Environmental Challenges and Remediation Operations at the Former Antimony-mine of Le Cetine di Cotorniano (Tuscany, Italy): Monitoring and Water Treatment Solution at Laboratory and Field Scale

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Abstract

The main criticality at the former Sb-mine of Le Cetine (Tuscany, Italy) is the high content of Sb in surface and shallow ground waters (up to 24 mg/L). To minimize the Sb concentration, a laboratory-scale Permeable Reactive Barrier (PRBL) was built to mimic the effect of a full-scale PRB, which is expected to be operative in the forthcoming months to abate the initial Sb content up to 75%. A kinetic model to verify the fate of Sb into the PRB is presented and highlighted that the minimum residence time of waters to reduce Sb in PRB is 168 hours.

Keywords: Antimony, kinetic reactions, geochemical monitoring, permeable reactive barrier

Introduction and study area

The exploitation of Sb at Le Cetine di Cotorniano mine (Southern Tuscany, Italy, Fig. 1A) began in 1878 and ceased in 1948 (Menchetti *et al*. 2015). Over time, even though the Sb demand was mostly related to weapons manufacturing, the mining activity was discontinued due to poor technology and complexity of the geological environment. The Le Cetine mine is part of a series of epigenetic Sb-rich ore deposits characterizing the southern part of Tuscany and generated by hydrothermal fluids related to the "Tuscan Magmatic District". These deposits are located on a structural high mainly due to direct and oblique faults, developed after post-collisional extensional tectonic activity (Middle Miocene) (Menchetti *et al*. 2015). In particular, the mine expanded at the contact with the Calcare Cavernoso Fm (CC, a Rhaetian vacuolar dolomitic limestone) where an intense silicification produced jasperoids. Permian siliceous schists and Oligocene-Cretaceous Ligurian and Sub-Ligurian Units are unconformably under- and overlying CC, respectively (Menchetti *et al*. 2015). The latter two formations are made up by ophiolitic fragments, clays, gabbro, and marls (Fig. 1B). The mineralization, with a content of Sb between 5 and 50%, mainly consisting of stibnite (Sb_2S_3), was found within the jasperoids. Sometimes, stibnite and calcite veins were recognized in fractured areas or within non-silicified dolomitic zones. Where altered, stibnite turns into Sb-oxides and sulfates (Menchetti *et al*. 2015). Many Sb bearing minerals, including cetineite (a Sb-oxysulfide hydrate: $NaK_5Sb_{14}S_6O_{18}(H_2O)_6$, Sabelli and Vezzalini, 1987), cervantite (Sb^{3+} Sb^{5+} O_4, first reported by D'Achiardi, 1901), onoratoite ($SbO_{11}Cl_2$, Belluomini *et al*. 1968), and other minerals e.g. rosenbergite ($AlF[F_{0.5}(H_2O)_{0.5}]*H_2O$, Omi *et al.* 1993) and dacostaite ($K(Mg_2Al)[Mg(H_2O)_6]_2(AsO_4)_2F_6*2H_2O$, Biagioni *et al.* 2025), have been found over the years in this mine. The Corsaioli Creek (Fig. 1B) is the main receptor of the surface run-off of Le Cetine, limiting the mining area to the south, and it flows into the main watercourse in the study area: the Rosia River (Fig. 1C).

The high secondary permeability of CC favors the infiltration of meteoric waters circulating on the surface. This indeed provokes an irregular inflow. In particular, during the summer months (July to September), little or no water is feeding the Corsaioli Creek and the few occurring springs. The absence of water in the mining system was both an advantage (the tunnels were not flooded during mining operations) and a disadvantage (rainwater collecting areas were placed and used for various mining operations, Menchetti *et al.* 2015). Given the high solubility of Sb minerals, from a geochemical point of view, the lack of water is beneficial. Issues arise when mineralization in streams or mining tailings interact with meteoric and run-off waters in autumn-winter months. During these periods, Sb concentrations in surface water greatly exceeded the threshold concentration (CSC) of 5 µg/L for surface water imposed by Italian law (Lgs D. 152/06). In 2011, a preliminary characterization plan was carried out for both soils and waters from the mining area, which led to define an exhaustive reclamation project that is currently going on. Among other reclamation operations, the project includes the reshaping of the mine tailings, to be covered by an impermeable capping, followed by the construction of a reactive permeable barrier (PRB) to drain surface and ground

