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Assessment of long term mining waste behaviour by a dynamic leaching test : application to contrasted physico-chemical conditions.

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Abstract

Mining activity has generated large amounts of mining wastes abandoned on the site after extraction, concentration or metallurgic processes. In this study assessment of the long term behaviour of mining wastes has been performed by the realisation of a dynamic leaching test performed with a Soxhlet device on mining wastes from two contrasted sites : Bentaillou and Saint-Salvy from south-west France.

Sphalerite and galena are the source of heavy metals, (Zn, Cd and Pb) in both sites. Pyrite and pyrrhotite are the main potential acid source in Saint-Salvy and Bentaillou respectively. Although both wastes display high contents of carbonate minerals associated to the metal bearing phases, their composition is different, calcite for Bentaillou and siderite for Saint-Salvy allowing different minerals transformations and drainage mining water compositions. Due to different impoundment type, dumps for Bentaillou and a dam for Saint-Salvy, oxidation reactions are favoured in the former compared to the latter. Waste drainage waters generated in situ display lower pH, Eh and higher Fe and heavy metals in drainage waters from Saint-Salvy compared to those from Bentaillou.

The leaching experiments lasted 62 days and 84 days for Bentaillou sample and Saint-Salvy sample respectively corresponding to an equivalent time of 288 and 183 years respectively calculated from pluviometry in situ. During the experiment, the amounts of elements released was higher for Saint-Salvy sample (0.2 % of Zn, and Pb and 1,4 % of Cd) than for the Bentaillou one (9.7 % of Zn, and 0.15 % of Pb and 46 % of Cd). The comparison of experimental leaching results with site data on waste drainage waters demonstrated the validity of laboratory results under oxidic conditions at Bentaillou while the duration experimentally estimated for total sulphide oxidation overestimates the time calculated from the sulfate flow in field drainage waters under reducing conditions at Saint-Salvy.

Keywords: modified soxhlet, equivalent time, inertisation time, tailing drainage water

1. Introduction

Different processes of mineral industry such as prospecting, extraction, treatment and storage of mineral resources, induce large amounts of mining wastes enriched in heavy metals such Hg, As, Pb, Cd. They constitute potential sources of metal contamination for surrounding soils, groundwater and superficial.

Evaluation of the long term behaviour of mining wastes is being a lasting challenge for researchers, indeed besides the analysis of contaminant contents, their mobility has to be addressed to assess the potential impact of contaminants on the environment.

In this study, the assessment of the long term behaviour of wastes mining and the kinetic determination of the metallic and not metallic elements has been performed with a dynamic test. This test using a Soxhlet device was used formerly on Solidified/Stabilized wastes (Badreddine et al. , 2004, De Windt et Bardreddine, 2007).

The results exploitation and the validation of dynamic test were undertaken by calculation of equivalent time and inertisation time and the comparison of data obtained from laboratory and site drainage waters. This approach has been applied to treatment wastes from two distinct Pb-Zn mining sites, both resulting from flotation process of Zn-Pb ores and displaying similar physical parameters (grain size distribution, permeability,...) but differing by the type of impoundment and the mineralogical composition.

2. Description of study areas

2.1. Bentaillou site

The orphan mining Zn-Pb site of Bentaillou is located in the upstream catchment of the Lez stream (French Pyrenees, SW France, Fig.1). The Bentaillou site has been the second most important Zn-Pb mining site of the Pyrenees mountains. The sulphides are associated to gangue minerals, dominantly calcite and ankerite and secondarily illite and chlorite. The mineralisation is hosted by Palaeozoic and metamorphosed limestone. The carbonated context of the Bentaillou mining site is representative of most of the Pyrenean Zn-Pb mining sites. The ore was treated in a plant downhill by flotation process since 1920. More than 410,000 tonnes of treatment tailings were produced. They were impounded in four dumps on the Lez stream banks, varying from 10 to 26 m in height. Pluviometry averages $1347 \text{ l.m}^{-2}.\text{y}^{-1}$.

