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Incurred environmental risks and potential contamination sources in an abandoned mine site

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The mineralogical characterization of Fedj Lahdoum mine wastes measured by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) showed the presence of the following sulfide minerals: galena (PbS), sphalerite (ZnS), pyrite (FeS2), cerussite (PbCO3) and smithsonite (ZnCO3). The wastes were stored in tailing ponds. The results showed that the concentration of metals from tailings were up to 10 460 mg kg−1 for total Zn, 2 100 mg kg−1 for total Pb and 62.08 mg kg−1 for total Cd. The tailings have presented a fine unconsolidated texture that accelerated the dispersion of the particles rich in heavy metals. Geochemical analysis of soil has revealed high total contents of Pb, Zn and Cd, respectively: 3 646, 3 236 and 17 mg kg−1. Chemical analysis of cultivated and wild plants species inside the district contain high grades in heavy metals: 708.56 mg Zn. kg−1; 16.24 mg Pb. kg−1 (Thymus vulgaris (L)); 500.44 mg Zn. kg−1, 12.44 mg Pb. kg−1 (Laurus nobilis (L)); 128.33 mg Zn. kg−1 and 22.53 mg Pb. kg−1 (Ficus (L)) and 106.73 mg Zn. kg−1 (pimento). The high levels detected in soil and plants have exceeded the Tunisian and Canadian standards. These results showed that the abandoned site was contaminated by the presence of tailing dumps which were exposed to significant water and/or wind erosion. To solve this problem, we proposed an environmental desulphurization by froth flotation.

Key words: Heavy metals, mine tailings, abandoned mining-district, plant contamination.

INTRODUCTION

The depletion has led to the closure of nearly all the mines in Tunisia, generating large amounts of tailings stored in tailing ponds near mining areas of the pool without supervision and subject to the Mediterranean climatic variations.

As a result, several areas contain large quantities of tailings which are rich in heavy metals such as Pb, Cd, Zn, Sb, As and Hg from the abandoned mine sites (Bhattacharya et al., 2006). These mining sites are areas where high levels of metals pollution can reach 102 to 104 times the normal content of a soil.

Exposure of tailings to air, oxidation and climatic conditions favored the release of heavy metals (Smuda et al., 2008) which are often a threat to the environment (Chiu et al., 2006; Chakroun et al., 2010; Concas et al., 2006). They have a negative impact on the concepts of sustainable development. In fact, many heavy metals remain in quantities that exceed the environmental standards in mining areas. Zinc in the form of sphalerite and lead as galena, are present in mine tailings owing to their release mesh that has not been reached).

Within the frame of abandoned mine sites remediation, fits this work, which is the environmental characterization

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of an abandoned mine site and potential sources of contamination and risks for a further purpose which will be the environmental desulphurization. Different techniques are applied to the restoration of sites contaminated by heavy metals such as: phytoremediation: biological method using green plants to remove, or render less toxic environmental contaminants (phytoextraction, phytostabilisation). Among the physicochemical methods: Confinement in situ; leaching with water and pumped on site; excavation and incineration; mineral processing separation by froth flotation: this process is becoming more useful for the management of certain mine tailings. the method consist on separating mineral particles non-selectively and economic by bringing them to the surface despite their high densities, in adhesion of hydrophobic particles to air bubbles blown into the pulp, while the hydrophilic particles remain into the pulp. This treatment process generates two products: a non reactive fraction and a reactive sulfide fraction. Management of this fraction is as a paste backfill or placed under a coverage made from desulfurized thin residue. This technology offers a great potential mineral processing to remove contaminants from mine tailings.

MATERIALS AND METHODS

Study area

The district of Jebel Fedj Lahdoum, a mining area of Pb-Zn has been exploited from 1892 to 2004 and since then it was abandoned. It is located in North West of Tunisia in the diapir zone (Figure 1) between the Medjerda plain and Krib plain one, located 120 km southwest of Tunis. This mineral deposit was one of the main Pb-Zn deposits in northwestern Tunisia (Sainfeld, 1952).

This mine deposit was the subject of several studies, which include those of Laatar (1980), Perthuisot (1981), Abidi and Abdelouahed (1986), Charef et al. (1987), Kassaa (1990), Bouhlel (1993), Vila et al. (2001), Sebei (2007) and Boussen et al. (2010).

Fedj Lahdoum mine is located at the heart of a relatively high mountain peak at 954 m at the bottom of a valley drained (9°60'47"E and 36°22'06"N) by Tordfin wadi tributary of El-Mor-Arkou wadi which flowed into the Tessa wadi about 11 km west of the deposit (Figure 2). The river system consisted of a large number of small ravines and wadis drained by the El-Mor-Arkou Tordfin wadi (deriving from the Tessa wadi) that passed north of the mining sector. The study area was located in a sub-humid field,
characterized by a relatively abundant rainfall, which ranged between 400 and 600 mm/year.

Jebel Fedj Lahdoum is formed by a breach of Triassic dolomite. Its mineralization is of the type: Pb, Zn (Sr, Ba, S), Fe. The soils of Fedj Lahdoum region are characterized by a basic pH in the range of 8.29. They have a dominant clay texture of the order of 68%.

