MET Grow +

Metal Recovery from Low Grade Ores and Wastes Plus

Deliverable 3.6
Report on metal extraction of low grade ores and wastes

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Deliverable Number	D3.6
Deliverable Name	Report on metal extraction of low grade ores and wastes.
Deliverable Duration	M5-M27
Due Date of Deliverable	30/04/2018
Actual Submission Date	27/04/2018
Deliverable Lead Partner	VTT
Dissemination Level	Public
Work Package	WP3
No of Pages	20
Keywords	Extraction, leaching, heap leaching, bioleaching, solvometallurgy, ionometallurgy, deep eutectic solvent, plasma, pyrometallurgy, carboreduction
In bibliography, this report should be cited as follows:	D3.6 Report on metal extraction of low grade ores and wastes. METGROW+ H2020 project, grant agreement Nº 690088.

Executive Summary

This deliverable, D3.6 "Report on metal extraction of low grade ores and wastes", summarizes the research done in WP3 of the METGROW+ project. The materials selected for metal extraction research were low-grade Polish and Greek laterites (including both limonitic and saprolitic ores), Fe-Ni slag, landfilled Cr-rich sludge, jarosite, landfilled Zn-rich sludge, goethite, fayalitic slag, steel sludge and automotive shredder residue. The extraction methods applied were atmospheric acid leaching, heap leaching, autotrophic oxidative and reductive bioleaching, heterotrophic bioleaching, solvometallurgical leaching, ionometallurgical extraction and plasma-pyro.

For Polish and Greek laterites atmospheric acid leaching resulted in >90 % leaching yield for the main target element, nickel, by utilizing H_2SO_4 or HCl. Acid consumption was decreased by combined limonitic-saprolitic ore leaching. For laterites, also a promising solvolixiviant was found, resulting in >90 % nickel yield with high selectivity against iron. Solvometallurgical leaching was as well a promising method for treating landfilled Cr-rich sludge, with leaching yields of 82 % and 83 % for chromium and nickel, respectively. In addition, >90 % yields for chromium and nickel was obtained with heterotrophic bioleaching. The third promising method for landfilled Cr-rich sludge was heap leaching, with selective nickel extraction. For jarosite, direct extraction was challenging, but with deep eutectic solvents (DES), >90 % yield was obtained for zinc. By utilizing roasting as a pre-treatment, >90 % of zinc and lead were extracted from jarosite with high selectivity. Plasma-pyro appeared to be another suitable method for jarosite, resulting in >90 % recovery of zinc and lead to fly ash. The observations and results with goethite were rather similar compared to jarosite. For landfilled Zn-rich sludge, a promising DES was found, resulting in >90 % leaching yield for zinc, with high selectivity. In addition, solvometallurgical leaching resulted in >90 % yield for zinc from this material. The third promising method for landfilled Zn-rich sludges was plasma-pyro, resulting in >90 % recovery of zinc to fly ash. Fayalitic slag, as well as Fe-Ni slag, were challenging materials for direct leaching, as the high silicon content caused severe filtration difficulties for the resulting process solutions. Therefore, fayalitic slag was also treated by plasma-pyro, resulting in fly ash with >90 % yields for zinc and lead. For steel sludge, a promising DES was found, resulting in >90 % leaching yield for zinc. Automotive shredder residue was studied mainly with heterotrophic bioleaching, resulting in 68% leaching yield for copper, with very high selectivity against iron.

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List of acronyms

DES   deep eutectic solvent

IL   ionic liquid

PLS   pregnant leach solution; leachate obtained from the extraction process

S/IL   solid/ionic liquid ratio

S/L   solid/liquid ratio

SI   selectivity index; calculated according to concentrations in the produced leachate; concentration of target elements divided by concentration of undesirable elements

Ti(Gr2)   Titanium, grade 2.

TRL   technology readiness level

WC   water content (percentage), referred to dry mass in a solid

CHAPTER 1   Introduction

The objectives of METGROW+ work package 3 "Metal extraction" were:

- To develop and apply innovative, versatile raw material treatment and metal extraction processes for the valorization of a wide variety of low grade ores and secondary (waste) materials in the framework of a Hydroflex process concept for the recovery of Ni, Co, Zn, Fe, In, Ga, Ge, Sb, and Cr.
- To improve yield (>90 % target) and selectivity.
- To apply integrated hydrometallurgical, biohydrometallurgical, solvometallurgical and pyrometallurgical methods to maximize extraction yield and obtain non-hazardous residues that are adequate for valorization in line with the zero waste approach.
- To develop and apply metal extraction processes within the developed new metallurgical system which are characterized by i) a high degree of innovation, ii) flexibility in varying processing conditions, iii) high efficiency, low operating cost and as low as possible environmental impact, and iv) enhanced degree of sustainability.
- To test plasma-pyro technology for its potential utilisation making more pure residues and improved recovery of volatile metals. The energy usage cost and waste valorization benefits are both looked at.
- To gather valuable information on metal extraction methods as input for the METGROW+ toolbox.

