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## (6) SÃO DOMINGOS MINE WASTES PHYTOSTABILIZATION USING SPONTANEOUS PLANT SPECIES

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### 1. Introduction

Past mining activities produced large amount of waste materials which were deposited at land surface becoming sources of soil and water contamination. Frequently, these materials are physically instable due to the huge dimensions of tailing piles and their deep slopes and contain high concentrations of several hazardous chemical elements as antimony, arsenic, cadmium, copper, lead, mercury, tungsten and zinc (Abreu *et al.*, 2007, 2008, 2012a, 2012b; Ávila *et al.*, 2008; Carbonell Barrachina *et al.*, 2004; Conesa *et al.*, 2007; Rieuwerts *et al.*, 2008; Tavares *et al.*, 2008). These mine areas, often represent a serious environmental risk and can be a threat for human health. Recovery of contaminated sites is a need and a challenge.

Current engineering type remedial approaches of mine areas have been proven to be economically prohibitive, and sometimes ecologically unfriendly. These types of remediation methods for mine tailings can also, in some cases, reactivate the waste materials creating conditions for increasing acid mine generation and even for improvement of erosion conditions during the reclamation works. After excavation both the cleaned area and the repository need reclamation, besides more land is used for the removed soil deposition (Abreu & Magalhães, 2009). Therefore, lower cost and environmental friendly alternatives must be applied for mine areas recovery.

Phytoremediation is a less expensive, non-invasive, and more acceptable technology for remediation of contaminated media (soils, sediments, water, and air) that uses plants and their associated rhizospheric microorganisms (Arthur *et al.*, 2005; Pilon-Smits, 2005; Singh *et al.*, 2003). It includes a variety of techniques that takes advantage of the natural ability of plants to uptake, accumulate and/or immobilize trace elements. The benefits of phytoremediation are quite obvious as it is non-expensive and non-disruptive to the landscape and to those living near the contaminated site.

The phytoremediation techniques can be based on soils contaminants stabilization (the containment processes) or on soils decontamination (removal processes). Remediation of substrata, contaminated with trace elements, can be achieved by phytoextraction (a removal process) or by phytostabilization (a containment process) (Mendez & Maier, 2008; Wong, 2003). Phytoextraction involves the use of plants for removal or reduction

of the contaminants by plant uptake and translocation to the aboveground biomass, which is then harvested for processing. Phytostabilization uses plants to convert soil trace elements into less mobile forms, but not remove these elements from the contaminated site. Phytostabilisation has the advantage, over phytoextraction, to eliminate the need of treating harvested shoot residues as hazardous waste.

Phytostabilization is a technology which aims a sustainable mining rehabilitation, based on the use of appropriated plant species to immobilize contaminants in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants, reducing or eliminating the risk to both human health and the environment (Abreu & Magalhães, 2009; Cunningham *et al.*, 1995; Padmavathiamma & Li, 2007; Pilon-Smits & Freeman, 2006; Wenzel *et al.*, 1999). This is achieved using specific tolerant plants and can be improved by applying soil amendments in order to enhance the biogeochemical processes in soils that can contribute to immobilise trace elements.

Phytostabilization is based on the contaminants tolerance of the plant species used for successful revegetation of the contaminated area. The use of autochthones and pioneer plants is crucial on phytostabilization programs and has a number of advantages such as lower cost and impact, adaptability to mining and climatic conditions, minimal environmental disturbance, reduction of erosion, and increasing of organic matter (Abreu & Magalhães, 2009; Tordoff *et al.*, 2000; Wong, 2003). Plant candidates for phytostabilization should, preferentially, accumulate trace elements in the roots and do not translocate and accumulate high quantities of the contaminants in shoots to avoid further transfer into the food-chain (Mendez & Maier, 2008; Wenzel *et al.*, 1999).

Considering the size of São Domingos area ( $\approx 50 \text{ km}^2$ ) affected by the old mining processes, the volume and type of waste materials, and the elemental contamination, phytostabilisation should be considered one of the best strategy for recovering the wastes and soil characteristics and diminishing the risk for human health.

