar et al., 1998). Thermal stratification was observed only in April 2005, but it did not result in remarkable vertical differences in water chemistry. The lack of differences was likely due to the fact that the thermal stratification had just begun its development. An overview of the water chemistry is given in Table 1.

The main reasons for the variability in water chemistry are (1) the use of the lake as disposal site for contaminated material (ranging from organic matter-rich soils to pyritic ashes) and (2) the water management of the mine site. Every new input of contaminated material is accompanied by the dissolution of substances. More than a million cubic meters of solids were deposited in the lake since 2002. As mentioned above, the water management has also a remarkable impact on the water quality. Surface runoff and ground water from the remediated former tailings pond, from the former ore processing facility and from a part of the waste rock piles are collected in a small pond and periodically pumped to the lake if the pond is filled. This mixture of clean and contaminated water accounts for about 80% of the total superficial inflow into the lake. The remaining 20% is a direct inflow of contaminated water from the waste rock piles (approximately 100 hectares footprint). In order to keep the water level below the

groundwater table, lake water is periodically pumped, treated and then diverted to the Agrio river. At a pH of approximately 9.5, the sludge produced in the treatment facility is pumped back into the lake. As a consequence of this procedure, in addition to the seasonal variations in runoff, the inflows into the lake are highly variable both with respect to the flow rates and with respect to their chemistry and contaminant load.

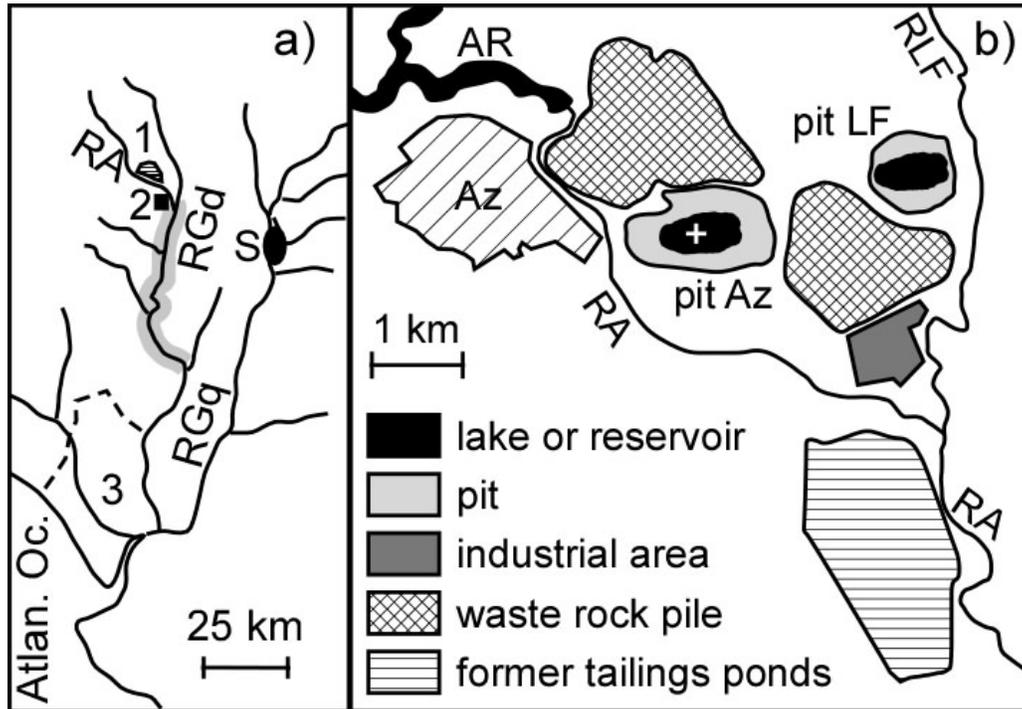


Figure 1. Location of the Aznalcollar pit lake. Panel a): 1 – mining area, 2 – former tailings ponds, 3 – Donana national park, S – Sevilla, RA – Rio Argio, RGd – Rio Guadiamar, RGq – Rio Guadalquivir, Atlan. Oc. – Atlantic Ocean, gray area – area contaminated by the failure of the tailings dam in 1998. Panel b): Az – Aznalcollar, RA – Rio Agrio, AR – Agrio reservoir, RLF – Rio Los Frailes, pit Az – pit Aznalcollar, pit LF – pit Los Frailes