Extraction of metals has led to mining wastes. Discharges of Fedj Lahdoum occupy an area of 10 ha with a volume = 157,270 m³; 393,175 tons (0.39 Mt). These wastes were deposited around the immediate vicinity of the Fedj Lahdoum site, which is a rural area exclusively. This zone is characterized by extensive agriculture based on a cereal production system associated with breeding (Figures 3 and 4).

Mine wastes sampling and characterization

The sampling is the crucial step in the process of tailings characterization. The purpose is to obtain a range of representative samples in terms of size and mineralogy, which reflect all the physical and chemical characteristics of all the dumps. The sampling method adopted is the release surface sampling on a square mesh screen 100° 100 m with 4 samples taken at 4 points
arranged on a circle of 80 m around a central point fixed on the
grid, with the directions SW, SE NW, NE according to the diagram
(Figure 5). This grid is sufficiently flexible to be adjusted during
sampling, tightened or relaxed depending on the constraints
encountered in the field. Along the upright, samples were collected
from the surface, half-height and base of each stock releases. All
the samples were taken from different tailings dumps were mixed
and then homogenized, quartered through a riffle sampler (Sample
Splitter: splitter falls). All of the samples obtained are similar in
content (Figure 6). They were kept in plastic bags until used for two
purposes: the mineralogical characterization and treatment process
by flotation. The representative sample must have the same grain

Figure 3. Tailings deposit in an agricultural area.

Figure 4. Breeding sheep in the vicinity of Fedj Lahdoum abandoned mine site.
size (by homogenization and quartering) to ensure that the flotation can be carried out.

In this study, the raw sample and the different size fractions of a representative waste sample were used for the characterization by XRD (X Ray Diffraction), SEM (Scanning Electron Microscope), chemical analysis which involved the determination of Pb and Zn total and other heavy metals. The samples were dissolved by triacid attack (HClO₄, HNO₃ and HF) whose purpose is to measure Zn, Pb, Fe, Mn, Cr, Co, Cd and Cu spectrometry atomic absorption (AAS) Thermo-elemental type.

Soils and plants sampling in the surrounding area and chemical analysis

Soil samples are collected around the mining district with a sample of control soil (control) outside the area (Figure 7). The determination of total contents of Pb, Zn and Cd in soils required a solution treatment and chemical analysis with the same protocol as for the solid waste.

To monitor the transport of PTE (Potentially Toxic Elements) at the first link in the food chain, wild and cultivated plant species were collected and represented (Figure 7) on the basis of their suitability to the inside or outside Fedj Lahdoum mining District: P1: olive tree (Olea (L)), upstream of the study area near the water source Ain Tordfin S1. P2: Plant shrub outside the mining district. P3: Aleppo pine (Pinus halepensis (L)), located far from tailings, upstream of the river Tordfin. P4: Aleppo pine (P. halepensis (L)), taken away from tailings. P5: pimento, plant along the left bank of the river Tordfin; P6: rosemary (Rosmarinus officinalis (L)), sampled on the left bank of the river Tordfin. P 7: fig tree (Ficus (L)) on the left bank of the wadi near the tailing dam N° 4. P8: Acacia (Acacia (L)), located on the right bank of the river Tordfin. P9: olive tree (Olea (L)), near the old gallery. P10: olive tree (Olea (L)), located near the old gallery and the tailing dump N° 1. P11: Cistus (Cistus (L)), located on the west bank of the river. P12: laurel (Laurus nobilis (L)) situated on the right bank of the river. P13: thyme (Thymus vulgaris (L)) on the right bank of the wadi.

The fresh material was washed with distilled water and treated with ultrasound to remove all dust and soil. The upper parts (leaves) are separated and then dried in an oven (40°C) for 48 hours, and then it was finely ground, calcined at 450°C for 12 hours. The calcination product was dissolved after an attack in pure nitric acid and pure perchloric acid [HNO₃ (70 to 71%)]: HClO₄ (70 to

Figure 5. Diagram of Fedj Lahdoum sampling tailings.
72%), 2:1(v/v)]. The concentrations of heavy metals Pb, Zn and Cd in the plants were measured by atomic absorption spectrometry (AAS), type Solar Thermo Elemental.

RESULTS

Tailings

The analyzed mine waste samples showed a light gray color with a texture that is closely applied to the ore mineral processing. These mining wastes are poorly consolidated; unstable seat erosion with traces of gullies (Figures 8 and 9).

Particle size analysis of a representative sample of tailings dumps in the Fedj Lahdoum determined the size distribution ranging between 315 and 20 μm with the finest fraction (< 25 μm) 20% (Figure 10).

The observation under the binocular microscope of different size fractions (> 315 μm, [315 to 250 μm], [250 to 160 μm], [160 to 125 μm], [125 to 100 μm], [100 to 80 μm] and [80 to 63 μm]) showed the presence of grains of galena (PbS),

![Diagram of sample homogenization and division](image-url)
sphalerite (ZnS), pyrite (FeS₂), calcite (CaCO₃), quartz (SiO₂) and dolomite (CaMg(CO₃)) (Figure 11) in a mixed form (formed from two or more mineral species), or free (only one mineral species). The finest fraction presented 20% which is the richest in sulfide minerals. The waste of fine texture is considered as a source of contamination of the entire mine site perimeter.

