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# Re-Processing of Mine Tailings: Discussion on Case Studies

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**Abstract.** Mining waste are regularly cited as potential secondary resources that could give access to residual concentrations of the exploited metals and also unrecovered metals, nowadays of economic importance for new high-tech applications. This article describes the investigation of three distinct mine tailings, and discusses the opportunity of re-processing such secondary mining resources, as part of the overall mining site management.

**Keywords.** critical metals, sampling, portable X-ray fluorescence spectroscopy, separation techniques, process development

## 1 Introduction

In France, a large number of mining sites operated in the past, generated large amounts of wastes, either tailings discarded at the end of the comminution/ concentration stages, waste produced by hydrometallurgical treatments, or slag recovered at the end of pyrometallurgy processes. In some cases, these wastes contain rare metals, including strategic or critical metals necessary for high-value applications (EU list 2014). These rare metals were not extracted in the past or were exploited by technologies which performance has greatly evolved since then. In addition, these sites often require rehabilitation works, mainly because of their impact on the environment (particle release, metal/pollutant leaching, acid mine drainage, etc.).

In this context, BRGM has investigated in more detail three different mining wastes dumps in connection with rehabilitation projects in progress. Three case studies are presented and discussed, after selection of the site using criteria of volume, date of exploitation, process techniques, etc. (see Bertrand et al. this congress)

## 2 Tailings of a former lead and silver mine

### 2.1 Site description

The investigated former Pb-Ag mining site (Auvergne, France) consists in four stockpiles accounting for 87,000 m<sup>3</sup> of physical treatment tailings. The rehabilitation project and the first sampling results in order to evaluate metal potential were described respectively in Bellenfant et al. (2013) and Guezennec et al. (2013).

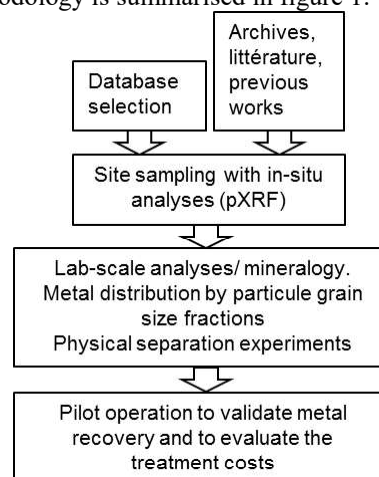
The mine was operated till 1905 for Pb and Ag production: 50,000 t and 100 t were produced respectively. The polymetallic mineralization consists of quartz veins containing silver-bearing galena [PbS], sphalerite [ZnS], pyrite [FeS<sub>2</sub>], arsenopyrite [FeAsS], bournonite [PbCuSbS<sub>3</sub>], tetrahedrite [(Cu,Fe,Ag,Zn)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>], and chalcopyrite [CuFeS<sub>2</sub>]. It is hosted by

hydrothermalized granite and gneiss gangue.

The historic beneficiation schemes comprised successive steps of grinding and physical separation at millimetric scale. Flotation was performed only during the late stages of the mine life; the treatment mainly consisted in gravimetric separation and manual sorting. Gravimetric separation at that time did not enable to treat particles lower than 100 µm. This usually led to significant losses of silver.

### 2.2 Methodology

The methodology is summarised in figure 1.



**Figure 1.** Methodology performed on the Pb-Ag mining residues

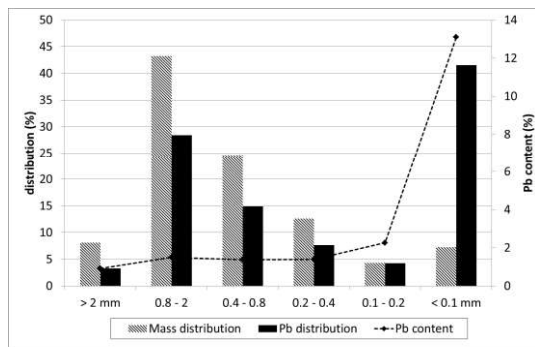
A representative sampling was performed for each dump, in order to evaluate more accurately the remaining metal content. On-site pXRF (portable X-ray fluorescence spectroscopy) chemical screening analyses were performed on the dump surface and on samples taken at regular intervals down to 5 m depth using a shovel; the bottom being estimated at 67 m. In the laboratory, bulk samples of approximately 5 kg were dried at 40°C, homogenised and re-analysed on a selection of samples. ICP-AES after total alkaline digestion, X-ray diffraction and microscopic observations were also performed to investigate metal speciation and liberation size. This was intended to determine namely how far tailings should be ground further for metal recovery.