A comparison of the observed water quality with results from other pit lakes in other ore mining districts (Levy et al. 1997, Parshley and Howell 2003, McNee et al. 2003, Lewis et al. 2003, Lu 2004, Dowling et al. 2004, Pellicori et al. 2005) shows that the metal concentrations in the Aznalcollar pit lake lies within the wide variation of reported data. But also within this comparison the concentrations in the Aznalcollar pit lake have to be called very high, especially for Zn and Cu. The mentioned variation is caused by the different geological settings of the pit lakes and the differences in the dominating ore minerals as well as by the limnological conditions of the pit lakes (e.g. occurrence of permanent chemical stratification, rate of water renewal, application of remediation technologies).

Table 1. Water chemistry in the Aznalcóllar pit lake between 2002 and 2005 (selected parameters, all concentrations in mg/L except pH, n.a. – not analysed).

	November 2002	December 2003	November 2004	April 2005
pH	5.3-5.4	3.7	3.8	4.0-4.5
SO ₄ ⁻²	4700-4920	5490-5720	8070-8290	7790-8220
Cl ⁻	106-110	65.9-85.3	84.1-98.0	59.2-63.2
Na ⁺	84.0-86.0	73.3-75.9	51.4-75.2	70.5-94.5
K ⁺	33.0-34.0	25.6-26.5	13.2-19.0	17.0-24.5
Mg ⁺²	n.a.	777-807	806-1140	1120-1540
Ca ⁺²	600-620	490-509	418-591	523-730
Al	1.6-3.3	51.5-56.9	108-157	109-130
Fe	130-140	3.8-10.7	1.6-2.8	0.2-2.0
Mn	135-140	161-169	141-201	183-218
Zn	310-320	434-450	638-899	834-1010
Cu	0.03-0.13	7.9-8.2	37.0-40.0	31.8-35.2
Cd	0.65-0.68	1.01-1.05	2.10-2.20	1.90-2.05

Options of remediation

Recently there is no clear concept for the future use of the pit lake (at the present moment (December 2005), the pit lake is being used as a disposal site for pyrite-rich rocks from the adjacent S-3 waste-rock pile, and this situation is expected to continue during the year 2006). In addition, the hydrologic regime is not completely known for the recent state as well as for a future final state. Therefore only some general options of remediation are briefly discussed here.

Chemical neutralization:

The chemical neutralization of lake water is based on the introduction of alkaline substances as lime, soda or ashes into the lake. It removes the acidity by acid-base reactions and metals by the precipitation of metal hydroxides. The availability of experiences from the neutralization of acidic lakes in Scandinavia and North America using lime or soda (e.g. Olem 1991, Lu 2004) and from AMD-treatment plants can be seen as an advantage of this approach of remediation, although the majority of neutralized lakes had been acidified by acid rain. But risks result from the different geochemistry of different metals: not all metals are precipitated in the pH-range 7-8 which is typically required for aquatic life and lake use. Higher pH-values may result in re-dissolution of precipitated metals from the sediment. The results of Loop et al. 2003 indicate that the addition of alkaline substances may easily result in very high pH (>11) due to the lack of sufficient buffering systems for the circum-neutral range in formerly acidic waters.

Neutralization based on sulphate reduction

The microbial reduction of solid Fe^{+3} and SO_4^{-2} is accompanied by a consumption of acidity and, thus, can contribute to the neutralization of acidic mine water. Additionally, metal sulfides are formed which are nearly insoluble under reducing conditions. Numerous technological approaches try to use this effect to neutralize pit lakes (e.g. Klapper et al. 1998, Castro & Moore 2000, Glombitza 2001, Frömmichen et al 2003, 2004, Lu 2004). The use of naturally occurring processes is an advantage of these technologies with respect to the public acceptance of such approaches. But on the other hand, organic material has to be introduced into the lakes. This may be seen as a new source of hazards. Reports of long term success of such an approach are not available. A number of tests failed (Brugham et al. 1995, Brugham and Stahl 2000, Lessmann et al. 2003a). Some technological approaches are still under development (Koschorreck et al. 2002a, b). In addition, the contact of the produced sulfides to O_2 , NO_3^- or Fe^{+3} has to be avoided to prevent re-oxidation. Otherwise the remediation would fail because of the processes described by Peine et al. 2001.