The observation under electron microscope (SEM) of fine particle size fractions confirmed the presence of galena, sphalerite and pyrite in the finest fractions of Fedj Lahdoum tailings (Figure 12).

The total contents of heavy metals in the raw sample and a sieved sample in Fedj Lahdoum waste rock piles are presented in Table 1. The raw sample showed levels of zinc of about 1.46% (14 600 mg.kg⁻¹), lead: 0.21% (2 100 mg.kg⁻¹) and iron: 3.2% (32000 mg.kg⁻¹). Strontium has a maximum of about 3.51% (35 100 mg.kg⁻¹), for manganese, the maximum (Figure 13) is about 1.63% (16 300 mg.kg⁻¹). The variation in grades, the contents of the other heavy metals are shown in the histogram (Figure 14).

The sieved sample showed that zinc concentrations ranged between 5.900 mg.kg⁻¹ (0.59%) and 32,300 mg.kg⁻¹ (3.23%). The lead content ranged from 800 mg.kg⁻¹.
Zinc and lead were concentrated preferentially in the fraction > 315 μm and that of < 25 μm (= 20 μm) (Figure 15). The iron has an average grade of about 32 000 mg.kg\(^{-1}\) (3.2%). The levels of manganese can reach 17 600 mg.kg\(^{-1}\) (1.76%). Iron and manganese showed a homogeneous distribution in all size fractions. The strontium levels high enough up to 61 800 mg.kg\(^{-1}\) (6.18%). Cadmium (Cd), cobalt (Co), chromium (Cr) and copper (Cu) are in small proportions (Table 1).

The correlation curves Zn / Cd and Pb / Cd (Figure 16 and 17) showed a good positive correlation between zinc...
Figure 10. Histogram of size distribution.

Figure 11. Different size fractions photographs of Fedj Lahdoum dumps.
and cadmium, and between lead and cadmium.

Environment of the abandoned site soil analysis in the vicinity of the study area

The results of chemical analysis of different soils that are taken from topsoil (arable and pasture lands) and control soil are presented in Table 2.

Chemical analysis of soils (FH₁, FH₂, FH₃, FH₄) showed high levels of Pb, Zn and Cd from a soil sample collected far from the mine site considered as control (FHT) whose contents are: 118 mgPb/kg⁻¹, 312 mgZn/kg⁻¹, 1 mgCd/kg⁻¹. The contents of the heavy metal increased progressively outside Fedj Lahdoum district and the highest grades were found inside the mine site (Figure 18 (a), (b), (c)) at Soil FH₁: 3 646 mgPb/kg⁻¹, 3 236 mgZn/kg⁻¹, 17 mg Cd/kg⁻¹.
Table 1. Total content of heavy metals (mg.kg\(^{-1}\)) in a raw sample and in different size fractions of a representative sample from Fedj Lahdoum tailings.

<table>
<thead>
<tr>
<th>Sample tailing (µm)</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
<th>Sr</th>
<th>Mn</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sample</td>
<td>14600</td>
<td>2100</td>
<td>32000</td>
<td>35100</td>
<td>16300</td>
<td>62.08</td>
<td>75.04</td>
<td>29.57</td>
<td>39.33</td>
</tr>
<tr>
<td>+315</td>
<td>32300</td>
<td>6200</td>
<td>35000</td>
<td>51000</td>
<td>16700</td>
<td>77.17</td>
<td>28.21</td>
<td>32.48</td>
<td>17</td>
</tr>
<tr>
<td>-315 to 250</td>
<td>17000</td>
<td>4800</td>
<td>32000</td>
<td>44400</td>
<td>17500</td>
<td>44.21</td>
<td>23.93</td>
<td>35.96</td>
<td>11.67</td>
</tr>
<tr>
<td>-250 to 160</td>
<td>10900</td>
<td>2200</td>
<td>32000</td>
<td>48100</td>
<td>17600</td>
<td>28.97</td>
<td>56.92</td>
<td>32.12</td>
<td>45.93</td>
</tr>
<tr>
<td>-160 to 125</td>
<td>8200</td>
<td>1400</td>
<td>32000</td>
<td>54700</td>
<td>17000</td>
<td>22.27</td>
<td>25.29</td>
<td>29.59</td>
<td>23.31</td>
</tr>
<tr>
<td>-125 to 100</td>
<td>7000</td>
<td>1100</td>
<td>34000</td>
<td>61000</td>
<td>16500</td>
<td>20.93</td>
<td>77.17</td>
<td>56.22</td>
<td>49.59</td>
</tr>
<tr>
<td>-100 to 80</td>
<td>6300</td>
<td>1000</td>
<td>34000</td>
<td>61800</td>
<td>17600</td>
<td>19.71</td>
<td>77.17</td>
<td>56.22</td>
<td>49.59</td>
</tr>
<tr>
<td>-80 to 63</td>
<td>5900</td>
<td>900</td>
<td>31000</td>
<td>52300</td>
<td>16200</td>
<td>20.51</td>
<td>23.39</td>
<td>23.09</td>
<td>23.09</td>
</tr>
<tr>
<td>-63 to 50</td>
<td>5900</td>
<td>900</td>
<td>31000</td>
<td>52300</td>
<td>16200</td>
<td>20.51</td>
<td>25.66</td>
<td>25.66</td>
<td>35.23</td>
</tr>
<tr>
<td>-50 to 40</td>
<td>6600</td>
<td>800</td>
<td>30000</td>
<td>42900</td>
<td>15600</td>
<td>18.82</td>
<td>18.16</td>
<td>28.16</td>
<td>40.69</td>
</tr>
<tr>
<td>-40 to 25</td>
<td>6700</td>
<td>900</td>
<td>34000</td>
<td>46200</td>
<td>15200</td>
<td>19.86</td>
<td>29.21</td>
<td>30.45</td>
<td>10.62</td>
</tr>
<tr>
<td>&lt;25 (=20)</td>
<td>30000</td>
<td>2000</td>
<td>36000</td>
<td>16900</td>
<td>14000</td>
<td>47.86</td>
<td>51.85</td>
<td>70.76</td>
<td>98.01</td>
</tr>
<tr>
<td>Min.</td>
<td>5900</td>
<td>800</td>
<td>30000</td>
<td>16900</td>
<td>14000</td>
<td>18.82</td>
<td>9.33</td>
<td>23.39</td>
<td>10.62</td>
</tr>
<tr>
<td>Max.</td>
<td>32300</td>
<td>6200</td>
<td>36000</td>
<td>61800</td>
<td>17600</td>
<td>77.17</td>
<td>75.04</td>
<td>70.76</td>
<td>98.01</td>
</tr>
</tbody>
</table>

