CHARACTERIZATION OF EXTRACTIVE WASTE FACILITIES FOR SRM RECOVERY FROM MINING SITES: CASE STUDIES FROM THE SMART GROUND PROJECT

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CHARACTERIZATION OF EXTRACTIVE WASTE FACILITIES FOR SRM RECOVERY FROM MINING SITES: CASE STUDIES FROM THE SMART GROUND PROJECT

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Abstract
The paper shows the first results, arising from Smart Ground H2020 project, connected to the characterization of the Secondary Raw Materials in two selected Italian Extractive Waste facilities: Campello Monti (Piedmont) and Gorno (Lombardy). The first was important for Ni exploitation. The area is characterized by the presence of waste rock and operating residues in several extractive waste facilities. The results from the sampling campaign show that operating residues are strongly enriched in Ni, Cu, Co and waste rock in some areas are enriched in the same metals. PGE analysis shows scattered Pd and Pt enrichments. Gorno mining district was an important of Zn and Pb exploitation. The area is characterized by the presence of several EW facilities, mainly represented by waste rock deposits and tailing basins. The study shows that the RW shown a high content in Zn, often associated to Cd.

Keywords
Extractive waste facilities, secondary raw materials, Smart Ground project

1. Introduction

Raw Materials are becoming always more important for the EU economy, thus considering the increasing scarcity and raising prices, the recycling and recovery of these materials is relevant. Rational waste management practices could lead to a more efficient use of raw materials and to waste reduction. If we consider that in Europe there are between 150k to 500k highly variable landfills, the EU Secondary Raw Materials (SRM) potential is significant. However, there is no inventory available of SRM present in EU landfills and existing knowledge and reporting standards actually used seem to be inefficient [1]. In this context, Smart Ground project intends to foster resource recovery in landfills by improving the availability and accessibility of data and information on SRM in the EU, while creating synergies among the different stakeholders involved in the SRM value chain. Hence, the Smart Ground consortium will integrate all the data from existing databases and new information collected during project activities in a single EU database.

One of the main purposes of the Smart Ground project is testing some operative methodology for the pilot sites characterization as for: extractive waste facilities, industrial and municipal solid waste landfills, and construction & demolition waste treatment plant. To do this 15 pilot-sites among the five countries involved in the project have been selected. Table 1 reports the general info connected to the investigated extractive waste facilities.

Table 1: Selected landfill pilots for characterization (EW facilities). [2].

Country	Name of the Pilot	Type and content of the pilot
Italy	Montorfano mining area	Feldspar production from granite dumps exploitation.
Italy	Gorno mining district	Mine landfill content metals as Zn, Pb and possible CRM as Ge, Te, In, Cd etc.
Italy	Campello Monti mining district	Mining landfill content principally nickel, copper and possible CRM as PGE.
Finland	Aijala mining area	Waste facilities of extractive industries. Tailings from mining containing Cu, Zn, S, Ag, Au.
Hungary	Rudabánya mining area	Waste facilities of extractive industries. Complex ores containing siderite, barite, pyrite, chalcopyrite).
Hungary	Pátka mining area	Waste facilities of extractive industries. Tailings of the critical fluorite.
Spain	Los Santos mining area	Open pit Scheelite skarn deposit.

The present paper reports the first results connected to two of the selected Italian pilots: Campello Monti and Gorno, both located in the northern Italy, respectively of nickel and lead-zinc exploitation.

2. *Materials and methods: pilot site characterisation*

2.1 Campello Monti pilot site

The Campello Monti mining area is located in Strona Valley (Piedmont, Western Italian Alps), ca. 20 km from the Swiss border. In the area, the mine waste deposits are related to the homonymous nickel mine, operating intermittently from the second half of the nineteenth century to 1945. In the area were exploited Fe-Ni-Cu-(Co) magmatic sulphide deposits occurring, from the Sesia to the Strona valleys, mostly in ultramafic layers, dykes and pipes of the so called "Mafic Complex", in the Ivrea Verbano Zone (Figure 1), [3,4,5].
These deposits were exploited for nickel (average grade: from 1-2 to 0.5 wt. % Ni in the last years of activity), with an estimated production which probably never exceeded 50 short tons per year [5]. The treatment activities in the area were intensive during the II World War and included a first phase of manual sorting, outside the mine adits, followed by mechanical (grinding, milling) and chemical (flotation) dressing activities. Over the last decades, localized PGE enrichments were documented in some mineralizations [7,8,9]. There are no previous data on EW facilities present in the area.

