Use of Industrial By-Products to Prevent/ Reduce Water Contamination with As and Hg

Rafael Rodríguez[1], Efrén García[1], Begoña Fernández[2], Julia Ayala[2]

[1]Department of Mining Exploitation and Prospecting, Polytechnical School of Mieres, University of Oviedo, Gonzalo Gutiérrez Quirós s/n, 33600 Mieres, Asturias, Spain; rrodrifer@uniovi.es, ORCID 0000-0002-5518-1481; garciaefren@uniovi.es, ORCID 0000-0001-9138-7076

[2]Department of Materials Science and Metallurgical Engineering, Polytechnical School of Mieres, University of Oviedo, Gonzalo Gutiérrez Quirós s/n, 33600 Mieres, Asturias, Spain; fernandezbegona@uniovi.es, ORCID 0000-0003-1239-4839, jayala@uniovi.es, ORCID 0000-0002-6404-1296

Abstract

Based on two real scale trials carried out in an abandoned mercury mine waste dump, a solution to prevent and reduce the contamination of water with arsenic (As) and mercury (Hg) is proposed. First, the waste surface is covered with a layer of fly ash preventing 90% of the water to be contaminated. Second, the leachate is treated in filtering channels with fly ash and steel slags to reduce the As concentration in four stages with reduction of 60% in each stage. The results demonstrate the feasibility and usefulness of the proposed solution.

Keywords: Fly ash, steel slag, physical remediation, abandoned mines, passive mine water treatment

Introduction

The European Union produces about 64 million tons per year of fly ash (ECOBA, 2016) and 15 million tons per year of slags (EUROSLAG, 2022). About 57% and 12% respectively are not reused with the problem of its storage and very expensive management. It has been demonstrated that some byproducts can fix potentially toxic elements. On the other hand, there are in Europe many mining dumps containing high concentrations of toxic elements being a problem both for the environment and human health. In this context, the SUBproducts4LIFE project was developed within the LIFE program of the European Union. First, the use of fly ash from coal burning power plants and slags from blast furnace and steel making were tested at a laboratory scale with positive results, Ayala and Fernández (2020). Then, several real scale tests were carried out in an abandoned mercury mine (Fig. 1) to demonstrate the reuse of byproducts to reduce the contamination of leachates produced in waste dumps.

The main problem is that rainwater is contaminated by the waste producing leachate with very high concentration of As and Hg, which becomes a very serious environmental problem. The average annual rainfall P in the area is of about 900 mm/a (Chazarra *et al.*, 2018), and the average evapotranspiration ET_0 is of about 800 mm/a (Sancho *et al.*, 2012). Under these conditions, the main goal is to prevent and reduce this contamination of the water.

Materials and Methods

The mine, located in Asturias (Spain), is a paradigmatic case of arsenic (As) and mercury (Hg) contamination that has been studied many times during the last years, i.e. Loredo *et al.* (1999, 2006), Fernández *et al.* (2020), García *et al* (2021), Rodríguez *et al.* (2021). In the present work the test was carried out in the upper waste dump with about 13,000 t of solid waste from metallurgical process highly contaminated with As and Hg. Seven soil samples were collected as described in Fernández *et al.* (2020) with the results shown in Table 1.

Two different tests were carried out. The first consisted in covering the waste with fly

Table 1 Arsenic and mercury concentration in the waste.

Potentially Toxic Element	N	Average mg/kg	Min mg/kg	Max mg/kg	SD
Arsenic (As)	7	16,107	2594	38,841	13,312
Mercury (Hg)	7	3646	240	7266	2645

ash to prevent water contamination. This measure is quite interesting because it has also the advantage of preventing gaseous Hg emissions to the atmosphere after Rodríguez *et al.* (2023).

For this purpose, two areas of about 1000 m^2 each one, were selected in the waste dump. One was covered with a layer of 30 cm of ash (Fig. 2) to prevent the rainwater infiltration. Under this layer another layer 30cm thick of blast furnace slag was put as a drainage. In this case, ash, with porosity of 58.8% and permeability of 2.83×10^{-6} m/s, act as physical barrier preventing the entry of water. No loss of efficiency of the materials has been observed; in no case are the slags or ashes loaded with As or Hg. Although slags were also used, the more important role is due to ashes. Slags contribute to the stability and drainage.

Water samples were collected from the ditch at the toe of the dump in each area. The ditches receive surface run off as well as leachates that have passed through the waste materials. Due to ditches are independent, the comparison between As and Hg concentration in leachate in both ditches allowed determine the efficiency of the ashes to prevent contamination.

In the second test the contaminated water passed through filtering channels to reduce the Hg and mainly As concentration as much as possible. The channels consisted in a half of a 40 cm diameter pipe, 6 m long, arranged with a slope of approximately 10%.

These channels were filled with two layers of steel making slags 3–4 cm thick alternating with two layers of fly ash 1–2 cm thick. The steel slag base layer is shown in the Fig. 3. In total, 189 kg of material were used (45 kg of ash and 144 kg of slag). The composition of the material is as follows:
80 kg of slag + 27 kg of ash + 64 kg of slag + 18 kg of ash.