## 2. Phytostabilization of São Domingos mine area

### 2.1. Soils

Soils were mainly developed on waste materials, weathered rocks mixed or not mixed with waste materials with different composition, and river bank sediments. As a consequence, soils presented a wide range of pH values (1.8 – 7.8) and, in general, low nutrient contents. Soils from the mine area are heterogeneous, due to different characteristics of original materials. They showed a wide range of total concentrations (mg/kg) of trace elements (mainly antimony (103-5640), arsenic (10-15900), copper (10-6207), lead (18-32170), zinc (31-14850)) (Abreu & Magalhães, 2009) which in the majority of the cases exceeded the normal values for a non-contaminated area of the region (Tavares *et al.*, 2008). Some soils contain high mercury concentrations (mean values 2.9-459 mg/kg), especially those collected in Achada do Gamo subarea (up to 9300 mg/kg), where pyrite was burned, and also in Telheiro soils (up to 420 mg/kg)

developed on riverbank sediments located downstream from Achada do Gamo (Quental *et al.*, 2002; Tavares, 2003; Tavares *et al.*, 2008).

Although contaminated, a great part of the São Domingos soils are relatively covered by vegetation. A sort of species in general colonizes soils developed on riverbank sediments, *gossan* materials, and mixtures of different waste materials and/or host rocks. However, slag piles and brittle pyrite are bare or contain very few plants. Species belonging to the genera *Erica* and *Cistus* have the ability to grow on these extreme substrata, presenting a good vegetative development, and without apparent signs of toxicity disorders. These species are, among the spontaneous species, the most abundant in São Domingos mine area.

## 2.2. Plants from genus *Cistus*

Plants from *Cistaceae* family (*Cistus ladanifer* L., *Cistus salviifolius* L. *Cistus crispus* L. and *Cistus monspeliensis* L.) are widespread in all the mine area growing on a diversity of substrata. *Cistus ladanifer* L. is a species that occurs in regions with climate typically Mediterranean with diverse edaphic conditions, being indigenous to Spain, Portugal and north-west Africa. It is a species well adapted to widely stress related to low water and nutrients soil availability and high levels of soil contamination in trace elements (Kidd *et al.*, 2004; Santos *et al.*, 2009). It is a shrub growing 1-2.5 m tall and wide. The flowers are 5–8 cm diameter, with five papery white petals, usually with a red to maroon spot at the base, surrounding the yellow stamens and pistils. The whole plant is covered with sticky exudates of fragrant resin (Fig. 1A, 2A).



Figure 1. *Cistus* plants growing in São Domingos mine area. (A) *Cistus ladanifer*; (B) *Cistus salviifolius*.

*Cistus salviifolius* L. is a Mediterranean shrub distributed in all Mediterranean basin occurring over a wide range of environments (Farley & McNeilly, 2000). This species grows in non-contaminated areas, but it is also well adapted to areas submitted to environmental disturbances such as recurrent fires and mine contamination. This shrub reaches on average 30–60 cm in height, with a maximum of 100 cm, the inflorescence holds one or more round flowers, long-stalked, arranged at the leaf axils. The five white petals have a yellow spot at the base, forming a corolla (Fig. 1B).

*Cistus monspeliensis* is a shrub with evergreen leaves and a hairy, glandular, sticky texture. The leaves are linear to lance-shaped, green, wrinkly, and up to 5 cm long. The inflorescence is generally a panicle of two to eight flowers, each with five sepals and white petals. It is native to southern Europe and northern Africa, in the Mediterranean forests, woodlands, and scrub ecosystems of matorral–maquis shrublands (Fig. 2A, 2B). *Cistus ladanifer* and *C. salviifolius* can be found in São Domingos mine area colonizing different substrata containing a wide range of hazardous chemical elements. They can be found even on fine slag materials, brittle pyrite and/or pyrite ashes, in general mixed with host rocks, with very high arsenic and lead concentrations (e.g. 7360 and 6000 mg/kg, respectively) and did not display visual symptoms of toxicity. *Cistus monspeliensis* is frequently observed on soils developed on riverbank sediments also containing high concentrations of trace elements (up to 3030 mg As/kg; 9210 mg Pb/kg; 496 mg Sb/kg). *Cistus ladanifer* plants can uptake and translocate to the aboveground part considerable quantities of lead (56 mg/kg (mean value) but in one some plants can attain 279 mg/kg), whereas the other *Cistaceae* species attain the lowest lead concentrations (e.g. *C. salviifolius*: 23.2 mg Pb/kg; *C. monspeliensis*: 10.3 mg Pb/kg). Nevertheless, these plants accumulate lead in root system being the concentration ratio of the element in aboveground part/root < 1. These plant species are also tolerant to arsenic, another major contaminant of the mine area (*C. ladanifer*: 14.5 mg/kg; *C. salviifolius*: 2.48 mg/kg; *C. monspeliensis*: 25.4 mg/kg). As well as for lead, arsenic was not translocated to the aerial part of the plants (Abreu & Magalhães; Abreu *et al.*, 2012a, 2012b; Santos *et al.*, 2012). Several plant communities belonging to these species can be observed near the open pit, industrial zone near the open pit - Malacate, Telheiro site, etc.