2.2. Saint-Salvy site

The Saint-Salvy mining district is located 70 km ENE of the city of Toulouse, at the southwestern in south-west France (Fig. 2). The mine has been operating between 1975 and 1994. It has produced 450,000 tons of Zn with Pb, Ag and Ge as byproducts. The ore was composed of sphalerite and galena associated with minor pyrite and chalcopyrite. Associated gangue mineral are mainly composed of quartz and siderite. Host rocks are composed of black shales and aplopegmatites sills. Four million tonnes of flotation wastes have been impounded in a storage dam, located in a small catchment 4 km to the south of the mine, covering 2 hectares at altitude around 300 m. Pluviometry averages $1200 \text{ l.m}^{-2}.\text{y}^{-1}$.

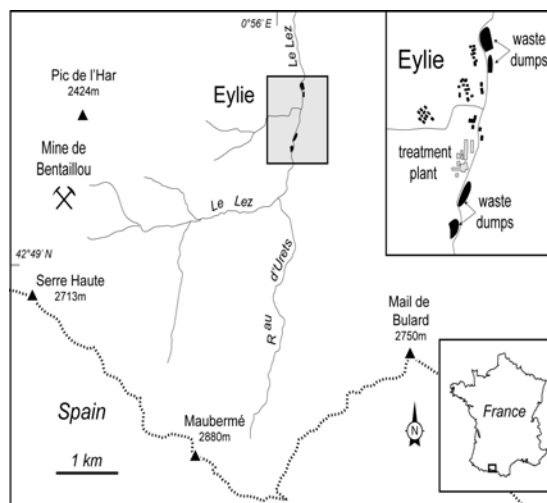


Figure 1 Bentaillou site localisation

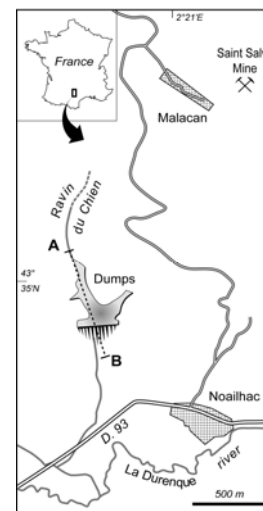


Figure 2. Saint-Salvy site localisation

3. Material and experiments

3.1. Solid samples collection and characterisation methods

A representative sample was collected from both sites taking into account the centimetric-scale variations of the laminae composition. The height, width and thickness of sampling were around 70 cm, 40 cm and 10 cm respectively. This representative sample was collected on a profile at the edge of the dump after removal of the surface (15 cm) tailing at Bentaillou, and, for Saint-Salvy, at the northern edge of the storage dam, where it is not covered by the clay land layer. Sub-samples were used for characterisation and experiment after mixing and quartering.

Qualitative and quantitative characterisation of metal-bearing mineral phases was carried out, after gravimetric separation, using optical metallographic microscopy, X-ray diffraction, Electron Probe Micro Analysis.

3.3. Dynamic leaching test

The samples of mining wastes from Bentaillou and Saint-Salvy mines were leached during 62 days and 84 days respectively in a water extractor, similar to the Soxhlet device. The system is adapted to mimic cyclic wetting and drying in open conditions. A detailed description of the extraction procedure was given by Humez *et al.* (1997), Humez & Prost (1999) and Badreddine & *al.* (2004) who used it to study the leaching of heavy metals from mainly Solidified/Stabilised (S/S) wastes. This extractor allows to keep the leaching water temperature at 18°C. In the apparatus employed, distilled water is introduced into the extractor after evaporation from a flask and condensation in a condenser open to the air. The extraction vessel contains 120g in average of mining wastes sample and the water flow is 250ml/hour. The progressive addition of water dribbling on the sample results in a decrease of the solution concentration in the extraction vessel and as a result, in the diffusion of solutes from the pore solution of the solid to the bulk solution. By analysing the leachate in the evaporation flask at fixed intervals, it is possible to follow the kinetics of elements release from the solid matrix. pH and Eh, the concentrations of SO₄, Ca, Mg, Fe, Zn, Pb and Cd were measured.