In this case, the removal of As and Hg from the water is due to physicochemical reactions, and the byproducts retain these elements (Ayala and Fernández, 2020). Therefore, as they work, they become loaded with As and Hg, reaching a point where they are exhausted, and their efficiency is null. The efficiency and the life span of the byproducts are determined by comparing the As and Hg concentration at the inlet and outlet of the channel.

Figure 1 La Soterraña mercury mine facilities (image: courtesy of Quercus Media).

Figure 2 *The two areas (covered and uncovered) of the waste dump (image: courtesy of Ax1 Ahora).*

Results

Four campaigns of water sampling in ditches of waste dump were carried out. Campaigns 1, 3 and 4 are related to days with intense raining while campaign 2 is related to rain of moderate intensity for several days (Fig. 4). The cumulative rain for each period was 42.8, 6.6, 45.6 and 53.4 mm respectively.

Nine samples of water were taken in each ditch. The results show that there is a huge variability in the concentration of As and Hg for different samples. High concentrations of As and Hg are usual when it rains after a dry period. The relationship between Hg concentration in waste and Hg concentration in leachate is according to Vaselli *et al.* (2017).

The results (Tables 3 and 4) show the effect of the ash capping: the contamination of the water was reduced more than 90%, from 10,203 to 1040 µg/L for As, and from 5.46 to 0.1 µg/L for Hg. This is in accordance with a study in another area described in Rodríguez *et al* (2025). When $P/ET_0 \approx 1$, with a 30 cm of ash layer, only 10% of the rainwater crosses

Figure 3 *One of the channels used for trials (image: R. Rodríguez).*

Table 2 Chemical composition of fly ash (FA), and blast furnace and steel making slags (BFS, SMS) after Ayala and Fernández (2020).

	Weight percentage (%)									Concentration (mg/kg)								
	SiO2	Fe2O3	MgO	K2O	Al2O3	CaO	SO3	TiO2	MnO	Hg	As	Zn	Cu	Cr	Pb	Ni	Cd	pH
FA	56.5	9.5	0.9	2.61	23.9	3.4	2.04	0.85	-	2	59	90	57	83.6	16	65.4	1.84	10.9
BFS	34.2	0.34	5.7	0.44	12.8	42	3.29	0.64	0.31	5.5	10.3	4	2.18	27	1	0.4	-	11.3
SMS	13.8	37.9	1.1	0.3	2.1	38.3	1.14	0.53	3.49	16.3	37.8	57.5	26	49	9	24	0.16	11

the ash, contact to the waste and become contaminated.

This result is very important because this solution reduces the Hg concentration from 5.46 to 0.10 µg/L, which is lower than 1 µg/L which is the maximum allowable concentration of Hg in water before being discharged in a river.

It must be taken in mind that companies which supply byproducts have a huge experience in managing these materials. More concretely in Asturias there are several large landfills in which these byproducts are deposited and consequently their potential effects on the environment, of very low intensity, and the measures to avoid them are well known. The main goal, more difficult to achieve, is to reduce the high concentration of Hg and As in water, mainly in the later which can reaches 400 times the maximum allowable value.

The effectiveness of the filtering channel was also analysed. Due to Hg concentration (0.38 µg/L) was lower than the maximum allowable value, only the As removal is analysed. The test was conducted over a period of two weeks (334 hours), with a total volume of 11,234 L of water flowing through the channel (average flow rate of 0.56 L/min). Samples were also collected on the initial days to ensure the representation of high adsorbent dosages.

A total of six water samples were collected at the inlet and outlet of the channel to analyse

Table 3 Arsenic concentration in the ditch water.

Sampling point (ditch)	N	Average (mg/L)	Min (mg/L)	Max (mg/L)	SD
Uncovered waste dump area	9	10,203	1525	26,304	6965
Ash-covered waste dump area	9	1040	23	220	980

Table 4 Mercury concentration in the ditch water.

Sampling point (ditch)	N	Average (mg/L)	Min (mg/L)	Max (mg/L)	SD
Uncovered waste dump area	9	5.46	0.67	23.25	9.00
Ash-covered waste dump area	9	0.10	0.00	0.29	0.12