Some samples were then sieved to produce particle size fractions (+2 mm, 800 µm, 400 µm, 200 µm and 80 µm) which were weighed and analysed by pXRF and ICP. Lab scale experiments were then performed to concentrate the most promising size fractions and evaluate the interest of performing a pilot operation.

## 2.3 Results

Field investigations using pXRF demonstrated the homogeneity of waste piles from similar beneficiation schemes, while piles produced by different schemes yielded slightly different results.

The mass balance of particle size fractions and associated Pb content are summarised on Figure 2. Results show that the major part of Pb, Ag and As is confined in the fine fraction <100 µm, which represents only 7 % of the total mass.



**Figure 2.** Distribution of Pb with particle grain size in the tailings

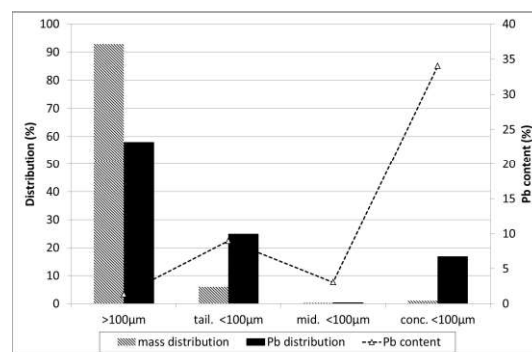
In view of specific interest for further separation experiments, a mineral characterisation of this concentrated fraction (< 100µm) revealed that most of primary galena, which is the major ore mineral, is destabilised in favour of secondary anglesite [PbSO<sub>4</sub>] with minor beudantite and Pb-bearing jarosite. This result was verified all along the profile of the four spoil heaps, in agreement with the quite homogeneous yellow colour of all samples. Ag occurs as micron-sized grains included in residual primary galena and in secondary sulfates. It is difficult to define its distribution due to its small size and its dissemination. Small grains of Ag<sub>2</sub>S were suspected in several phases.

Due to these mineralogical characteristics, concentration tests were carried out on the fine fraction (<100 µm) using gravimetric methods: Mozley laboratory table and Falcon gravimetric centrifugal concentrator. The best results were obtained with the Mozley table: as can be seen in Figure 3, 17% of the total Pb is concentrated in 1% of the total mass of tailings (including the fractions over 100 µm). Pb content reaches 34 % in the concentrate.

As the mineralogical analyses revealed that a significant amount of lead remained in the finest particles of the light fraction produced by the Mozley table (tailings), micro-hydrocyclone tests were performed on this fraction to separate the particles under 10 µm. Finally, by combining the concentrate produced with the Mozley table and the fine particles of the light fraction, 40% of total Pb is recovered in 4.6% of the initial mass of tailings with a Pb content of 18%. In addition Ag recovery reaches 11% with a content of 152 ppm.

It must be noticed that elements with potential environmental impacts (such as As or Sb) behave similarly to lead and can be concentrated at a high level

(not shown here). This, on one hand could be penalizing for metallurgical processes, but on the other hand, contribute to reduce site pollution.



**Figure 3.** Gravimetric concentration tests using Mozley table. Pb distribution in the different fractions.

## 2.4 Conclusion

The study of this former mining site was very important to check each step of the methodology we propose, to evaluate properly the concept of metal recovery from sampling and analyses to laboratory tests and finally a pilot operation. These latter results will be the subject of a full paper. Briefly, from the results obtained at laboratory scale, a continuous piloting operation was designed including separation, classification and concentration steps. Four tons of tailings were treated, which enable to determine the recovery of Pb and associated metals. The secondary recovery scheme can be integrated into a global site management and rehabilitation strategy, reducing a large part of metals and pollution. On the other side further reuse of the concentrate will be a new issue considering the sulphate carriers and also the arsenic content. Further re-use of the mineral residues, now metal-poor, could be evaluated in connexion with the local industrial needs.

The results are very encouraging and allow developing a methodology to investigate a larger Pb/Ag site identified elsewhere. In a more general way the methodology could be applied to investigate bigger former mining sites in Europe and include re-processing in their whole rehabilitation management.

## 3 Tailings of a former lead and zinc mine

### 3.1 Context

In with the framework of the French Ing-ECOST-DMA project (see references), the chemical composition of the tailings from the former mine of Carnoulès, Gard, France has been determined in respect to its content in potentially recoverable rare metals. Namely, indices of germanium associated to sphalerite in primary ores, sampled at the same location was the starting point.

On the other hand several environmental studies have been conducted over the past 15 years on this site (not exhaustive list: Leblanc et al. 1996; Koffi et al. 2004; Casiot et al. 2003; Casiot et al. 2009) in relation with acid mine drainage related to the oxidation of arsenic-bearing pyrite by underground waters. This drainage which contains significant concentrations of As is still a

great matter of concern.

