Motivation

Waste material deposits from mining activities in Spain lasting for more than 2500 years are a threat to environment and society. Methodologies to detect, assess and mitigate these environmental issues are desired.

Main Results

A comprehensive methodology for assessment of affected sites including long term plans for recovery have been developed and demonstrated in Spanish tailing ponds. The vegetation cover has been successfully restored.
18-1 Introduction

Cartagena-La Unión Mining District in southeast of Spain constituted an important mining focus for more than 2500 years until its closure in 1991. Phoenicians, Carthaginians, Romans, Arabsians, and Spaniards have been mining silver, lead, zinc, tin, iron, and manganese in this district [Conesa and Faz, 2009; Faz et al., 2001]. Those mineral deposits were likely to be mined for profit, thus, overburden and waste materials (accumulated in tailing ponds) with their consequent environmental risks appear as the fundamental components in the post-mined landscapes [Acosta et al., 2011; Collins, 2001]. Tailing ponds contain materials rich in Fe-oxyhydroxides, sulphides, sulphates, and heavy metals (mainly Cd, Pb, and Zn). As a consequence, these soils remain bare and have low soil organic matter content [Acosta et al., 2011; Conesa et al., 2007]. Consequent environmental risks, especially water and wind erosion and mobility of heavy metals in soil-plant systems stand out with propensity to adversely affect both human health and the functioning of ecosystems. Therefore, it is necessary to take action towards remediation of this contamination [Doumett et al., 2008; Ji et al., 2011].

While surface mining has relatively ancient origins, reclamation is a relatively recent phenomenon with a global concern about the potentially damaging effects which can originate from mining [Burley, 2001]. In this recent phenomenon, phytoremediation takes its place as a newly emerged reclamation technique in the removal or stabilization of soil heavy metals by the usage of plants providing advantages in costing, in in situ applications and in environmental compatibility, among other expensive and often impractical techniques [Pérez-Esteban et al., 2011; Sasmaz and Sasmaz, 2009]. Restoration of a vegetation cover can fulfil the objectives of stabilization, pollution control, visual improvement and removal of threats to human beings (phyto-stabilization) [Wong, 2003]. Vegetation cover is very effective in reducing surface erosion; can return a large proportion of percolating water to the atmosphere through transpiration, thus reducing the concentration of soluble heavy metals entering watercourses; reduces the visual scars in the landscape, so that successful re-vegetation may allow recreational use of the land [Tordoff et al., 2000]. Several studies on the use of metallophytes for re-vegetation of metal toxic mine wastes appear in the literature (e.g. [Peters, 1984; Smith and Bradshaw, 1979; Wong, 2003]). According to these studies, combining metal-tolerant species with proper application of fertilizers and pH adjusters resulted in the successful and rapid re-vegetation of contaminated soils.

The general objective of this chapter is to show an effective methodology for improving soil fertility and environmental risk reduction in mining tailing ponds using organic and inorganic amendments and phyto-stabilization. This general objective can be divided in the following specific objectives:

1) to evaluate the evolution of tailing properties after amendment application,
2) to evaluate the risk reduction for human and ecosystems after amendment application,
3) to study the effect of amendments in the growth of native vegetation (vegetation cover, richness and biodiversity), and finally
4) to design a new landscape for the reclaimed areas.
18-2 Study Areas and Experimental Design

Two areas affected by mining activities were selected, El Lirio and El Gorguel tailing ponds. These areas are representative of the rest of existing mining affected areas in the Mining District of Cartagena-La Unión, SE Spain, with similar problems and characteristics (F.18-1). The selection of these two areas was based on their access facilities, physicochemical characteristics (based on previous studies), hydrological conditions, slope, distance from towns, surrounding landscape, etc. Thus, the conclusions that can be extracted from these zones can be applied to the rest of the areas, at the same mining district, or in other areas from similar metallic mining activities under the same environment. A distribution of the surface areas of the tailing ponds to delimitate the zones with the different treatments was carried out as show in the F.18-1.

Zone A: Application of marble waste is added to increase soil pH for metal immobilization, and to improve soil structure and metal retention. A superficial area of 3750 cm² and 1300 cm² in El Lirio and El Gorguel, respectively, were amended with marble waste on the top soil and then mixed to the upper first 30 cm, and immediately incorporated into the soil taking care to give several passes to get a good mixture.

Zone B: Marble waste and pig slurry are applied in a superficial area of 3750 cm² in El Lirio and 2300 cm² in El Gorguel. First, marble waste was applied on the surface soil and then pig slurry allowing the liquid to be absorbed by the soil/marble mixture. After 24
hours amendments were incorporating into the soil and mixed with the first 15–20 cm of soil by ploughing. This assay allows us to study the influence of amendments in the soil-plant system, and to establish comparisons with zones A and D.

**Zone D:** Pig slurry is applied to increase soil organic matter and nutrients. Pig slurry was added in a surface area of 3500 cm² and 1900 cm² in El Lirio and El Gorguel, respectively. We were waiting 24 hours for the water to be adsorbed by the soil and incorporated in 15–20 cm into subsoil. This assay allows us to study the influence of amendments in the soil-plant system, and to establish comparisons with zone B.

**Zone C:** In this plot none of the amendments studied was applied. It acts as a reference to contrast the effects of the different amendments in the soil-plant system, and to monitor the evolution of physico-chemical and biological soil properties.

### 18-3 Waste Residues Used as Amendments

Two types of waste materials were used as amendments in this large-scale plot experiment for improving tailing properties and increasing the possibilities of reclamation of the El Lirio and El Gorguel tailing ponds. We chose marble waste and pig slurry as inorganic and organic amendment, respectively, because they are generated in huge quantities, representing a significant disposal problem for pig producer and stone industry in the Region of Murcia.