Figure 13. Variation in the contents of Pb, Zn, Fe, Sr, and Mn from a raw sample of tailing.

Plants grades of metals at risks

The results of the chemical analysis of the aerial parts of these plants are shown in Table 3.

Plants that are located outside the mining district have shown low grades, while all plants located inside abandoned mining district are strongly contaminated (Figure 19(a), (b), (c)).

Zinc concentrations (Zn) in the plant species located inside Fedj Lahdoum mining district are extremely high (Figure 19(a)): Thyme (Thymus vulgaris (L)): 708.56 mgZn.kg\(^{-1}\), laurel (Laurus nobilis (L)): 500.44 mgZn.kg\(^{-1}\), pimento: 106.73 mgZn.kg\(^{-1}\). High concentrations of lead (Pb) were also registered (Figure 19(b)): Olive (Olea (L)): 18.08 mgPb.kg\(^{-1}\), fig tree (Ficus (L)): 22.53 mgPb.kg\(^{-1}\). High grades of cadmium (Cd) were shown (Figure 19(c)): Olive: 5.62 mgCd.kg\(^{-1}\), pimento: 3.23 mgCd.kg\(^{-1}\) laurel (Laurus nobilis (L)): 5.01 mgCd.kg\(^{-1}\).

DISCUSSION

Tailings: Potential source of contamination

The mineralogical characterization of the tailings showed
that bearing phases of lead and zinc are generally the size of about 20 microns, lead and zinc are mainly associated with sulfides and carbonates. In carbonate context and under a Mediterranean climate, Boussen et al. (2010) show that the environmental risks associated with mining activities are mainly related to the dispersion of fine particle that were emitted under the action of wind and to a lesser degree in erosion of the dumps and
Figure 16. Correlation diagram of zinc-cadmium.

Figure 17. Correlation diagram of lead-cadmium.

Table 2. Concentrations of Pb, Zn and Cd (mg.kg$^{-1}$) in the soil of Fedj Lahdoum region.

<table>
<thead>
<tr>
<th>Soil Sample</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil FH$_1$</td>
<td>3 646</td>
<td>3 236</td>
<td>17</td>
</tr>
<tr>
<td>Soil FH$_2$</td>
<td>1 768</td>
<td>3 294</td>
<td>12</td>
</tr>
<tr>
<td>Soil FH$_3$</td>
<td>842</td>
<td>3 184</td>
<td>10</td>
</tr>
<tr>
<td>Soil FH$_4$</td>
<td>506</td>
<td>1 432</td>
<td>6</td>
</tr>
<tr>
<td>Control soil FHT</td>
<td>118</td>
<td>312</td>
<td>1</td>
</tr>
</tbody>
</table>
transport water from rivers during winter when it rains heavily.

High concentrations of zinc and lead in the 315 μm fraction were due to the presence of mixed grains of sphalerite and galena that were not broken (the mesh is not optimal liberation reached) during the enrichment. In
the finest fraction, the high content of zinc and lead owe their origin to overgrinding. It resulted in the production of a large quantity of fines making it difficult to flotation. Thus, these fines were found in the tailings. The positive correlations between Zn/Cd and Pb/Cd could deduce the possibility to recover cadmium simultaneously in the same phase with lead or zinc, in the reprocessing of tailings by flotation with the aim of environmental desulphurization. In fact, these elements have ionic radii neighbors, which allow partial replacement of Zn by Cd in sphalerite: $R_{Zn} = 1.34 \text{ Å}$, $R_{Cd} = 1.51 \text{ Å}$ or partial replacement of Pb by Cd in galena $R_{Pb} = 1.46 \text{ Å}$, $R_{Cd} = 1.51 \text{ Å}$ (Rosler and Lange, 1972).

