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# The Aznalcóllar Disaster: An In-depth PIXE Study of the Pyrite Mine Spill of 1998.

H. Calvo del Castillo[a,b], J.L. Ruvalcaba Sil[b], M.A. Álvarez, T. Calderón[a]

*(a) Dpto. Geología y Geoquímica, Universidad Autónoma de Madrid (Spain)*
*(b) Instituto de Física, Universidad Nacional Autónoma de México (Mexico)*
*(c) Dpto. de Cristalografía, Mineralogía y Química Agrícola. Universidad de Sevilla. (Spain).*

**Abstract.** In 1998 a contention wall from a pyrite mine broke in Aznalcóllar (Sevilla, Spain). As a result, tons of toxic heavy metal enriched tailings and acidic water were spilled through agricultural soils and reached the Doñana Natural Park, covering a surface of 4.402 Ha and affecting the rivers Agrio, Guadiamar and Guadalquivir. The fact has been known since then as the "Aznalcollar Disaster".
Despite the remotion of the mud and other soil decontamination processes, residuous pollutants from the spill were still found in 2002, and the following of the Natural Park's recovery and its surroundings is generating many information in different science fields up to date. Many independent studies have been carried out to valutate the extent of the disaster since 1998. PIXE studies in precedent works have been done with scarce number of samples and/or extended to little areas.
In this paper we present the PIXE analysis of the samples that horticultural exploiting companies FRUTANSA and AFREXPORT had analysed after the disaster during 1998 to 1999 with techniques such as SEM/EDS, INAA or IPC covering the areas of the Finca de Guadiamar, Finca de Coto and Finca de Quema.
The main pollutants found with PIXE have been lead and arsenic. There are some differences between the results obtained in the 1998-1999 analyses and the current PIXE results.

**Keywords:** *Aznalcóllar, mine spill, PIXE, arsenic, lead, pyrite.*

## INTRODUCTION

In the early morning of April 25th in the year 1998, the contention wall of a decantation pool from the *Explotación Minera Aznalcóllar* pyrite mine broke, in the province of Sevilla (Spain). As a result, 0.9 $Hm^3$ of toxic heavy metal enriched tailings and 3.6 $Hm^3$ of acidic water were spilled through agricultural soils overflowing the rivers Agrio and Guadiamar, both affluents to the Guadalquivir river[1].

The mud flood, reaching 400 m wide and 1.5 m high at some points, expanded over 40 km arriving to the so-called "pre-park zone" next to the Doñana Natural Park, covering a surface of 4,402 Ha, equivalent to 2.7 Tm of toxic tailings. Water continued up to 50 km thus gaining the external part of the park and joining the Guadalquivir River, leading latter to the Atlantic Ocean at Sanlúcar de Barrameda (Sevilla)[1].

This fact has been known since then as the "Aznalcóllar disaster", and has been held responsible for the disappearance of many animal species in this unique and protected natural area.

Despite the remotion of the pyrite mud and other soil decontamination processes, residuous pollutants from the spill were still found in 2002[2], and the following of the natural park's recovery and its surroundings is generating many information in different science fields up to date.

Many independent studies have been carried out to valutate the extent of the disaster since 1998. Except for some analyses of the area done before the flood [3], the rest of them have been carrried out after the spill [1, 2, 5, 6, 7, 8, 9, 10, 11]. Most of these studies are based in techniques that involve sample digestion[1, 5, 6, 7, 8, 9, 10, 11] some used ICP-AS [6] (Inductively Coupled Atomic Spectrometry) or ICP-MS [8] (Inductively Coupled Mass Spectrometry). PIXE studies in precedent works have been done with scarce number of samples and/or extended to little areas through the spill's course[2, 3].

We have applied PIXE to a large set of samples (35) elsewhere studied[1], affected by pyrite enriched

tailings and water coming from the mine spill. The scope of these measurements is to compare the PIXE results with those obtained before by other means (XRD, SEM/EDS, INAA and ICP-AES[1].

PIXE allows the simultaneous analysis of most of the elements present in the sample and does not involve any chemical digestion for sample preparation avoiding too the transformation of stable isotopes into radioactive ones.

The samples employed for the PIXE study came from three different areas: Finca de Guadiamar (GU) from Sanlúcar la Mayor, Finca de El Coto (CO) from Benacazón and Huévar, and Finca de Quema (QM) from Villamanrique de la Condesa and Aznalcázar, all of them in the province of Sevilla. These areas were affected by the toxic flood that consisted of pyrite ($FeS_2$), sphalerite (Zn, Fe)S, galena (PbS), chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS), bearing heavy metals such as zinc, lead, arsenic, copper, cobalt, talium, bismut, cadmium or mercury.