#### 18-3-1 Marble Waste

In this region the volume of residues generated by non metallic extractive industry, and concretely marble extraction, is relevant with a total of 147 000 m³ of process product, generating an annual residue of 128120 tons. Thus, one of the main environmental problems of this extractive industry is the low output in the profit of the material (10–20%) generating a huge volume of inert residues that are normally taken to industrial disposals. The application of alkaline materials has been considered to prevent the acid conditions to either neutralize the acidification process or stop the oxidation of pyrite, and to promote recovery of plant cover by means of improving soil structure. When limestone dissolves in aqueous media it provides alkalinity and assists in neutralization of acidic solutions and

---

Generation of marble waste: cutting marble stone, wet and dry conditions
immobilization of metals through precipitation and/or adsorption. Marble waste was obtained from marble industries located in Cehegín, Murcia (F.18-2) and had approximately 20% humidity and 94% CaCO₃ in dry condition, pH was 8 and salinity 2.2 dSm⁻¹.

The applied amount is based on the equivalent CaCO₃ required to neutralize the acidity generated in terms of percentage of oxidizable sulphur present in the mine soil. Eq CaCO₃ was calculated according to the method proposed by [Sobek et al., 1978]. Additionally, in management plans which involve liming, a first engineering safety factor, (fs), is considered of at least 1.5 to 2 times the theoretical lime requirements and needs to be used, to allow the slow reactivity of lime and reduce the negative effects of non homogeneous mixing in the field. The second is the purity factor, (fp), to reach the equivalent of pure lime.

Analyses of representative soil samples from each tailing pond reported a mean content of 0.25% and 0.57% of sulphur for El Lirio and El Gorguel, respectively; which allows neutralizing the soil potential acidity supplied by sulphur. Thus, we have calculated a mean of quantity requirements for the current conditions of potential acidity in each tailing pond corresponding to 1.4 kg marble/m² and 4 kg marble/m² for El Lirio and El Gorguel respectively. Marble wastes were applied only once at the beginning of large-scales plot experiments A and B.

18-3-2 Pig Slurry

The Region of Murcia has more than 8% of pig production in Spain, with almost 2000000 pigs in 7486 farms. This quantity of pigs generates an annual production of 6.5 Hm³ of pig slurry (F.18-3). Using pig slurries as soil amendment will address two environmental problems in southeast Spain – disposal of industrial wastes from pig production and reclamation of mine soils. Pig slurry could ameliorate mine soil by providing available nutrients (e.g. nitrogen, phosphorous, potassium etc.), improving physical properties and possibly lowering the availability of toxic metals through complexation with the organic matter. Nitrogen, carbon and nutrients are usually deficient in mine soils and limit vegetation establishment and sustained productivity. Soil organic matter improves nutrient retention by increasing cation exchange capacity (CEC), enhances the availability of nutrients (e.g., NH₄⁺, NO₃⁻, PO₄³⁻, SO₄²⁻) and traces elements by mineralization, improves soil buffering capacity, chelates metallic ions, increases the availability of some nutrients, and decreases the toxicity of others [McBride, 1994; Stevenson, 1994].
The calculation for application of pig slurry was made according to the agronomic rate established by Spanish legislation RD 61/1996: 170 kg N ha$^{-1}$ yr$^{-1}$ (framed within the Directive 91/676/CEE), to avoid contamination of groundwater by nitrates. Pig slurry was added in plots B (marble and pig slurry) and D (pig slurry) at a rate of application of 3.3 L m$^{-2}$ and 5.9 L m$^{-2}$ in El Lirio and El Gorguel, respectively. Pig slurry was obtained from a pig farm located in Fuente Álamo, Murcia, which was directly pumped from the pond and transported for application by spreading the tank in movement towed by a tractor (F.18-3). The chemical characterization of pig slurry includes a pH of 7.8 and salinity of 39.1 dSm$^{-1}$, its moisture was 96 %, total nitrogen 5.1 g L$^{-1}$ and total organic carbon 18.7 g L$^{-1}$. Concentration of metals were 19.3 mg Cu L$^{-1}$ and 28 mg Zn L$^{-1}$.

### 18-4 Initial Site Preparation and Amendment Application

First initial activities including the construction of drainage structures around the plots in order to conduct the runoff water and prevent flooding into the plots in rainy seasons. As the soil surface presents a hard cemented layer it was necessary to use machinery to break-up dense soil through its spiralling action in surface (up to 50 cm depth). Then, soil was redistributed across the surface to produce a relatively uniform reconstructed soil. Finally, after tillage soil surface was levelled, guaranteeing the drainage of waters after rainfalls. Each step can be observed in detail in the F.18-4, F.18-5, F.18-6 and F.18-7 shows the steps taken during the addition of the marble waste and pig slurry amend-
Incorporation of amendments (marble waste and pig slurry) into the soil

At the beginning of the experiments soil samples were taken in each plot (A, B, C and D) in order to have a reference to compare with results from periodical sampling planning during this long-term experiment. After application of amendments soil samples were again taken in three different periods: one week (to determine the first changes in soil properties), six months and twelve months after application. Soil samples were collected in five replicates distributed into each plot (F.18-8).

In each sampling point, we collected surface soil (0–30 cm) because the roots of the vegetation and the preparatory tillage of the mining lands reached the 30 cm of the soil. The collected samples were transported to the laboratory for analyses. Samples were air-dried for seven days, passed through a 2-mm sieve, homogenized, and stored in plastic bags at room temperature prior to laboratory analyses. In addition, a subset of each sample was grounded for several analytical determinations.
The analyses for this study were determined as follows: pH and electrical conductivity [Peech, 1965]; total carbon, sulphur and nitrogen in an elemental analyzer, cation exchange capacity [Chapman, 1965], particle size [FAO-ISRIC, 2006], aggregate stability [USDA, 1999], total metals [Risser and Baker, 1990], bioavailable metals [Lindsay and Norwell, 1978; Norvell, 1984] and water soluble metals [Ernst, 1996]. Measurements of metals were carried out using atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer).