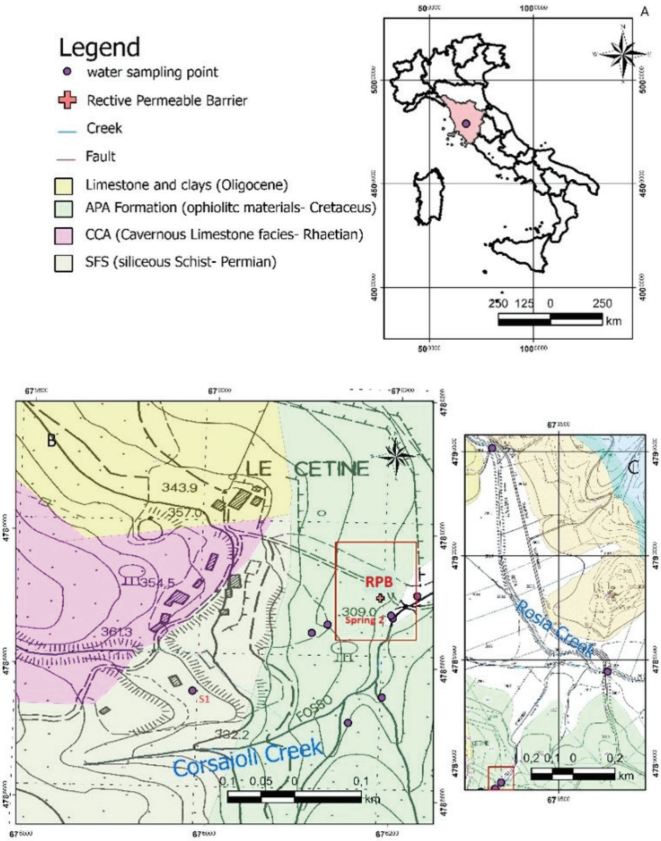

Figure 1 *Simplified geological maps of Le Cetine di Cotorniano mine. The violet circles represent the water sampling points and the red cross the location of the Permeable Reactive Barrier.*

waters. The PRB to abate Sb is expected to be done early this year. Since June 2024, a monthly geochemical survey of the waters within the mining area and nearby (violet circles in Fig. 1B and 1C) has been carried out and a PRB, at laboratory scale, was built to test the efficiency of the PRB on-site.

The aims of this work were to: i) geochemically characterize the surface and ground waters in the Le Cetine mine, ii) investigate the reaction kinetics of the various minerals characterizing the study area to optimize the PRB functionality with the aim to reduce the Sb concentrations by least 75% before discharging the treated waters into the local watercourse.

Methods

For the geochemical monitoring of the waters from the former mining area, ten sampling points were selected, as follows: two piezometers (i.e., S1 in the tailing body, and S6 at the foot of the tailing body); one spring; seven surface waters, i.e., five from the Corsaioli Creek (respectively named F1, F2, F3, FCP, F4) and two from the Rosia Creek (one upstream and one downstream after the confluence of the Corsaioli Creek). During the various surveys, F1, S6, and the spring could not be sampled because they were dry. In October 2024, however, a new spring, named "spring 2", was found with a flow rate of 0.1 L/min. For each sampling, measurements of pH, electrical conductivity (EC), redox potential (Eh), temperature (T), and in the case of sample S6 hydraulic head, were carried out in situ. The main cations and anions, as well as Fe, Al, Mn, Hg, As, Sb, Se and some other trace metals, were analyzed. The software PHREEQC version 3.5.0 (Parkust and Appelo, 1999) with Minteq.v database, modified by Meloni *et al.* (2024), was used to calculate the Saturation Index (SI) and determine Sb speciation. Furthermore, four mine tailings samples (named from Cet1 to Cet4), with different grain sizes, were collected and leached (ratio soil-MilliQ-water 1:10) to study the reaction kinetics of the minerals contained in the tailings. The leaching tests were performed on the four samples after 1 hour, 1 day, and 7 days. The leaching tests were carried out progressively (from 1 hour to 7 days) on the same sample aliquot after filtration at 0.45 µm. In total, the material was leached for 8 days and 1 hour. For each leaching test, the main cations and anions, as well as the same trace elements as those measured in the water samples, were analyzed. Subsequently, the kinetic model that best represented the mineral dissolution was calculated. Additionally, by using the PHREEQC software, the reaction conditions leading to the mineral dissolution were reconstructed. This process allowed us to define the origin of the Sb-pollution in

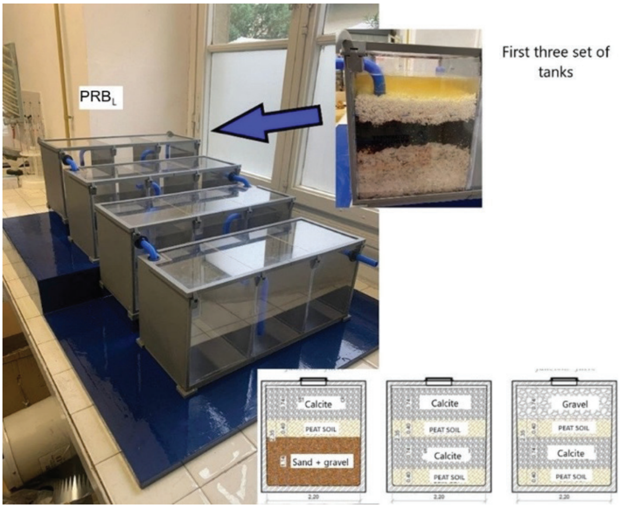

***Figure 2** Laboratory-scale Permeable Reactive Barrier (PRBL) and a schematic representation of the tanks and relative proportions of the materials to be filled with.*

