Metal Recovery from Low Grade Ores

and Wastes Plus

Deliverable 2. 6.

Report on optimised pre-treatment methods of low-grade ores and wastes

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This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 690088.

Public

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This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 690088.

Deliverable Number	2. 6.
Deliverable Name	Report on optimised pre-treatment methods of low-grade ores and wastes
Deliverable Duration	from 01/02/2016 to 30/09/2017
Due Date of Deliverable	2017-09-30
Actual Submission Date	2017-10-04
Deliverable Lead Partner	IMN
Dissemination Level	Public
Public Summary enclosed	No
Work Package	WP2
No of Pages	12 (incl. cover and annexes)
Keywords	laterites, jarosite, fayalitic slag, fine-grained sludge, beneficiation, sulphidation, roasting, WHIMS, flotation, magnetic separation
In bibliography, this report should be cited as follows:	D2.6 : Report on optimised pre-treatment methods of low-grade ores and wastes

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1. Introduction

The deliverable summarizes the studies conducted by Metgrow Plus project partners in the first stage of the project, i.e. the part focused on selection and optimisation of the most flexible technologies for pre-treatment of low-grade primary and secondary materials. Based on the performed detailed analysis and characterization of the materials, including analyses for determination of potential contents of critical metals, specific techniques and methods were selected and then tested to produce enriched materials at high efficiency, low operating costs and limited environmental impact. Screening and selection of the methods for verification and optimisation was performed based on the expertise of the project partners and literature review with a specific objective of determination whether a pre-treatment step is required in order to optimise targeted metal extraction yield and what methods are the best for preparation of the given material for further steps of metal value recovery. The comprehensive analysis of the composition of the materials studied in the project and the studies of their pre-treatment were conducted with:

- laterite ores (Greek and Polish),
- iron-rich sludges,
- landfilled fine-grained sludges,
- fayalitic slags.

The performed quantitative and qualitative analyses provided a good picture of the potential of the materials with respect to metal value recovery thus making identification of valuable components possible, and constitute a first step in the selection of best pre-treatment options in the subsequent project actions. Pre-treatment and beneficiation studies of the addressed in the project materials were conducted by different partners and their results will be exploited in the studies planned in further stages of the project.

2. Summary of results

Below public summary of the main results of studies conducted for development of optimised pre-tretment methods is presented. In the project two sources of laterites have been made available (i.e. from Poland and from Greece) therefore the pre-treatment studies addressed both types of the materials in comprehensive and complementary tests. For more specific information please contact the responsible institution as listed at the end of each subsection.

2.1. Polish laterite

The Polish nickel deposit was formed by serpentinization of ultramaphic rocks followed by chemical weathering of the resulting serpentinites. The Szklary (city) serpentinite massif is located in the southern part of the Niemcza zone (Fore – Sudetic Block, NE Bohemian Massif). It forms a chain of hills which are situated ca. 7 km north of Ząbkowice Śląskie. The serpentinites are cut by granitoids, aplites, pegmatite and lamprophyre veins.

The investigated laterite ore contained about 1.34% Ni, while the content of the remaining main elements was as follows: Fe – 9.56%, Si - 17.63%, Mg – 10.64%. Based on the phase analysis, the examined ore is characterized by complex mineralogical composition resulting from the chemical and physical serpentinite weathering. In the ore there are minerals from the group of oxides of spinal structure (magnetite, chromite) and hematite, quartz, silicates and aluminosilicates.

Ore flotation studies have been carried out using various collectors (butyl xanthate, isooctyl xanthate, isoamyl xanthate, amine, oleic acid) and sulphidation, however no product with increased nickel content was obtained as a result of the flotation tests. The grade of the obtained concentrates was slightly higher than the raw ore - at the level of 1.44 to 1.55% of nickel. In order to improve nickel recovery, ore roasting tests were carried out prior to the flotation tests. A number of roasting tests was carried out at different ratios of Ni to $CaCl_2$ and coke. Roasting process was carried out in stationary and rotary furnaces, with and without flow of nitrogen. The best results were reached in flotation of the ore after roasting in a rotary furnace under inert atmosphere and then additional activation of the ore in $CuSO_4$.

