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CHARACTERIZATION OF SECONDARY RAW MATERIALS FROM MINE WASTE: A CASE STUDY FROM THE CAMPELLO MONTI Ni±Cu±Co±PGE MINING SITE (WESTERN ALPS, ITALY)

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SUMMARY: The present research is within the framework of Smart Ground project (G.A. 641988), which intends to foster resource recovery from different types of waste deposits by improving the availability and the accessibility of data and information on secondary raw materials (SRM) in the EU. The evaluation of the SRM potential requires the estimation of a number of factors which must include technical, economic and environmental considerations. A first factor is a thorough characterization of the waste material, that can be performed with different methodologies, depending on the waste typology. This issue has been addressed, within the project, on a number of pilot sites which include municipal solid waste landfills, industrial landfills and waste deposits related to the extractive industry. The present study shows the methodologies adopted for waste characterisation (sampling protocols and analysis), with the aim of evaluating the secondary raw materials potentiality from extractive waste facilities. In particular the study has been carried out on the extractive waste facilities of the Campello Monti Ni+Cu (±Co±PGE) mining site (Western Alps, Italy).

1. INTRODUCTION

1.1 Issues and challenges connected to extractive waste and extractive waste facilities

During the last decades the mining industry has been mainly considered for the environmental problems associated to Raw Materials (RMs) exploitation and Extractive Waste (EW) facilities management, rather than for the fundamental role that RMs perform in developed society. The legislation and the actions associated to mining sectors have brought to a general negative opinion; moreover, the common thought that mining industry represents a risk for the environment has been facilitated and disseminated thanks to accidents that occurred at EW facilities (Guerrero et al., 2008; Luino & De Graff, 2012; Dash et al., 2016; Petticrew et al., 2016). This approach is clearly visible when observing the quantity of researches connected to environmental issues compared to those connected to EW recovery (Rybicka, 1996; Banks et al., 1997; Fields, 2003; Samecka-Cymerman & Kempers, 2004; Talavera et al., 2016).

But RMs and Critical Raw Materials (CRMs), are crucial for EU economy and for guaranteeing and improving citizens life quality. Thus, their supply needs to be programmed at
national and EU level, in order to guarantee the economic development of each country. At present, developed countries have found more profitable to import RMs from developing countries or from countries, as China, India, Turkey, etc., where the RMs are abundant and their exploitation is easier (also due to less strict regulations for environment and social rights and lower salaries).

From the beginning of the XXI century something has changed in EU policy, and RMs supply came to the forefront, with a consequent new EU funding program (H2020) and new roles to share as for RMs exploitation. The European Commission's actions to ensure a sustainable supply of these materials can be divided into two interlinked parts: the Raw Materials Initiative and the European Innovation Partnership (EIP) on Raw Materials. In particular, the Raw Materials Initiative, adopted in 2008, set out a strategy for guaranteeing the access to RMs in the EU. This strategy, which covers all RMs except the ones connected to agriculture and to fuel supply, is based on three pillars, which aim at ensuring: i. fair and sustainable supply of RMs from global market; ii. sustainable supply of RMs within the EU; iii. resource efficiency and supply of Secondary Raw Materials (SRM) through recycling.

The EW facilities often occupy large areas, and can lead to negative impacts on soil, water and air quality and on human health, that have to be evaluated (Tiruta-Barna et al., 2007). A sustainable and efficient waste management and recovery is based on the reduction of the environmental impact and on the improvement of their market and environmental acceptability. If we treat and recover fluent waste, we preserve different areas from the presence of new EW facilities. Furthermore, on the basis of suitable results it is possible to think about the recovery and treatment of huge quantity of SRMs/CRMs from historic EW facilities. These approaches are in line with the 3rd pillar of the Raw Material initiative. Indeed, the EU guidelines aim to the exploitation, based on environmental protection, of any kind of material which can be recovered and recycled, with consequent natural resources preservation (Dino et al., 2016). To reach the effective recovery of such materials, operators, public bodies and small and medium enterprises (SME) associations have to encourage the use of waste, also giving practical examples of implementation of the “End of The Waste criteria”, lined by the EU Commission.

1.2 Potentialities and issues connected to EW exploitation

In 2012 the extractive industry represented the second most important sector in terms of waste quantities produced in the EU-27 (29%, i.e., 734 million tons), after Construction and Demolition Waste (C&DW) (Eurostat Statistics, 2012). Total amount of mining waste stored in whole EU exceeds 5.9 billion tons (BRGM, 2001). As introduced above, the necessity to reduce the use of non-renewable natural resources and, at the same time, to minimize the negative impacts on environment has led to an increasingly high interest in recovery and recycling.

