Metal Recovery from Low Grade Ores
and Wastes Plus

Deliverable 4.4
Report on metal recovery processes

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Executive summary

This deliverable, D4.4 "Report on metal recovery processes", summarizes the research done in WP4 of the METGROW+ project. The selected input streams were complex pre-concentrates produced in the extraction processes developed in WP3 ("Metal extraction") of METGROW+. The recovery methods applied were solvent-chemical recovery, supported liquid membranes, supported ionic liquid phases, biosorption, bioprecipitation and electrowinning.

The recovery process that combines Alkaline Oxidation (AO) and Acid Leaching (AL) provided good Ni and Co recovery results. However, the process requires further optimization, to reduce Ni and Co losses in the solid residues. The process compounded by the steps of Fe and Al precipitation, Ni precipitation and scavenger precipitation allowed a proper separation of the Ni from Greek laterite leachates by means of two steps in which the Ni precipitated partially. Promising results were obtained with solvent extraction for sulphate reduction, ionic exchange and hydroxides precipitation methods with an efficiency higher than 95% for Ni separation from Polish laterites leachates. On the other hand, the supported liquid membrane-based separation led to a good recovery of Zn from pre-concentrates. However, a pretreatment step was required for the removal of the Fe from the stream. Supported ionic liquid phases were applied for the recovery of Ge and In from goethite pre-concentrates with a recovery of 99% and 66%, respectively, showing excellent selectivity in comparison with the adsorption of Fe. The biosorption tests have shown promising results using chitosan as an adsorbent for the selective recovery of Ni over Ca (100%), Zn over Mg (100%) and Mn (94-100%). For both laterite and jarosite pre-concentrates, the sulfide precipitation experiments using indirect bioprecipitation techniques produced relatively low recoveries (43% for Ni and 79% for Co) but high selectivity (>97%). The use of direct bioprecipitation method led to the separation of Cu using strains of *Pseudomonas putida* and *Shewanella oneidensis*, which also allowed Cr recovery from the solutions. The use of microbial-electrochemical systems significantly increased the recovery of Cr. Besides, the assessment of carbon sources for biorecovery processes has pointed at acetate as the most promising energy and carbon source. Finally, electrowinning methods showed good results for the selective recovery of Cu and also for the use of Deep Eutectic Solvents as electrolytes.

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List of acronyms

AAS	Atomic Absorption Spectrometry
CTS	Chitosan
CE	Counter Electrode
ChCl	Choline chloride
COD	Chemical Oxygen Demand
CV	Cyclic Voltammogram
DES	Deep Eutectic Solvent
ELM	Emulsion Liquid Membranes
EW	Electrowinning
FSSLM	Flat Sheet Supported Liquid Membranes
HFSLM	Hollow Fibre Supported Liquid Membranes
IX	Ion Exchange
MA	Malonic Acid
MES	Microbial-Electrochemical Systems
PC	Pre-concentrate
RE	Reference Electrode
SILP	Supported Ionic Liquid Phase
SX	Solvent Extraction
WE	Working Electrode

I.   Introduction

Work package WP4 ("Recovery of metals from dilute and concentrated solutions") is devoted to the development of techniques for the capture and concentration of target metals from the dilute and complex pre-concentrates produced in the extraction processes developed in WP3 ("Metal extraction") of METGROW+. The specific objectives of WP4 are listed below:

- To further develop novel approaches for metal recovery from dilute and concentrated solutions based on physicochemical, biological and electrowinning approaches
- To define the optimal operational parameters for the selected technologies, *i.e.* operational conditions that maximise metal recovery (yield and selectivity) and minimise costs, resource use and environmental impact
- To achieve > 90% of metal recovery yield or adequate yield sufficient for following unit operations from the pre-concentrates produced in WP3
- To achieve > 85% of metal recovery selectivity from the pre-concentrates produced in WP3
- To assess the reuse of process liquid effluents in order to decrease process OPEX and environmental impact
- To reduce waste by achieving end-products with a value that can be reused in a circular economy approach
- To retrieve and gather information to be included in the METGROW+ toolbox

The pre-concentrates (PC) from WP3 used as input in the processes developed in WP4 are reflected in Table 1. The used PCs origin from the following materials: Polish saprolitic laterite, Greek limonitic laterite, landfilled Cr-rich sludge, steel sludge, landfilled Zn-rich sludge, jarosite, goethite, fayalitic slag, automotive shredder residue and old heap from copper leaching. The selected streams were treated by atmospheric acid leaching, heap leaching, solvometallurgical leaching, heterotrophic bioleaching and ionometallurgical leaching.

