

# Mineral Processing Technologies for the Remediation of Soils Polluted by Trace Elements †

Carlos Boente <sup>1,\*</sup>, Carlos Sierra <sup>2</sup>, Eduardo Rodríguez-Valdés <sup>1</sup>, Diego Baragaño <sup>1</sup>, José Luis Rodríguez Gallego <sup>1</sup> and Juan María Menéndez Aguado <sup>1</sup>

<sup>1</sup> INDUROT and Environmental Technology, Biotechnology and Geochemistry Group, University of Oviedo, C/Gonzalo Gutiérrez Quirós s/n, 33600 Mieres, Spain; rodriguezreduardo@uniovi.es (E.R.-V.); diegobcoto@uniovi.es (D.B.); jgallego@uniovi.es (J.L.R.G.); maguado@uniovi.es (J.M.M.A.)

<sup>2</sup> Department of Mining, Topography and Structural Engineering, University of León, Av/Silverio Fernández Tirador, 24007 León, Spain; csief@unileon.es

\* Correspondence: boentecarlos@uniovi.es; Tel.: +34-985-45-82-03

† Presented at the 2nd International Research Conference on Sustainable Energy, Engineering, Materials and Environment (IRCSEEME), Mieres, Spain, 25–27 July 2018.

Published: 5 November 2018

**Abstract:** Soil washing is a remediation technology based on the adaptation of techniques habitually used in mineral processing to recover contaminants from polluted soils. Its main scope is the reduction of the total volume of contaminated soil, which could later be treated by biological, chemical, or thermal procedures. Since the contaminants are usually associated to the soil finer fractions, direct classification is the most widely employed technique. Moreover, other procedures, such as indirect classification, density and magnetic separation, as well as froth flotation are also extended. Soil washing is usually applied by means of on-site mobile plants which are located in the study sites. However, previously to these field applications, a detailed soil characterization and some trials are required in order to optimize the process. In this work, soils affected by heavy metals as a result of mining, metallurgical, and industrial activities are evaluated and pilot-scale treated. The diversity of soils and residues treated, together with the variety of the methodologies employed enabled the elaboration of a general feasibility protocol.

**Keywords:** soil pollution; mineral processing; soil washing; heavy metals

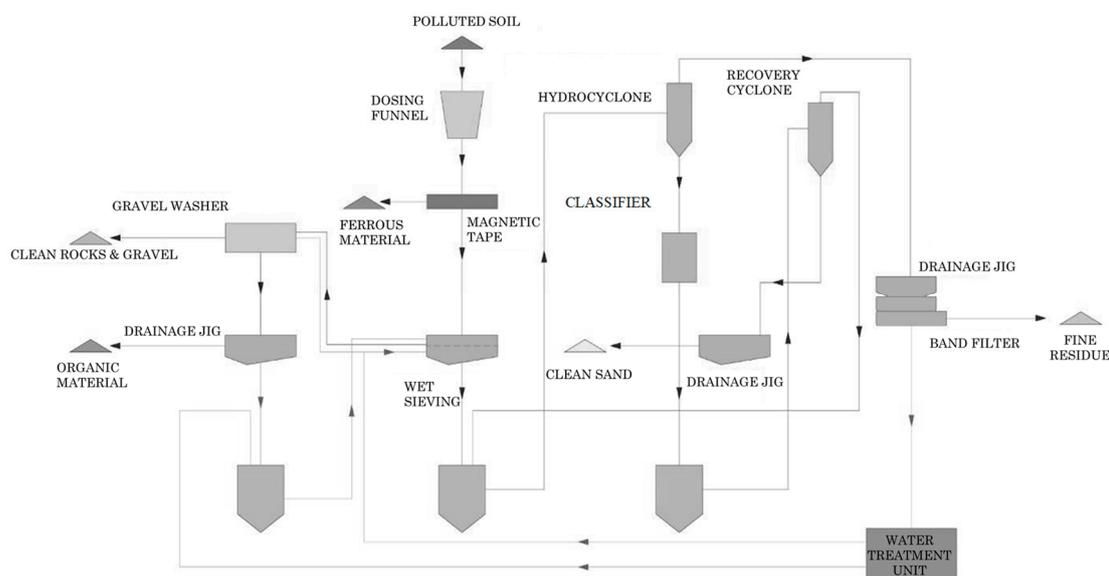
---

## 1. Introduction

There are three main alternatives to dealing with polluted soils, namely [1]:

- Isolation/landfill transportation: Conceptually cannot be categorized as remediation procedures, since they do not remove the pollutants from the soil or change its physicochemical characteristics.
- Solidification/stabilization: Solidification encapsulates the waste to form a solid material. Stabilization converts the contaminants into less soluble, mobile, or toxic forms.
- Pollutant removal: This group of technologies can be divided, in its turn, in:
  - Physicochemical: They remove, extract or transform the pollutant via physicochemical procedures.
  - Thermal methods: They warm the contaminant up to high temperatures in order to destroy or immobilize it.
  - Biological methods: They use the activity of living organisms (plants, fungus and bacteria) to degrade or accumulate the contaminants.

Regarding the physicochemical methods, they can be divided into: a) physical soil washing, which exploits the differential physical properties (size, density and magnetism) of the soil itself and between the soil and the pollutants; and b): chemical soil washing, which employs chemical agents such as acids, bases, solvents or surfactants (Figure 1). In the first case the aim of the process is the reduction of the total volume of polluted soil, in the later the complete removal of the pollutants [2].



**Figure 1.** Scheme of a mobile plant of soil washing (Courtesy of Soldec Tecnologías Ambientales).

## 2. Experiments

In this work, a protocol for pilot-scale soil washing studies is presented. This methodology has been developed on the basis of different case studies covering a wide range of both soils and pollutants. The most relevant are:

- Soils and sediments polluted by As and other heavy metals in the surroundings of the Los Ruedos abandoned mine (Asturias, Spain) [3].
- Soils and sediments polluted by As, Hg and other heavy metals in the surroundings of the former La Soterraña mine and metallurgical plant (Asturias, Spain) [4].
- Soils polluted by pyrite ashes from the former fertilizers plant of Nitrastur (Asturias, Spain) [5].
- Soils by Pb and other heavy metals from different environments affected by the mining and metallurgical activities in the Linares mining district (Andalucía, Spain) [6].

## 3. Results

### 3.1. Protocol

All things considered, we suggest a five-steps protocol, which includes:

- I. Representative samples obtention. Soil are extremely heterogenous so this steep is key for the rest of process.
- II. General pedological study: The recommended parameters include: Texture, structure, density, field capability, total nitrogen, organic matter, C/N, pH, electrical conductivity, total carbonates, extractable bases (Na, K, Ca, Mg) and effective cation exchange capacity (sum of cations + exchangeable Al).
- III. Grain size characterization: The granulometric fractionation (<63; 63–125; 125–500; 500–2000; 2000–4000  $\mu\text{m}$ ) should be obtained by wet sieving in order to improve classification efficiency which might be hindered by the presence of clays. The end of these fractions would not only be the obtention of the granulometric curve, but samples supply to further chemical analysis and mineralogical observations.

- IV. Study of chemical parameters: This steep would include an exhaustive study of the typology, evolution and origins of the pollutants present in the site. The characterization would encompass the determination of metal concentrations, sequential extraction, chemical speciation, etc.
- V. Mineralogical study: Predominant mineral species could be determined in soils by X-Ray diffractometry. Additionally, petrographic microscope and scanning electron microscope observations would aid in mineral species determination (sulphides, oxides, etc.) and liberation degree assessment.
- VI. Physical separation feasibility assessment: Apart from the previous, a complete mineral processing feasibility study would be required. This would include:
  - Milling study: Although milling previous to soil washing makes the process expensive, it is for this precise reason that Bond mill tests should be performed if this process is suspected to be necessary for the separation process.
  - Classification: Direct classification with screens and trommels, as well as indirect by sedimentation and hydrodynamic classification with hydrocyclones.
  - Gravimetric study: Its aim is to determine, for each size fraction, the feasibility of density separation. It is carried out through heavy liquid separation (HLS) or direct use of density separators: shaking tables, spirals, jigs, multigravimetric separators (MGSs), etc.
  - Magnetic susceptibility study: Each grain size fraction could be subjected to magnetic susceptibility determinations in order to assess the magnetic separation feasibility. Alternatively and complementary direct tests with dry-/wet- and high/low- magnetic separators are advisable.
  - Pilot scale tests: In accordance with the previous tests, a complete lab plant should be constructed so the results could later be scaled-up to the industrial plant.