## EXPERIMENTAL

Powdered samples coming from GU, CO and QM including pyrite mud and sediments taken in different points of the three areas and at different profile depths were measured (Table 1). Samples were labeled as XGUY, where X means the number of the profile, GU (CO or QM), the area, and Y differences profile height. Pellets (7mm in diameter) had to be made of the mud and sediments. 70mg of each sample were needed for this purpose. Samples were mounted on an aluminum support. Time for measurements was 5 minutes per sample.

PIXE measurements were accomplished at the Pelletron Accelerator on-air line of the Instituto de Física (Universidad Autónoma de México). A 3 MeV proton beam was used for sample excitation, with current intensity of 10-20 nA (on sample surface), beam diameter being of 1.5 mm. Set-up included two detectors; Si-Pin with a helium flux of 0,85 sl/min., whereas LEGe Canberra with an 8μm Kapton window and a 158 μm Aluminium absorber was employed for heavy elements characterization. Detectors were placed at 40º within the beam direction.

## RESULTS AND DISCUSSION

PIXE allowed the detection of 21 elements for each sample. Elemental concentrations of Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb, As, Rb, Sr, Zr, Sn, Sb and Ba were obtained. Table 1 shows the most important elements for this study. Previous informs[¡Error! Marcador no definido.] yielded concentrations for other elements as well that were not detected by PIXE (Mo, Ag, Br, Co, Cs, Au, Cd, Bi, V, Hg, Rb, Sc, Y, Ta, Th, U, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and W).

In spite of this fact, PIXE brings a general idea for the characterization of the mud and soils and allows the following of some important contaminants such as Mn, Ni, Cu, Zn, Pb or As.

The local government Junta de Andalucía, has established some levels to classify contaminated areas: (a) *Reference level* corresponds to the typical concentration of elements (natural background) present in the area for uncontaminated soil. (b) *Recomended investigation level* points out the presence of contaminants in small quantities and advises to investigate their origin. (c) *Compulsory investigation level* corresponds to higher concentrations of pollutants that need to be investigated. (d) *Intervention level* implies an obligation to remove the contaminants, for their concentrations are high enough to be considered perilous.

### Mud Analysis

In general, the pyrite mud carries a 32% w-w of iron and 17% w-w of sulphur, accompanied by high average percentages of metals: Mn (0,50%), Ni (0,09%), Cu (0,30%), Zn (0,18%), Pb (2,31%), As (0,91%), Sn (0,05%), Sb (0,13%), Ba (0,11%).

Ni, Cu, Zn, Pb, As or Sn bear concentrations that fall in the *intervention level.*

### Sediments Analysis

Metal concentrations in samples appertaining to one same profile typically descended with depth, so that in most cases, pollution does not reach a profundity of 70 cm under the surface.

*Finca de Guadiamar (GU)*

The pollutants found in the mud have passed into the sediments that lie underneath them. For profile nº1, for instance, shows large concentrations of As (30 ppm) reaching the *intervention level* established by the local government Junta de Andalucía at 20 cm, this concentration remains almost the same (29 ppm) even at 45 cm under the surface. Copper falls into the *recommended investigation level* at that same profundities. Other metals present are not so significant.

Profile nº2 shows more quantity of lead (173 ppm) than that allowed (100 ppm) for sample 2GU1, which does not correspond to mud sample but to sediment, as the mud did not reach this area.