Figure 2. *Cistus* plants growing in São Domingos mine area. (A) *Cistus ladanifer* (right) and *Cistus monspeliensis* (left); (B) *Cistus monspeliensis*.

### 2.3. Plants from genus *Erica*

Two species of the genus *Erica* (Ericacea family) deserves special attention in São Domingos, *Erica australis* L. and *Erica andevalensis* Cabezudo & Rivera. The latter species was described for the first time by Cabezudo & Rivera (1980). It grows on the banks of Tinto and Odiel rivers as well as on mining tailings in the same zone being its

distribution limited, at the time, to the mining region of Andévalo (Spain). Nowadays, the species can be found in almost all mine areas of the Spanish Iberian Pyrite Belt. *Erica andevalensis* (Fig. 3A) was classified as an endangered species by the Andalusian (southern Spain) Regional Government, as its geographic distribution is limited to the pyrite mine environments (Aparício & García-Martin, 1996).

In Portugal, this species was identified in São Domingos mine for the first time by Capelo *et al.* (1998), where it grows on soils developed on the sediments along the bank of the São Domingos river that carries acid water from the abandoned mine (Abreu *et al.*, 2008) and, more recently on the slopes nearby. Several plant communities can be observed along the banks of São Domingos river, as well as at Moitinho, Achada do Gamo, between Achada do Gamo and Telheiro and Telheiro sites, etc.

*Erica australis* (Fig. 3B), the other species of Ericaceae family is endemic in the Iberian Peninsula and NW Africa. It is widely distributed in various climates and soil types, but it can also grow on soils with high concentrations of trace elements, such as As, Cu and Pb (Abreu *et al.*, 2008; Freitas *et al.*, 2004). This spontaneous shrub is very well established in São Domingos mine area, colonizing almost all kind of waste materials where it can attain up to 1–2 m high (Abreu *et al.*, 2008). Several plant communities belonging to these species can be observed near the open pit, industrial zone - Malacate, Moitinho, Telheiro sites, etc.



Figure 3. *Erica* plants growing in São Domingos mine area. (A) *Erica andevalensis*; (B) *Erica australis*.

The implantation of these plant species may be a valuable element for mining landscape restoration because of its compact growth as a shrub plant up to 1–2 m high, showing striking pink to crimson blossoms from June to December. In addition, *E. andevalensis* is the only angiosperm species adapted to extreme ecological conditions (pH<2.5, strong impoverishment in nutrients, high heavy metals content) (Soldevilla *et al.*, 1992) and it has never been observed growing out of Iberian Pyrite Belt mining habitats.

Both *Erica* species are well adapted to the extreme mine environments with low pH (3.0–4.5) and high hazardous chemical elements contamination (175–11600 mg As/kg; 25–989 mg Cu/kg; 218–24930 mg Pb/kg; 19.2–2150 mg Sb/kg; 36.4–1369 mg Zn/kg) (Abreu *et al.*, 2008). Concentrations of trace elements in the aerial tissues are, in general

higher in *E. andevalensis* (e.g. 7.8 mg As/kg; 10.9 mg Pb/kg - median values) than in *E. australis* (e.g. 3.6 mg As/kg; 8.04 mg Pb/kg - median values) (Abreu *et al.*, 2008). Besides the high concentrations of antimony in soils, plants uptake of this element is very low (< 0.2 mg/kg). Translocation of the hazardous chemical elements to the aboveground part of these plant species is < 1 which indicate that they are adequate to use in phytostabilization programs.

### 3. Conclusion

Among the plants identified in the São Domingos mine area some are autochthon and pioneer species, like those belonging to genera *Cistus* and *Erica*. In spite of the high concentrations of hazardous chemical elements in São Domingos soils/wastes none of the spontaneous plants growing in the mine area are hazardous chemical elements (mainly antimony, arsenic, lead) accumulators. The concentrations of antimony, arsenic, copper, lead, manganese and zinc in the aboveground part of the plants are, in general, below the range of domestic animal toxicity. In addition, *C. ladanifer*, *C. monspeliensis*, *C. salviifolius*, *E. andevalensis* and *E. australis* are species well adapted to the extreme conditions found in São Domingos mine area, and do not present any signs of toxicity, consequently they can be used for phytostabilization purposes. These species can be the key for stabilization and environmental rehabilitation of the São Domingos degraded and contaminated areas, because they can also contribute for ecological succession evolution by increasing weathering conditions and pedogenesis of the waste materials.

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