Removal of the metals by artificial eutrophication

Algae can act as “collectors” for heavy metals and trace elements by adsorption and incorporation during their growth. Some laboratory and field tests have been performed to test this remediation approach in the last years (Martin et al. 2003a, McNee et al. 2003, Poling et al. 2003, Dessouki et al. 2005). Remarkable success was reported. But little is known about the long-term stability of the binding of the metals in the lake sediments. The microbial decay of the biomass of the algae may force SO_4^{-2} reduction and, thus, the formation of sulfides with very low solubility under reducing conditions, which are common in lake sediments. But if SO_4^{-2} reduction does not occur with sufficient rates the only effect of microbial decay will be the liberation of the heavy metals and trace elements which had been accumulated by algae before. Martin et al. (2003b) and Martin and Pedersen 2004 reported remarkable risks of re-dissolution of the precipitated metals and trace elements.

Introduction of river water

The introduction of river water may be used to prevent acidification of pit lakes during their filling and to neutralize filled pit lakes as well (Klapper and Schultze 1995, Lessmann et al. 2003b, Schultze et al. 2005). The neutralization is caused mainly by the HCO_3^- content of the river water. Other processes also contribute to the neutralization. The extent of these contributions depends on the particular circumstances (Schultze et al. 2005). Good experiences were obtained by the use of this approach in Germany to remediate pit lakes which result from lignite mining (Lessmann et al. 2003b, Schultze et al. 2005). Problems may result from a lack of river water, from poor river water quality and the overflow of still contaminated water if the remediated lake is already filled.

Artificial creation of meromixis

Meromixis, i.e. the exclusion of a part of the water body of lakes from periodic overturn, result in extremely low exchange rates between the upper periodically mixed part of the lakes (called mixolimnion) and the lower stagnant part (called monimolimnion). Sedimentation transports substances from the mixolimnion into the monimolimnion. But diffusion is the only mechanism exporting substances from monimolimnion to mixolimnion. In this way the monimolimnion acts as an accumulation site within meromictic lakes. Fisher (2002) reports the creation of an artificially meromictic lake in the former Island Copper Mine (Vancouver Island, Canada): The first and main step of filling was done with sea water from the nearby ocean.

Fresh water was used to form a layer with much lower density on top of the sea water and to get the filled lake permanently stratified. Acid rock drainage (ARD) from the surrounding waste rock piles and tailings is collected and diverted into the deep of the lake. In this way the contact of ARD to O₂ is minimized. The formation of further acidity by ongoing oxidation is prevented in this way and the occurrence of SO₄⁻² reduction is favored. As reported by Poling et al. (2003) the meromixis is stabilizing the success of artificial eutrophication for the removal of metals too. But the use of this approach is limited to mine sites where highly saline water is available for the artificial formation of meromixis. The planning of artificial meromixis may be complicated because the mechanisms governing the occurrence of meromixis are not completely understood (Boehrer and Schultze 2006). In addition, the ongoing pyrite oxidation in the monimolimnion of the Berkeley pit lake indicate that some of the mechanisms responsible for the advantages of artificial meromixis may be counteracted by other processes to a remarkable extend. Sudden unexpected overturns of water from the monimolimnion may liberate enormous amounts of accumulated hazardous substances (e.g. H₂S, toxic metals) to the mixolimnion or to other water bodies downstream. This may cause total fish kills there or other damages to wild life or water users.

As far as known today, there is no chemical, biological or physical treatment option which would be able to serve as single approach for a successful remediation. Additional alternatives may include control of the runoff from waste rock piles, submergence of sulfide pit walls, partial and complete backfill of the pit. The different approaches can be employed successfully only if there is no or only a very limited further introduction of acidity, heavy metals and trace elements. Some measures are necessary for the management of the water quality and solids that enter the pit, such as sludges, partially and untreated non pit waters, and contaminated wastes. Otherwise the remediation approach will fail completely or has to be employed frequently causing more and more costs. But combinations of some of the mentioned options may provide approaches for the primary rehabilitation of the Aznalcóllar pit lake, as well as for a sustainable long-term management of the lake.

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