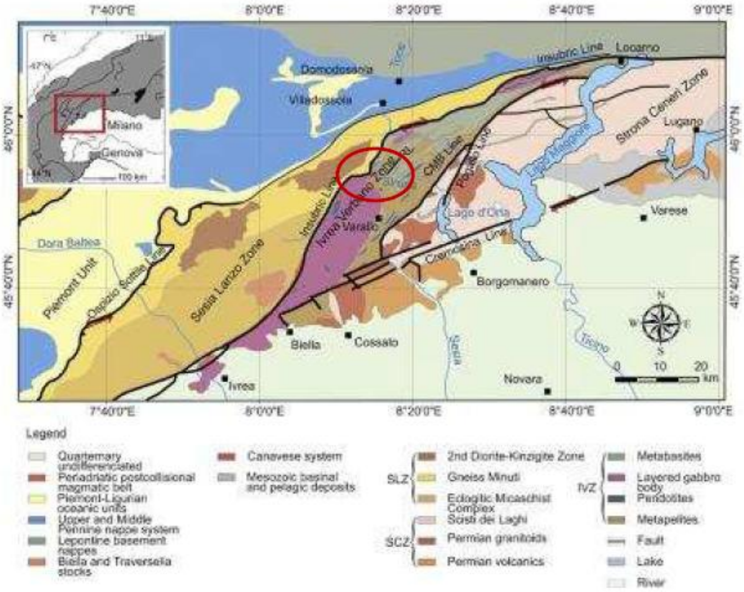

Figure 1: Tectonic sketch-map of the Central-Western Alps [10] . The ellipse shows the location of the Campello Monti area in the Western Italian Alps.

2.1.1 Field survey and sampling

The field surveys were developed into two phases:

- Phase 1: field activities, aimed at the recognition of the main characters of each waste deposit;
- Phase 2: mapping and sampling;

The preliminary field activity led to the recognition of two types of waste: waste rock (in dumps (Figure 2) and operating residues. The latter include coarse-grained accumulations of sorted ore material and fine-grained, reddish material – close to the old dressing plant – related to a first phase of treatment (Figure 3).

Figure 2 : Typical rock waste dump. The adopted sampling grid is also shown.

Figure 3 : Operating residues deposit close to the ruins of the dressing plant.

Based on these first observations, eight waste deposits were selected for characterization. All deposits were sampled, according to a protocol shared among all project partners, by adopting a grid method. Each sample was collected, due to poor accessibility in the mountain area, using hand shovel in an area of 1.5 square meters, after cleaning the sampling point from organic residues. 41 samples of rock waste and 12 of operating residues were collected.

2.1.2 Laboratory analyses

All samples were processed at the Mineral Dressing and Sampling Laboratory (Earth Science Department – UNITO) following the operative protocol shared among project partners. the samples have been characterized by:

- Petrographic characterization: performed at the Optical Microscopy and at the Scanning Electron Microscopy Laboratories (Earth Science Department – UNITO).
    - Geochemical characterization (at external lab): performed adopting the following methods: Multielements analysis of all 61 samples by ICP-MS method, in order to obtain a general geochemical screening. Analysis by ICP-OES using 4 acid digestion for samples with Ni and/or Cu exceeding the upper limit for the previous analytical package.
    - Fire Assay - ICP-MS analysis of Au, Pt and Pd of samples strongly enriched in Ni and Cu.
    - NiS Fire Assay – INAA analysis of Pt, Pd, Os, Ir, Ru, Rh, Au and Re of selected samples among those strongly enriched in Ni and Cu.

2.2 Gorno

The Gorno mining District is located in the Seriana, Riso and Brembana valleys (Lombardy, Northern Italy). The District lies in the "Lombard Basin" of the Italian Southern Alps, where a strong subsidence during Permian-Triassic time allowed the accumulation of a thick sedimentary pile, composed of Permian continental deposits overlain by shallow sea Triassic sediment [11]. (Figure 4) .

The Gorno Zn-Pb (±Ag, fluorite and barite) mining district belongs to the Alpine Type Zinc-Lead-Silver stratabound ore deposits (sub-type of the Mississippi Valley Type deposits), associated with the middle – upper Triassic carbonatic series. The mineralization mostly occurs within the "Metallifero" (i.e., "ore-bearing") Formation of upper Ladinic – lower Carnian age. The dominant distribution trend of the orebodies is approximately N-S, as tabular "columns" up to over 2 kilometers long, with a width ranging from 50 to 400 meters and thickness between 3 and 20 meters [12, 13]. The primary mineralization is mainly composed of sphalerite and galena (average Zn/Pb ratio= 5:1), ± pyrite, marcasite, chalcopyrite and argentite. A secondary mineralization is composed of oxidation products of sphalerite, i.e., Zn-carbonate and silicate. The dominant gangue minerals are calcite, dolomite and quartz (± ankerite).