Also application of wet magnetic beneficiation did not result in favourable nickel recovery index. The received concentrate (magnetic product), despite a relatively high Ni recovery, was characterized by only slightly higher Ni content in relation to the ore content. The conducted research does not provide grounds for development of a viable technology for beneficiation of the nickel ore by means of mineral engineering methods. The main reason behind the negative results of beneficiation seems to be the complicated mineralogical composition of the material. However, even though beneficiation of the material is not possible, the pre-treatment of both Polish and Greek laterite ore for hydrometallurgical metal recovery needs to be done according to the method defined in the next subsection.

The studies were performed by the following project partners: Tecnalia, Profima, IMN.

More information available at Institute of Non-Ferrous Metals.

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2.2. Greek laterite

Greece is one of the few EU countries with extensive but low-grade nickel laterites. The Greek laterites are unique in the world in that they are sedimentary and have originated by transport and sedimentation of laterite-derived material, generated by weathering of ultramafic rocks, on karstic Triassic –Jurassic limestones or on ultramafic ophiolites. In Greece, there are more than 110 nickel iron-ore occurrences with nickel content ranging from 0.4 up to 1.2% and iron from 20% to 79%. The total reserves are estimated to be over 500 Mt of which the 200 Mt are exploitable. The mineral resources of lateritic nickeliferous iron-ore deposits are spread mostly in the areas of Euboea (Evia), Boeotia (Agios Ioannis) and Kastoria.

Selective sulphidation aims at converting nickel oxides to nickel sulphides so that higher Ni yields can be obtained after flotation. In sulphidation tests Greek laterites were mixed with various proportions of reagent grade elemental sulphur, namely 100kgS/t, 300 kgS/t and 500 kgS/t. The mixtures were compressed at 50 MPa so that small briquettes were obtained. Sulphidation experiments were performed in a laboratory furnace at 500, 600, 700 and 800 °C, under inert atmosphere (flow of N_2 with a constant heating rate of 10 ^{o}C/min). Reaction time was set either to 1h or 3h. Flotation tests were carried out in a 1 L Denver flotation cell using material (90% passing 30 μm) that was subjected to sulphidation. Different collectors and agents to prevent agglomeration of fine particles were used during flotation.

Sulphidation and flotation studies indicate that:

- Sulphidation resulted in the formation of nickel (and iron) sulphide phases.
- After sulphidation, the content of millerite (NiS) was 4.8% and 6.4% in various samples of the Greek laterite, while the content of heazlewoodite (Ni_3S_2) was 1.3% in the laterite.
- Both nickel sulphide phases were present in all flotation concentrates as well as (with lower content) in tailings of all tests.

Reduction roasting aims to reduce nickel oxides and obtain (Fe,Ni) phases, so that an enriched (Fe,Ni) fraction can be obtained after magnetic separation. Experiments were carried out using LK and LAI laterites. Each laterite was mixed with different dosages of $CaSO_4$ and lignite. After mixing, the green samples were pressed at 50 MPa so that small briquettes were obtained. Reduction roasting experiments were performed using porcelain crucibles in a Limm high therm laboratory furnace, under nitrogen atmosphere at 800 °C, 900 °C and 1000 °C.

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Reaction time was set to either 1h or 2h. Magnetic separation tests were carried out in a Carpo Model WHIMS 3x4 high intensity wet magnetic separator The roasted samples were ground and a slurry with pulp density 20% wt was produced. The slurry was fed to the separator and the products obtained at different flux densities (0.2-0.8 Tesla) were weighted and analyzed to obtain their chemical and mineralogical analysis.

The analyses indicate that (Fe, Ni) phases were enriched to a certain degree in the magnetic products. Additional tests are required, both for reduction roasting and magnetic separation, to optimize the process and fully assess the potential of the proposed approach.

