Geochemical Modelling Applied to the Study of Arsenic Mobilization in Abandoned Mines

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Abstract

The end of mercury mining activities in the Spanish region of Asturias from the 1970s has left significant sources of arsenic contamination in tailings piles, some of which are abandoned. The mobility of arsenic in water and its incorporation into the hydrological cycle add to the hazards of the leachates that continue to be produced constantly in many of these tailings piles. This work proposes a protocol for characterizing the leachates, which are regularly sampled in the field, analysed in the laboratory and geochemically modelled. The proposed methodology has been applied to the dumps of La Soterraña mine, which contributes concerning amounts of arsenic to the natural waters in its surroundings. Although the results presented here are still considered to be preliminary, the protocol seems to be ideal for evaluating the leachates and their hazards, offering explanations regarding the mobility of the contaminants and the formation of efflorescences that appear in the tailings piles during certain periods of the year.

Keywords: Geochemical modelling, abandoned mines, arsenic, mine tailing pile.

Introduction

The region of the Principality of Asturias (NW Spain) has been an important mercury producer since ancient times. By the late 1960s, it produced 5% of the world's mercury. However, from that point on, the economic conditions that led to the drop in the price of this metal caused the gradual closure of all the mining operations, and the last mercury mine in the region, La Soterraña, ceased its activity in 1974. A characteristic feature of many mercury mines in Asturias is a strong geochemical anomaly in arsenic, which was also exploited as a byproduct and has left significant contamination in the spoil heaps, recognized as an important source of local pollution (Marques, 2020).

The La Soterraña mine, currently inactive, is located in the municipality of Lena, on the southwest slope of a mountain called Las Campusas, next to the AS-231 road. In the field and on satellite photographs, it is identified by the abundance of mining facilities in ruins and by an impressive waste dump (43°11'31.6"N 5°50'37.7"W), which reveals the significant volume of material extracted during an extended mining period. The small stream Muñón runs along the western edge of the spoil heap, collecting leachate water that is permanently channeled in the roadside ditch. The spoil heap is heterogeneous, with almost no vegetation, and recurrent efflorescences, more or less ephemeral, develop on it, although their nature has not been completely determined. Currently, actions are being taken regarding the spoil heap in connection with a remediation and decontamination project (SUBproducts4LIFE) funded by the European Union.

From a geological point of view, the La Soterraña deposit is classified by Luque (1985) and Luque-Cabal and Gutiérrez – Claverol (2010) as part of the Central Coal Basin. The materials in which the mineralization is hosted are sandstones and shales from the Lena Group, of Carboniferous age, which also contains some carbonated banks and coal seams (Luque 1985). The main tectonic structure in the area is the Muñón anticline, with an approximate N-S direction, affected on its western flank by two fault systems: one with an approximate NNE-SSW trace (like the Pajares fault, according to Alonso *et al.* 2009) and another with a predominant E-W direction (like the Aramo fault). The deposit, which is considered of tardi-Hercynian epithermal character (Luque *et al.* 1989), has cinnabar, realgar, and orpiment mineralization, generally associated with limestone beds.

This work proposes a protocol for the geochemical modelling of natural waters that have leached the spoil heaps of these abandoned mines, aimed at understanding their current state after several decades of mining abandonment. The focus is on arsenic, which is highly dangerous and mobile in water, in a hydrogeologically complex context, of rural nature and strong human alteration. It has been applied to the La Soterraña mine, and here we present the main results, which, although preliminary in some aspects, are of interest for potential remediation efforts or actions on the spoil heaps and in the hydrogeological system.

Methods

The methodology applied in this study primarily involves sampling leachate waters at different times of the year, their chemical analysis, and geochemical modelling using the PHREEQC code. The results are interpreted and discussed in correlation with meteorological conditions. The following details the procedure followed for each of these tasks; however, it is important to note that the selection of sampling points, which is not discussed here as it is outside the scope of this study, requires a deep understanding of the regional and local geological and hydrogeological context. Additionally, it is stated that the sampling period extended from late December 2022 to late April 2023, a time of year when precipitation is more likely, according to data from the Spanish State Meteorological Agency. Within this period, efforts were made to maintain regularity, with sampling approximately every 10 days.

Two sampling points, very close to each other, were selected. At the first point (P1), leachate water is directly collected from the lowest point of the waste dump, and at the second (P2), at the same level, from the stream described above, which borders the dump at its most western part. The mixing of waters occurs practically at the sampling site; that is, the leachates are discharged directly into the stream, with no specific treatment currently in place (Marques *et al.* 2018). Fig. 1 shows the location of the collection sites on a satellite image, along with its coordinates.