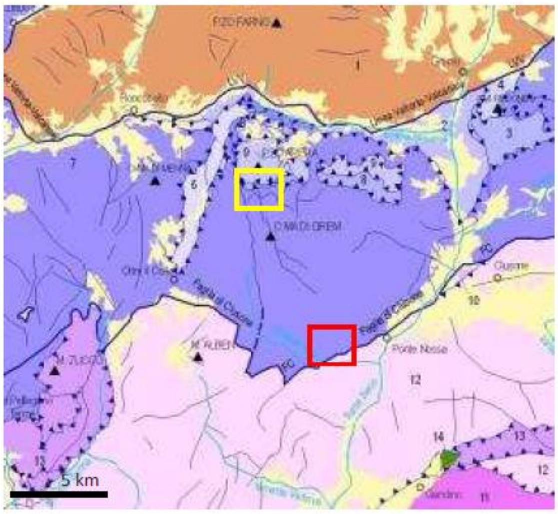

Figure 4 : Left: tectonic sketch-map of the Gorno District area [14]. The "intermediate structural units", which host the mineralizations, are shown with various shades of purple. The yellow rectangle shows the location of the Arera mining area while the red rectangle shows the location of Gorno tailings basins. Above: location of Gorno mining district in N Italy (blue rectangle).

Field survey

After a preliminary field survey, the field activity was focused on two areas:

- Arera mining area (extractive waste facilities in Oltre il Colle municipality);
- Gorno tailings deposits (Gorno municipality)

The sampling activity in Arera area was focused on 6 extractive waste facilities (rock waste deposits, Figure 5), generally located at the exit of main mine tunnels. The sampling method was shared and agreed by project partners. In particular, the rock wastes have been sampled using hand shovel, while an hammer was used where necessary. Each sampling spot covers an area of approximately 4 m^2. A total of 30 samples were collected in different EW facilities.

Figure 5 : Rock waste dumps of the Arera mining area

Sampling activity on tailings was focused on one of the tailings deposit close to the Riso river (Figure 6) in the lower part of the Riso valley. Sampling was performed by hand drilling (Figure 7), after removing of the top soil covering the tailing basin; samples of the tailing deposit were taken at different depth. 4 sampling points have been identified within deposit and a total of 18 samples were collected.

Figure 6: Gorno mine tailings deposits (rehabilited)

Figure 7: sampling and hand drilling activity

All samples were processed at the Earth Science Department, University of Torino, following a shared operative protocol; the geochemical analyses were instead performed in an external laboratory. The following geochemical methods were adopted:

- Multielements analysis of all samples by total digestion ICP-MS/ICP-OES method to obtain a general geochemical screening;
- Fusion Specific Ion Electrode-ISE method for fluorine;
- Analysis by ICP-OES using 4 acid digestion for samples with a content of Zn and/or Cd exceeding the upper limit for the previous analytical package;
- Additional analysis by IR for samples with a content of S exceeding the upper limit for the previous analytical package;
- Additional analysis by cold vapour FIMS for samples with a content of Hg exceeding the upper limit for the previous analytical package.

Also the mineralogical and petrographic characterizations have been performed: such analysis are important because the possibility of extracting a metal from a rock is strongly dependent on its mineralogical form a microstructure.

3. *Results*

3.1 Campello Monti pilot site

The main geochemical features of all samples are typical of ultramafic rocks affected by processes of exsolution and accumulation of sulfide liquid, as typical of Ni-sulfide magmatic mineralization worldwide. The SRM potential of waste materials connected with Ni-sulfide mining is represented by metals as Ni, Cu, Co and (possibly) PGE.

Resuming the results of samples analysis, variable, but generally high to very high Ni, Co, Cu and relatively high Cr and Mn contents are found. The REE are low in the investigated samples and PGE enrichments, where present, are strongly localized.
In particular, the whole rock geochemistry shows that the rock waste materials are characterized by up to 0.5 wt% Ni, 0.1 wt% Cu and 0.02 wt% Co. The operating residues, especially the fine grained ones, show even stronger metals enrichments: up to 2.4 wt% Ni, 0.9 wt% Cu and 0.1 wt% Co.