Several ore beneficiation experiments were conducted, however, none of them resulted in the production of nickel concentrate, which could constitute a feed for hydrometallurgical or pyrometallurgical treatment. None of the pre-treatment methods used - neither flotation nor magnetic separation, result in a concentrate which meets the targets set in the project i.e. 5-6% Ni content with approximately 80% recovery. The produced results are considered as non satisfactory, as they cannot adequately justify a novel laterite ore beneficiation technology.

The main reasons behind these results seem to be the complicated mineralogical composition of the material and the distribution of the target metals in various phases exhibiting different behaviour.

The studies were performed by the following project partners: Tecnalia, TUC.

More information available at Technical University of Crete

These studies of pre-treatment of laterite ore showed that recovery of nickel must therefore be investigated by another method, i.e. by hydrometallurgical processing.

The only applicable pre-treatment method for the preparation of the material and the extraction/recovery of target metals via hydrometallurgy is proper comminution of the ore by initial crushing and grinding. In conclusion, proper grinding seems to be the only suitable method for laterite ore pre-treatment. The currently recommended grain size of the bulk mass to be treated hydrometallurgically in reactors is below 1mm.

2.3. Iron-rich sludges

Jarosite sludge is an iron-rich sludge residue produced during the hydrometallurgical production of zinc. The sludge is mainly composed of jarosite, a mineral primarily comprising iron sulfate. The investigated jarosite sludge was received from the metal producing company.

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About 500,000 tonnes of Fe-rich sludges from zinc production and recycling are annually landfilled in the EU. In addition, there is a vast historical reserve of stockpiled materials.

Precipitation of iron is an important issue in many hydrometallurgical processes, due to the association of the target metals with Fe-rich minerals. Co-dissolved iron must be removed from the pregnant leach solutions before further processing to recover the desired metals, which is most often done by precipitation leading to the formation of (large amounts of) iron rich sludges. An example of this is zinc production, with concomitant production of iron rich compounds such as jarosite or goethite, depending on the process used. In Metgrow Plus project jarosite was investigated as a model stream. The jarosite sludge pre-treatment was studied to concentrate and/or convert valuable metals into a form that can be further processed in the following WPs. The two main pre-treatment techniques were investigated:

- Wet high intensity magnetic separation (WHIMS) and
- Roasting of the jarosite sludge.

Based on the results, it can be concluded that WHIMS is not a suitable method for pre-treatment of jarosite sludge mainly due to the very fine particle sizes of the material ($d50 = 2.9$ μm, $d99 = 27$ μm). On the other hand, roasting seems to be an effective pre-treatment step mainly due to the decomposition of jarosite to simpler and more soluble phases. The optimal roasting temperature depends on the objective of the further processing steps and the methods to be used in metal value recovery.

Furthermore, to enable heap leaching, which is studied in Metgrow Plus project, the permeability must be enhanced. Agglomeration tests are conducted within the scope of the WP focused on metal recovery.

The studies were performed by the following project partners: Tecnalia, Outotec, VITO.

More information available at Outotec.

2.4. Fine-grained sludges

Within Metgrow Plus, landfilled fine-grained sludges are considered to represent small quantity inorganic waste streams currently delivered to specialized landfills. Representative industrial materials were studied as model streams. The selected materials give a good overview of the challenges to face for these materials, such as the fact that the annual amounts are limited

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(in the range of a few 10,000 tons/year), different metals may occur in low grades, the materials are very fine, and in some cases high organic matter content may be present.

The investigated pre-treatment techniques included low and high intensity wet magnetic separation, density separation (wet shaking table, sink-float), thermal treatment, milling and sieving, flotation and pulping method. The results showed that magnetic or density separation are not suitable for pre-treatment of very fine sludges (d50 < 50 µm). They can be valuable however for slightly coarser grained materials (> 250 µm), where a promising flowsheet was developed that can recover up to 16% of the material as pure metals. Further research on a wider set of model streams could help to identify the cut-off size at which these techniques become efficient.