However, the SRM estimation of waste deposits connected with the mining activity is not straightforward. A pre-requisite is a reliable characterization of waste deposits: in other words, a comprehensive characterization of all the deposits. Over the last decades, several studies have dealt with the issue of extractive waste characterization. However, most studies addressed the problem from the environmental point of view only (e.g., Jamieson et al., 2015, with refs.). Moreover, studies were generally performed with a strictly disciplinary approach, geochemical (e.g., Alpers & Nordstrom, 1999; Al et al., 1994, with refs.) or mineralogical (e.g., Blowes et al, 2013; Corriuveau et al., 2011; Jamieson et al., 2015, with refs.) and, being focused on the environmental impact, were often concentrated on tailings.

Aim of this paper is to propose a multidisciplinary approach for EW characterization, which have been tested in the former Campello Monti mining site.
1.3 Campello Monti case study

Resource efficiency and supply of SRM through the recycling is the core of the Smart Ground H2020 project (G.A.641988), which aims at storing the existing standards for RMs and waste inventory, and at developing a new methodology for data gathering (about sites and materials characterization), validated on selected pilot sites (15 in total, including EW facilities and Municipal Solid Waste (MSW) Landfills).

One of the investigated pilot sites has been Campello Monti (Verbano Cusio Ossola district, Piedmont Region, Northern Italy). Campello Monti village is located at 1305 m a.s.l. in the upper Strona Valley, near the Lakes District (Maggiore Lake and Orta Lake) (Fig. 1). Characterized by typical alpine mountain scenery, the area is well known as a touristic attraction, being an important center for trekking along the “Altavia” alpine walk path and hosting a Walser historical village.

The former Campello Monti mine is located on the left side of the valley just upstream of the homonimous village, at altitude between 1300 and 1600 m a.s.l. About fifteen small Fe-Ni-Cu(-Co) sulphide deposits occur in the investigated area and nearby, between the Sesia and Strona valleys. They were exploited for nickel, with an estimated production which probably never exceeded 50 short tons per year.

2. GEOGRAPHIC AND GEOLOGICAL SETTING

The Campello Monti area is located in the Ivrea Verbano Zone, a tectonic unit which extends, from NE to SW for about 120 km from Locarno to Ivrea, with a maximum width of 14 km (Fig. 1) and is considered a classic example of lower continental crust which has not been affected by the alpine metamorphism. The Ivrea Verbano Zone consists of three main Formations: Mantle Tectonites, Mafic Complex and Kinzigite Formation (Garuti et al., 1980). The Mantle Tectonites, which occur within the Mafic Complex, are considered obducted fragments of subcontinental mantle. The Mafic Complex, made of gabbroic to leucodioritic rocks and ultramafic cumulates, represents a deep-seated layered intrusion intruded in a metasedimentary sequence, the Kinzigite Formation. The latter is composed of metapelites with minor marbles (metamorphosed under granulite to amphibolite facies conditions) intruded by (and in part structurally overlying) the Mafic Complex (Garuti et al., 1980; Rivalenti et al., 1984; Sinigoi et al., 1994).
3. THE CAMPELLO MONTI ORE DEPOSITS

Several small Fe-Ni-Cu-(Co) sulphide deposits occur in the area, mostly in ultramafic layers, dykes and pipes of the Mafic Complex. As similar Ni sulphide deposits worldwide, they are related to the concentration of immiscible sulphide liquid in the magma chamber during the earliest stage of crystallization. The occurrence of strongly localized platinum-group elements (PGE) enrichments in some of the mineralizations was initially pointed out by Ramdohr (1960) and Mastrangelo et al. (1979) and later documented by a number of studies (Fiorentini & Beresford, 2008, with refs.).