The mineralogical and petrographic characterization on the coarse fractions confirms that these materials are composed of mafic silicates associated with a variable amount of metal sulfides. The mineralization is made of sulfides consisting of pyrrhotite, pentlandite, chalcopyrite and minor cubanite. Pentlandite, the main ore mineral, generally occurs as subhedral to euhedral crystals (ca. 0.1-2 mm across) enclosed by anhedral pyrrhotite (± chalcopyrite).
The electron microprobe study shows that:
- pentlandite is the main Ni(±Co) mineral, with a Ni content of 32.5-33.6 wt.% and up to 1.4 wt% Co;
- Cu occurs as chalcopyrite ± cubanite (ca. 34.5 and 23.4 wt. % Cu, respectively).

Furthermore, the very fine-grained (<1–100 micron-m across) operating residues are composed of: iron oxides/hydroxides and sulphate; Mg-rich silicates; partially oxidized pyrrhotite, pentlandite and chalcopyrite; covellite; native sulphur. Ni occurs in partially oxidized pentlandite (23.2 to 36.0 wt. % Ni, up to 1.8 wt. % Co), while Cu may occur both in chalcopyrite and in chalcocite (Cu_2S, ca. 80 wt. % Cu).

3.2 Gorno
A strong difference is observed between the waste rock samples (Monte Arera area) and tailings deposit.
The waste rocks are characterized by:
- strong to very strong Zn concentration (avg. content of each dump: 3.9 to 12.8 wt.%);
- relatively high Cd (avg. content: 123 - 366 ppm) and moderate Ga values (avg. content: 7 – 21 ppm);
- very low Ge and In content (mostly <1 ppm);
- low Pb and Ag content.

The tailings show instead:
- lower Zn (avg. content: 0.6 wt%), Cd (avg.: 29 ppm) and Ga (from <0.1 to 7 ppm) contents;
- a Pb content much higher than the waste rocks, but still rather low as absolute values (avg.: 0.14 wt%).

Considering the industrial minerals fluorite and baryte, their relative abundance can be inferred by the F and Ba analyses. The fluorine content variable, but moderately high (0.01 – 0.12 wt.%) and no fractionation between waste rocks and tailings is observed. Conversely, the Ba content is low in the rock waste (avg.: 22 ppm) and strongly enriched in the tailings (avg.: 979 ppm).
Zn is positively correlated with Cd and Ga, which occur as minor elements in sphalerite.

As for mineralogical and petrographic characterization we can say that, in the Gorno District, zinc can occur as sulfide or oxide ore; historically the oxide ore has been preferred, and for this reason some EW facilities can be rich of sphalerite. Such characterization was performed by optical and electronic (SEM-EDS) microscopy.

In the waste rock deposits both primary and secondary ore occur. In the primary ore Zn occurs as sulphide (sphalerite). ICP analysis of a pure sphalerite concentrate shows that is almost devoid of iron, but contains Cd in significant amount (1970 ppm). The secondary ore ("calamine") is typically composed of very fine-grained intergrowths of Zn-carbonate (smithsonite and/or hydrozincite) and hemimorphite. A rough estimate of the relative proportions of sphalerite and oxide, calculated from the geochemical analyses, suggests that in the rock waste most of the zinc is contained in sphalerite, even if some zinc "oxides" also occur and are dominant in few samples.

4. Conclusions

Smart Ground project has allowed to investigate several pilot sites connected to EW facilities: the characterization of the selected pilot site was useful to test shared protocols for site and materials investigation, in order to obtain preliminary data about the SRM present in waste and an estimation of the SRM potential to exploit. The first pilot-testing site (Campello Monti pilot), after a field and laboratory activity, clearly shows that Ni, Cu and Co (± PGE) represent potential SRM in the mineral waste. In fact, not only these metals always occur well above the typical rock content, but – above all - within minerals (metal sulfides) suitable for metals recovery. The metals distribution is not homogeneous, but strong differences occur among the different waste deposits.

In the second pilot-testing site - Gorno mining district, mineralogically different from the previous one - our data suggest that Zn and Cd (± Ga) represent potential SRM in the mineral waste. Other metals which may be present in sphalerite, like Ge and In, are instead in extremely low concentration. Strong differences occur between rock waste and tailings: despite of the obvious variability, all the analyzed rock from waste dumps are enriched in Zn (+Cd±Ga), while the tailings are strongly depleted in the same metals.

This study emphasizes the complexity of the SRM estimation in waste deposits connected with the extractive industry, suggesting that a thorough characterization of each waste deposit is a prerequisite for a reliable resource evaluation.

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