18-5-2 Monitoring of Vegetation

After application of amendments we hope that in time for the chemical stabilization and nutrients added by pig slurry promote the creation of initial structured soil, with immobilization of heavy metals, and increases in organic matter, nutrients, water holding capacity and active microbial communities, in order to initialize the establishment and survival of spontaneous species by the surrounded vegetation. In order to evaluate the evolution of the colonization of spontaneous vegetation, the vegetation cover, richness and biodiversity were quantified every six months.
Results and Discussion

18-6-1 Tailing Properties Evolution

Soil Acidity (pH)

Soil pH is a measure of active soil acidity. The pH of a given mine soil can change rapidly as the rock fragments weather and oxidize. Pyritic minerals (FeS₂), when present, oxidize to sulphuric acid and drastically lower the pH, while carbonate (Ca/MgCO₃) bearing minerals and rocks tend to increase the pH as they weather and dissolve. Unweathered (or unoxidized) mine soils containing an amount of pyritic-S higher than the amount of their neutralizers (e.g. carbonates), will result in a fast drop of the pH to a range of 2.2 to 3.5 after exposure to water and oxygen.

In El Lirio tailing pond, soil pH in plot treatment with marble waste was increased after amendment application (F.18-9). Contrarily, plot amended with pig slurry and control remained with a pH of 4.0 and 5.0 respectively. The change in pH might indicate the “liming effect” of marble waste to modify soil acidity. In El Gorguel, the effect of the amendments on soil pH is not observable, which is due to the fact that initial pH in this pond is already high (~8.0) for all plots. This shows that, after amendment applications, the pH of these ponds is currently adequate for natural plant colonization.

Electrical Conductivity

Electrical conductivity (EC) of a soil solution indicates the concentration of total soluble salts in solution, thus reflecting the degree of soil salinity. Plants are detrimentally affected, both physically and chemically, by excess salts in some soils and by high levels of exchangeable sodium in others.

Initial soil salinity on both ponds and for all plots was high (>2 dSm⁻¹), indicating that salinity is an important limitation for plant colonization; and only resistant plant species will be able to colonize these ponds. Soil EC values for both tailing ponds decreased significantly in plots amended with marble waste, on the contrary that happened when pig slurry was applied (F.18-9). However, for all plots in El Lirio and marble plot in El Gorguel, the general pattern is an increase of EC during the next months after application; this can be explained by the effect of soluble salt movements to the surface due to evaporation and capillary rise and subsequent salt precipitation during the summer period.

Redox Potential

Redox potential (Eh) is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species’ affinity for electrons and tendency to be reduced. Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution.

For both ponds and all plots, including control plots, the observed general pattern was a decrease of the redox potential values during the time, however, some differences
were observed. In El Gorguel, an increase of Eh in the plots treated with pig slurry was observed, however, after six months the values of Eh were even lower than the Eh values before application for these plots (F.18-9). This indicates that the climatic conditions of this area are responsible for the changes in the redox potential.

**Total Sulphur**

Sulphides in the ore deposits and tailing ponds derive from the metalliferous minerals originated by the intense hydrothermal alteration of sub-volcanic rocks from Miocene or Pliocene [Manteca and Ovejero, 1992]. Main sulphides come from pyrite (FeS₂), sphalerite ((Zn,Fe)S) and galena (PbS). The content of sulphides determine the potential acidity of the material, since sulphides oxidize in the presence of O₂, releasing sulphates and protons, as indicated in the following reaction:

\[
\text{FeS}_2 + \frac{7}{2} \text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 2\text{H}_3\text{O}^+ + e^-.
\]

The content of total sulphur in both tailing ponds is very high (25–30 gkg⁻¹), especially in El Gorguel tailing pond, which indicates the potential acidity that can be generated in these ponds, whose data were used for the calculation of the marble waste doses. As can be observed in F.18-10, the variations of total sulphur in the plots do not follow any specific pattern and no effect between treatments was reported. Therefore, the slight differ-

Evolution of pH, EC and Eh in the different plots from El Lirio and El Gorguel tailing ponds

![Graphs showing pH, EC, and Eh values for El Lirio and El Gorguel tailing ponds](F.18-9)
ences between plots and periods of time are likely due to the heterogeneity of the tailing material forming the ponds. From the point of view of vegetation, sulphur is an essential element for plant growth, and therefore it must be present in the soil for adequate plant colonization. The amounts of this element in the ponds are more than enough to meet the requirements of potential plants and therefore no deficiencies are expected for this element. However, the generation of acidity and the excessive presence of sulphates could be a limiting factor for plant growth.

**Total Nitrogen**

Total soil N includes all forms of inorganic soil N. Inorganic N includes soluble forms (e.g., NO$_2^-$ and NO$_3^-$), exchangeable NH$_4^+$, and clay-fixed non-exchangeable NH$_4^+$. Organic N content includes numerous identifiable and non-identifiable forms [Stevenson, 1986] and can be determined by the difference between total soil N and inorganic soil N content. In the abandoned mining areas the loss of soil nutrients due to rapid decomposition of vegetation is an important degradation process. Specifically, losses of nitrogen (N) are often greater than losses of other nutrients [Vitousek et al., 1982].