spring 2, and the runoff waters that are going to be conveyed to the PRB. As part of the reclamation project, the PRB is constructed with four cascading tanks, each one divided into three smaller compartments. The first set of tanks consists of alternating layers of gravel + sand, peat soil, and calcite with mixed grain sizes (Fig. 2). The second and third sets are composed by alternating layers of peat soil and calcite with mixed grain sizes (each of this layer is repeated twice). The final set of tanks is composed by peat soil, calcite with mixed grain sizes, and a final layer of gravel. All tanks are sealed airtight to create reducing redox conditions. This model was recreated at a laboratory scale using a 3D printer (Fig. 2) and filled with the previously described materials. A peristaltic pump was used to circulate the water through the barrier by setting the flow rate to the downscaled version of the PRBL, preserving the interaction time as the water passes through the PRB (ca. 8 days).

Results and discussion

The surface waters exhibited a Ca(Mg)-HCO_3 geochemical facies. Sample S6, on the other hand, had a Ca(Sb)-SO_4 composition, while spring 2 showed an intermediate (Ca(Sb)-$HCO_3(SO_4)$) composition between S6 and the surface waters. All waters, except for the samples from the Rosia stream in July, consistently exceeded the Sb concentrations for CSC limits. Specifically, the concentration of Sb in S1 was 24,407 µg/L, whilst that of spring 2 was 10,993 µg/L. The Corsaioli creek showed a Sb content of 865 µg/L after the inflow of spring 2 into the creek. All analyzed waters were relatively low in Fe and Al (up to 220 and 68 µg/L, respectively). Notably, spring 2 and sample S1 were characterized by Fe and Al concentrations below the detection limit (5 µg/L).

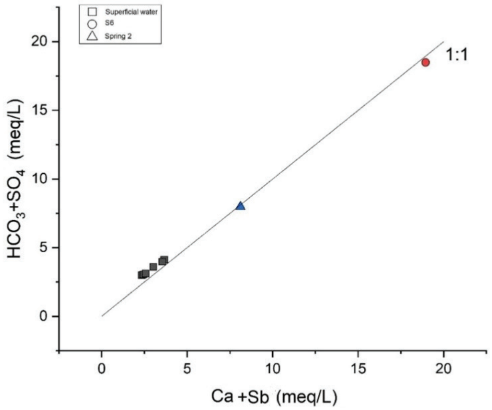

Figure 3 Binary diagram Ca+Sb (meq/L) vs. HCO_3+SO_4 (meq/L) for the October 2024 water samples. Th stoichiometric line is also drawn.

By calculating the SI of the waters and the speciation of Sb and given the generally basic pH of the waters and an oxidizing Eh (always above 200 mV), Sb was found as Sb^{5+}, in the form of romeite ($Ca_2Sb_2O_7$) or SbO_2. Occasionally, tripuhyite ($FeSbO_4$) appeared to be slightly oversaturated. If we consider Sb^{5+} dominating over Sb^{3+} and construct a binary graph of Ca+Sb vs. HCO_3 + SO_4 (in meq/L, Fig. 3, with concentrations relative to the October 2024 sampling), the sampled waters distribute uniformly along the stoichiometric 1:1 line, demonstrating that the waters derive from water-rock interaction processes involving meteoric water, carbonate, sulfide, and sulfate.

Scanning electron microscopy (SEM) of the four sampled tailings showed that antimony was found as metallic Sb, Sb bound to Ca and S (likely as romeite) and occasionally as stibnite, and Sb-oxides. However, the presence of Sb sulfosalts cannot be ruled out, as they were found in both the mine and the landfill materials. Gypsum, calcite, pyrrhotite, and pyrite (sometimes containing As) were also present.