### 3.2 Site description

The lead-zinc mineralization from the SE Cevennes Mountains Region (detritic layers) was mined mainly over the period 1833-1962 for the production of Pb (2 Mt at 5-2.5 %), 3500 t Zn and Ag (estimated at 50-60 g/t), Alkaady (1986). The sulphide ore mineralization is dominantly composed of marcasite, pyrite, galena, sphalerite, Ag-sulphoarsenides and As-Ag-Fe-Cu sulpho-antimonides. Quartz and barite are the main gangue minerals. The historical process consisted mainly in gravimetric separation, but it was not optimal because of the small size of metal-bearing grains. Flotation was undertaken at the very end of the operating life.

The current tailings pile, mainly composed of the so called Fe-Pb-Zn-As sulphide sand (Leblanc et al., 1996) was estimated at 1.2 Mtons (Koffi, 2004). The sequence consists of a surface clay layer (30-70 cm) which limits meteoric infiltration, fine sulphide sand (2 – 9 m) of <30 µm to 1 mm particle size, sand with gangue rocks, gangue rocks and quartzite (substratum). Hydrology modelling of the heap allowed describing a bilayer aquifer with three hydrological zones exhibiting different physico-chemical characteristics (Koffi et al., 2004).

### 3.3 Materials and methods

Sixty-three samples of powdery materials from four vertical profiles (T1-T4) were prepared and analysed in this study. The four profiles were drilled by HydroSciences Montpellier in 2002; samples were taken every one meter from surface downwards to 13 to 21 m depth. They were partly analysed for Fe, As and S in a previous study (Casiot et al. 2003). The samples have been preserved since at -20°C (T1, T2) or at ambient temperature (T3, T4). Decaking, splitting and drying at 40°C were performed to prepare composite samples for analyses.

Portable X-ray fluorescence spectroscopy (pXRF) analyses were performed on all samples. Laboratory ICP-AES analyses were performed on selected samples containing various amounts of Pb, Zn and As, after total alkaline digestion with sodium peroxide at 450°C. Correlation curves were established between pXRF and laboratory analyses. They are linear for Pb (up to 10000 ppm), Zn (2000 ppm) As (6000 ppm) and also Ba (12000 ppm) and Sr (1000 ppm). The correlation curves were therefore used as a simplified calibration for pXRF measurements. Ga, Ge, In content could not be measured by pXRF and were analysed by ICP-MS after total digestion on the samples with the highest Zn concentrations.

### 3.4 Results

Pb, Zn, As contents in the four vertical profiles (figure 4) show a large variability, apparently independent of the three different hydrological zones described previously.

The decreasing trend towards the bottom of the deposit, seems to be linked to sulphide oxidation zoning, which itself resulted in metal leaching over time thus metal depletion at depth, especially for T1; this result

was already described for Fe, As and S in Casiot et al. (2003). Median values for 63 samples are 6,665 ppm Pb and 560 ppm Zn. These values are very low and do not justify further metallurgical tests. Median As content is 2,141 ppm.

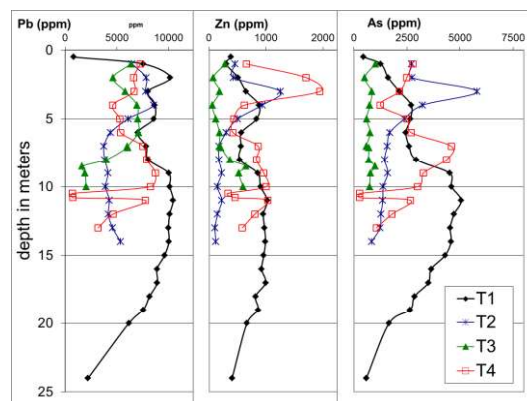


Figure 4. Pb, Zn, As contents along the four vertical profiles.

Considering the very low Zn content of the tailings for re-processing objectives –tailings from other mines are known to contain up to several % of Zn- three analyses of Ga, Ge, In, Ta, Tl were performed to document further the site (Table 1); they confirm the conclusion that element values are too low to justify further work.

Table 1. Rare element content in the most concentrated Zn samples (mg/kg DM)

| Zn | 964  | 1,287 | 1,985 |
|----|------|-------|-------|
| Ga | 7.1  | 3.3   | 4.4   |
| Ge | 1.8  | 1.6   | 1.9   |
| In | <0.2 | <0.2  | <0.2  |
| Ta | 0.54 | 0.41  | 0.32  |
| Tl | 24   | 24.4  | 32.2  |

### 3.5 Conclusion

Zn (Pb) analyses on 63 core samples (0-20 m depth) on four distinct locations revealed very low base metal content of the tailings and logically, of associated rare elements (Ge, Ga, In). These results do not justify further sampling and lab treatment tests to evaluate the benefit of re-processing the tailings to recover valuable (rare/critical) metals.