The following materials were selected for WP3: low-grade Polish and Greek laterites (including both limonitic and saprolitic ores), Fe-Ni slag, landfilled Cr-rich sludge, jarosite, landfilled Zn-rich sludge, goethite, fayalitic slag, steel sludge and automotive shredder residue. The extraction methods applied were atmospheric acid leaching, heap leaching, autotrophic oxidative and reductive bioleaching, heterotrophic bioleaching, solvometallurgical leaching, ionometallurgical extraction and plasma-pyro. The summary of materials and technologies tested is presented in Table 1.

Table 1. Studied materials, technologies and obtained TRL increase in WP3 of METGROW+. AAL = Atmospheric acid leaching. HL = Heap leaching. AO/RB = Autotrophic oxidative and reductive bioleaching. HB = Heterotrophic bioleaching. SML = Solvometallurgical leaching. IME = Ionometallurgical extraction. PP = Plasma-pyro technology.

	AAL	HL	AO/RB	HB	SML	IME	PP
Polish laterite	3→4	3→4			2→4		
Greek laterite (saprolitic)	3→4	3→4	3→3				
Greek laterite (limonitic)	3→4	3→4	3→3			3→3	
Fe-Ni slag	2→2	2→2					
Landfilled Cr-rich sludge		3→4		2→3	2→4		
Jarosite		3→4	2→3	2→2	2→3	3→4	3→4
Landfilled Zn-rich sludge		3→4	2→2	2→2	2→3	3→4	3→4
Goethite		3→4	2→3		2→3		3→4
Fayalitic slag			2→3	2→2		3→4	3→4
Steel sludge				2→2	2→4	3→4	
Automotive shredder residue				2→3			

CHAPTER 2   Summary of the work done and main achievements

2.1.   Subtask 3.1.1 Atmospheric acid leaching (IMN, PROFIMA, OUTOTEC, TUC, VTT)

Atmospheric acid leaching refers to hydrometallurgical processes that utilize non-pressurized, stirred reactor applications with temperatures <100 ˚C. In METGROW+, atmospheric acid leaching was studied for nickel bearing laterite ores from different EU locations, and for Fe-Ni slag. Atmospheric acid leaching of laterites was conducted by IMN, PROFIMA, OUTOTEC, TUC and VTT, while Fe-Ni slag was studied by IMN and PROFIMA. The role of OUTOTEC and PROFIMA was to steer the work towards industrial applications by helping in parameters selection and economic aspects of the processes.

Polish laterite, studied by IMN, contains nickel and cobalt with the dominant amount of silicon, magnesium and iron. Among many preliminary tested leaching chemicals, H_2SO_4 and HCl were selected for further studies, and 1-3 L reactor experiments were conducted with variable parameters of pH (0.0-2.1), temperature (20-80 °C), process duration (15-240 min), S/L-ratio (10-40 %). As a result, targeted 90 % nickel yield has been achieved, as well as improved selectivity of Ni leaching over undesirable metals. However, this required sulphuric acid leaching combined with neutralization by $Ca(OH)_2$. The atmospheric HCl leaching caused a significant increase in iron dissolution. Additionally, reaction mixture neutralization with $Ca(OH)_2$ caused filtering problems due to the formation of iron hydroxide precipitate without gypsum matrix, as in the case of H_2SO_4. According to the research done, optimized parameters for Polish laterite leaching are H_2SO_4 as an acid, S/L-ratio of 20-40 %, temperature of 50-75 °C, leaching time of 2-3 h and neutralization of reaction mixture by $Ca(OH)_2$. Process flowsheet has been prepared for validation/upscaling (WP6).

Fe-Ni slag, studied by IMN, is a waste from pyrometallurgical processes containing also nickel and cobalt, but the dominant elements are iron and silicon. Fe-Ni slag was studied using a similar approach to the Polish laterite, but found unsuitable to any of the chemicals used, due to the formation of silica gel that prevented filtration.

Greek laterites, studied by TUC, included ores from Kastoria, in NW Greece (LK; saprolitic laterite) and Agios Ioannis, in central Greece (LAI; limonitic laterite), both containing Ni and Co, as well as Fe, Ca, Al and Mg. Reactor leaching tests were carried out with the use of H_2SO_4 or HCl in mechanically agitated glass reactors of 500 mL and 1000 mL. Three parameters, i.e. temperature, acid concentration and S/L-ratio were investigated. Special emphasis was given to the co-extraction of Co, as well as to the dissolution of Fe, Al, Mg and Ca. For the saprolitic ore (LK), atmospheric acid leaching results were very encouraging, with both acids, as Ni and Co extractions over 90 % were obtained. Increase of acid concentration and temperature, and decrease of S/L-ratio, improved the extraction of Ni but had no major effect on the extraction

of Co. The maximum acid consumption (kg pure acid/t of dry ore) varied and reached 850 kg/t. For the limonitic ore (LAI), Ni and Co extractions with HCl exceeded 90 and 80%, respectively, while the use of H_2SO_4 was less efficient. Increase of temperature improves in general metal extraction, while increase of S/L-ratio resulted in decreased iron dissolution with both acids. The maximum acid consumption reached 650 kg/t. Leaching residues, based on mineralogical analyses, are considered suitable for alkali activation and the production of alkali activated inorganic polymers (AAIP) and binders (WP5). Process flowsheet has been prepared for validation/upscaling (WP6).