For the very fine grained materials, flotation can be a promising technique, but the operational procedure (collector, frother etc.) as well as the efficiency depend on the mineralogy of the sludge and the fraction to recover.

Removal of organics is necessary to avoid contamination of the equipment used for physical separation, as well as for operational problems in the downstream leaching. Both flotation and pulping did not succeed in removing the organics from the tested material. A thermal treatment can be used to remove the organics, however, whether this is economically feasible depends on the metal content and further processing needed.

The work has shown that physical pre-treatment does not have an added value for all fine-grained sludges. Especially the fineness is a great challenge, but this can be beneficial for the leaching process due to the large specific surface. For some sludges, such as the steel and shredder sludge, it is recommended to go directly to leaching. However, for heap leaching, and possibly also for other leaching methods developed among the project, permeability of the materials must be improved. Similarly to pre-treatment of iron-rich sludges the agglomeration tests are conducted within the scope of the WP focused on metal recovery.

The studies were performed by the following project partners: Tecnalia, VITO, JMR, URBASER.

More information available at VITO.

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2.5. Fayalitic slags

Million tons of slags are produced annually from various metallurgical industries. These slags exhibit different physical and chemical characteristics and may (i) pose risk to the environment if they are disposed of without care, (ii) contain valuable or critical elements that need to be recovered, and (iii) utilized in various industrial sectors as aggregate or inert material. Thus, prior to their further management (pre)treatment is often required.

The assessment of their environmental risk is carried out with the use of established environmental tests, to assess their contamination potential prior to their use or disposal in landfills or in other suitable sites. These tests assess the leachability of potentially hazardous elements and indicate the risk for the environment (soil, surface- and groundwater).

The potential recovery of metals from slags may (i) minimize to a noticeable degree mining of raw materials and reduce the carbon footprint of metals production, and (ii) result in the production of an inert material that can be either disposed of safely or valorized to produce secondary materials that can be used mainly in the construction sector or in other uses (as back fill in underground mines etc.).

The obtained results deal with the assessment of the risk of fayalitic slag and the study of pre-treatment options, mainly towards its potential valorization as binder in the construction industry.

The study involved the following steps (i) Magnetic separation, (ii) Environmental characterization and (iii) Leaching tests for the assessment of its toxicity, the removal of contaminants and assessment of the quality of the final product

The experimental results indicate that (i) Magnetic separation can separate to a good degree the magnetic and non-magnetic fractions of the slag, (ii) Environmental characterization of the as-received slag indicates that slag has a certain toxicity and further steps are required prior to its valorization or disposal, (iii) Leaching tests, mainly with HNO_3, indicate that solubilisation of several elements is possible and thus the toxicity of the obtained residue is substantially reduced. It is believed that the use of slag or its leaching residue as binder for the production of building elements will further reduce its toxicity and result in the production of suitable and environmentally safe products.

The studies were performed by the following project partners: Tecnalia, TUC.

More information available at Technical University of Crete.

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3. Conclusions

Following the Metgrow Plus project work plan, the analyses and pre-treatment work package represents adequate starting point of further research by providing the necessary information for the studies in technology development. The ongoing and coming WPs shall be based on the analyses and pre-treatment methods results obtained in the initial phase of the project. The relevant technological processes will be incorporated in the Toolbox as developed within the scope of the project.

Nevertheless the pre-treatment methods, analyses and all the rest of obtained results should be controlled, validated or supplemented whenever required during further experimental work. The most preferred pre-treatment methods (considering their application in further steps of metal recovery) are presented below:

- Laterite ores (Greek and Polish) - proper grinding/comminution (grain size <1mm).
- Iron-rich sludges – roasting and agglomeration (for heap leaching).
- Fine-grained sludges - For some sludges, it is recommended to go directly to leaching. Agglomeration required in case of heap leaching.
- Fayalitic slags - Magnetic separation.

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