The initial content of nitrogen in both ponds is very scarce, indicating that the presence of nutrients for plant growth is one of the main limiting factors for plant colonization in these ponds. As can be seen in F.18-10, the application of pig slurry results in a significant increase of total nitrogen in the first week and remains six and twelve months after application, however, a decrease after six months is observed, likely due to consumption of nitrogen for plant species and organic matter mineralization and loss for runoff or leaching. Therefore, we can conclude that pig slurry is an important source of this essential element and probably other nutrients, favouring plant colonization; however, a decrease of this element is expected after twelve months.

**Total Carbon**

Soil carbon is the generic name for carbon held within the soil, primarily in association with its organic content. Soil carbon is the largest terrestrial pool of carbon. Humans have significant impacts on the size of this pool. Soil carbon plays a key role in the carbon cycle and thus is important in global climate models.

The content of total carbon in both studied tailing ponds is very low; however, there are important differences between them. In general, El Gorguel pond has higher content of total carbon than El Lirio (F.18-10), therefore it is expected that the soil conditions in El Gorguel will be more favourable for plant establishment than in El Lirio. However, it must be taken into account that the total carbon in soils is divided in inorganic and organic carbon; and the content of these two pools of carbon in the ponds affects the soil conditions in different ways. A higher presence of inorganic carbon indicates a better buffer capacity against changes of acidity, a better retention of toxic metals and an improvement of the soil structure. On the other hand, a higher presence of organic carbon increases the soil fertility, release of nutrients, better water holding capacity, etc. For these reasons, it is important to study the effect of the used amendments in both organic and inorganic carbon contents.
Evolution of total sulphur, nitrogen and carbon in the different plots from El Lirio and El Gorguel tailing ponds

**Total Inorganic Carbon**

Inorganic carbon occurs in soils generally as carbonate minerals e.g. calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$) and siderite (FeCO$_3$). Carbonate in soils can be of primary (inherited from parent material) or secondary (pedogenic) origin. Secondary carbonates are usually aggregates of silt- and clay-sized calcite crystals that are easily identified in grain mounts. Large crystals of calcite or dolomite are of primary origin [Doner and Lynn, 1989]. Soil carbonates affect root and water movement, soil pH [Nelson, 1982], and the nature of the exchange complex [Arnaud and Herbillon, 1973]. The authors showed that soil retention of P, Mn, Zn and Cu was directly related to carbonate content and to the distribution of total and active calcium carbonate between the clay and silt fractions. When total CaCO$_3$ is less than 20%, the retention of those elements is affected mainly by the total amount of carbonates, but, when it is above 20%, nature of the carbonates was more important in governing retention.

The effect of marble waste application in the inorganic carbon content is immediately observed in both plots where the marble was applied, especially in El Lirio (F.18-11). However, after six months from the application, a slight decrease in the inorganic carbon contents is appreciated, which is likely due to the dissolution of the carbonates in the process of acidity neutralization.
Total Organic Carbon

Soil organic matter is a complex and varied mixture of organic substances. Commonly, soil organic matter is defined as the percentage of humus in the soil. Humus is the unidentifiable residue of plants and animals that becomes fairly resistant to further decay. Soil organic matter, from this point of view, can be divided into two fractions: 1) the recognizable organic material (straw, woodchips, roots, mulches, insects, etc.) with their partially decomposed remains, and 2) humus. Organic matter is very important for the functioning soil system for various reasons. It increases soil porosity, thereby, increasing infiltration and water holding capacity of the soil, providing more water availability for plants and less runoff that may potentially become contaminated. This may be specifically helpful at mine sites where runoff may become acidic and contain high concentrations of heavy metals. The increased porosity also aids in easing tillage of the soil.

In general, El Gorguel tailing pond shows a higher content of organic carbon than El Lirio, indicating that the soil conditions in this pond are better for the spontaneous plant colonization. The effect of pig slurry application in the content of organic carbon in soil is slightly observable after the amendment application (F.18-11). El Lirio tailing pond shows a slight increase in the organic carbon content in plots amended with pig slurry; however, in El Gorguel the effect of pig slurry application in the content of organic carbon is not appreciable, which indicates that the amount of carbon added with the amendment is not enough for increasing significantly the organic carbon content in soil, and therefore future application of organic amendments are recommended.
Cation Exchange Capacity

Cations are positively charged ions such as calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), potassium (K$^+$), sodium (Na$^+$), hydrogen (H$^+$), aluminum (Al$^{3+}$), iron (Fe$^{2+}$), manganese (Mn$^{2+}$), zinc (Zn$^{2+}$) and copper (Cu$^{2+}$). The capacity of soil to hold these cations is called cation exchange capacity (CEC). These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces (negative soil particles attract the positive cations). The cations on the CEC of the soil particles are easily exchangeable with other cations and as a result, they are plant available. Thus, the CEC of a soil represents the total amount of exchangeable cations that the soil can adsorb. F.18-11 shows the effect of amendment application in the cation exchange capacity (CEC) values of the tailing ponds. In general, the cation exchange capacity of El Lirio is higher than in El Gorguel, which is likely due to the different mineralogical composition among both ponds, this indicates that the soils from El Lirio have a higher capacity of retain nutrients. Values of CEC do not significantly change with any of the amendments, and the observable variations are due to heterogeneity of the tailing ponds during the sampling.

Texture

Texture influences plant growth by its direct effect on soil aeration, water infiltration, cation exchange capacity (CEC), and erodibility. Infiltration and permeability are rapid in sandy soils, very slow in clay soils, and intermediate in loam soils. Soils that are granular, with a large diversity in particle size, have many large and small pores, a desirable characteristic for plant growth. Due to the fact that particle soil distribution is very stable during long periods of time, the effect of the amendments has not been evaluated for this soil property. However, the particle size distribution of each plot in both tailing ponds is presented in the F.18-12. The main fraction in both ponds is the sand fraction, with the highest percentages in El Lirio (50 to 80%), followed by silt content, and finally clay percentage, with contents lower than 15%. This particle size distribution indicates that the water holding capacity of these materials is low, and the porosity high.