Currently, X-ray powder diffraction (XRD) and quantitative XRF analysis are in progress. The leaching tests on the tailing samples showed a change in the geochemical facies over time, i.e., transitioning from Ca(Sb)-SO_4 to Ca(Sb)-HCO_3 (Fig. 4A,B C). Unlike Fig. 3, Fig. 4C shows a deviation of the leachate samples from the 1:1 stoichiometric line to a Ca+Sb enrichment. When Ca is removed from the graph (Fig. 4D), the samples realign along the stoichiometric line, indicating a greater contribution of Ca due to an increased presence of calcite, gypsum and romeite. From the kinetic model, it is observed that Sb follows a second-order kinetics equation (Eq. 1), while the main anion and cation components follow a first-order kinetics equation (Eq. 2):

$y = B(1\text{-}e^{(-x/c)})$ Eq.1

$y = B \times log(C \times x) + A$ Eq.2

By entering the obtained parameters into PHREEQC, it is evident that the dissolution kinetics of the minerals are governed by the dissolution of pyrite (FeS_2) and the precipitation of magnetite. Calcite buffers the acidity of sulfides (primarily Sb_2S_3 and FeS_2), raising the pH up to > 9.3.

Calcium ions are related to the dissolution of gypsum. Sulfate is also likely related to the chemical oxidation of FeS_2. In some cases, an excess of sulfate is found due to the presence of soluble salts (e.g. mirabilite, peretaite, batoniite), which immediately increase their concentration in the aqueous phase. The kinetic model indicates that after 168 hours the concentration of Ca^{2+}, Sb^{5+}, $Fe^{3+\text{ or }2+}$, SO_4^{-2}, HCO_3^- in the leachates tends to be stabilized. Therefore, this coincides with the minimum residence time of the water with a flow rate of 0.00167 L/s (i.e., the flow from "spring 2") in the PRB to achieve a reduction of Sb concentrations. To test the PRB_L, synthetic waters with increasing concentrations of Sb (i.e., 20, 50, 100 µg/L) were produced. After the required contact time with the barrier filling material had passed, an aliquot of water was collected for pH, EC, Eh, and T measurements, and main cations and anions and trace metals analysis. The water flowing through the barrier showed a reduction in Sb of approximately 75%. Tests with concentrations of around 1000 µg/L are also planned.

Conclusion

This study presented the results of geochemical surveys of surface and piezometer waters at the former Sb mine of Le Cetine di Cotorniano. The waters had high concentrations of Sb largely exceeding the Italian CSCs. The remediation project, which is still ongoing, includes the creation of a PRB to channel run-off and spring waters and to reduce Sb concentrations in the nearby river. To optimize the PRB, reaction kinetics of minerals, characterizing the mine tailings, were investigated. In addition, a laboratory-scale PRB was tested with a

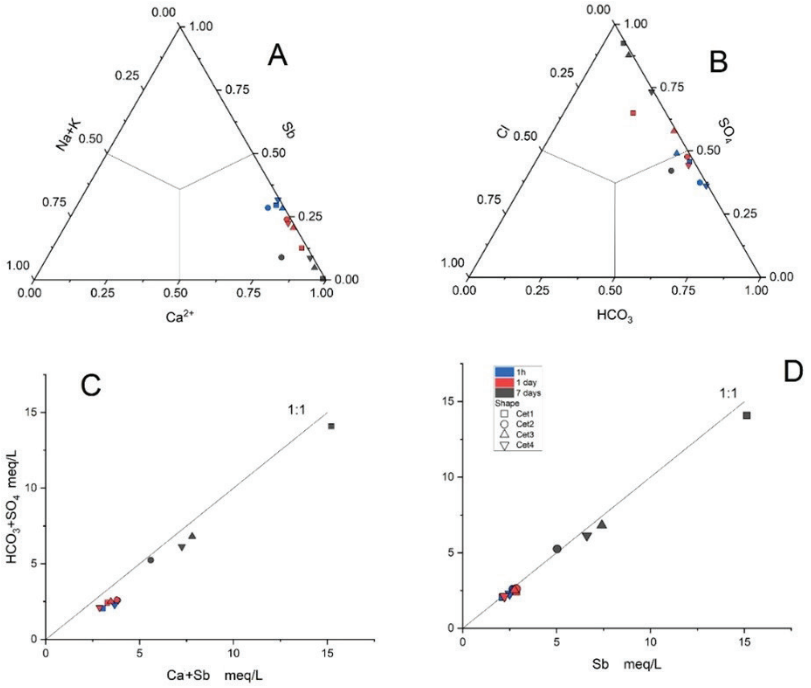

Figure 4 *A) Main cation ternary diagram, B) main anion ternary diagram, C) binary diagram Ca + Sb (meq/L) vs.* $HCO_3 + SO_4$ *(meq/L), D) binary diagram Sb (meq/L) vs.* $HCO_3 + SO_4$ *(meq/L) of the four tailing leachates.*

synthetic water at increasing concentrations of Sb to assess whether the designed PRB would be able to reduce the initial concentration of Sb. The barrier is currently able to retain approximately 75% of the Sb input. Forthcoming studies involving waters with higher Sb concentrations are already planned by also adding As and Se, the latter two exceeding the Italian CSCs. Whether the physicochemical processes that retain Sb in the barrier are related to adsorption or precipitation of mineralogical phases are also to be investigated.

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