Pre-concentrate preparation method		Greek limonitic laterite	Polish saprolitic laterite	Landfilled Cr-rich sludge	Steel sludge	Landfilled Zn-rich sludge	Jarosite	Goethite	Fayalitic slag	Automotive shredder residue	Old heap from copper leaching
Atmospheric acid leaching	HCl as a leaching agent	PC1	PC5								
	H_2SO_4 as leaching agent	PC2	PC4					PC8			
Heap leaching	H_2O/NaCl as leaching agent						PC9[a], PC10[b]				
	Na_2SO_4/H_2SO_4 as leaching agent			PC11[a], PC12[b]							
	NaAc/HAc as leaching agent					PC13[c], PC14[d]					
	NH_4Cl as leaching agent						PC6[c]				
	NaOH as leaching agent						PC7[d]				
Solvometallurgical leaching			PC3			PC15					
Heterotrophic bioleaching				PC16						PC17	
Ionometallurgical extraction		PC18			PC19	PC20	PC21		PC22		
Mine leachates											PC23, PC24, PC25, PC26

[a] From the first step of leaching

[b] From the second step of leaching

[c] From raw material

[d] From thermally pre-treated material

II.   Work done and main achievements

Subtask 4.1.1 Solvent-chemical recovery methods development (VTT, TUC, IMN, OUTOTEC, PROFIMA) – Pre-concentrates PC1, PC2, PC3, PC4 and PC5

Pre-concentrate **PC1** from Greek laterites has been treated by TUC through several steps for the separation of impurities and valuable metals. HCl leaching involved batch tests and counter-current leaching (CCL). CCL was used to increase the extraction of metals, which is rather limited at high pulp densities and maintain the co-dissolution of Fe at low levels. Emphasis was placed on the purification of the pre-concentrate obtained from leaching tests using near-industrial conditions (e.g. solid: liquid (S/L) ratio = 30% w/v).

The first step (preliminary purification of **PC1**) involved the removal of Fe and other trivalent metals, e.g. Cr^{+3}, Al^{+3}, *etc.*, in the form of hydroxides, using Mg $(OH)_2$ as neutralisation agent by maintaining the pH at relatively acidic conditions, *i.e.* 3.5. The solution resulting from this step contained all divalent metals, including Ni, Co, Mn, Mg and Ca. The following process steps aimed at separating Ni and Co from Mn and the alkaline earth Mg and Ca. Separation was carried out by the combination of two processes, namely Alkaline Oxidation (AO) and Acid Leaching (AL) of AO solid residue. During the AO the pH was increased to basic values. To facilitate the separation of Mn H_2O_2 was used to oxidise divalent Mn to higher valence states (Mn^{+3}, Mn^{+4}). Mg and Ca remained in the aqueous phase, while Ni, Co and Mn were recovered in the form of a solid residue. The AL process involved the treatment of the solid residue at acidic conditions, to enable the selective dissolution of Ni and Co, given that high valence Mn is expected to remain in the solid state. To improve the effectiveness of the separation, the combined processes AO-AL could be repeated. The aqueous solutions of all AO steps contained mainly Mg, Ca and Cl. Calcium can be removed by precipitation as $CaSO_4 \cdot xH_2O$. The final stream containing Mg and Cl could be treated by pyrohydrolysis. By this process, it would possible to regenerate HCl which may be recycled in the leaching step and produce Mg$(OH)_2$.

Prior to the actual pre-concentrates purification, initial thermodynamic calculations were carried out by means of Visual Minteq software, to identify the best conditions that could allow the selective separation of impurities from the valuable metals. Visual Minteq is a free geochemical equilibrium model that can be used to determine the chemical speciation of ions in aqueous solutions and to predict precipitation of possible solid phases under variable conditions. The composition of the pre-concentrate, as simulated in Visual Minteq, is based on the experimental results. The molality of Cl^- anions was considered equal to the initial concentration of HCl used in the leaching tests. The molality of metal cations was calculated based on the chemical analysis of the pre-concentrates, and residual H^+ was estimated from the electroneutrality condition. The main objective of the simulation was to identify the pH ranges, where precipitation of metal hydroxides enables the separation of impurities from the

useful elements. Thus, the model was run by using fixed pH values, in the range 0-14. The metal hydroxides considered as possible precipitates were ferrihydrite (Fh), $Al(OH)_3$, $Cr(OH)_3$, $Ni(OH)_2$, $Co(OH)_2$, pyrochroite ($Mn(OH)_2$) or pyrolusite (MnO_2), brucite ($Mg(OH)_2$) and portlandite ($Ca(OH)_2$). The solid residues and precipitates formed in various stages were examined by XRD and SEM, while mass balance calculations were carried out in all stages.