Stable Aggregates

An aggregate is a group of primary particles that adhere to each other more strongly than to surrounding soil particles [Kemper and Rosenau, 1986]. Aggregate stability can be defined as the resistance to disruption or breakage of the bonds within the aggregates by external forces of impact, shearing, abrasion and internal forces arising from the escape of entrapped compressed air (slaking) and differential swelling. Aggregate stability can serve as an indicator of the resistance of soils to water erosion, surface seal or crust formation, compaction leading to decreased infiltration and subsoil aeration, and as a general soil quality indicator [Doran and Parkin, 1994; Larney et al., 1996; Le Bissonnais and Arrouays, 1996]. Soil aggregates control soil hydrology [Wu et al., 1990], affect soil oxygen diffusion and nutrient availability [Sextone et al., 1985; Wang et al., 2001], influence soil erodibility [Barthes and Roose, 2002] and constitute a pathway of organic carbon stabilization and long term sequestration [Six et al., 2004].

F.18-12 shows the effect of amendment application in the formation of stable aggregates. This parameter was not analysed one week after applications because the aggregate formation needs more time to be observed. After six months the formation of
aggregates was identified in the plots amended with marble and pig slurry alone and in the plots amended with both amendments for both ponds. This indicates that both amendments contribute to the aggregate formation; although, in accord with our results, the marble waste increases the stable aggregates more than pig slurry.

18-6-2 Risk Reduction for Human and Ecosystems

Effect of the Amendments in the Risk of Tailing Pond Erosion

In order to evaluate the effect of the amendment in the risk of tailing pond erosion, land degradation indexes were used. Land degradation, defined as the loss or reduction of the potential utility or productivity of the land [Lal, 1994], is a major environmental problem in arid and semi-arid areas [Chikhaoui et al., 2005], and it can be divided into three classes [Barrow, 1991; Snakin et al., 1996]:

1) physical degradation: including compaction, erosion, loss of water retention, sealing of soil surface etc.,
2) biological degradation: including loss of biodiversity, changes in the rates of microorganisms, contamination by pathogens etc., and
3) chemical degradation: including salinity, alkalinity, heavy metal accumulation, loss of nutrients etc.
Due to the main soil parameters affecting soil erosion are included in the degradation indexes (physical and biological degradation), such as organic matter, aggregate stability and particle size distribution, the evaluation of the amendment effect in these indexes will indicate if the risk of erosion has been reduced by the application of the mentioned amendments. In addition, the evaluation of the total metal content (chemical degradation) in the tailing ponds will be useful to estimate the amount of toxic metals that can be transported by the eroded tailing materials.

**Physical Degradation (PDI)**

This index was developed by [FAO, PNUMA, UNESCO, 1980] modified by [De Paz et al., 2006]. It is considered the main parameters and properties that play an important role in the evaluation of physical properties of the soil such as porosity, permeability, structure and water retention capacity. They are closely related to water movement, nutrient transport, root penetration, and plant emergence.

\[
PDI = \left( \frac{CI}{\%SA} \right) \cdot 100
\]

\[
CI = \frac{(1.5 \cdot FS + 0.75 \cdot CS)}{(\%Cy + \%OM \cdot 10)}
\]

\[
FC = 0.2391 - 0.0019 \cdot \%Sn + 0.0036 \cdot \%Cy + 0.0299 \cdot \%OM
\]

\[
WP = 0.0260 + 0.005 \cdot \%Cy + 0.0158 \cdot \%OM
\]

**Physical and biological degradation indexes for El Lirio and El Gorguel**

<table>
<thead>
<tr>
<th>El Lirio</th>
<th>El Gorguel</th>
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<tbody>
<tr>
<td><img src="image1" alt="Physical degradation index" /></td>
<td><img src="image2" alt="Physical degradation index" /></td>
</tr>
<tr>
<td><img src="image3" alt="Biological degradation index" /></td>
<td><img src="image4" alt="Biological degradation index" /></td>
</tr>
</tbody>
</table>

- Before application
- 6 months
- 12 months
F.18-13 shows the effect of the amendments in the physical degradation index for El Lirio and El Gorguel tailing ponds. Physical degradation in both tailing ponds is generally high, being much higher in El Lirio, which is mainly due to a low content of organic matter and clay, and a high percentage of silt. The relative amounts of these soil constituents result in low water retention capacity, soil crusting etc. causing high physical degradation.

The application of the amendments results in a decrease of the degradation index and therefore less susceptibility to the erosion processes in both ponds, this effect is more intense when marble waste is applied than when pig slurry is used, probably due to formation of stable aggregates using as cemented agent the carbonates (F.18-13). However, after twelve months, the degradation index increased up to the initial values in plot amendments with pig slurry from El Lirio tailing pond; contrarily, the effect of the amendments in the reduction of the physical degradation is maintained over time in El Gorguel.

Biological Degradation (BDI)

This index was proposed by [De Paz et al., 2006], biological degradation is related to the depletion of organic matter content and litter due to a rapid mineralization or soil erosion. This degradation is in part caused by bad soil management practices. Organic matter is the main nutrient source for plants and microorganisms, and also affects the soil aggregation, facilitates the air-entry and water flow and prevents crusting. The biological soil degradation index is: \[ \text{BDI} = \frac{1}{\text{OM}} \] (OM: organic matter).

Content of total heavy metals in the different plots from El Gorguel and El Lirio tailing ponds
As shown in F.18-13, the biological degradation in the tailing ponds is, generally and taking into account the mean of the data, very high for El Lirio and low for El Gorguel, which is, due to the content of organic carbon in El Gorguel, much higher than in El Lirio, therefore it is expected that the erosion processes are more intense in El Lirio.