**TABLE 1.** Elemental concentration determined by PIXE (%).

| Sample | P | S | Ti | Cr | Mn | Fe | Ni) | Cu | Zn | Pb | As | Rb | Sn | Sb | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| **1GU1** | 2,0077 | 15,2 | | | 0,5324 | 33,9 | 0,1321 | 0,2574 | 0,2452 | 2,2066 | 0,8593 | | | 0,1092 | 0,1517 |
| **1GU2** | 0,2179 | 0,115 | 1,1467 | | 0,1369 | 3,04 | 0,0091 | 0,0059 | 0,0083 | 0,0073 | 0,0030 | 0,0099 | | | |
| **1GU3-f** | 0,1381 | 0,012 | 1,4957 | | 0,1686 | 5,0 | 0,0212 | 0,0068 | 0,0036 | 0,0076 | 0,0046 | 0,0167 | | | |
| **2GU1** | 0,3251 | 0,050 | 3,5505 | | 0,3464 | 8,6 | 0,0298 | 0,0315 | 0,0090 | 0,0173 | 0,0090 | 0,0273 | | | |
| **2GU2** | 0,1647 | 0,049 | 2,4485 | | 0,1554 | 3,2 | 0,0106 | 0,0052 | 0,0027 | 0,0055 | 0,0016 | 0,0142 | | | |
| **1CO2** | 0,2399 | 0,203 | 1,2472 | 0,0571 | 0,1319 | 3,9 | 0,0118 | 0,0205 | 0,0124 | 0,0297 | 0,0137 | 0,0091 | | | |
| **1CO3** | 0,2147 | 0,030 | 3,7423 | | 0,1497 | 3,2 | 0,0083 | 0,0127 | 0,0036 | 0,0099 | 0,0026 | 0,0091 | | | 0,0701 |
| **3CO1** | 2,1873 | 16,87 | | | 0,5456 | 32,5 | 0,0958 | 0,2433 | 0,0199 | 2,0879 | 0,8628 | | 0,0459 | 0,1308 | 0,1296 |
| **3CO2** | 0,4111 | 0,042 | 1,3182 | | 0,1430 | 3,5 | 0,0152 | 0,0039 | 0,0024 | 0,0039 | 0,0022 | 0,0156 | | | |
| **1QM1** | 2,2441 | 16,4 | | | 0,4575 | 30,4 | 0,0885 | 0,3982 | 0,2715 | 2,3510 | 0,7843 | | | 0,1069 | 0,1188 |
| **1QM2** | 0,0216 | 0,032 | 0,6384 | 0,0844 | 0,1093 | 3,3 | 0,0098 | 0,0214 | 0,0074 | 0,0161 | 0,0054 | 0,0081 | | | |
| **1QM3** | 0,2105 | 0,025 | 0,6643 | 0,0558 | 0,0823 | 2,1 | 0,0064 | 0,0029 | 0,0011 | 0,0046 | 0,0008 | 0,0105 | | | |
| **2QM2** | 0,1511 | | 1,2044 | | 0,1857 | 3,0 | 0,0085 | 0,0035 | 0,0016 | 0,0056 | | 0,0094 | | | 0,0301 |
| **2QM3** | 0,1720 | 0,019 | 1,8399 | | 0,1153 | 3,8 | 0,0105 | 0,0024 | 0,0015 | 0,0029 | 0,0025 | 0,0130 | | | |
| **3QM1** | 2,3942 | 17,6 | | | 0,4753 | 32,4 | 0,1004 | 0,2633 | 0,1651 | 2,7339 | 1,3882 | | 0,0479 | 0,1080 | 0,0901 |
| **3QM2** | 0,2328 | 0,062 | 0,5920 | | 0,1280 | 3,8 | 0,0095 | 0,0222 | 0,0091 | 0,0233 | 0,0067 | 0,0115 | | | |
| **3QM3** | 0,1607 | 0,042 | 0,7595 | | 0,1607 | 4,50 | 0,0099 | 0,0360 | 0,0146 | 0,0140 | 0,0130 | 0,0096 | | | |
| **3QM4** | 0,2068 | 0,017 | 1,5164 | 0,0490 | 0,1079 | 2,9 | 0,0098 | 0,0044 | 0,0025 | 0,0048 | 0,0017 | 0,0103 | | | |
| **2CO3** | 0,2235 | 0,037 | 1,2570 | | 0,1191 | 2,7 | 0,0065 | 0,0057 | 0,0023 | 0,0062 | 0,0024 | 0,0077 | | | |
| **2CO2** | 0,2796 | 0,034 | 0,2318 | | 0,0751 | 2,0 | 0,0039 | 0,0050 | 0,0018 | 0,0047 | 0,0011 | 0,0079 | | | |
| **2CO1** | 2,5375 | 18,2 | 2,6644 | | 0,5090 | 33,1 | 0,0576 | 0,2510 | 0,2075 | 2,1048 | 0,8005 | | 0,0552 | 0,1470 | 0,0735 |
| **4QM1** | 2,1708 | 16,74 | | | 0,4603 | 30,7 | 0,0585 | 0,1886 | 0,0865 | 2,2825 | 0,8155 | | 0,0502 | 0,1181 | 0,1572 |
| **4QM2** | | 0,085 | 0,6453 | | 0,1021 | 3,1 | 0,0068 | 0,0153 | 0,0066 | 0,0113 | 0,0045 | 0,0107 | | | |
| **4QM3** | | 0,059 | 0,7538 | | 0,1656 | 2,3 | 0,0061 | 0,0047 | 0,0013 | 0,0034 | 0,0015 | 0,0086 | | | |
| **4QM4** | | 0,040 | 0,6879 | | 0,1429 | 3,2978 | 0,0079 | 0,0036 | 0,0015 | 0,0060 | 0,0018 | 0,0105 | | | |
| **5QM1** | 0,2760 | 0,016 | 0,7392 | | 0,0982 | 2,6 | 0,0059 | 0,0076 | 0,0027 | 0,0146 | | 0,0102 | | | 0,0731 |
| **5QM2** | 0,1959 | 0,037 | 1,1348 | | 0,1374 | 3,5 | 0,0072 | 0,0172 | 0,0057 | 0,0162 | 0,0061 | 0,0101 | | | |
| **5QM3** | 0,1905 | | | | 0,1119 | 3,47 | 0,0076 | 0,0235 | 0,0050 | 0,0075 | 0,0055 | 0,0087 | | | |
| **6QM1** | 2,1779 | 17,35 | | | 0,4849 | 31,9 | 0,0609 | 0,3534 | 0,2607 | 2,4265 | 0,8590 | | 0,0462 | 0,1434 | 0,1077 |
| **6QM2** | 0,2217 | 0,048 | | | 0,1108 | 2,9 | 0,0057 | 0,0126 | 0,0049 | 0,0095 | 0,0048 | 0,0104 | | | |
| **6QM3** | 0,1780 | 0,046 | | | 0,1138 | 3,0 | 0,0082 | 0,0122 | 0,0040 | 0,0081 | 0,0031 | 0,0116 | | | |
| **6QM4** | 0,2662 | 0,016 | | | 0,1703 | 2,3 | 2,6912 | 0,0037 | 0,0014 | 0,0054 | 0,0011 | 0,0081 | | | |