Particularly, in the Campello Monti area magmatic rocks belonging to the Mafic Complex crop out, consisting of cumulate peridotites, pyroxenites, gabbros and anorthosites and of a large body of gabbro-norite grading to gabbro-diorite and diorite. The mineralizations occur as lens-shaped sulphide-rich, subvertical bodies broadly striking N-S to NNE-SSW within the pyroxenites. The dominant primary ore assemblage is given by pyrrhotite (Fe$_{1-x}$S), pentlandite ((Ni,Fe)$_3$S$_8$), chalcopyrite (CuFeS$_2$), mackinawite ((Fe,Ni)S$_{0.9}$) and cubanite (CuFe$_2$S$_3$); accessory metallic phases include ilmenite (FeTiO$_3$), magnetite (Fe$_3$O$_4$), chromite (FeCr$_2$O$_4$), hematite (Fe$_2$O$_3$), sphalerite (ZnS), pyrite (FeS$_2$), marcasite (FeS$_2$) and graphite. Some PGE enrichments have been locally reported, though specific platinum-group minerals (PGM) have not been found so far in the area. The primary sulphides occur as interstitial aggregates around the silicates, passing to massive concentrations that usually include roundish silicates. Secondary sulphides also occur, as microscopic vein networks, very fine fissure fillings or, alternatively, sulphide cementing microgranular silicate breccia.
4. MINING ACTIVITIES IN THE CAMPELLO MONTI AREA

Development of the Campello Monti mine began in the second half of the 19th century (ca. 1865) and the mining activity went on – with some interruptions - until the first half of the 20th century. After 1936, during the period of the economic autarchy declared by the fascist regime, a new treatment plant was built, initiating a period of intensive exploitation that only lasted, however, until 1943. The mining activity ceased in the immediate post war (1945).

The average grade of the ore was ca. 1-2 wt. % Ni (0.5 wt. % in the last years of activity). Nickel was extracted from pentlandite, occurring as both coarse-grained intergrowths and very fine-grained exsolutions in pyrrhotite. A concentrate of 5-6 wt. % Ni was recovered by enrichment through a flotation process.

Exploitation was organized into (sub-) levels connected by shafts and excavation was performed with drilling and blasting method. The ore was transported by Decauville railway to the surface, where it underwent a first (manual) sorting process before being stockpiled and then taken by ropeway down to the processing plant.

5. MATERIALS AND METHODS

An appropriate methodology for waste characterization is fundamental for the assessment of the SRM potential. For this reason, within the Smart Ground project a series of methodological protocols have been developed for both MSW and EW facilities. These protocols represent general guidelines that must be tailored to specific situation. The adopted methodology for the Campello Monti pilot site is described in detail below.

5.1 Reconnaissance survey

A comprehensive study of the waste materials connected with the mining activity in the area is lacking. Therefore, a preliminary field reconnaissance survey was carried out in order to verify location and typologies of extractive waste facilities. Using GPS, adits of the mine tunnels were located and mapped, as access roads, pedestrian paths and waste facilities. This early survey also included the recognition of the main characters of each dump, including some geochemical features with the help of a handheld X-ray fluorescent (XRF) analyzer. Such a survey led to the recognition of 8 main waste deposits (Fig. 2) belonging to two different typologies: waste rock and operating residues.
Figure 2. Location of the investigated areas, including sampling point (waste rock in red and operating residues in blue).

Waste rock is the most common typology, occurring in dumps located on the left side of the valley from Campello Monti village uphill, at the outlet of mine tunnels (Fig. 3). Generally each dump is related to a single tunnel activity, even if dumps originating from different levels also occur.

Operating residues occur in two areas: close to the dressing plant (area 1, Fig. 4) and on the opposite side of the valley (area 8). The two deposits show strongly different features.

The deposit close to the dressing plant only crops out over an extension of ca. 20 m² with an average thickness of ca. 2 meters; such exposed part is only the downward termination of the deposit, as suggested by previous analyses performed by ARPA Piemonte (Regional Environmental Protection Agency) along the slope upstream of the deposit (ARPA, 2006). The material is fine grained, red/orange to grey/brown in color, and shows a slightly hardened superficial crust. These features and its location, confirmed by the laboratory studies (see below) suggest that such a “waste” is related to a first enrichment activity.

The deposit of area 8 represents instead coarse grained sorted ore material coming from a mining area on the right side of the valley (not shown in Fig.2) that was connected to the Campello Monti dressing plant by ropeway.

The XRF analyzer was useful for highlighting compositional differences between different deposits which were later confirmed by the geochemical data.
5.2 Sampling campaign

For each waste facility, sampling was performed by adopting the following protocol:
- due to poor accessibility, sampling activity was made using hand shovel, following a net scheme (or grid method). Each sample was collected in an area of 1.5 square meters; after cleaning the sampling point from organic residues, a sample of 8-10 kg was collected using hand shovel and, where necessary, hammer to reduce the grain size of the rock. For each sample point all relevant information (operator, date, UTM WGS84 coordinates, type of material, photos etc.) was collected. 41 samples of rock waste and 12 of operating residues were collected. Sampling map and distribution of the studied waste deposits are shown in Fig. 2.