Greek laterites, were also studied by VTT and OUTOTEC, including the above mentioned saprolitic LK and limonitic LAI laterites, but also another laterite sample from the island of Evia, Greece (LEV; limonitic laterite). The focus was on determining optimum leaching conditions for H_2SO_4 process; the effect of pH for nickel extraction was studied by pH-static experiments (from pH 0.25 to 2.0) with 5000 mL Ti(Gr2) standard reactor apparatus. It was found out that nickel from saprolitic LK laterite can be dissolved at pH 1.5 that is suitable also for simultaneous jarosite precipitation, whereas limonitic LAI and LEV need more acidic conditions. The iron precipitation as jarosite in case of saprolitic laterite generates sulfuric acid, which in certain cases can be used again for the leaching. Combined limonitic-saprolitic laterite leaching and precipitation tests were conducted to make use of this effect. Promising results were obtained from these tests, which aimed to first dissolve nickel from LEV or LAI in lower pH, then, after sulfate addition (as Na_2SO_4; to increase the reaction), increase the pH by LK addition and simultaneously dissolve nickel from LK and precipitate iron from the solution. High selectivity values of Ni over Fe using the respective ratios and concentrations in the PLS were achieved in these combined leaching and precipitation tests. In the combined leaching and precipitation tests, the SI was for LAI+LK 1.1 and for LEV+LK 0.9, whereas in the test where laterites were leached separately, SI varied from 0.09 to 0.33. The preliminary leaching tests showed that around 650 - 1100 kg/t of acid was needed with the Greek laterite samples LAI, LEV and LK. Combined leaching and precipitation process has a potential to reduce acid consumption and decrease iron removal cost. The acid consumption was only around 400 kg/t when LK laterite was used as neutralization agent for jarosite precipitation. Iron concentration decreased from 10 g/L to around 2 g/L during the jarosite precipitation stage. That indicates significant savings in iron removal cost because in the conventional process all the iron is removed from the solution using lime or limestone. The Ni yield to the solution was still relatively good being 79% for combined Ni leaching and Fe precipitation experiment, LEV+LK. Yields for Mg, Al and Cr were 91%, 99%, 79%, respectively. The valorization of leaching residues was preliminary studied at KULEUVEN in WP5. Results of the studies suggest that suitability of the residues for alkali activated inorganic polymers (AAIP) could be enhanced by increasing its amorphous content, for example through heating treatment and fast cooling. Process flowsheet has been prepared for validation/upscaling (WP6).

2.2. Subtask 3.1.2 Heap leaching (VITO, TUC, TECNALIA, IMN, PROFIMA, JMR)

Heap leaching is a controlled process whereby a complex or low-grade ore is stacked in short lifts, usually crushed and often agglomerated on a carefully prepared containment system (the leach pad) and irrigated in a controlled manner with a solution to extract the optimum amount of metal from the material. Heap leaching technology is low cost and flexible, and can consist of either acid or alkaline leaching. Heap leaching method was used for variety of METGROW+ materials: landfilled Cr-rich sludge, jarosite, goethite, landfilled Zn-rich sludge, Polish laterite and Greek laterites. Heap leaching was conducted by IMN, TUC, VITO and TECNALIA, while industrial partners (PROFIMA, JMR) gave advices for industrial applications, regarding to the process parameters and economic aspects.

Landfilled Cr-rich sludge, studied by VITO, concentrated on extraction of Cr and Ni. Analysis of theoretical Pourbaix diagrams of the studied systems in combination with preliminary leaching tests showed that selective recovery of Cr and Ni from the material is possible at pH 5-6. However, a major challenge for this material is the large solubility of gypsum, which makes up the majority of the material (app. 60 w-%). A first column experiment with 1 M HNO_3 demonstrated that the pH must be well controlled to avoid complete dissolution of the material. In industrial heap leaching applications, recirculation of the leaching liquor must be performed to improve economics by 1) concentrating metals for better recovery and 2) reusing leaching liquor to minimize the use of solvents/reagents. In a heap leaching set-up fresh leaching liquor will be saturated in gypsum through gypsum dissolution after a first leaching cycle. When the liquor is then subsequently circulated through the heap, the dissolution of gypsum will be strongly reduced due to the gypsum saturation. Metals of interest can be stripped selectively from the pregnant leach solution. This concept was proven in a column experiment by leaching with a solution saturated in gypsum, buffered at pH 2.3. Based on the results, it is possible to extract about 50% of Ni very selectively in the pH interval 4-7 before Cr and Fe start to dissolve. Agglomeration of the materials is necessary to ensure sufficient permeability for heap leaching. Stable granules could be obtained by rapid mixing using only water. Further optimization is ongoing in view of upscaling in WP6.