The application of the amendments, especially pig slurry, results in a decrease of the degradation index in El Lirio, although no effect is appreciable in El Gorguel. However, after twelve months in El Lirio, the degradation index increased up to the initial values, showing that this application is not effective for reducing the biological degradation over time. Therefore, future applications of organic amendments are recommended.

### Chemical Degradation

In order to evaluate the chemical degradation of the tailing ponds, total heavy metals were analysed and compared with different legislations. F.18-14 shows the mean values of metals in the plots and in the four sampling periods for both tailing ponds. In addition, the allowed levels of metals for different countries are presented in T.18-1.

The metal with the highest concentrations was zinc, following lead, copper and cadmium in both ponds. In El Lirio tailing ponds some important differences were found between plots, such as the case of cadmium, where the plots amended with pig slurry and

<table>
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<tr>
<th>Country</th>
<th>Allowed levels in soils</th>
<th>Reference</th>
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<tbody>
<tr>
<td><strong>Italy</strong></td>
<td><strong>Limit A</strong>&lt;sup&gt;1&lt;/sup&gt; Zn: 150 Pb: 100 Cu: 120 Cd: 2</td>
<td>[Ministerial Decree, 1999]</td>
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<tr>
<td></td>
<td><strong>Limit B</strong>&lt;sup&gt;1&lt;/sup&gt; Zn: 1500 Pb: 1000 Cu: 600 Cd: 15</td>
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<tr>
<td><strong>The Netherlands</strong></td>
<td><strong>Level A</strong>&lt;sup&gt;2&lt;/sup&gt; Zn = 50 + 1.5(2C + OM) Pb = 50 + C + OM Cu = 15 + 0.6(C + OM) Cd = 0.4 + 0.007(C + 3OM)</td>
<td>[Ewers, 1991]</td>
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<tr>
<td></td>
<td><strong>Level B</strong>&lt;sup&gt;2&lt;/sup&gt; Zn: 500 Pb: 150 Cu: 100 Cd: 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Level C</strong>&lt;sup&gt;2&lt;/sup&gt; Zn: 3000 Pb: 600 Cu: 500 Cd: 20</td>
<td></td>
</tr>
<tr>
<td><strong>The Netherlands</strong></td>
<td><strong>Target value</strong> Zn: 140 Pb: 85 Cu: 36 Cd: 0.8</td>
<td>[Ministry of Housing, 1994]</td>
</tr>
<tr>
<td></td>
<td><strong>Intervention value</strong> Zn: 720 Pb: 630 Cu: 190 Cd: 12</td>
<td></td>
</tr>
<tr>
<td><strong>Spain</strong>&lt;sup&gt;*&lt;/sup&gt;</td>
<td><strong>pH &lt; 7</strong> Zn: 150 Pb: 50 Cu: 50 Cd: 1</td>
<td>[B.O.E., 1990]</td>
</tr>
<tr>
<td></td>
<td><strong>pH &gt; 7</strong> Zn: 450 Pb: 300 Cu: 210 Cd: 3</td>
<td></td>
</tr>
<tr>
<td><strong>Canada</strong></td>
<td><strong>Level A</strong>&lt;sup&gt;3&lt;/sup&gt; Zn: 110 Pb: 50 Cu: 40 Cd: 1.5</td>
<td>[Ministere de l’Environnement du Québec, 2001]</td>
</tr>
<tr>
<td></td>
<td><strong>Level B</strong>&lt;sup&gt;3&lt;/sup&gt; Zn: 500 Pb: 500 Cu: 100 Cd: 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Level C</strong>&lt;sup&gt;3&lt;/sup&gt; Zn: 1500 Pb: 1000 Cu: 500 Cd: 20</td>
<td></td>
</tr>
<tr>
<td><strong>Turkey</strong></td>
<td><strong>Clean</strong> Zn: 300 Pb: 100 Cu: 50 Cd: 1</td>
<td>[T.S.P.C.R., 2000]</td>
</tr>
<tr>
<td></td>
<td><strong>Polluted</strong> Zn: 500 Pb: 150 Cu: 100 Cd: 5</td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> Limit A: public and private green areas and residential use; limit B: commercial and industrial use.

<sup>2</sup> Limit A: reference value; level B: maximum allowable limits; level C: decontamination measures.

<sup>3</sup> Limit A: background level; level B: maximum acceptable limit for residential, recreational and institutional sites; level C: maximum acceptable limit for commercial and industrial sites.

<sup>*</sup> Agricultural soils
control showed lower concentration than in the other two plots; also the plot amended with pig slurry presented the lowest concentration of zinc compared with the others plots. This behaviour indicates that the waste material forming the ponds is very heterogeneous in the concentration of some metals. Contrarily, in El Gorguel the concentration of each metal in the different plots is more homogeneous, and no important differences between plots were found. Total Cd, Cu, Zn and Pb were above European legislation thresholds [Directive 86/278/ECC, 1986] and most of the compared laws for both ponds and all plots. In accord with the results, no changes with the application of amendments were found, and the variations between concentrations for a specific plot in the different periods of sampling are due to the natural heterogeneity of the tailing materials.

**Effect of the Amendments in the Risk of Metals Mobility to the Food Chain**

Heavy metals were extracted using DTPA, which is a chelating agent that adsorbs the amount of metals that can be potentially uptaken by plants. Therefore, with the results from this analysis we can determine the potential risk of metal mobility to the food chain, these data are shown in F18-15 for El Lirio and El Gorguel.