5.3 Laboratory work

5.3.1 Samples processing

All samples were weighed and dried into oven for at 24 hours at 80°C. After slow cooling to room temperature, samples were weighed (dry) and subsequently sieved, in order to obtain three size classes: > 20 mm, 2 – 20 mm and < 2 mm. Each grain size class has been weighed. After quartering (using the coning and quartering sampling method), 100 g of representative sample of class < 2 mm was obtained for environmental analysis; the remaining part was subsequently crushed (with a jaw crusher) and milled (with a ring mill) for the geochemical analyses.

5.3.2 Geochemical characterization

For any geochemical characterization, the analytical method must be chosen based on the type of waste material, taking into account the potential SRM. For waste related to Ni sulphide ore mining, the potential SRM are mainly represented by metals as Ni, Cu, Co and possibly PGE.

Accordingly, the following geochemical methods were adopted:
Multielements analysis of all samples by ICP-MS method, for a general geochemical screening. A “near total” attack method was chosen, i.e., the most vigorous digestion used in geochemistry, employing hydrochloric, nitric, perchloric and hydrofluoric acids.

Analysis by ICP-OES using 4 acid digestion for samples with a content of some metals (Ni and/or Cu) exceeding the upper limit for the previous analytical package (5,000 and 10,000 ppm, respectively).

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.

Analyses were performed by an external laboratory (ACTLABS, Canada). Preliminary analyses were performed on samples of the three size classes (>20 mm, 20-2 mm, <2 mm) in order to verify the existence of significant compositional differences. As differences were not significant, geochemical analyses were performed on the whole sample.

5.3.3 Mineralogical and petrographic characterization

For samples from EW facilities, a mineralogical a petrographic characterization is necessary because i) the metals recovery is strongly dependent on mineralogy: nickel, for instance, can be easily recovered from sulphides, while if contained in olivine its recovery is virtually impossible; ii) ore processing is strongly influenced by rock microstructure. Depending on grain size and type of intergrowths, the separation of an ore mineral from the gangue can be easy or impossible. In nickel sulphide ores, for example, pentlandite, the typical Ni ore mineral, can be easily separated when it occurs as granular aggregates, while its physical separation is problematic when occurring as very fine grained exsolutions within pyrrhotite.

The petrographic and mineralogical characterization of coarse grained waste materials has been performed by optical (transmitted and reflected light) microscopy on thin-polished sections of representative samples. On the same sections, after carbon coating, the chemical composition of the ore minerals was obtained by electron microscopy (SEM-EDS) technique.

The operating residues of area 1, which are very fine grained, requested a different approach: representative samples were incorporated in epoxy resin and, after polishing and carbon coating, observed and analyzed with electron microscopy (SEM-EDS) technique.

6. RESULTS

6.1 GEOCHEMICAL CHARACTERISATION

6.1.1 Main geochemical features

The main geochemical features of all samples are typical of ultramafic rocks affected by processes of exsolution and accumulation of sulphide liquid, as typical of Ni-sulphide magmatic mineralizations worldwide. Concerning the metals content, the samples show a) variable, but generally high to very high Ni, Co, Cu values; b) relatively high Cr and Mn; c) low REE content; d) strongly localized PGE enrichments.
6.1.2 Potential Secondary Raw Materials

As already mentioned, the SRM potential of waste materials connected with Ni-sulphide mining is represented by metals as Ni, Cu, Co and (possibly) PGE. The content of Ni, Cu and Co in all samples is shown in Fig. 5. The geochemical data allow the recognition of four groups of samples:

- **group I (area 1):** very strong Ni (>10000 ppm), Cu (≥5000 ppm) and Co (>600 ppm) values.
- **group II (areas 3, 4, 8):** strong Ni (2000-10000 ppm), Cu (600-1500 ppm) and Co (100-300 ppm) values.
- **group III (areas 2, 6):** moderate Ni (700-1600 ppm), Cu (200-600 ppm) and Co (100-200 ppm) values.
- **group IV (areas 5, 7):** relatively low Ni (100-700 ppm), Cu (50-200 ppm) and Co (50-100 ppm) values.

The good positive correlation observed between Ni, Co and Cu suggests that all these chalcophile elements occur within metal sulphides, as confirmed by the mineralogical study.

