

### **Innovative Approaches to Remediate Waterways Contaminated with Mercury in a Mining Area in the Iberian Pyritic Belt, Southwest Portugal**

Conference

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Session

#### Part of - Field-Scale Application of In Situ Treatment Technologies

#### **Track: E4. Field-Scale Application of In Situ Treatment Technologies**

#### **Background/Objectives**

Heavy metal pollution is the biggest environmental issue facing the mining industry worldwide. Whenever the target is metal ores, it is generally associated with acid mine drainage (AMD), a multi-factor pollution formed from complex chemical, physical, and biological interactions that takes place under ambient conditions in abandoned and active mines. In areas impacted by mining of metallic sulphides, mercury (Hg) is one of the most critical contaminants in the environment, due to its potential toxicity and the ease with which it leads to widespread contamination over a wide area. This is the case of mining areas in the Iberian Pyritic Belt (IPB), a well-known volcanogenic massive sulfide mining district of worldwide significance in southwest Europe, where many abandoned mines prevail, leaving behind large accumulations of oxidizing sulfide-bearing mine wastes, without suitable corrective measures. One of the most serious examples in Portugal is Caveira mine, where the occurrence of stable forms of Hg reported at the surface around the mine is responsible for generating Hg-rich fluxes of AMD that represent a potential focus related to water quality degradation. The main purpose of this study is to assess the present impact of Hg on local populations around Caveira mining area through (1) the assessment of the most potentially mobile and/or toxic fractions of Hg in the sediments of the aquatic systems in the surrounding area, and (2) based on the greater or lesser mobility of Hg, to test the effectiveness of different types of geomaterials in retaining Hg from the drainage water and which could also be used as cover materials in areas of sediments with a higher degree of contamination.

## **Approach/Activities**

Sediments were collected in the winter of two consecutive years (2022, 2023), with 2022 corresponding to a very dry winter and 2023 to a rainy winter, reflecting a scenario of climatic disruption over one year. Total mercury was determined in samples stored at about 4°C using a mercury analyzer (NIC MA-3000) based on thermal decomposition, gold amalgamation, and cold vapor atomic absorption spectroscopy detection. Given that contents of total Hg in sediments do not provide sufficient information on potential toxicity in water lines, the evaluation of Hg contamination was complemented with the knowledge of the chemical forms in which this element occurs in sediments using a sequential extraction method, i.e., subdivide the Hg content of the samples into four fractions with different solubility: mobile (M), semi-mobile (SM), non-mobile (NM) and residual (R) with toxicity decreasing in this order. A laboratory-scale assessment was conducted to evaluate the effectiveness of different types of geological and waste materials (limestone and marble powders, Fe-oxides, clays, terra rossa, cellulose, biochar, activated carbon) in increasing pH and retaining Hg from the acid drainage water of Caveira mine. The retention capacity of the geo/waste materials in relation to Hg was determined by analyzing the cation exchange capacity, kinetic tests and simulation of “ponds” containing different proportions of geo/waste materials: mining water.

## **Results/Lessons Learned**

Sediments of the streams that receive the percolating water from the tailing's piles showed very high values for Hg (50-340 µg g<sup>-1</sup>). Hg is mostly distributed between the semi-mobile and non-mobile fractions, which correspond to less toxic and more stable forms. The average distribution is around 40% for each of the two fractions, with less than 1% occurring in mobile forms and a negligible proportion (< 20%) in the residual fraction. Kinetic tests and comparative analysis of the Hg content of the mining water before contact with the materials and after 10 days of contact showed that almost all of the Hg was retained by the activated carbon, followed by bentonite clay and cellulose. Cellulose, limestone and marble powders were the most effective materials in increasing pH. Control of sediment contamination (excavation, capping) should only be carried out after intervention in the upstream areas of the tailings piles. Before entering the streams, a technology should be applied in the confluence of drainage water fluxes to increase the pH (in conditions of extreme acidity, metals will not be able to be adsorbed by any material) through a pond with one of the most efficient materials for increasing the pH at the bottom, followed by another pond or permeable reactive barrier with layers of materials that have shown the greatest capacity for

retaining other polluting metals (Cu, Pb, As) - cellulose-lime powder, and a layer of activated carbon for retaining Hg.

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