

# CONTRIBUTION OF CIEMAT IN THE CONTROL OF CHEMICAL TREATMENT AND FLUSHING OF TOXIC WATER RETAINED IN ENTREMUROS FROM THE AZNALCOLLAR MINE ACCIDENT

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## INTRODUCTION

At dawn on April 25, 1998, the tailing dam of Aznalcóllar (Sevilla) pyrite mines, belonging to the Company Boliden-Apirsa, collapsed. The flood with sulphide slurry and acid water was retained within a channel (approximately 8 Km long and 1 Km wide) in the lower part of the Guadiamar river, in the Entremuros area, near the Doñana Park. The retained water volume was estimated about 4 millions of m<sup>3</sup>. The flushing of these waters is not permitted (BOE num. 103, 1986) due to their heavy metals content (Pb, Zn, Cu, Cd, etc.) and very low pH. Therefore this water is very toxic for plants, animals and groundwater in this area and it must be treated for decreasing the content of toxic species prior to its release.

Several laboratories studied the process involved in the chemical treatment of Entremuros water (Mujeriego et al., 1998; Gómez et al., 1998). The process consisted of the neutralisation of the water with a solution of either 25% Na<sub>2</sub>CO<sub>3</sub> or 50% NaOH. The chemical process selected was applied by Aguas Filtradas, S.A.

The contribution of CIEMAT (Centro de Investigaciones Energéticas Medioambientales y Tecnológicas) with the hydrogeochemical mobile unit "CIEMAT-ENRESA" was in collaboration with the following official organisms from the Ministerio de Medio Ambiente: Confederación Hidrográfica del Guadalquivir (CHG) and Instituto Tecnológico Geominero de España (ITGE). The latter was the director and co-ordinator for the overall operation carried out for the flushing.

The mobile unit has the necessary instrumentation for the "in situ" determination of species which are interesting to control the water treatment and the flushing. Measurements of pH and Zn were periodically performed at the outlet of the neutralisation vessels. Furthermore, pH, conductivity, sulphate, turbidity and heavy metals were analysed. The samples were taken from the pumping zone of the toxic dam, the decantation dam and the flushing water.

The performance of CIEMAT in the control of the chemical treatment and flushing of the waters retained in Entremuros took place in two phases. A first phase, in the last week of May and a second one in the months of July and August when the flushing of the waters was performed.

This paper describes the contribution of CIEMAT in the control of the detoxification treatment and the release of Entremuros retained water, the methodology used and the main results obtained.

## ANALYTICAL TECHNIQUES

Heavy metals were determined by electrochemical methods, polarography and anodic stripping voltammetry in accordance with the DIN commission. A Metrohm VA Processor 693 coupled to the 694 VA Stand, was employed. The electrodes used included, a hanging mercury-drop electrode (HMDE), as working electrode, a Ag/AgCl/KCl 3M, as reference electrode, and a platinum electrode, as auxiliary electrode.

Differential pulse anodic stripping voltammetry (DPASV) was used to analyse low levels of heavy metals in water samples. An aliquot of the samples was transferred to the polarographic cell and deaerated by purging with oxygen-free nitrogen for 300 seconds. After the preconcentration step, application of a deposition potential (-1.100 mV) under stirring (30-90 sec), the stripping voltammograms were obtained.

In samples with the highest concentrations of heavy metals, the preconcentration step was omitted, carrying out a cathodic potential sweep. All measurements were made using the differential pulse mode with a -50 mV pulse amplitude. The method of standard additions was used for quantitative analysis.

The anions were analysed by ion chromatography according to US EPA, 1989. An ion chromatograph Dionex 4500i was used. The analytical columns included a guard column Dionex AG14 and a separator column Dionex AS14. Detection was achieved by a conductivity detector. Eluent conductivity was suppressed by an anion self regenerating suppressor Dionex (ASRS).

The determination of Ca and Mg was also performed by ion chromatography. A separator column Dionex CS12 with an eluent solution 20 mM methanesulfonic acid (MSA) was used. As suppressor device, a cation self regenerating suppressor Dionex (CSRS) was used.

The pH measurements were made on an Orion Model EA 920 digital pH-meter calibrated with adequate buffers solutions.

Electrical conductivity measurements were performed on a WTW LF325 conductimeter. The conductivity cell was calibrated with KCl solutions.

The turbidity was measured on an Hach DR/2000 nephelometer by comparison of the intensity of light scattered by the sample and a formazin polymer standard reference suspension under the same conditions (A.P.H.A., A.W.W.A. & W.E.F., 1995)

The standard solutions were prepared from standard stock solutions by dilution as required. All chemicals had the purity degree p.a. All solutions were prepared with deionized water with a specific resistance of at least 18 M $\Omega$ .