### 3.2. Treatment Example

For instance, for the particular case of Olicio (Asturias, Spain) the following recommendations were obtained after applying the protocol. Soils showed a notable content of As and Hg (up to 200 and 300 mg/kg in some areas) as a result of lixiviation and dispersion processes of materials wasted in the dump and abandoned for more than 40 years. Grain-size fractioning via wet sieving and chemical analysis revealed high concentrations of heavy metals in the finest fractions (< 125  $\mu\text{m}$ ). These results were complemented with a specific gravity study and magnetic separation assessment. The integration of all this information eased the design of a pilot-scale diagram [7]. The strategy mainly consisted in wet high intensity magnetic separation (Wet-HIMS) for >125  $\mu\text{m}$  particles, combined with hydrocycloning for the <125  $\mu\text{m}$  fraction.

## 4. Conclusions

Physical soil washing is a technology that concentrates the contaminants in a small volume of soil, leaving most of the soil matrix with a minor concentration of them. The physical soil washing proposal is based on the use of mineral processing technologies which were historically used by the mining industry to separate the ore from the gangue. It differentiates from chemical soil washing in the fact that almost none chemical additives are used and there is neither chemical transformation of the pollutants nor of the soil. To meet this end, the process combines attrition, classification, gravity and magnetic separation.

In this context, it is recommended to perform a study of the soil properties and separation feasibility that will finally lead to the pilot-scale tests. This kind of study is complex, involving the use of a diversity of techniques difficult to master in conjunction, so a feasibility protocol has been established. Its advantages are evident: eases the implementation and increases laboratory and plant efficiency thus reducing costs. All things considered, the proposed protocol proved to be appropriate at a number of contaminated sites.

**Author Contributions:** C.B., D.B., C.S., E.R.-V. and J.M.M.A. conceived and designed the experiments and gathered the information, C.S. designed the protocol, J.L.R.G. and C.B. wrote the manuscript.

**Acknowledgments:** Carlos Boente and Diego Baragaño obtained a grant from the “Formación del Profesorado Universitario” program, financed by the “Ministerio de Educación, Cultura y Deporte de España”.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Sharma, H.D.; Reddy, K.R. *Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies*; John Wiley & Sons: Hoboken, NJ, USA, 2004.
2. Dermont, G.; Bergeron, M.; Mercier, G.; Richer-Lafleche, M. Soil washing for metal removal: A review of physical/chemical technologies and field applications. *J. Hazard. Mater.* **2008**, *152*, 1–31.
3. González-Coto, F.; Sierra, C.; Villa, R.; Menéndez-Aguado, J.M.; Gallego, J.R. Textural distribution of arsenic and heavy metals in soils affected by abandoned mining works: Consequences for soil washing. In Proceedings of the 8th International Scientific Conference on Modern Management of Mine Producing, Geology and Environmental Protection, SGEM, Varna, Bulgaria, 16–20 June 2008; pp. 2349–2354.
4. Sierra, C.; Menéndez-Aguado, J.M.; Afif, E.; Carrero, M.; Gallego, J.R. Feasibility study on the use of soil washing to remediate the As-Hg contamination at an ancient mining and metallurgy area. *J. Hazard. Mater.* **2011**, *196*, 93–100.
5. Boente, C.; Sierra, C.; Rodríguez-Valdés, E.; Menéndez-Aguado, J.M.; Gallego, J.R. Soil washing optimization by means of attributive analysis: Case study for the removal of potentially toxic elements from soil contaminated with pyrite ash. *J. Clean. Prod.* **2017**, *142*, 2693–2699.
6. Sierra, C.; Martínez, J.; Menéndez-Aguado, J.M.; Afif, E.; Gallego, J.R. High intensity magnetic separation for the clean-up of a site polluted by lead metallurgy. *J. Hazard. Mater.* **2013**, *248–249*, 194–201.
7. Boente, C.; Sierra, C.; Martínez-Blanco, D.; Menéndez-Aguado, J.M.; Gallego, J.R. Nanoscale zero-valent iron-assisted soil washing for the removal of potentially toxic elements. *J. Hazard. Mater.* **2017**, *350*, 55–65.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).