Jarosite, studied by VITO, concentrated on extraction of Zn, Pb and Ag. In VITO, the jarosite process included roasting pre-step, followed by extraction. Process development started with batch leaching tests to determine the optimal leaching conditions. This resulted in a three-step process able to selectively extract >95 % of Zn, 90 % of Pb and >95 % of Ag, with very little Fe dissolution (<1%). Through an additional step, also >90 % of As can be removed. This was important, as the arsenic enrichment after leaching has a very negative impact on the reuse options of the residual solid. In a next step, the batch leaching results are being validated by column experiments. For the column leaching, it was vital to ensure sufficient permeability. The agglomeration experiments showed that addition of a binder (in this case bentonite) was necessary to achieve sufficient strength. Performance of the agglomerates will

be evaluated during the column experiment. Process development for goethite was similar to that of jarosite.

Jarosite was also studied by TECNALIA, with the target element of Zn. The jarosite process was studied at lab scale in glass columns (d=55 mm, h=350 mm). The sample placed inside the column was irrigated (gravitational down flow) with several leaching agents from acidic to alkaline. For the selection of the leaching agent, preliminary pH-static tests were conducted according to standard EN14429 test. The final pH values covered the range between 2 and 12. Metals extraction rates for the column tests were obtained by analysing the obtained eluates at different time intervals, from days to several months. The objective was to optimise the Zn extraction rate while minimizing the matrix dissolution. According to extraction yield and selectivity criteria, two tests, performed at different operating conditions, were selected as the best performing. The test 1 (thermal pre-treatment followed by leaching with NaOH solution) resulted in 61% leaching yield for Zn, but it was seen that iron extraction competes with zinc extraction (40% leaching yield for iron), i.e. the leaching was not very selective. The test 2 (leaching with ammonium chloride of an agglomerated sample) resulted in lower zinc yield of 36%, but was very selective against iron (iron leaching yield <1%). The solutions and residual solids from these experiments were sent to WP4 (Recovery of metals from dilute and concentrated solutions) and WP5 (Valorization of solid residue) for further studies.

Landfilled Zn-rich sludge, studied by TECNALIA, concentrated on extraction of zinc. The apparatus and working protocol was similar as described in the respective jarosite research. Two tests of the conducted were selected as the most promising, according to selectivity criteria and their high Zn leaching yield comparing with the rest of the tests performed. The test 1 utilized buffered leaching agent based on sodium acetate, and resulted in Zn leaching yield of >90%, but iron was also extracted (50% leaching yield). The test 2 utilized thermal pre-treatment to eliminate the organic content of the landfilled Zn-rich sludge, and then leaching was conducted with leaching agent based on sodium acetate. This protocol resulted in a lower Zn leaching yield (67%) but, on the contrary, better selectivity was achieved (iron leaching yield <0.5%). The solutions and residual solids from these experiments were sent to WP4 (Recovery of metals from dilute and concentrated solutions) and WP5 (Valorization of solid residue) for further studies.

Polish laterite, studied by IMN, was the same ore as studied also in atmospheric acid leaching. Heap leaching tests were carried out in four types of test columns with variable flowrate and concentration of acid (H_2SO_4). Tests resulted in columns blockage by fine particles, caused by the presence of binders (confirmed by microscopic grains analysis). The agglomeration test did not result in satisfactory results. Therefore, tests were carried out with bigger grain size of raw laterite ore. The obtained results show >90 % nickel leaching yield, however the selectivity over iron was very low. Therefore, the product leachate requires major iron removal prior to nickel recovery. The leachate obtained in heap leaching tests without acid

solution recirculation contained large amounts of free sulfuric acid, due to the high acid consumption/neutralization at the beginning of tests in columns with the ore; too low concentration of acid caused the column blockage by iron hydroxide precipitate.

Fe-Ni slag, studied by IMN, was the same material as studied also in atmospheric acid leaching. Sulfuric acid was used as a leaching agent. Due to the formation of silica gel, resulting in severe blockage of columns, heap leaching with sulfuric acid was considered as unsuitable method for treating this material.

Greek laterites, studied by TUC, were saprolitic and limonitic ores. The saprolitic ore (LK) was the same used in atmospheric acid leaching, while the limonitic ore (LAIp) had lower nickel content compared to the original LAI ore in atmospheric acid leaching. Ores were tested in laboratory Plexiglas columns, with a diameter of 5 cm and length of 50 cm, using H_2SO_4 or HCl as leaching media. Solution recirculation was also considered. Results showed that H_2SO_4 was considered a more efficient leaching agent for both ores. Acid concentration of 1N does not seem sufficient to extract most Ni from laterites, especially those containing high Ca and Mg. When acid concentration is increased to 3N much better results (in terms of Ni extraction and selectivity of leaching) were obtained. The sulfuric acid consumption was 441 - 1366 kg/t ore in 3N experiments. The addition of Na_2SO_3 was also tested in 3N sulfuric acid process, resulting in higher Ni and Co extraction yields, without an increase in iron dissolution.