Kovacs et al. (2006), in Gyöngyösoroszi, North Hungary, show that the contamination of the site by mining activity is the result of the transfer of trace elements by wind and water processes.

Recent studies conducted by Conesa et al. (2007) and Liao et al. (2008) prove that mining waste fine textured rich in heavy metals pose serious environmental problems. Once released into the environment, these heavy metals have a potentially negative impact on the quality of the environment (Jang and Kim, 2000). The toxicity of heavy metals (Pb, Zn, Cu and Cd) is one of the main constraints to remediation (Lan et al., 1998).

A recent study similar to the present work was carried out by Rashed, 2010 shows that when processed mine minerals are finely divided, there is a potential risk that such materials may find their way through the environment and food chain to animals/humans, and can be toxic to plants, animals and humans through their interaction with the environment. The contamination of heavy metal has been reported in the vicinity of mining and smelting sites.

The tailings (from the fine grinding of ore and processed material) can seriously pollute the surrounding land with toxic dust due to the wind erosion. Jacob and Otte (2004a) and Ritecy (1989) confirms that the tailings deposits, the crushed and processed ore material, can severely pollute the surrounding land with toxic dust from wind erosion.

### Contamination of agriculture soil

All concentrations detected in soil inside and outside the Fedj Lahdoum mining district have exceeded the maximum allowable tolerance in soils: 100 mgPb·kg$^{-1}$, 300 mgZn·kg$^{-1}$ and 0.7 mgCd·kg$^{-1}$ (Henin, 1983).

According to the Canadian Environmental Quality Standard International for soils (CCME-EPC-CS34, 1991), grades of Pb, Zn and Cd in soil samples analyzed (FH$_1$, FH$_2$, FH$_3$, FH$_4$) greatly exceeded the tolerance contents in agricultural areas (50 mgPb·kg$^{-1}$, 100 mgZn·kg$^{-1}$, 3 mgCd·kg$^{-1}$) tolerance limits and in residential areas (300 mgPb·kg$^{-1}$, 500 mgZn·kg$^{-1}$, 5 mgCd·kg$^{-1}$). For soil FH$_5$, it can be considered below the tolerance levels in industrial areas (600 mgPb·kg$^{-1}$, 1 500 mgZn·kg$^{-1}$, 20 mgCd·kg$^{-1}$). The levels detected in soil samples (FH$_1$, FH$_2$, FH$_3$ and FH$_4$) also exceeded the Tunisian standard (INORPI 2002, 2003 (a), (b), (c)), NT 106.20, NT 91.12; NT 91.33; NT 91.10 in agricultural areas (100 mgPb·kg$^{-1}$, 300 mgZn·kg$^{-1}$, 3 mgCd·kg$^{-1}$).

Control soil contained significant grades of heavy

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**Table 3. Grades of Pb, Zn and Cd (mg·kg$^{-1}$) in plants located in the vicinity of the Fedj Lahdoum abandoned mine site.**

<table>
<thead>
<tr>
<th>Localisation</th>
<th>Plant leaves</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Outside the mining district</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1 (Olea (L))</td>
<td>38.73</td>
<td>3.23</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>P2 (Plant shrub)</td>
<td>67.98</td>
<td>2.53</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>P3 (Pinus halepensis (L))</td>
<td>77.78</td>
<td>3.84</td>
<td>-0.001</td>
<td></td>
</tr>
<tr>
<td>P4 (Pinus halepensis (L))</td>
<td>92.20</td>
<td>8.68</td>
<td>2.11</td>
<td></td>
</tr>
</tbody>
</table>

|                | P5 (pimento)                 | 106.73   | 2.25     | 3.23     |
|                | P6 (Rosmarinus officinalis (L)) | 113      | 4.98     | 0.25     |
|                | P7 (Ficus (L))               | 128.33   | 22.53    | 1.44     |
|                | P8 (Acacia (L))              | 130.68   | 7.92     | 0.5      |
|                | P9 (Olea (L))                | 181.70   | 4.98     | 2.32     |
|                | P10 (Olea (L))               | 212.20   | 18.08    | 5.62     |
|                | P11 (Cistus (L))             | 229.05   | 2.59     | 0.69     |
|                | P12 (Laurus nobilis (L))     | 500.44   | 12.44    | 5.01     |
|                | P13 (Thymus vulgaris (L))    | 708.56   | 16.24    | -0.001   |
Figure 19. Grades variations of Zn (a), Pb (b) and Cd (c) according to plants approximinity from mining site.
metals that exceed the standards, which proved that contamination exceeded the internal territory of the former mine and progresses to the vicinity of the mine site. Simon et al. (2001) show that the soil contamination is related to the distance from the storage site and fine texture of tailings.

High concentrations of heavy metals in soil samples reflect the blocking of these metals risk surface, from the input of mineral dust from operating activities of the mining field and the deposit of waste around the site (Schippera, 2008).