3.4. Tailing drainage water sampling, analysis and modelling

On Bentaillou site, tailing drainage waters (TDW) were collected nine times, in contrasted moisture conditions, between march 2002 to February 2004 from the permanent source. At Saint-Salvy, TDW sampling was carried at the dam outlet under base and high flow conditions between October 1998 to august 2002. Five samples have been collected. In both sites, redox potentials, pH and alkalinity were measured *in situ*. Chloride, nitrate and sulphate concentrations were measured using ion chromatography (HPLC, Dionex 2000i), base cations concentrations using atomic absorption Perkin Elmer 5100PC spectrometer, and dissolved Organic Carbon (DOC) using a Carbon Total Analyser (Shimadzu TOC 5000). Trace metal concentrations were determined by inductively coupled plasma mass-spectrometry (ICP-MS, Perkin Elmer, Elan 6000). Geochemical modelling of aqueous data was realised with CHESS geochemical code (Van der Lee *et al.*, 2002) using SUPCRT92 and MINTEQ databases (Johnson *et al.*, 1992), in order to determine theoretical distribution of metal species in solution and the saturation state of TDW relatively to different metal-bearing species.

4. Results and discussion

4.1. Mineralogical characterisation

Mining wastes from Bentaillou are mainly composed of quartz and calcite which amounts estimated by X-ray diffraction are about 50 % and 20 % respectively. The clay minerals are present in small amount in illite and chlorite forms. The mining wastes were composed equally by ankerite, amphiboles, diopside, micas, feldspars and minor dense minerals as magnetite, zircon and ilmenite.

Pyrrhotite, sphalerite, galena and scarce willemite, chalcopryrite, arsenopyrite and nickelite were identified as primary minerals of the ore. Sphalerite contains in average 5.4 wt% of Fe and up to 0.2 wt% of Cd. Cerusite, Fe-(oxy)hydroxide and scarce smithsonite were identified as secondary minerals (Brunel, 2005).

Bulk chemical composition was obtained by analysing four samples. Only the analyses concerning the representative samples BEN-R and STS-R are presented (Table 2). These mining wastes are mainly composed of silica (49.3 - 52.9 wt%). They are enriched in Ca (13.4 - 17.8 wt%) and in inorganic C (14.8 - 16.6 CO₂ wt%). Pb, Zn are dominant metals with 4.8 - 10.9 g.kg⁻¹ and 13.3 - 29.0 g.kg⁻¹ respectively. Cd concentration is in the range 38 - 92 mg.kg⁻¹.

Table 1: Chemical composition of representative samples

SAMPLE	BEN-R	STS-R
	% wt	
SiO ₂	49.43	67.82
Al ₂ O ₃	6.57	6.40
Fe ₂ O ₃	4.58	12.76
MnO	0.24	0.60
MgO	1.63	0.77
CaO	16.27	0.50
Na ₂ O	0.06	0.09
K ₂ O	1.72	1.79
TiO ₂	0.44	0.32
P ₂ O ₅	0.07	0.16
S tot	0.14	1.04
CO ₂	15.24	7.06
C.org	0.36	0.54
	mg.kg ⁻¹	
Zn	18 290	18 560
Cd	53	50
Pb	7 520	550
As	44	310

Mining wastes from Saint-Salvy are mainly composed of quartz, siderite, mica and kaolinite associated to sulphide minerals. Siderite (FeCO₃), the dominant carbonate, is enriched in Mn with around 29 g.kg⁻¹. Pyrite (FeS₂), sphalerite (ZnS) and galena (PbS) are the sulphide minerals identified in these wastes. Fe and Cd cations are substituted to Zn in sphalerite, hence iron content ranges between 2.2 and 3.3 wt%. and cadmium content averages 2500 mg.kg⁻¹ (Munoz et al., 2003).