2.3. Subtask 3.2.1 Autotrophic oxidative and reductive bioleaching (VTT, UMICORE)

Autotrophic oxidative and reductive bioleaching refers to biohydrometallurgical methods, which rely on bacterial activity to oxidize/reduce different sulfur and iron species. This results in production of leaching agent (sulfuric acid), oxidant (ferric iron), or reduction of iron enabling enhanced leaching of certain oxidized minerals. These methods were tested for jarosite, goethite and Greek laterites (both oxidative and reductive bioleaching), and for fayalitic slag and landfilled Zn rich sludges (only oxidative bioleaching).

All materials were first screened in 100 mL batch experiments (incubated at rotary shaker at 30 °C and 150 rpm), to assess the suitability of bioleaching (either oxidative or reductive) for the material in question. All materials, except landfilled Zn-rich sludge, proved to be suitable for bioleaching bacteria, even though the leaching efficiency varied among the materials. The most interesting results and the highest novelty was observed with oxidative bioleaching of jarosite and fayalitic slag and these experiments were continued in reactor scale (1000 - 5000 mL). Reductive (anaerobic) experiments proved to be either the same or lower in efficiency compared to oxidative ones, and were not studied in reactor applications. In the aerobic reactor experiments, S/L-ratio, agitation and impeller type, temperature and pH was studied to reach the highest elemental yields and the fastest possible process. Because of its high elemental sulfur content, **jarosite** experiments were very rapid (retention time of app. 3 days

with S/L-ratio of 15 %) and pH decreased even too low values, inactivating the bioleaching bacteria. Therefore, also longer experiments were conducted by controlling the pH with NaOH in optimal area (pH = 1-2, retention time of app. 2 weeks). Despite of these strategies, the main commodity, zinc, was not efficiently leached (zinc yield in all experiments app. 35 %). However, bioleaching resulted in selective zinc leaching over iron (SI = 8.1), and jarosite was dissolving very slowly in the pH area of 1-2.

Fayalitic slag experiments had 5-7 day retention time with S/L-ratio of 10 % (stable pH of 1.5, controlled with H_2SO_4), and resulted in copper, zinc and cobalt yield of 51 %, 44 % and 36 %, respectively. The selectivity of target elements (Zn, Cu, Co) over iron was poor (SI = 0.11). The chemical H_2SO_4 leaching experiment was conducted for comparison, resulting in copper, zinc and cobalt yield of 71 %, 65 % and 70 %, respectively. However, the selectivity of target elements over iron was even lower (SI = 0.08). This was caused by different behavior of iron in biologic and chemical process: in bioleaching the iron oxidizing bacteria were able to oxidize Fe^{2+} to Fe^{3+}, resulting in iron precipitation (most likely as jarosite) simultaneously with leaching process, while in chemical leaching iron remained in Fe^{2+} form. Resulted iron precipitation generates acidity, that can be used to decrease the external acid need (50 % acid consumption decrease was observed in bioleaching), but also saves chemical costs later when iron is removed from the leachate (prior to target elements recovery). A downside with fayalitic slag was very challenging separation of solids from leachate. From both jarosite and fayalitic slag bioleaching processes, residual solids were analyzed, but found unsuitable for reuse (WP5).

2.4. Subtask 3.2.2 Heterotrophic bioleaching (UGent, Umicore)

Heterotrophic bioleaching involves the production of diverse biogenic lixiviants *via* microbial (yeast, fungi and bacteria) respiration using organic carbon. As part of METGROW+, research aimed for sustainable, green (i.e. non-toxic, biodegradable lixiviants) and less energy intensive (i.e. processes carried out under ambient conditions) approaches for metal recovery. In addition to testing metal leaching using organic acids produced by fungi and yeast, research aimed and achieved an expansion of the heterotrophic biolixiviant portfolio with investigations of metal leaching with biogenic NH_4^+, surfactants and bacterial siderophores. Materials tested for heterotrophic bioleaching were Polish laterite, fayalitic slag, jarosite, landfilled Zn-rich sludge, landfilled Cr-rich sludge, steel sludge and automotive shredder residue.

The most promising results were obtained with an automotive shredder residue; copper yields of up to 68 % and extremely high selectivity against iron (SI > 800) were achieved with biogenic ammonia. Leaching with biosurfactants (seven different sophorolipids, boro-lipids and rhamnolipids), produced by the fungi Starmerella bombicola, resulted in yields of <40 %

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

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for target elements, with all studied materials. Given that the same biosurfactants have been successful at leaching metals from metal contaminated soil, the poor leaching observed in these experiments was a surprise.

Organic acid biolixiviants have been researched extensively for heterotrophic bioleaching. Synthetic organic acids (like citric, gluconic and oxalic acid) where tested as analogues to those produced by the archetypal heterotroph *Aspergillus niger* and a novel yeast strain *Candida viswanathii*. The most potential results were observed with landfilled Cr-rich sludges, using mixtures of 100 mM oxalic and 100 mM citric acid, resulting in nickel and chromium leaching yield of 96 % and 91 %, respectively. Furthermore, routes for the sustainable production of organic acids using fungi and yeast was also investigated, using microbial strains cultured with cheap waste streams, typically produced by industry as carbon and nitrogen sources for microbial respiration. Here, glycerol and urea was used. Proof of principal was achieved with up to 32 mM oxalic and 6 mM citric acids using the yeast strain *Candida viswanathii* and *Aspergillus niger* respectively.