Water samples were collected and preserved according to a standardized procedure that ensures the absence of contamination and the stability of the sample. Essentially, the procedure requires constant water flow, in-situ measurement of pH and water temperature, the use of gloves,

Figure 1 *Detailed location of the sampling points at La Soterraña on the Google Earth satellite image.*

the addition of three drops of nitric acid (1N) per 200 mL to prevent precipitation, and preservation in decontaminated polypropylene containers, stored in a refrigerator at 8 °C until the chemical analysis is performed. For each collection, 500 mL of sample was obtained per sampling point.

All water samples collected were analysed at the Technical Services of the University of Oviedo. The samples were filtered using a 0.45-micron PTFE syringe filter, and the arsenic concentration was determined in all of them by ICP-MS, using an Agilent Technologies HP 7700 instrument. Additionally, based on the results, a complete analysis of the concentrations of B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Tl, Pb, and U was conducted in one of the samples using the same instrumental technique, along with the determination of the anions F^-, Cl^-, and SO_4^{2-} by ion chromatography with a METROHM 883 Basic IC plus system. For this complete analysis, the sample with the arsenic concentration closest to the mean of all the samples was selected.

From the results of analyses, geochemical modelling was carried out using the PHREEQC Interactive code version 3.7.3 (Parkhurst and Appelo 2013), from the USGS (United States Geological Survey). The modelling utilized the llnl.dat database, which includes a comprehensive set of thermodynamic data compiled by the Lawrence Livermore National Laboratory and is considered an ideal database for mine water modelling.

Calculations of the effective rainwater, that is, water that percolates into the waste dump, were obtained using the TRASERO 2.0 code, developed by the Alicante County Council. The input data were obtained from the Spanish meteorological service (AEMET) website, *meteosolana.net*, for the station nearest to La Soterraña mine, called Lena-Ronzón. The code uses an empirical correlation method known as the *Thornthwaite approximation*, whose fundamentals and detailed development can be found in the manual (Diputación de Alicante 2005) and the references therein.

Results

The arsenic content in the samples from the water of the tailings piles at the two locations is shown in Tab. 1. A variation in the data is observed, but within the same order of magnitude, without any major gradients or values that could be considered anomalous within the data series. The arsenic content in all samples is several orders of magnitude above the tolerable levels for water intended for human consumption (not exceeding 10 µg/L according to Spanish regulations in Real Decreto 3/2023 and WHO recommendations), or even for uses such as irrigation (not exceeding 25 µg/L according to Spanish regulations Real Decreto 60/2011).

The full analysis of the sample selected as the most representative in terms of arsenic concentration yields the results shown in Tab. 2. Both the arsenic content data and the data for other elements are consistent with those found in historical records from monitoring conducted at La Soterraña (Marqués, 2020).

The complexity of the waters whose analyses are shown in Tab. 2 and the high number of species and phases that can

Table 1 As concentration in the water collected from the tailings of the abandoned La Soterraña mines.

	As content µg/L (LQ=2 µg/L)	
Date	P1 (dump)	P2 (stream)
29/11/2022	35322.35	41532.55
10/12/2022	36634.21	34116.58
20/12/2022	34625.11	33250.48
02/01/2023	35250.36	32928.79
11/01/2023	31667.58	29985.45
20/01/2023	29514.29	29754.02
31/01/2023	31725.43	32260.17
09/02/2023	39533.81	34599.84
18/02/2023	43552.76	40837.89
02/03/2023	36237.60	32906.1
11/03/2023	39472.46	36680.75
20/03/2023	40260.21	42168.88
31/03/2023	41685.37	49421.26
20/04/2023	40266.83	43360.43
27/04/2023	40534.92	43518.9

form presents a complicated geochemical modelling. The modelling with PHREEQC predicts that native mercury (Hg), barite ($BaSO_4$), tiemannite (HgSe), $Sb(OH)_3$, and Sb_2O_4 could precipitate. The saturation indices for each of these are shown in Tab. 3, that also includes the saturation indices for the phases containing arsenic.

Thus, according to modelling, all arsenic species are dissolved, and therefore, their mobility in the natural environment is very high. Based on the PHREEQC modelling, an attempt has been made to determine the hypothetical precipitation sequence of arsenic phases in a system where water is removed through evaporation. However, the concentration required for the precipitation of these phases is so high that the ionic strength increases significantly. When this ionic strength reaches such high levels, the database used in the modelling becomes insufficient, and thus the simulation cannot be performed. Consequently, it can be concluded that arsenic phases will only appear when the presence of water is minimal. In the event that they precipitate, and due to their high solubility, these phases can be considered ephemeral in the tailings, and with any rainfall episode, they would re-enter the aqueous system. Probably, some of these phases appear as efflorescences in the tailings during dry periods.