Only Fe-(oxy)hydroxide compounds have been identified as secondary minerals. Chemical analysis of this compound evidences Zn, Pb, and Cd enrichment (up to 10 g.kg⁻¹, 0.045 g.kg⁻¹ and 0.015 g.kg⁻¹ respectively) (Munoz et al., 2003).

Bulk chemical composition indicates that these wastes are mainly composed of silica (60.0 - 67.8 wt%) and are enriched in Fe (10.0 - 18.1 wt%) and in total C (5.56 - 10.7

CO₂wt%). Among heavy metals, Zn is dominant with 13.6 - 18.7 g.kg⁻¹ while Pb and Cd concentrations range between 221 – 550 mg.kg⁻¹ and, 25 – 53 mg.kg⁻¹ respectively. Sample STS-R is the most representative one and used for the comprehensive study. Its carbon organic content amounts was 0.54 wt%.

4.2. Tailing drainage waters (TDW) and geochemical modelling

TDW from Bentaillou are lightly basic (7.2 - 7.5). On field, Eh potential (450 mV) reflects oxidising conditions within tailing dump. TDW present a relatively low TDS (112 mg.l⁻¹ as a mean). Calcium and hydrogenocarbonate ions are the main cation and anion, respectively. This bulk composition reflects the carbonated feature of tailings with calcite dissolution. Sulphates are the second main anions reflecting sulphides oxidation. Zn and Pb which are the main heavy metals in the tailings are also dominant in the TDW with concentrations ranging between 34 and 269 µg.l⁻¹ and between 0.1 and 21-µg.l⁻¹ respectively. Cd concentration ranges between 0.2 and 1.8 µg.l⁻¹. The average discharge is 10.3 m³.day⁻¹.

Geochemical modelling indicates that TDW from Bentaillou are under-saturated with respect to sulphate minerals (Saturation Index (SI) lower than -2.0). Carbonate minerals display higher saturation index. Cerussite (PbCO₃) is close to equilibrium in agreement to mineralogical observations (SI ranging from 0.0 and -0.6). Although the TDW are undersaturated with respect to smithsonite (SI ranging from -1.5 and -2.0), it has been occasionally found in these mining wastes probably because it was formed locally during drought periods or at the dryer edge of the tailing dump limiting the mobility of Zn. Similarly, ferrihydrite might precipitates in such circumstances as TDW are very slightly under-saturated with respect to this iron phase (SI ranging from -1.0 and -0.2) and ferrihydrite can be considered as a potential scavenger for heavy metals in these TDW.

TDW from Saint-Salvy are slightly acidic (6.3 < pH < 6.5) with a redox potential (200-244 mV) indicating reducing conditions. They are high mineralised Ca-SO₄ dominated waters (TDS = 1013-1264 mg/l⁻¹), the lower values corresponding to the rainy period in spring (Table 4b). They are enriched in Fe (total Fe = 13.4-23.1 mg.l⁻¹), Mn (4.7-10.5 mg.l⁻¹) and Zn (1.9-3.3 mg.l⁻¹). They presents rather low Cd (2.3-4.9 µg.l⁻¹) and Pb (0.1-1.4 µg.l⁻¹) contents. The average discharge is 360 m³.day⁻¹.