Scaled-up tests (1 L) were preformed for selective copper leaching from automotive shredder residue using biogenic NH_4^+ and organic acid leaching of landfilled Cr-rich sludge, providing data to WP1 for economic and environmental assessment, leachates to WP4 for the recovery of the metals and solid residues to WP5 for the residue valorisation into innovative building materials. Depending on those studies and the conclusions from the comparative evaluation of approaches in WP1, a final decision will be taken in order to perform validation activities in WP6.

2.5. Subtask 3.3.1. Solvometallurgical leaching (KULeuven)

Solvometallurgical leaching consists of applying organic liquids (solvents, extractants, organic acids, modifiers, …) to extract metals from a solid source. The aim is to reduce the volume of the aqueous phase (<50 %) compared to conventional leaching. The main advantage of solvometallurgical leaching, compared to conventional hydrometallurgical leaching, is that a higher selectivity may be obtained for the targeted metals.

In METGROW+, many solvolixiviants were tested. Among the ones tested, two solvolixiviants performed best with regard to the leaching extraction of valuable metals, separately from the main impurity (Fe), which is typically present in concentrations of about one order of magnitude higher, and avoiding high-temperature processes (>100 °C). One solvolixiviant is the ionic liquid (IL) Aliquat 336 after loading with HCl (HA336). It was applied to five materials: Polish laterite, jarosite, landfilled Cr-rich sludge, steel sludge and goethite. The other solvolixiviant is the acidic extractant Cyanex 272 diluted in the Shell GTL solvent GS190 (Cy272). It performed better than HA336 or versatic acid - 10 in the case of landfilled Zn-rich sludge.

The extraction of Ni from Polish laterite (21 % S/IL ratio and 80-90 °C) was efficient (96 % Ni in the acidic aqueous leachate) and selective (0.3 % Fe and SI = 27 Ni/Fe) using wet sample (75 % WC), HA336 leaching and 2 M NaOH for the IL regeneration. The extraction of Ni and Cr from Cr-rich sludge (27 % S/IL ratio and no temperature control required) was efficient (82 % Cr, 83 % Ni in the acidic aqueous leachate) and selective (4 % Fe and SI = 4.5 Cr/Fe and 3.5 Ni/Fe) using wet sample (75 % WC), HA336 leaching and 2 M NaOH for the IL regeneration. The extraction of Zn from steel sludge (37 % S/IL ratio and no temperature control required) was efficient (92 % Zn in a basic NH_3 aqueous stripping liquor) and selective (0.02 % Fe and 4 % Ca, with SI = 4.2 Zn/Ca and 600 Zn/Fe) using wet sample (45 %), HA336 leaching and 3 M aqueous NH_3 for the Zn recovery and IL regeneration. The extraction of Zn, Pb and Cu from jarosite and goethite (11 % S/IL ratio and no temperature control required) was less efficient (33-37 % Zn, 30-90 % Pb and 20-60 % Cu in the IL leachate), but still selective (1-6 % Fe) using wet sample (34 %) and HA336 leaching. However, the calcium-rich aqueous leachates formed as a by-product probably hold the highest value, because they contain In and Sb, the most valuable (and critical) metals in these materials, without the main impurities. This aqueous acidic leachate obtained after IL leaching had almost no iron or copper and only low concentration of zinc (SI of In and Sb 3.4 versus iron, 1.6 versus zinc and 2.3 versus copper). These are important interfering elements in the downstream recovery processes of In and Sb. The selectivity for In and Sb against Pb and As was poorer (SI = 0.4), but their mutual separation is much easier. Finally, the extraction of Zn from landfilled Zn-rich sludge (12 % S/L ratio and no temperature control required) was between 56-76 % (acidic sulphate aqueous stripping liquor), and very selective (6 % Ca and 4 % Fe, SI = 21.4 Zn/Ca and 16.8 Zn/Fe) using dried sample, 2 M Cy272 leaching and 2 M H_2SO_4 for both the Zn recovery, separately from Fe and Ca, and Cy272 regeneration, at the same time.

The upscaling of solvometallurgical leaching tests was performed at the optimum conditions of the laboratory scale experiments, with 0.6 – 0.8 L of organic lixiviants mixed with 0.1 – 0.2 kg of Polish laterite, landfilled Cr-rich sludge, steel sludge, goethite and landfilled Zn-rich sludge. This represented a 1000 – 2000 times increase in terms of mass of material (100 in the case of Cr-rich sludge) and 600 – 800 times increase in terms of volume of lixiviant (40 in the case of Cr-rich sludge). Results were similar compared to small scale, with the highest difference found in the upscaled process for the steel sludge (small scale: 92 % Zn extraction, 0.02 % Fe extraction, and SI = 4 Zn/Ca, 600 Zn/Fe, whereas at large scale: 83% Zn extraction, 18 % Fe extraction, and SI = 3 Zn/Ca, 2 Zn/Fe). Still, a high selectivity for the valuable elements over iron was reached. These upscaling tests with selected samples allowed to provide data to WP1 for the economic and environmental assessment, leachates to WP4 for metal recovery, and solid residues to WP5 for the residue valorisation into innovative building materials.