Tailings dumps were subject to atmospheric transport under wind action and presenting a dust emission source and an inhalation risk for people (Haneef and Yanful, 2003; Conesa et al., 2007). Mining waste are subject to water erosion that results in a transport of rich particles in toxic elements in particulate form or dissolved form causing degradation of soil quality (Boussen et al., 2010). These tailings (from the fine grinding of ore and processed material) can seriously pollute the surrounding land with toxic dust due to wind erosion (Ritcey, 1989; Jacob and Otte (2004b).

Soil pollution by lead, zinc and cadmium were characterized in an old Spanish mine Pb-Zn (Rodriguez et al., 2009), in abandoned mine sites Tunisia: Jalta (Boussen et al., 2010), Jebel Sidi-Hallouf Bouaouane (Chakroun et al., 2010). In the same context, Lee et al. (2001) showed that the soil located around an abandoned mine site in Korea is less contaminated than those detected in Fedj Lahdoum (northern Tunisia).

Other previous studies on this topic led by Shu et al. (2001), Liu et al. (2007), Yang et al. (2003) and Schipper et al. (2008) have shown that the tailings that are deposited in agricultural areas are suspected of being sources of heavy metals to the environment. The potential toxicity and the risk of contamination of the food chain have been described in the USA by Pichtel et al. (2000), in New Zealand by Taylor and Percival (2001), in the Rio Pilcomayo basin, Bolivia by Miller et al. (2004) and in China by Liu et al. (2006). The exploitation of mineral deposits is a major anthropogenic source of soil pollution by heavy metals which is confirmed by Wang et al. (2008), Jiménez et al. (2009), Wang et al. (2009), Wei et al. (2009) and Schindler et al. (1987).

**Heavy metal concentrations in plants**

Plants located outside the mining district have grades below the limits of tolerance. While all plants located inside the abandoned mining district were highly contaminated.

These concentrations of Zn, Pb and Cd exceeded the limits of toxicity in plant tissues: 100 mgZn.kg\(^{-1}\), 5 mgPb.kg\(^{-1}\) and 2 mgCd.kg\(^{-1}\) (Bedell et al., 2006).

Plants react differently depending on the variety. Some are less tolerant than others and die on contact with heavy metals. Other defense reactions and prevents the absorption by secreting acids that will increase the pH and therefore reduce the mobility of toxic elements. Others are tolerant to metals and even accumulate and concentrate them. These plants are called: hyperaccumulators and metallophlic (Bhattacharya et al., 2006). Several studies have demonstrated that heavy metals (Pb, Zn, Cu, Cd) are preferentially absorbed by certain plants hyperaccumulator such as: *Thlaspi caerulescens* and *Brassica napus*;*Colza* (Ben Ghnaya et al., 2006); *Rhododendron annae* (L), *Llex puleuera* (L), *Fargesia dura* (L), *Arundinella yunnanensis* (L) (Yanqun et al., 2004).

In fact, these plants accumulate heavy metals that can be assimilated by humans and can cause the contamination of the whole food chain (Kabata-Pendias, 2004).

Heavy metals are absorbed by the roots and remain the most often. The shift in aerial parts (stems, leaves) vary depending on the metal and are indicators of an increased concentration of metals in the soil. Lead remains in the roots, cadmium and zinc pass more easily into the aerial parts (Boularbah, 2006).

Plant contamination by heavy metals is done: either through root and in this case only the mobile fraction (phytodisponible) can be assimilated by the plant (Van Gronsveld et al, 1995; Pratas et al,2005 ), or through passive contamination: it is the wind transportation. The performed analysis showed that the plants were contaminated at the leaves. Mine wastes are suspected to be a source of plants contamination and therefore contamination of the environment (Rodriquez et al., 2009; Yang et al., 2003; Lan et al., 1998). In Mediterranean countries, and in the case of Tunisia, eolian transport plays an important role in the dispersion of fine particles when released around former mine sites (Boussen, 2010). Plants and crops can uptake toxic elements through their roots from contaminated soils and even leaves can absorb toxic elements deposited on the leaf surface (Rashed, 2010).

**Diffusion process of contamination to the environment**

The Mediterranean climate is characterized by long dry periods interspersed with heavy rains, high winds and
high temperatures that induce wind and erosion. They are the two major processes of the spread of contamination to the various compartments of the environment and to local populations. The relative importance of wind and water processes depend on the climate zone that varies greatly according to a north-south gradient. In addition, in a changing climate where the frequency of droughts and extreme rainfall events are increasing, the spread of contamination becomes a more prevalent concern.

The transfer through wind plays a leading role in the spread of contamination in semi-arid climatic conditions in arid areas around the Mediterranean. Aeolian transport depends also on weather events and surface characteristics subjected to wind erosion. All natural resources are vulnerable to anthropogenic assaults and for this reason, the ecological balance had been broken.

The cultivation of almost all land is originally starting the process of malfunction and degradation of all components of the landscape: changing the water balance of land with higher rates of runoff, erosion of land sloping (Cappuyns et al., 2006) and siltation in low areas. These phenomena are still shaping the abandoned mine site of FH and determine its regressive evolution marked by:

(i) Extensive land degradation;
(ii) Shaping the landscape by water runoff and erosion which cause environmental risks arising from this dynamic resident, a very special way, the potential transfer by runoff, contaminating mineral particles that could settle the land surface and landing in areas of spreading or in waterways.