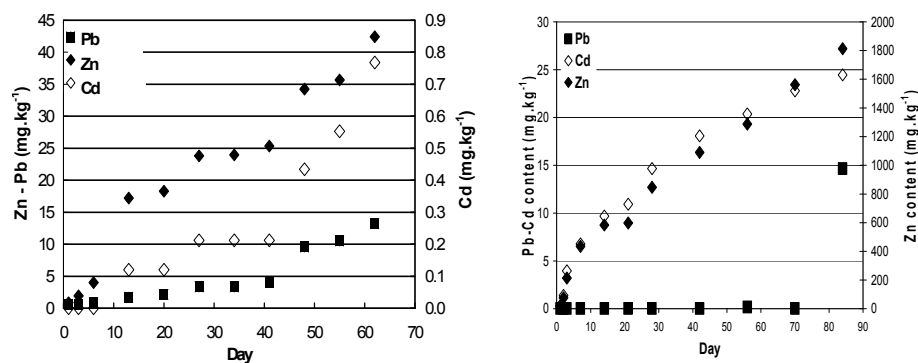
Fe(II) and Fe(III) concentrations, determined assuming that the redox potential refers to the Fe(II)/Fe(III) system, were used to calculate the degree of saturation for potential iron secondary minerals. In the measured pH and Eh range, the TDW are close to equilibrium with respect to ferrihydrite, Fe(OH)_{3(s)}, indicating that Fe(III) concentration in drainage water is controlled within the waste material by this amorphous phase (SI ranging from 0.0 and -0.4), while the high log SI values for goethite are the result of none, or very slow crystallisation, because of kinetic constraints (SI ranging from 4.0 to 4.6). The waters are under-saturated with respect to Fe(II) mineral phases.

In spite of the high sulphate concentrations, drainage waters are slightly under-saturated with respect to gypsum, CaSO₄, (SI ranging from -0.4 and -0.7) and under-saturated with respect to jarosite, KFe₃(SO₄)₂(OH)₆, mineral commonly found in this type of site (SI ranging from -0.8 and -1.8). None of the sulphate minerals present in the data base appears to control the sulphate content of the drainage waters and in this case, this species behaves conservatively. However, as gypsum SI values are slightly negative at the dam outlet, it is possible that locally saturation is reached.

In addition, drainage waters are strongly under-saturated with respect to all oxide, hydroxide, carbonate and sulphate minerals of Zn, Cd and Pb included in the database, indicating there is no secondary phase other than ferrihydrite which precipitates from this solution in the tailings. Hence, the scavenger potential of this mineral phase is to be considered for the control of heavy metals in the drainage waters.

4.3 Dynamic leaching test results

For the waste sample from Bentaillou, the dynamic leaching test was performed during 62 days with analysis of the leachate after 1, 3, 6, 13, 20, 27, 34, 41, 48, 54 and 62 days.



At the end of experiment, the amount of elements released was very low in comparison with the initial content of mining wastes Figure 3. It reached 0.2% for Zn and for Pb and 1.4% for Cd, 3.6 % for SO_4^{2-} and 2.5 % for Ca. The metals amount released into solution were very small reflecting a retention mechanism of Pb, Zn and Cd in the mining wastes.

The pH value of eluates varied from the beginning to end of experiment between 9.3 and 8.4 whereas, during the experiment, the lower value reached is 7.1.

Half of sulphates was released in the beginning of the experiment, probably resulting from the dissolution of sulphate mineral such as gypsum rather than from sulphide dissolution.

The dynamic leaching test was performed on the mining wastes of Saint-Salvy during 84 days. Lead was mainly retained in the solid matrix while the release of Zn and Cd during the experiment was more important than for the Bentaillou Site. The release amounts of Pb, Zn and Cd were 0.15%, 9.7% and 46 % respectively. Third of the liberation was operated in the beginning of the experiment (Figure 3).

The sulphates leaching was fast in the beginning of the experiment. The total amount liberated is 1500 mg.kg⁻¹ corresponding to 5% of initial amount of sulphur. The high calcium release was operated in the beginning of the experiment whereas 30% was mobilised by the end of experiment. The pH values varied from 7.1 to 5.3 from the beginning to end of the experiment.

4.4. Equivalent time and inertisation time estimations

The determination of equivalent time is based on an extrapolation of the experimentation duration to the leaching duration in the field by comparison of the

amount of water passed through the sample during the experiment with the rainfalls flows of the area.