2.6. Subtask 3.3.2 Ionometallurgical extraction development (IDENER, VTT)

Deep Eutectic Solvents (DESs) are eutectic mixtures of Lewis or Brønsted acids and bases. Most of the reviewed DESs are based on the quaternary ammonium cation: ChCl. These liquids are simple to prepare, relatively unreactive with water, biodegradable and relatively cheap. DESs have been widely used as lixiviants for metal extraction, being possible to bring them into direct contact with the solid material. DESs can contain a variety of anionic and/or cationic species, which result in a wide range of different properties. The solid to leach can be a crushed and grinded ore, but it can also be a fine-grained industrial process residue. After the solvent leaching, the liquid organic phase and the solid residue can be separated by centrifugation and filtration. In METGROW+ materials tested for DES were jarosite and fayalitic slag (both IDENER and VTT), and Greek limonitic laterite (from Agios Ioannis, in central Greece: "LAI"), landfilled Zn-rich sludge and steel sludge (IDENER).

Nine different DESs were tested: equimolar combination of choline chloride and malonic acid (fayalitic slag, Greek limonitic laterite, jarosite, steel sludge, landfilled Zn-rich sludge), equimolar combination of choline chloride and malonic acid with iodine addition (fayalitic slag, Greek limonitic laterite, jarosite, steel sludge, landfilled Zn-rich sludge), equimolar combination of choline chloride and boric acid (fayalitic slag, jarosite), combination of choline chloride and urea (1:2) (fayalitic slag, jarosite), combination of sodium acetate and urea (1:2) (fayalitic slag, jarosite), combinations of choline chloride, malonic acid and oxalic acid (1:0.9:0.1 and 1:0.5:0.5) (Greek limonitic laterite, steel sludge) and combinations of choline chloride, oxalic acid and ethylene glycol (1:0.75:0.25 and 1:0.5:0.5) (jarosite). For the preparation of DESs, components were mixed in a fixed molar ratio at 100 °C until homogeneous liquid was formed and iodine was aggregated to the experiments with I2 addition. Then, the leaching extractions were carried out varying the following parameters: duration (8-48 h), S/L-ratio (5-20 %) and presence of iodine or not. The most suitable DESs, according to the experimental results, were selected for each material.

The objective of the optimization has been focused on maximizing target metals in each material and minimizing the amount of iron extracted. For jarosite Zn leaching yield was 65-100 %, while Pb was not extracted. The selectivity against unwanted elements was poor (SI = 0.27). For fayalitic slag Zn leaching yield was 60-80 %, but the selectivity poor against unwanted elements (SI = 0.07). For steel sludge and landfilled Zn-rich sludge Zn yields were 90-100 %, and also high selectivity against unwanted elements was observed (SI = 15.6 and 1.65 for landfilled Zn-rich sludges and steel sludge, respectively). For Greek limonitic laterite, Ni yield was low, 10-30 % and selectivity against unwanted elements poor.

Regarding leaching yield, the best results were obtained for the recovery of Zn in fayalitic slag, jarosite, steel sludge and landfilled Zn-rich sludge. The equimolar combination of choline chloride (ChCl) and Malonic acid (MaA) with iodine addition was the selected DES among

those tested in the screening. The addition of I_2 seems to increase the extraction percentages of most of the metals, including Zn, the most presenting and therefore interesting one in the material. Thus, it can be stated that the iodine oxidized the metals effectively, allowing them to be solubilized in the DES. However, the ChCl:MaA DES leads to a poor extraction of Ni, Cr and Mg in Greek limonitic laterite. The DESs product of the combination of choline chloride, malonic acid and oxalic acid leads to lightly higher extraction of all metals and, specifically, an increase of 10 % in the leaching yield of Ni. The recovery of Pb was very low in jarosite that shows the low capability of ChCl:MaA DES to leach this metal. ChCl:Boric acid DES reached a higher Pb leaching yield (app. 47 %) but a lower recovery of Zn (app. 60 %). S/L-ratio of 20 % was suitable for all the materials expect to fayalitic slags. In this case, high S/L-ratio caused compaction of the solid mixture with DES, which did not make possible to separate the solid and the liquid by neither centrifugation nor filtration.

The regeneration of the solvents (DES) was tested in order to assess the possibility to reuse the DESs in the leaching step after the separation of the recovered metals. Two different strategies were considered: (1) the extraction of metals from DES using ILs and (2) the recovery of metals using electrodeposition techniques. The first strategy was tested using leachates from fayalitic slag. It was found a good recovery of metals from DES using the IL as well as a good performance for the reuse of the treated DES in a new extraction cycle.