In El Lirio, the effect of marble waste was observed in the concentration of available copper, but especially efficient were the levels of available lead (F18-15). The concentrations of these metals decrease immediately with the application of marble. In the case of lead, the available lead decreased from 17% to 5% and was maintained over time,
also in the plots amended with marble waste and pig slurry an important decrease was observed, from 10% to 2% and also maintained over time. Likely, the formation of stable compounds of carbonates-lead promotes the precipitation of Pb and its reduction in the concentration of available lead. Oppositely, the application of pig slurry alone increased the available Pb after six months from the amendment application, which can be due to formation of organic ligands with lead increasing its mobility. For the rest of the metals no significant differences were observed after amendment application.

In El Gorguel, the effect of marble waste in the reduction of available lead and copper was observed after six months from the amendment application, however, after twelve months the concentrations of these metals went back to the initial concentrations, which indicates that the efficiency of the treatment was not maintained over time. In the case of zinc, a similar pattern was observed for all plots, after six months the concentration of available zinc was increased independent of the treatment, therefore likely an external factor produced this behaviour and cannot be attributed to the applied amendments.

**Effect of the Amendments in the Risk of Heavy Metal Leaching**

In order to determine the potential concentration of metals that can be mobilized by the effect of rainfall, runoff or leaching, heavy metals were extracted using deionised water. With the results from this analysis we can determine the potential risk of metals leaching, these data are shown in F.18-16 for El Lirio and El Gorguel.
The effect of marble waste reduced the water soluble fraction of cadmium, copper, zinc and lead in El Lirio tailing pond (F.18-16), this decrease can be due to the formation of insoluble carbonates from marble waste [Alvarenga et al., 2008; Liu et al., 2009]. Oppositely, the application of pig slurry increased the concentration of water soluble metals (Cu, Pb, Zn and Cd), which was probably achieved by the effects of complexation by organic matter from pig slurry. In the case of El Gorguel (F.18-16), due to the initial concentrations of soluble metals are very low, the effect of amendments is not easily observed, and probably the variation in the water soluble concentrations are due to other factors more than the effect of the applied amendments.

18-6-3 Evolution of Vegetation after Amendment Application

Soil erosion is increased if the soil has no or very little plant cover. Vegetation cover protects the soil from raindrop impact and splash, tends to slow down the movement of surface runoff and allows excess surface water to infiltrate. The lack of permanent vegetation cover also results in extensive erosion by wind. Loose, dry, bare soil is the most susceptible. The erosion-reducing effectiveness of plant covers depends on the type, extent and quantity of cover. Plant diversity completely covers the soil and intercepts all falling raindrops at and close to the surface, and thus is most efficient in controlling soil erosion. The effectiveness of any vegetation community depends on how much protection is available at various periods during the year, relative to the amount of erosive rainfall that falls during these periods. In this respect, perennial plants, principally grasses, provide a protective cover for a major portion of the year. The absence of vegetation rapidly increases erosion rates and transfer of toxic heavy metals by wind and runoff to the surroundings, including populated areas. Thus, vegetation cover can be used as indicator of erosion risk.

Evolution of vegetation in El Gorguel (top) and El Lirio (bottom) ponds (0, 6 and 12 months)
At the beginning of the experiments in El Lirio and El Gorguel tailing ponds, vegetation cover was practically null (F.18-17), with the presence of some sparse stems of *Piptatherum miliaceum*, *Dittrichia viscosa*, *Zygophyllum fabago*, *Diplotaxis lagascana*, *Phragmites australis* and *Tamarix canariensis*.

Although the vegetation in the tailing ponds was practically absent, the application of amendments conducted to spontaneous colonization of vegetation by the surrounding environment (T.18-2, F.18-17). After six months from the amendment application, in El

<table>
<thead>
<tr>
<th>El Lirio</th>
<th>Richness</th>
<th>Vegetation cover [%]</th>
<th>Biodiversity</th>
<th>Plant species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 months</td>
<td>12 months</td>
<td>6 months</td>
<td>12 months</td>
</tr>
<tr>
<td>MW</td>
<td>1</td>
<td>1</td>
<td>0.26</td>
<td>0</td>
</tr>
<tr>
<td>MW + PS</td>
<td>5</td>
<td>5</td>
<td>0.52</td>
<td>1.1</td>
</tr>
<tr>
<td>PS</td>
<td>2</td>
<td>5</td>
<td>0.02</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>C</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>El Gorguel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 months</td>
<td>12 months</td>
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<tr>
<td>MW</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MW + PS</td>
<td>5</td>
<td>10</td>
<td>1.1</td>
<td>25.0</td>
</tr>
<tr>
<td>PS</td>
<td>5</td>
<td>10</td>
<td>2.4</td>
<td>33.3</td>
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<td></td>
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</tr>
<tr>
<td>C</td>
<td>1</td>
<td>2</td>
<td>0.1</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Lirio tailing ponds, only *Zigophyllum fabago* was present in the marble waste plot; however, in the plots amended with pig slurry the biodiversity was higher with the presence of *Zigophyllum fabago*, *Monocotidelónea*, *Phragmites australis*, *Sonchus tenerrimus*, *Cakile maritime* in the plot amended with marble waste and pig slurry. In the Gorguel, the results were slightly better with the presence of *Piptatherum miliaceum*, *Zigophyllum fabago*, *Sonchus tenerrimus*, *Atriplex halimus*, *Cakile maritime* in the plots amended with pig slurry and a vegetation cover higher than in El Lirio tailing pond.

After twelve months from the amendment application (T.18-2, F.18-17), in El Lirio tailing ponds, only *Zigophyllum fabago* was still present in the marble waste and control plots, however, in the plots amended with pig slurry the biodiversity was higher with the presence of *Piptatherum miliaceum*, *Zigophyllum fabago*, *Sonchus tenerrimus*, *Atriplex halimus*, *Cakile maritime*, also the vegetation cover was slightly higher than six months before but still very low.