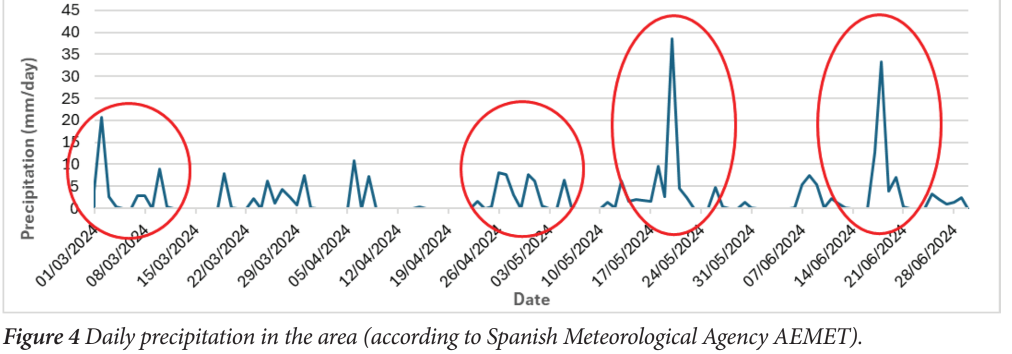

Figure 4 Daily precipitation in the area (according to Spanish Meteorological Agency AEMET).

the As concentration by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The average concentration of As was reduced from 21,510 to 11,192 µg/L with an average global efficiency of 47.9%. According to Ayala and Fernández (2020) ashes and steel slags exhibit comparable retention curves, suggesting that about half of the arsenic was retained in the slags and half in the ashes.

If it is assumed that the entire mass of material (189 kg) is involved in removing As, the relationship between the volume of water treated at a given time and the mass of material represents the adsorbent concentration which diminishes with time. According to these results, if the volume of water is limited to an adsorbent concentration of 25 g/L, the As reduction reaches the 60% (Fig. 5).

Case study

Based on the previous results, we can carry out a case study assuming the use of filtering channels in conjunction with the use of fly ash capping to prevent and diminish the contamination of the rainwater over 1000 m^2 of a dump with waste from mercury metallurgical process. We can consider that the yearly precipitation is 900 mm/a, and the total rainwater volume over the 1000 m^2 of waste surface is 900 m^3/a.

Let us assume that the concentration of As and Hg in leachate from the waste dump is 10,000 and 5.0 µg/L respectively. The maximum allowable concentration for As and Hg to discharge water into a river are 25 and 1 µg/L respectively according to Spanish regulations.

The waste surface is covered a layer of ash 30 cm thick which means that only 10% of water is contaminated. The water collected in the ditch is driven to a filtering channel with steel making slag and fly ash. The efficiency of the channel is 60% for a dosage of 25 g/L.

Under these hypotheses, the concentration of Hg in leachate after covering the waste with ash would be 0.5 µg/L, lower than the maximum allowable value 1 µg/L. Nevertheless, the concentration of As would be 1000 µg/L, so it is necessary the treatment in a filtering channel to reduce the As concentration to 25 µg/L. We can achieve this by using 4 stages in series:

$1000\ \mu g/L \times (1 - 0.60)^n = 25\ \mu g/L\ \mu$ then $n \approx 4$

The total mass of adsorbent material is:

$4 \times 900\ m^3/a \times 25\ g/L = 4 \times 900\ m^3/a \times 25\ kg/m^3 = 90{,}000\ kg/a = 90\ t/a$

Each stage must have 22.5 t of ashes and slags with a total volume of about 11.2 m^3. An example of a possible distribution could be four channels of 25 m ×2.5 m × 0.2 m.

The result could be improved if the layer of ashes covering the waste is of 40 cm thick. In this case, the water infiltrating through the ash would be 5%, the As concentration in the ditch would be 500 µg/L and only 3 stages should be necessary. After using, the exhausted byproducts should be stored in the site and covered with clean ash.

Conclusions

The solution described for the elimination of As and Hg from the leachate produced in a waste dump has been demonstrated to be feasible and useful to reduce mainly the As contamination by reducing the concentration of As from 10,000 to 25 µg/L.

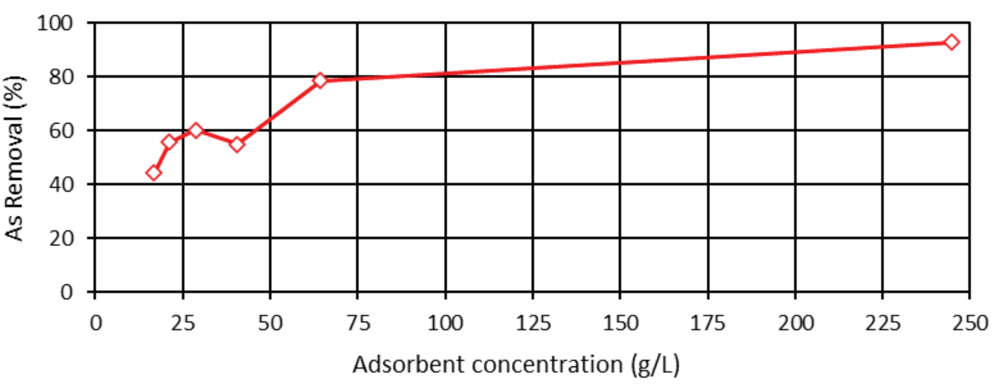

***Figure 5** Relationship between As removal and adsorbent dossage.*

On the other hand, it must be considered that the results achieved are perfectly replicable since they were carried out under real conditions without taking special precautionary measures like in a laboratory.

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