## 4 Tailings of tungsten old mine

### 4.1 Site description and methodology

The last case study consists of two waste dumps accounted for 700,000 m<sup>3</sup> of tailings from a former tungsten mine. The mine was produced 12.4 kt of WO<sub>3</sub> (1963-86). The dump content is estimated to 1,500 t WO<sub>3</sub> and primary reserve around 3, 400t. The skarn-type mineralisation consists of dominant scheelite [CaWO<sub>4</sub>] and pyrrhotite, with minor galena, (arseno)pyrite, chalcopyrite, bismuthinite and traces of gold.

### 4.2 Preliminary results

On this site, only preliminary investigations were carried out: on-site pXRF analyses and sampling. The field



campaign allowed identifying two facies along a redox profile: red oxidized powdery sample on the top (around 0.5 m) and below, black-reduced sample corresponding to the initial flotation tailings (from 0.5 to around 1.6 m). In the difficult-to-sample reduced zone little chemical evolution apparently occurred in the mineralogical form of the metal bearing assemblage. The dumps were not evaluated deeper because of the lack of suitable equipment, due to the hardness of the materials.

In-situ chemical contents as measured by pXRF are in the range: W 1300-7000 ppm; Cu 600-5000 ppm; As 500-1800 ppm with a high As variability between the 2 heaps (figure 4). A copper concentration front at the redox interface was noticed along the four vertical profiles (figure 5), which might correspond to the leaching of chalcopyrite through weathering of the waste dump. This is also an indication that infiltration in the heap did not affect its contents further down.

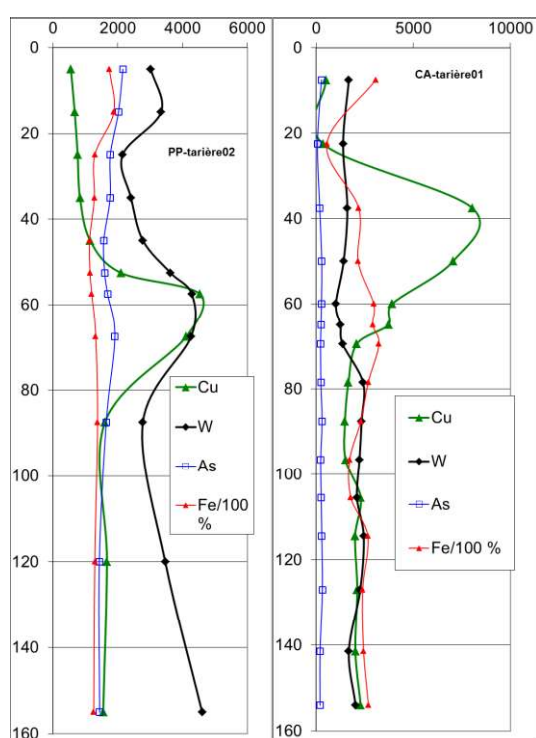


Figure 5. Metal content in a vertical profile of each dump.

### 4.3 Perspectives

The first results on metal contents are very encouraging to perform laboratory concentration tests on the two types of tailings to recover W and Cu, and Au. Namely flotation tests will be performed to evaluate the metal recovery potential of the two types of resources.

## 5 Conclusion - Discussion

This article presents three distinct case studies where metal recovery potential of former mine tailings were evaluated. These examples highlight the importance of analysing relevant data, namely on the process implemented and its efficiency in relation with the period of exploitation and, in addition, to geological and mineralogical data. The site survey or further analyses of available samples are essential then to estimate the

potential total metal contents and to assess the heterogeneity of the resource. Sampling efficiency is greatly enhanced by on-site analyses in order to guide the investigations and optimise sampling (Robbat 1997). Selected samples should be submitted to laboratory analysis program, including a mineralogical study. The latter should focus on the secondary host minerals, which can differ from the mineral phases contained in the primary ores depending on oxidation and weathering over time (i.e., sulphides into sulphates, etc). Metal distribution should be evaluated on particle grain size fractions. If metal concentration is effective, physical separation tests could be performed, at lab scale then at pilot scale.

Further processing reuse of the concentrate is still an issue to be evaluated, depending on the new metal mineral carriers and associated elements such as arsenic. Further re-use of the metal-poor mineral fractions could be evaluated in relation with local industrial needs.

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