*Finca de Coto (GU)*

Profile nº1 and nº3 have shown Ni concentrations (83 ppm) above the *reference level*. However, this feature has been observed for other samples studied in this work, meaning that perhaps the area is Ni rich naturally.

For profile nº1, samples have shown large quantities of Cu (205 ppm) and As (137 ppm) that reach the *intervention level* at 15 cm depth from the surface. Both concentrations diminish (Cu: 127 ppm, As: 26 ppm) at 40 cm arriving to the *recommended investigation level*.

In profile nº2, there are hardly any contaminants, however some quantity of As (24 ppm) exceeding the *reference level* can be found for 2CO3 whereas no As contamination is found for sample 2CO2 (placed 15 cm on top of 2CO3 in the profile). In this case the contamination does not decrease with profundity.

*Finca de Quema (QM)*

This is the most polluted area in this work. For profile nº1, at 20 cm from the surface down, arsenic (54 ppm) reaches the *intervention level* while Cu (214 ppm) arrives to the *compulsory investigation level*, and Pb (161 ppm) places itself on the *recommended investigation level.*

Profile nº3 shows large quantities – *intervention level*- of copper (360 ppm) and arsenic (130 ppm) at 50 cm and lead (140 ppm) appears on a *recommended investigation level*. In profile nº4 contaminants do not reach those depths, and mainly remain at 20 cm down from the surface, where Cu (153 ppm) and As (45) reach *compulsory investigation levels*. Lead (113 ppm)

is again at this profundity on a *recommended investigation level.*

As for profile nº5, lead (162 ppm) is found at 20 cm once more on the *recommended investigation level*. Arsenic reaches the *intervention level* both at 20 cm and 50 cm under the surface and copper is found too on a *compulsory investigation level*. The same thing happens with As in profile nº6, whereas copper appears in less quantity (6QM2: 126 ppm, 6QM3: 122 ppm) – *recommended investigation level*.

## CONCLUSIONS

Three different areas affected by the pyrite mine spill have been studied with the PIXE technique. This technique has detected 21 elements that give a general view on contamination problems aroused by the toxic flood. Amongst these elements some heavy metals have been detected: Mn, Ni, Cu, Zn, Pb and As.

Main contamination has come from Cu, As and Pb, being Cu and As the most important, for they have been found at considerable concentrations (*compulsory investigation level or intervention level*) in-depth in the profiles (50 cm approx.).

Generally, concentrations diminished as profundity increased for each profile, though there are some anomalies at certain points due to removal of muds that in some places started (in GU zone) before the samples could be taken.

Even though PIXE yielded fewer results than the combination of techniques elsewhere applied[1] for these same samples, we believe that this technique is helpful for a first approach to contamination disasters for it has provided nevertheless information on 21 elements in a quicker way and with a considerable sensitivity. Moreover, PIXE may be used within a general methodology to establish sampling areas and ample selection for further studies with other techniques.

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