In the case of El Gorguel tailing pond the results were different, the marble waste plot remained practically bare, with the presence of some sparse stems of *Salsola kali*. The only species able to grow in the control plot were *Zigophyllum fabago* and *Salsola kali*, while in the plots receiving the organic amendment a richness of 10 was reached, with higher vegetation cover (25–30 %) and biodiversity (H = 1.1–1.3). The understanding of the processes implied in the primary vegetation succession initialized after colonizer establishment is crucial to avoid degradation processes. The fact that two plant species are growing in the control plot may indicate that these concrete species are resistant to highly extractable metal concentrations and, therefore, the previous absence of them may be likely due to adverse physical conditions for vegetation establishment. The initial tillage contributed to reduce compaction and bulk density, increasing porosity, which triggered the germination of seeds and development of seedlings. The application of pig slurry contributed to the improvement of soil fertility facilitating a higher colonization of natural vegetation. In MW plot, the development of plants was inhibited likely due to the presence of higher contents of soluble sulphate salts and clay.

### 18-6-4 Landscape Design of Tailing Ponds

Mine reclamation has to be formed an integral part of the planning process which includes feasibility studies and environmental impact assessment for new mines. The following objectives have to be provided by the help of reclamation [Mchaina, 2001]:

1. to allow a productive and sustainable post-mining use of the site;
2. to protect public health and safety;
3. to alleviate or eliminate environmental damage;
4. to conserve valuable attributes,
5. to minimize adverse socio-economic impacts.

The aim of design approach is not only recovering the health and biodiversity of ecosystems across the site, but also the spirit and imagination of people who will use the new park by using the ecological process of environmental reclamation.

The problematic features of the area can be transformed to a functional stage by providing their association with landscape components (F.18-18). With a controlled us-
age such as tampon zones, fences etc., the physical character of tailing ponds and colour of acid mine drainage pools can be seen aesthetic and can provide a touristic attraction centre in the region. Solutions for environmental risks can be combined with the main landscape value or specifically with one of the landscape components. For example in our case, phytostabilization can be seen the way of solution for various environmental problems of the area. The phytostabilization process itself has a didactic value which can be utilized in a thematic park in order to improve the knowledge of users. Also mining elements (engine houses, shafts, headframes etc.) can be represented by providing their safeness and restoration; their educative and museum effect can be helpful in the reforming of the area. In this situation the didactic value can be the main value of the area which is prominent in all, or a sub-value which is auxiliary for the main value. Transformation of the ultimate land use decision to a landscape design has to be realized delicately by professions from different disciplines.

Landscape design approach, which is emerged related to phytostabilization studies in Cartagena-La Union Mining District, required associations between values and solutions. By considering this association, a general approach was tried to explain in order to light the way for similar cases.

Conceptual Landscape Design Application in Tailing Ponds

In available heavy metal distribution maps of El Lirio and El Gorguel (F.18-19) mine tailings it is possible to see nine different level polluted areas according to their heavy metal (Zn, Pb, Cd) content.

With respect to the soil plant toxicity levels, 400 mg Zn kg⁻¹, 100–500 mg Pb kg⁻¹, and 3 mg Cd kg⁻¹ [Kabata-Pendias, 2001], in El Lirio; Zn is not toxic in level 1 of the area and is partially acceptable in level 2, but in the rest of the mine tailing Zn is approximately from 1.8 to 19 times toxic for plants. Pb is not toxic in the levels 1, 2, 3, 4 and 5 of the area. However, Pb toxicity from levels 6 to 9 of the area reaches until three times more than index.
Spatial distribution of available metals in El Lirio and El Gorguel mine tailing pond

With respect to Cd amount, it is not toxic in levels 1, 2 and 3 of the area, is partially acceptable in level 4, while in the rest Cd toxicity is ranging from 2.5 to 8.3 times for the plants. In El Gorguel; Zn is not toxic in level 1 and 2, partially acceptable in 3, and in the rest almost 14 times toxic for plants. Pb is not toxic until level 7, partially acceptable in 8, and in the last level 2 times toxic. Cadmium is not toxic in 1, partially acceptable in 2, and in the rest until 4 times it seems toxic for plants.

In regard to these gradual changes of available heavy metal density of phytostabilization measures were separated into graded ranks and the areas which will serve to public use were determined. In F.18-20 toxic amount distribution of metals and the parts under toxic limits is shown. In order to observe the phytostabilization effect of native species triggered by amendments, we suggested establishing experimental trials in the most polluted parts of the tailing ponds. F.18-20 shows the proposed design of the experimental areas which are based on Mel Chin’s Revival Field [Collins, 2000; Felson and Pickett, 2005].

The aim is to reduce or eliminate the negative effects on environment and public health of the tailing ponds by creating functional and sustainable landscapes as shown in the F.18-21, which presents the ideal concept designs of tailing ponds.

In the conceptual landscape design of the ponds, only the area in which the toxicity level under limits was opened to the visitors as a resting-sitting area and viewpoint. Visitors were not allowed to enter the phytostabilization areas because of the maintenance requirement of phytostabilization processes. Beside phytostabilization plantation, the use
of native ornamental plant species was suggested, especially in non contaminated areas for several aims such as increasing attraction, redirecting of visitors. The surroundings of phytostabilization areas were closed by native ornamental plants and fences. In the most contaminated areas of the tailing pond, phytostabilization experimental areas were located in order to make investigations related to the improvement of the technique. Explanation panels of the landscape design and phytostabilization processes took place in required points. The paths were also suitable for the use of bicyclists. At the end of the paths, in the most scenic place of the area, resting and sitting areas were located. In order to provide shadow in this area, pergolas and/or gazebos were proposed. Connection with the cultural heritage was provided with the consideration of the restoration of ancient engine house and headframe.
References