2.7. Task 3.4 Plasma-pyro (TECNALIA, UMICORE)

A pyrometallurgical route to pre-concentrate different type of materials researched in the project was investigated by performing lab scale tests at TECNALIA. More specifically, this thermal approach aimed at extracting the metallic components (mainly the most volatiles ones such as zinc) to the fly ash fraction. To achieve that goal, tests at different operational conditions (temperature, flux addition, reducing agent content, time) were carried out. The different phases obtained during the tests were all characterized and conveniently distributed, according to the results, to other tasks partners (to WP5 for valorization of some slag residues, for example). The studied materials were landfilled Zn-rich sludge, jarosite, fayalitic slag and goethite. The nature of each material was different, requiring special design of research. In some cases, a combination of several thermal steps, some at oxidant condition and finishing with a carboreduction treatment at two possible temperatures, lower and higher, depending whether a separate metallic phase from a slag is possible or interesting to obtain.

For defining the range of temperatures in the thermal treatments, thermogravimetric analyses, under different atmospheres (air and argon), were performed for the studied materials. Preliminary thermal tests at oxidizing and reducing conditions (with some few grams of sample placed into a crucible and without capturing the fumes) were carried out to study the influence of several variables. Several temperatures, type of flux addition, waste to

flux ratios and, for the tests at reducing condition, also graphite percentages and graphite to waste ratios, were studied. Depending on the type of sample and of the treatment operating conditions, only one or two residual materials (metallic phase and slag phase) were obtained in each test. Furnaces were adapted so that the emissions could be controlled and captured to collect the produced fly ashes and to determine the quality of all the products. The chemical analysis allowed calculating mass balances of the processes and distribution of the valuable metals in the different phases produced during the treatments, thus obtaining conclusions about the performance of the plasma-pyro strategy within METGROW+.

For **landfilled Zn-rich sludge**, zinc, which was initially as zinc hydroxide, was nearly completely released and collected in the fly ashes as a zinc metal/zinc oxide concentrate including Pb, Na, Al, Mg, K and Ba at impurity levels (well below 1 % each element). The distribution coefficient to the fly ashes for the zinc was above 99 %. The residual material remaining in the crucible, under study in WP5, consisted of iron metal and some iron oxides (between 41 and 58 %) and the rest was a mixture of CaO, SiO_2 and Al_2O_3. For **jarosite**, zinc, which was initially as zinc sulphide, was completely released to the fumes at both temperatures used in the reducing step. Similarly, lead, initially bonded to the jarosite, was collected in the fly ashes. For both elements, the extraction yield was higher than 90 %. Consequently, a concentrate consisting of zinc and lead oxides (app. 50 % and 40 %, respectively) was obtained and its market potential is being analyzed in WP1. For **goethite**, zinc, which was initially as zinc iron oxide, was nearly completely released to the fumes (>95 %) at both temperatures used in the reducing step. Lead, initially as sulphate, was collected in the fly ashes. Consequently, a concentrate consisting of zinc and lead oxides (app. 84 % and 16 %, respectively) was obtained and its market potential is being analyzed in WP1. No additional improvement was achieved in terms of critical metals extraction (In, Ga, Ge, Ag) when comparing goethite to jarosite, as concentrations were not high enough. For **fayalitic slag**, zinc, which was initially bounded to fayalite and iron oxides, was nearly completely released to the fumes (>95 %) at both temperatures used in the reducing treatment, as Zn and ZnO. Lead was collected in the fly ashes as metal or suboxide form. Consequently, a concentrate consisting of a mixture of zinc/lead metal and oxides (app. 80 % and 10 % respectively, of each element expressed as oxides) was obtained and its market potential is being analyzed in WP1.

The residual solids, i.e. slags, were analyzed by WP5 and according to the preliminary results, they seem potential for hydraulic binders with SCM and AAIP binders. Depending on those studies and the conclusions from the comparative evaluation of approaches in WP1, a final decision will be taken in order to perform validation activities in WP6.

CHAPTER 3   Conclusions

In WP3 of METGROW+, several low-grade ores or wastes from European industry were studied with a broad range of metal extraction technologies. For all the materials (except for the Fe-Ni slag and for the automotive shredder residue), a potential technology was developed, based on the main criteria set in the objectives for WP3. As a result of the research performed in this work package, technology readiness levels were increased by 1-2 units, reaching TRL 4 for those technologies that fulfilled the work package objectives.

As a result of successful process development in WP3, METGROW+ continues with the original approach. From the developed hydrometallurgical metal extraction processes, target elements are recovered from leachates in WP4 (Recovery of metals from dilute and concentrated solutions) and residual solid reuse are studied by WP5 (Valorisation of residues). From plasma-pyro technology, no leachates are obtained, as the aim has been to produce solid fly ashes, being already market quality products. The economic aspects of developed metal extraction processes are studied in WP1 (METGROW+ Metallurgical System Toolbox), together with fully integrated processes developed as a cooperation of the whole project. The most potential processes will be validated in WP6 (Metallurgical system validation).