The methodology used in the mobile unit was checked by comparison with the methodology existing in the analytical laboratories in the Chemistry Area of Ciemat. Common anions were determined by ion chromatography. For heavy metals determination, atomic absorption spectrometry (AA), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) were used. These methodologies were validated by means of certified reference materials of the Community Bureau of Reference (BCR) of the Commission of the European Communities when it was applicable.

## FIRST PHASE: WATER CHARACTERISATION IN ENTREMUROS AREA

The first phase was performed in the last week of May 1998. Figure 1 shows the location of the 10 sampling points, selected according to the first sampling campaign carried out by the CSIC-UPC groups. Eight samples were collected in the northern area of the main containing wall. Sample P7 was taken from a parallel rice irrigation channel called "Canal de Aguas Mínimas". Two samples were taken in the south part of the main containing wall. (Gómez et al., 1998).

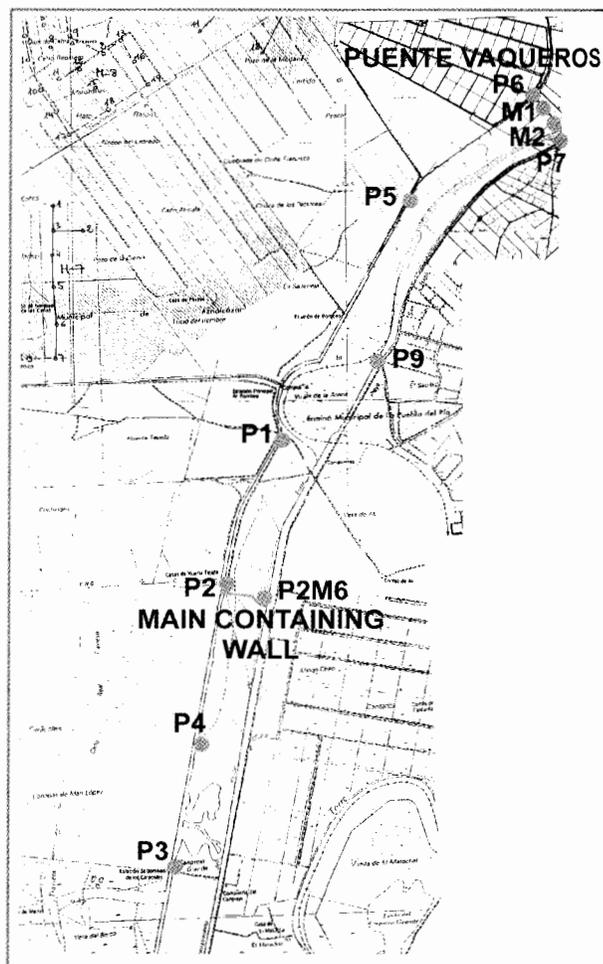


Figure 1. Location sampling points in the Entremuros area.

The analytical results obtained for the water samples were similar to those found by other analytical groups, although a decrease in the content of heavy metals was observed in relation to the first determinations due to a natural increase of the pH of the waters. The high content of sulphate was originated by the oxidation of the sulphides dissolved in the mine wastes spilled.

In Table 1 the analytical results obtained in the mobile unit (MU) are compared with those obtained in the laboratories of the Chemistry Area of CIEMAT. Only the parameters and chemical species of interest in the control of chemical treatment and flushing of the toxic waters are showed.

## CONTROL OF CHEMICAL TREATMENT AND FLUSHING OF TOXIC WATER RETAINED IN ENTREMUROS FROM THE AZNALCOLLAR MINE ACCIDENT

SAMPLE	PH		COND 20°C (mS/cm)		Zn (mg/l)		Cd (mg/l)		SO <sub>4</sub> <sup>2-</sup> (g/l)	
	MU	LAB	MU	LAB	MU	LAB	MU	LAB	MU	LAB
P2	7.1	6.8	7.13	6.93	153	135	277	250	3.3	3.3
P2M6	7.1	7.0	5.92	5.75	216	190	415	360	3.5	3.5
P3	8.6	8.5	12.5	12.2	0.51	0.35	<5	<1	1.3	1.3
P4	7.4	7.2	8.40	8.13	78	71	159	170	4.0	3.5
P1	6.9	6.8	5.50	5.37	130	125	302	280	2.9	2.9
P5	7.8	7.5	3.08	2.97	22	20	78	65	1.7	1.6
P6	8.1	7.8	2.47	2.41	6.1	6.0	32	24	1.2	1.2
P7	8.4	8.4	2.11	2.04	0.27	0.13	<5	<1	0.39	0.37
M1	7.8	7.6	2.50	2.42	6.8	6.8	26	18	1.2	1.2
M2	8.3	8.1	1.72	1.67	2.2	2.1	11	18	0.62	0.56

Table 1. Comparison between analytical results obtained in the mobile unit and the central analytical laboratories of the CIEMAT for the waters in Entremuros.