Table 2 Composition of a representative sample of the leachates from La Soterraña dump.

Element or ion	Concentration µg/L	LQ µg/L
B	56.81	20
Na	21904.54	200
Mg	27234.02	200
K	14896.46	200
Ca	235837.12	200
V	11.91	2
As	36634.21	2
Se	3.67	2
Sr	3247.53	2
Mo	8.97	2
Sb	59.88	2
Ba	28.51	2
Hg	0.56	0.2
U	0.82	0.2
	mg/L	**mg/L**
F^-	0.680	0.02
Cl^-	12.33	0.2
SO_4^{2-}	616.47	0.2
NO^{3-}	2.804	0.2

Discussion

In light of the data presented in the Results section, the situation regarding arsenic at the mining waste dump of the abandoned La Soterraña mine is concerning. The data from this study are consistent with historical records and with those from several research projects that have been developed and are still ongoing to try to mitigate the situation. Focusing solely on arsenic content, the waters circulating around the tailings pile and collecting its leachates are heavily contaminated with arsenic, and the Muñón stream exceeds legal limits for human consumption or even irrigation by more than three orders of magnitude. The efflorescences that recurrently appear are soluble, and instead of permanently fixing arsenic, they re-enter the water system when the short dry periods in the valley end.

The graph in Fig. 2 shows the concentration of arsenic in the analysed samples from La Soterraña along with effective rainfall data as calculated by TRASERO 2.0. Although the discussion is qualitative, it is clear that arsenic concentrations increase during dry periods. The amount of water flowing through the Muñón stream, and the percolation in

Table 3 Saturation indices for As species and the possible phases that could precipitate in lixiviates.

Phases	Saturation Index
Barite	0.52
Hg (native)	4.9
$Sb(OH)_3$	0.79
Sb_2O_4	6.4
Tiemannite (HgSe)	4.4
Arsenolite (As_2O_3)	-22.66
As	-33.04
As_2O_5	-24.77
As_4O_6 (cubic.)	-45.17
As_4O_6 (monocl.)	-44.95

the tailings pile increases during the rainy season, and the concentration of dissolved phases decreases. Establishing a quantitative correlation of data requires a longer sampling period, and most likely, the actions being carried out at the tailings pile and its surroundings in connection with ongoing projects complicate the achievement of a good quantitative correlation between rainfall and arsenic concentration, beyond the merely qualitative correspondence.

Conclusions

In light of the data presented in the Results section, the situation regarding arsenic at the tailings pile of According to the geochemical modelling, all the arsenic is in dissolved chemical species, making it highly mobile. Arsenic phases will only precipitate during very dry periods. Due to their high solubility, rainfall carries them back into the aqueous system.

Although the available data are preliminary, a correlation has been found between the arsenic leached from the La Soterraña tailings pile and the effective rainfall during the sampling period.

The proposed protocol for studying the leachates provides useful information for designing mitigation strategies and environmental monitoring in mining areas.

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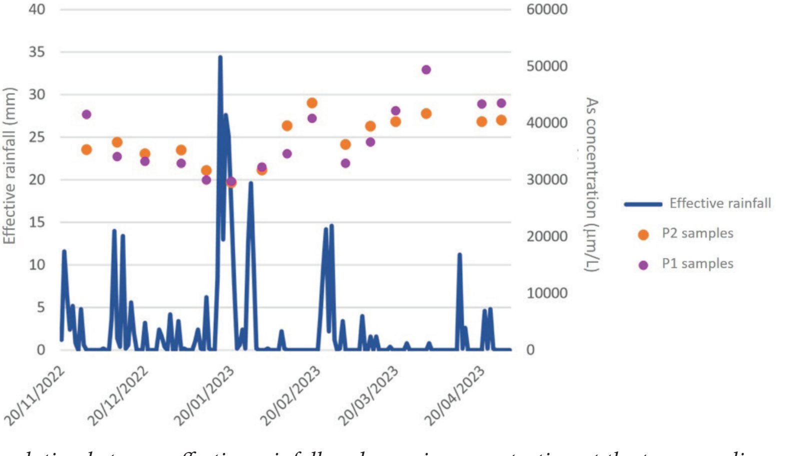

Figure 2 Correlation between effective rainfall and arsenic concentration at the two sampling points.