The 62 days lasting experiment performed on the Bentaillou mining wastes sample corresponds to an equivalent time of 288 years.

The equivalent time determined for the Saint-Salvy site from the experiment of 84 days would correspond to a leaching duration of 183 years in situ.

The inertisation time of system is defined as the time necessary for oxidation of the total amount of sulphide minerals which are the metallic contaminant providers. Its estimation is based on exportation of sulphate which must behave conservatively (Igarashi et al., 2003 ; Munoz et al., 2003, Brunel, 2005). Although a few percent of sulphur might occur as sulphate mineral in the waste sample and is released at the beginning of the experiment, the solution/solid ratio does not favour saturation of sulphate mineral during the experiment. If the sulphur release is linear with time, the inertisation time from site data is determined from the following equation :

$$T_{\text{inertisation}} = C_S / F_{\text{SO}_4}$$

C_S : Total molar stock of sulphur in the waste sample

F_{SO_4} : calculated mean molar flow of SO_4^{2-} annually exported.

Hence, the inertisation time determined experimentally for Bentaillou waste dump is of 7730 years approximately.

The inertisation time determined from the experimental data for Saint-Salvy wastes is of 4050 years approximately.

4.5. Validation of the modified Soxhlet experiment

For the validation of modified Soxhlet test, the estimation of inertisation time of mining wastes based on field data was compared to the estimation based on experimental data.

The inertisation time of system was defined as the time necessary for oxidation of the total amount of sulphide minerals in the dump and the dam of Bentaillou and Saint-Salvy respectively. Its estimation is based on exportation flow of sulphate by drainage waters in the sites. Assuming the sulphur release is linear with time, the inertisation time from site data is determined from equation : $T_{\text{inertisation}} = C_S / F_{\text{SO}_4}$

C_S : Total molar stock sulphur in the mining wastes drained in the site

F_{SO_4} : mean molar flow of SO_4^{2-} annually exported by drainage waters in the site.

The inertisation time estimated on the Bentaillou site is around 9400 years.

The inertisation time determined from site data of Saint-Salvy is approximately 1440 years.

Finally, the estimated inertisation times from experimental and site data are 7730 and 9400 years for Bentaillou and 4050 and 1440 for Saint-Salvy respectively. The same order of magnitude from the experimental and site data implies the efficiency of the modified soxhlet test for mining wastes characterisation aiming the prediction of their behaviour. However some uncertainties such as the flow rate, the representativity and not totally conservatives character of sulphates infer that the results are only approximate.

Hence experimental and field results are close for Bentaillou taking into account various assumption and approximations. Validation of the modified Soxhlet method for long term behaviour assessment can be proposed.

On the contrary, for Saint-Salvy wastes the duration experimentally estimated for total sulphide oxidation overestimates the time calculated from the sulphate flow exported by drainage waters in situ.

In the Saint-Salvy impoundment waste system, subsequently to sulphide oxidation and neutralisation reactions, elements are released and transported downwards by infiltrated waters to more reducing conditions. Oxidation reactions are allowed by infiltrated waters transporting oxygen which decreases with depth. The oxidation products of sphalerite, pyrite and galena are acidity and liberation of SO_4 , Zn, ferrous iron, Cd and Pb. The H^+ ions supply generates siderite dissolution whose products are HCO_3^- , Fe^{2+} and Mn^{2+} . In the Eh and pH conditions of site, only a part of ferrous iron oxidise favouring the ferrihydrite precipitation which can act as a screen protecting sulphides grains from further oxidation. Such a mechanism may explain the lower rate of oxidation obtained in the experimental leaching procedure performed under oxidising conditions while drainage waters in the field evidence more reducing conditions. Consequently the modified Soxhlet procedure is not validated for dam impounded wastes, this type of impoundment lowering oxygen availability.

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