In general, a good agreement between both sets of results was obtained. In this way, we had an up to date analytical information of these waters and a contrasted methodology for the control of chemical treatment and flushing of toxic waters. In a recent paper, we have studied quite extensively the geochemical aspects of the toxic waters retained in Entremuros. (Garralón et al., 1999).

## SECOND PHASE: FLUSHING OPERATION (8 JULY-21 AUGUST)

This phase included the whole period in which the flushing operation, of both the toxic water and the water located up, took place. In this phase, different stages can be considered:

- Experimental test with 25 % sodium carbonate solution.
- Characterisation of the dam waters up from the toxic dam.
- Flushing of the treated toxic waters and of waters in which chemical treatment was not necessary.

### Experimental test (8-17 July)

Firstly, a previous test with about 100 000 m<sup>3</sup> of toxic water was carried out in order to check the validity of the chemical treatment. The chemical process selected by the ITGE, was applied by Aguas Filtradas S.A. This process consisted of neutralisation of the water with 25 % sodium carbonate solution.

This company set up two linked tanks with a capacity of about 30 000 liters, connected to the reagent tank by means of a dispenser pump. The toxic water was impelled inside the mixture tanks by two pumps 1000 m<sup>3</sup>/hour flow. Inside them, two stirrers mixed and homogenised the water with the carbonate. The treated water was poured out through a ramp, from the up zone of the second mixture tank to a discharge-decantation dam. This dam had about 100.000 m<sup>3</sup> volume, 1 meter in depth

and approximately 900 m long. It was formed by the main containing wall and another parallel security containing wall built about 100 meters in the south part.

From 600 to 900 meters from the treatment plant, 6 tubes with opening/closing valves were placed at 30 and 60 cm from the bottom of the dam. The treated water advances toward the release tubes. In the meanwhile, the precipitate formed by addition of reagent decants. In this way the amount of toxic species in the water decreases to a level below the permitted limit by applicable legislation. So, the water can be released to the Guadalquivir river through the "Canal de Aguas Mínimas".

The mobile unit CIEMAT-ENRESA was located at the end of Entremuros, at the left margin, close to the treatment plant. It carried out the following functions:

- Characterisation of the pumping zone of the toxic dam. Determination of Zn, Cd, pH, SO<sub>4</sub><sup>2-</sup>, Ca and Mg were performed.
- Support to Aguas Filtradas S. A. in some previous test carried out to know the adequate dose of reagent. The Zn content, as a function of pH and the decantation time, was determined in order to select the optimum pH.
- Control of the "in situ" chemical treatment. The pH and Zn content of treated water were determined periodically at the exit of the mixture tanks. The obtained value of pH of this operation was 8.3.
- Control of evolution of pumping zone and decantation dam. pH, Zn and sometimes SO<sub>4</sub><sup>2-</sup> were determined periodically.

Many of the obtained results were used to carry out immediate decisions to adjust adequate conditions of operation. In Table 2 the data obtained for evolution of pumping zone and decantation dam in this experimental test are indicated. In the decantation dam three sampling points were selected: discharge point, the half point dam and the final point dam.

DATE		8/7	12/7	13/7	14/7	15/7	16/7	17/7
PUMPING POINT	PH	7.2	7.08*	7.20	7.14	7.13	7.26	7.26
	Zn (mg/L)	105	91	91	84	82	80	78**
	SO <sub>4</sub> <sup>2-</sup> (g/L)	3.8	3.7	-	-	3.9	4.0	-
DISCHARGE POINT	pH		7.62*	7.79	7.94	8.00	8.03	7.92
	Zn (mg/L)		1.4	1.4	1.1	0.75	0.58	0.28**
	SO <sub>4</sub> <sup>2-</sup> (g/L)		-	-	-	3.8	4.0	-
HALF POINT	pH		7.60*	7.75	7.90	7.93	7.98	7.90
	Zn (mg/L)		0.55	0.34	0.46	0.49	0.34	0.29**
	SO <sub>4</sub> <sup>2-</sup> (g/L)		-	-	-	3.9	4.0	-
FINAL POINT	pH		7.68*	7.78	7.89	7.92	7.93	7.91
	Zn (mg/L)		0.38	0.38	0.39	0.33	0.40	0.30**
	SO <sub>4</sub> <sup>2-</sup> (g/L)		-	3.8	3.7	3.8	4.0	-