![Figure 5. Ni, Cu and Co content of all samples from the Campello Monti area (values in ppm). The numbers at the base of the diagram are referred to the sample areas.](image)

Concerning the critical PGE and Au, the geochemical data show that the PGE content is highly variable (Pd+Pd: 5.8 to 821 ppb) and the main PGE are represented by Pd and Pt. Two of the sampled waste areas show significant PGE enrichments:

- **area 1 (fine grained operating residues).** Samples from area 1 display very strong PGE enrichments: in particular, samples not only show high Pd and Pt content, but also significant enrichments in Ru (106-133 ppb), Os (61-73 ppb), Ir (46-84 ppb) and Rh (38-66 ppb), with PGEtot up to 1213 ppb. The Pd and Pt contents are high: Pd ranges from 404 to 556 ppb (avg. 477 ppb) and Pt from 282 to 362 ppb (avg. 362 ppb). Au also shows relatively high values (170-241 ppb, avg. 194 ppb).
- area 3 (mine rock waste). Samples from this area show moderate enrichments (Pd+Pt = 50-164 ppb, avg. 114 ppb). The Au content is highly variable, from 3 to 190 ppb; Au is broadly correlated with the PGE content.

6.2 Mineralogical and petrographic characterization

6.2.1 Rock waste and coarse grained operating residues

Under the microscope these materials are composed of mafic silicates (olivine, pyroxenes, rare amphibole and their retrogression products) and minor oxides (chromite, magnetite, ilmenite, hematite) associated with a variable amount of sulphides. The mineralization is made of sulphides consisting of pyrrhotite (Fe$_{1-x}$S), pentlandite ((Fe,Ni)$_8$S$_8$), chalcopyrite (CuFeS$_2$) and minor cubanite (CuFe$_2$S$_3$). Pentlandite, the main ore mineral, generally occurs as subhedral to euhedral crystals (0.1-2 mm across) enclosed by anhedral pyrrhotite (± chalcopyrite) (Fig. 6).

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 (CuFeS$_2$) ± cubanite (CuFe$_2$S$_3$) (ca. 34.5 and 23.4 wt. % Cu, respectively).

Figure 6. Reflected light microphotos showing the typical microstructure of the Ni-Cu sulfide mineralization. Pn: pentlandite, Ccp: chalcopyrite, Po: pyrrhotite.
6.2.2 Fine grained operating residues

The electron microscopy study of the very fine grained material of area 1 shows that:

- very fine grained (<1–100 µm across) material is composed of: iron oxides/hydroxides and sulphate; Mg-rich silicates; partially oxidized pyrrhotite, pentlandite and chalcopyrite; covellite (CuS); 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$_2$S, ca. 80 wt. % Cu).

These data show that the waste material of area 1 is the partially oxidized equivalent of the coarser grained material of the other areas, after crushing, milling and some mineral dressing operation.

7. CONCLUSIONS

The present study, performed within the framework of the Smart Ground project, aimed at developing a suitable methodology for an in-depth characterization of the waste material connected with former Ni sulphide mining in the Campello Monti area.

The overall data suggests that Ni, Cu, Co (± PGE) represent potential SRM in the mineral waste from the Campello Monti mining area. Not only these metals occur well above the typical rock content, but also within minerals (metal sulphides) which are suitable for metals recovery.

This study also shows that the metals distribution in the former mining area is not homogeneous, but strong differences occur among different waste deposits; moreover, each deposit shows a relatively homogeneous “geochemical signature”, depending on its significance within the mine site. Such variability likely represents a factor typical of mine-related waste, which must be taken into account for any assessment of SRM potential. As a consequence, detailed information on the primary ore deposits, as well as on the former mining and dressing activities in the area, is important for any evaluation study.

Even if, in detail, each characterization study must be tailored to the specific situation, the multidisciplinary methodology tested in the Campello Monti area can be adopted also in other former mining sites, particularly those exploiting metal sulphides.

The results of this study emphasize the complexity of the SRM estimation in waste deposits connected with the mining activity, suggesting that a thorough characterization of each waste deposit is a prerequisite for any resource evaluation. An in-depth characterization is one of the key factors to assess the resource potential, other factors including the site location, waste tonnage, as well as environmental and social aspects of landfill mining. Moreover, data acquired through a proper characterization study can be used to improve risk assessment and optimize remediation design at closed or abandoned mining sites.

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