The starting points of potential dust hazards are all located inside the territory of the former mine, spread out along the route of the treatment with ore from its extraction to its shipment outside the region, the following steps: at the exit of the ore mining galleries and its transport to the area for crushing and stockpiling of material along the transport path of the ore to the ore processing plant, loading of ore processed for evacuation to the outside.

As for potential vectors of dust dispersal into the abandoned mine environment, they were:

(i) Wind: Its ability to transport these particles depends on its speed and humidity. In areas considered particularly windy, only the wind in the wet season was potentially able to disperse the load and potential pollutants in the territory of the former mine and in the vicinity of mine (Haneef and Yanful, 2003; Conesa et al., 2007).
(ii) Runoff: Potentially, these waters are important vectors of dispersal of dust hazards in the absence of specific arrangements for rainwater retention that does not infiltrate immediately locally. Potential areas of dust transported landing zones are spreading flood waters and waterways.
(iii) The drainage water: The fraction of rainwater that infiltrates into the soil must first saturate the topsoil prior to percolate deeply and eventually reach the groundwater (Pinte, 2000). In reality, the risk of leaching of heavy metals by vertical drainage are virtually zero for several reasons: the minerals at risk are insoluble in high pH calcareous soils, rainfall averages, even in the wet season, are not sufficient to saturate the soil and cause a drainage material in the context of Fedj Lahdoum soil. Previous mining activities caused a serious heavy metal contamination of surface waters, groundwater in different sites throughout the world. The effluent from mine site consists of mine drainage, water that flows at the outfall of tailings accumulation area, of runoff from waste rock pile or a combination of these types of water. The mine water is pumped to the surface to keep the mine dry and to permit the exploitation. It may contain contaminants emitted by blasting operations, the use of vehicles and other equipment, as well as by biological or chemical reactions that occur on the surface of the bedrock. In Sardinia (Italy) water is contaminated under the impact of mining activities (Concas et al., 2006). The same phenomena is detected in British Columbia, Canada (Azcue et al., 1995) and in south Africa (Winde and van der Walt, 2004).

Contamination of the aquatic environment caused by mining and ore processing metal comes mainly from the oxidation of sulphide minerals contained in the exposed walls of the underground galleries, the walls of the extraction sites, areas of accumulation of tailings and waste rock dumps. Sulphide minerals, when exposed to air, first undergo a relatively slow chemical oxidation and then gradually become more acidic environment: pyrite.

Oxidation of iron sulfide (FeS₂) in the presence of water is the starting reaction process. The first reaction is the conversion of sulfides to sulfates by means of an oxidation reaction (Pint, 2000) and the water is acidic values (pH 3 to 4).

$$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$

The second reaction is with the progressive acidification
of the medium (H⁺) and processing of ferrous iron to ferric iron (Fe³⁺), which produces a fast cyclical process and forms large amounts of acid (Toulhoat, 1996).

\[2\text{FeS}_2 + \frac{15}{2}\text{O}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 4\text{HSO}_4^- + 2\text{OH}^-\]

This acidification allows the growth of bacteria that act as catalysts in oxidation reactions, thereby causing an increase in the rate of acidification (Masson and Rice, 2002).

\[4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}\]

They are acidophilic bacteria that are involved in the oxidation of metal sulfides: Thiobacillus ferrooxidans, is a Gram-negative (optimal growth T: 30 to 35°C and low pH=2), chemolithotrophic bacterium able to derive energy for growth from the oxidation of ferrous to ferric iron and elemental sulfur or reduced inorganic sulfur compounds to sulfate using oxygen as electron acceptor. In waters strongly acidic (pH 2 to 3) mines, the iron type oxidation is bacterial (Buonfiglio et al., 1999).

Therefore, there is a production of highly acidic water that dissolves the heavy metals from sulphide minerals which generates acid mine drainage: AMD (Lawrence et al., 1991). Sulfidic mine tailings are the major source for AMD and contamination of the mine environment (Sima et al., 2011). In Kristineberg, northern Sweden and near Selebi-Phikwe, Botswana; Kock and Schippers (2006) reported the impact of microbiological metal sulfide oxidation on acid mine drainage generation. Sulfide oxidation is predicted to continue for centuries in the absence of remedial actions.

(iv) The work and the reversal of the surface layers of soil: ploughings could actually mix the possible pollutants that contaminate the surface of cultivated land.

(v) Direct contamination of natural and cultivated vegetation types through dust dispersion by the wind: it is possible inside the mine, particularly as a result of transport along the tracks inside the mine site. This is the case of contamination of aerial parts (leaves) of forestry training, relics of scrubland, and the remaining olive groves inside the territory of the mine.

(vi) The export of plant products, potentially contaminated harvested or consumed by sheep flocks: contamination could occur directly by deposition of dust risks on bodies consumed, or due to absorption of metal pollutants in contaminated soil and their concentration in parts consumed or collected. But the potential export of plant products contaminated outside the risk zone was extremely high. For the surrounding area the risks of plants contamination, directly or indirectly by dust from the mine are high.

Thus, Fedj Lahdoum abandoned mine site has vulnerable components but the environmental risks were very serious. However, if the risks were probable over short distances inside the mine, they were maximum for possible contamination of the surrounding land in view to the humidity of air, land and materials exposed to air in relatively rainy season. In this case, tailings are suspected being the source of contamination.