\* Measurements on 15th July

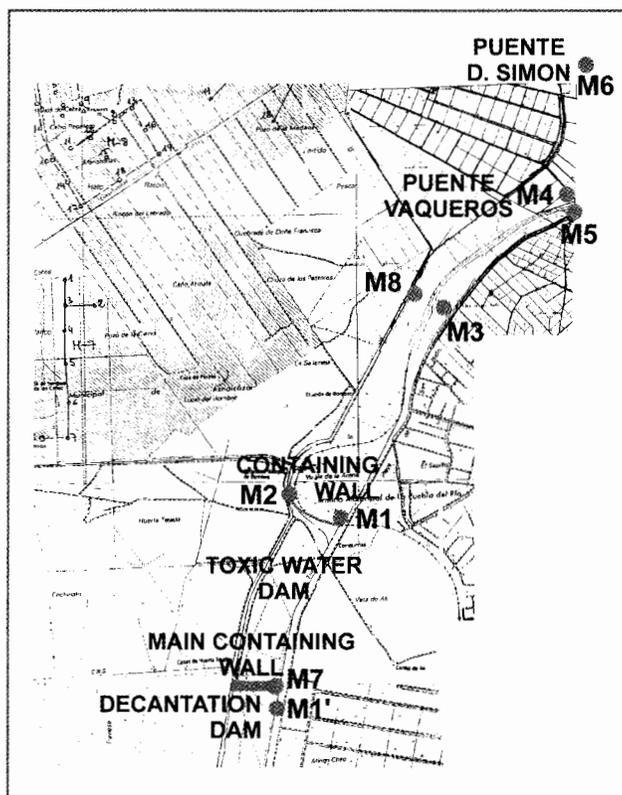
\*\* Measurements on 20th July

Table 2. Analytical results in the experimental test (1998).

The analytical results obtained show a decrease of Zn content after the water treatment as a function of time and distance to the treatment plant. In the release area the content is lower than that permitted by the legislation. The sulphate content in the water doesn't change after water treatment as it was expected.

## Characterization of waters up toxic dam

The river bed was separated in compartment. In order to reduce the volume of toxic water to be chemically treated, water above toxic dam was pumped to that dam, to decrease the heavy metals content. The pH, electric conductivity and Zn and  $\text{SO}_4^{2-}$  content of these waters were determined simultaneously to the first stage. The measurements were performed for 8 days. Figure 2 shows the location of the sampling points in the area.



In Table II the results obtained for these samples in the last day of sampling, prior to release to Guadalquivir river, are listed.

	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8
PH	7.91	7.76	7.62	7.53	8.00	7.88	7.54	7.67
Conductivity 20° (mS/cm)	3.29	3.98	2.81	2.36	2.11	2.07	6.92	5.20
Zn (mg/L)	2.7	2.7	2.4	0.38	0.34	1.4	59	1.5
$\text{SO}_4^{2-}$ (g/L)	1.6	2.0	1.1	1.0	0.82	0.93	3.9	3.1
$\text{Cl}^-$ (mg/L)	380	402	304	259	276	171	994	717

Table II. Analytical results for the samples up toxic dam

The concentration of the chemical species analysed is below the permitted values by applicable legislation in all cases, so it was unnecessary its chemical treatment.

## Flushing of treated toxic water and untreated water

The water in which chemical treatment was unnecessary was flushed through a tubing 4 Km long, placed along the left wall to "Canal de Aguas Mínimas". Determinations of pH, Zn, conductivity and sulphate were performed everyday in the

pumping point M1 and the flushing point M1' (Figure 2). The volume of water released in this way was about 1.4 millions  $\text{m}^3$  (Ministerio Medio Ambiente, 1999). Analytical results (minimum and maximum values) obtained from 24 July to 21 August for these waters are shown in Table 3.

SAMPLE	PH	Conductivity mS/cm 20°C	Zn mg/L	$\text{SO}_4^{2-}$ mg/L
M-1	7.75-8.09	3.12-3.48	1.6-3.5	1.3-1.8
M-1'	7.56-7.75	2.55-3.62	0.44-2.8	1.1-1.7

Table 3. Analytical results obtained in untreated waters.

Some of these results were contrasted with those obtained later in the conventional laboratories of CHG showing an excellent agreement between them. In view of the obtained results, we can conclude that the release of this waters was carried out, in all time, with concentration values and parameters, below those authorised by the Junta de Andalucía.

## CHEMICAL TREATMENT AND FLUSHING OF TOXIC WATER

Once the validity of the chemical treatment of contaminated water was checked in the experimental test, the flushing operation was authorised by the Junta de Andalucía. The chemical treatment plant was operated in continuous. The mobile unit laboratory participated in the following operations:

- "In situ" control of the toxic water treatment process. The 25 % sodium carbonate solution reagent was changed by the 50 % sodium hydroxide solution, as it was proposed by the ITGE. Addition of this reagent is cheaper than the addition of carbonate. It was necessary to increase the pH from 8.3 to 9.3 in order to keep the Zn content below 10 mg/l. At a pH of 9.3 also the Mn precipitates resulting in a dark solution with high turbidity values.

In order to treat a higher toxic water volume, and carry out the operation in continuous, several modifications were made. A new pump (1000  $\text{m}^3/\text{hour}$ ) was placed and two bigger section release tubes were added. In this way about 1.6 millions  $\text{m}^3$  toxic water were treated (Ministerio de Medio Ambiente, 1999).

- Periodic control of the released water to the "Canal de Aguas Mínimas". pH, Zn and turbidity were determined at least three times a day.
- Control of evolution of the pumping zones, toxic water dam and discharge-decantation dam, in order to prevent possible wrong operation conditions. pH, Zn and sometimes turbidity were analysed.
- On 10th August, close to the treatment plant, a conventional plant started to operate. Several controls of pH, conductivity, Zn and  $\text{SO}_4^{2-}$  in the exit of the plant were performed. This plant treated 1.2 millions  $\text{m}^3$  contaminated water (Ministerio de Medio Ambiente, 1999).

It is not the aim of this report to list all data obtained in this stage. Many of them were used to carry out decisions in order to adjust the chemical operation conditions. In table 4 the results obtained from 24 July to 21 August to release treated water are summarised. In order to avoid a long listed data, only the minimum and maximum values obtained and the most common ones in this period, have been shown.

	pH	Zn mg/L	Turbidity FTU
Min and Max values	7.9-8.9	0.45-4.2	74-280
Common values	8.2-8.4	1.0-3.0	130-140

Table 4. Analytical results obtained of the treated water flushing.

Figure 3 shows the Zn contents before and after of chemical treatment. The means values obtained everyday have been represented (1998).

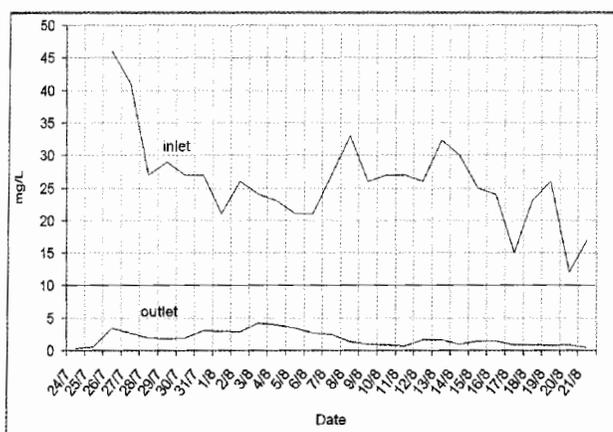


Figure 3. Zn concentration obtained in the chemical treatment.

As in the case of untreated water, the values of the chemical species and parameters in the release water, were always below those authorised by the Junta de Andalucía. Many results were contrasted later with those obtained in the analytical laboratories of ITGE of Madrid, with a good coincidence between them.

## CONCLUSIONS

CIEMAT had a significant contribution in the control of chemical treatment and flushing of the toxic waters retained in the Entremuros area, as a result of the Aznalcóllar mine accident on April, 1998. It was used a mobile unit laboratory CIEMAT-ENRESA with appropriated instrumentation and methodology. The analytical data obtained were immediately informed to official organism of Ministerio de Medio Ambiente. These data were also used to ask for the flushing authorisation to the Junta de Andalucía.

The electrochemical techniques, voltammetry and polarography have demonstrated to be a good tool for "in situ" determination of heavy metals. Their selectivity and sensitivity allows to obtain a very fast and reliable results at different concentration levels.

The advantages of owning a mobile laboratory for "in situ" determinations with a validated methodology have been shown. On the other hand, additional advantages encountered are minor risk of the samples alteration and the possibility of repetition both the sampling and the analysis in order to confirm an uncertain result. This allows to carry out immediate decisions that can be adjusted to the appropriate operation condition of the treatment process and therefore to guarantee the flushing water quality.

CIEMAT collaborated successfully to a satisfactory development of whole flushing operation in time, and therefore guaranteed the flushing water quality all time.

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