The methods that are available to decontaminate the toxic metals contained in the tailings include phytoremediation such as phytoextraction: use of plants to extract organic pollutants from soil and metals and concentrate in the organs of the plant for harvest (Wong, 2003) and phytoextraction: use of plants to reduce erosion and immobilize pollutants in the surface layers, in particular avoiding their migration to the water surface and groundwater (Dourmet et al., 2008; Rutten et al., 2006); soil flushing; pneumatic fracturing; solidification/stabilization; vitrification; electrometallurgy; (Zhongning et al., 1997), phytodegradation: use of the combination plant/microorganisms to degrade organic pollutants from the soil; chemical reduction/oxidation; soil washing and excavation, but these methods are usually expensive (Chiu et al., 2006). The most profitable method in the long term and less expensive is froth flotation using the appropriate collector chosen according to the mineralogical and chemical characterization of mine wastes (López Valdivieso et al., 2006).

Froth flotation is a separating process, by bringing them to the surface despite their high densities, particles of searched minerals (galena, sphalerite, pyrite and even cerussite, anglesite, smithsonite), by adhesion of these particles (hydrophobic particles) to air bubbles blown into the pulp, while the other particles of these minerals (hydrophilic particles) does not cling to the air bubbles and remain in the pulp (Fuerstenau, 1976; Herrera-Urbina et al., 1999). In a pulp, the most important factor to separate particles of the gangue is useful to the specific surface behavior versus the products that are added to the air and some chemical agents: collectors, depressants, activators and regulators of pH (Blazy, 1970).

To apply the flotation process, it is necessary to mill the representative sample in a steel rod mill during the
required time (up to the mesh liberation minerals) in the presence of water and the necessary reagents. The milled slurry was transferred to a Denver flotation stainless steel cell, the impeller speed is fixed depending on the cell size, at a constant air flow rate (the maximum permitted by the system). Pulp density is adjusted by tap water. The pulp is conditioned in the flotation cell for few minutes with the appropriate reagent after adjustment of pH. The collector is added to the pulp for few minutes. The global flotation is carried out to have finally: total concentrate and a final tailing (non reaction fraction). The froth height was kept constant at 2 cm throughout using frother. Feeds, concentrates and tails were filtered, dried and weighed before analysis for heavy metals (Havre, 1952).

This technique is essential to the prosperity of several mines producing ore complex. It can lead to open new mines or to reprocess tailings from old mines (Benzaazoua et al., 2000). With flotation, dumping of old mines in Canada have been treated by the flotation process for an environmental desulphurization (Benzaazoua et al., 2003). Heskeh et al. (2010) developed a conceptual integrated approach for sulfide removal from flotation tailings in AMD mitigation and presents preliminary findings in the technical feasibility of flotation desulfurization. It is the aim in North Africa, especially in Tunisia: desulphurization of contaminated mine sites by froth flotation. This method was chosen for possible decontamination of Fedj Lahdoum mine site after the mineralogical study which has shown the finesse of mine waste and mineralogical complexity (mixed minerals).

Conclusion

This study showed that Fedj Lahdoum abandoned mine site was contaminated with heavy metals originating tailings. The concentrations of mine wastes were: 10.240 mgZn.kg⁻¹ and 2.100 mgPb.kg⁻¹ and 62.08 mgCd.kg⁻¹.
Tailings are suspected of being the primary source of environmental contamination. The soils of the former mining site of the deposit and various materials were contaminated by zinc, lead and cadmium (3 646 mgPb.kg⁻¹, 3 236 mgZn.kg⁻¹ and 15 mgCd.kg⁻¹). As for the plants growing inside this abandoned mine, they had already revealed significant accumulations of Zn, Pb and Cd, particularly in the leaves of thyme (Thymus vulgaris (L)): 708.56 mgZn.kg⁻¹; 16.24 mgPb.kg⁻¹. Laurel (Laurus nobilis (L)): 500.44 mgZn.kg⁻¹, 12.44 mgPb.kg⁻¹ and 5.01 mgCd.kg⁻¹. Heavy metals concentration in pepper was: 106.73 mgZn.kg⁻¹, 3.23 mgCd.kg⁻¹.

Fedj Lahdoum area is strongly contaminated by mineral dust rich in Zinc and Lead. In Tunisia, several mine sites are located in rural zones where the population depends on agriculture. In this environmental context, the contaminants were dispersed from mining sites (transfers wind, water) to land surrounding the areas. Therefore, there has been a transfer from soil to plant of these contaminants and their accumulation in plants. The spread of contamination into the food chain via local agriculture can then lead to people exposure to a health risk in relation to regulatory limits. Environmental risks inherent in mining activities reside in the potential dispersal of dust from zinc materials exploited and stored in tailings ponds without any precautions previously. The former mining activity can generate pollution from mining.

Current methods to combat this problem remain limited, often very costly and environmental guarantee is never assured in the very long term. Assistance in the management of contaminated sites and the choice of modes of prevention and protection is already started in our laboratory involving the environmental remediation. Therefore, we suggest adapting the method of environmental desulphurization by froth flotation.

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