One-step HCl leaching of LK laterite at 10% pulp density indicated that the most important steps determining the final recovery of Ni and Co and the purity of the Ni-Co stream are those involved in the combined AO-AL process. Repetitive application of the AO-AL steps greatly improved the separation of Mg and Mn from the valuable metals. For instance, the Mg/Ni ratio dropped from 6.9 to 0.05, when three cycles of the combined treatment were considered. Based on mass balance considerations, it was seen that after three stages of AO-AL the overall Ni and Co extraction can be considered good. A considerable advantage of the CCL operation at 30% S/L, in comparison with the one-step leaching operation at 10% S/L, is the drastic reduction of the volume of iron sludge produced. The percentage of extracted Fe dropped from over 60% to 0.5%. However, the overall Ni and Co extractions achieved were considerably lower compared to the previous case (purification of pre-concentrates obtained from one-step leaching). Some Ni and Co remained in the residue produced after CCL. It should be noted that the experimental simulation of CCL cannot accurately predict the performance of the process under industrial operating conditions and probably underestimates its effectiveness. Some Ni and Co were also lost in the produced MnO_2. Most of the extracted Mn was removed together with the MnO_2 solids, while more than 90% of the extracted Mg was fed in the pyrohydrolysis step for MgO recovery and HCl regeneration. Both CCL and AO-AL processes require further optimisation, pilot tests included, to reduce Ni and Co losses in the solid residues. For instance, Ni and Co losses in the MnO_2 solids could be probably reduced by decreasing the pH below 1 during the AL steps.

VTT has developed a Ni recovery and solution purification process that contains several steps. These include Fe and Al precipitation, Ni precipitation and scavenger precipitation. Pre-concentrate PC2, from Greek laterite, has been used as input. There is no technical or economical reason to precipitate Mg out from the process solution, but it is highly recommended because of environmental reasons. Mg precipitation would be part of the water treatment process and probably part of the process solution coming from the scavenger precipitation stage.

The purpose of precipitating Fe and Al was to remove both metals from the solution prior to Ni precipitation and thus improve the purity of the Ni product. Almost all Fe and Al were precipitated during the first 4 h. Based on the solids analyses also some Ni precipitated together with Fe and Al. Ni precipitation was carried out in two stages. The first stage aimed at precipitation of a pure Ni-Co hydroxide product while the second stage involved the so-called scavenger precipitation. The idea of the scavenger precipitation was to precipitate residual Ni as an impure precipitate that is circulated back to the leaching stage. The main

reason for the scavenger precipitation is Mn, which precipitates at a similar pH as Ni. Ni was precipitated as a hydroxide using MgO in the first stage, while lime was used in the second stage. Lime is cheaper and a more reactive reagent than MgO, but the advantage of MgO is that gypsum is not formed in the precipitation and thus the product is purer. Ni did not fully precipitate during the lime precipitation step. However, when the solution was used as the starting solution for Mg precipitation it was found that Ni precipitated during the test and thus its concentration was reduced. It should be notified as well that Mg precipitation was very low at this time.

Mg and Mn were the only major metallic components left in solution after the Ni precipitation stages. In some cases, depending on the environmental regulation, Mg could be removed directly from the process. The cost of Mg removal is high, but also the environmental burden of $MgSO_4$ removal is significant. $MgSO_4$ can be quite easily precipitated from the solution using slaked lime ($Ca(OH)_2$). Mg precipitation increased significantly when pH 10 was achieved and almost all Mg precipitated at a pH level of 10.5. Mn fully precipitated when the pH was 10. It seems that the precipitation pH should be 10.5 or higher to enable efficient Mg removal from solution.

IMN in cooperation with PROFIMA has developed several Ni separation techniques. The tests were carried out using three solutions obtained from WP3 leaching tests: two chloride solutions (after solvometallurgy-**PC3** and after HCl leaching- **PC4**) and one sulphate solution (after H_2SO_4 leaching-**PC5**). The following technologies have been tested:

• Solvent extraction – SX (for sulphate solution),

• Ion exchange - IX (for sulphate solution),

• Hydroxide precipitation (for chloride solutions),

• Sulphides precipitation (for sulphate solution).

The first of the tested techniques was solvent extraction. In the first stage of the study, the dependence of extraction yields and pH level was tested from the **PC4** solution for 3 different extractants at various concentrations and at two different temperature levels. The Versatic acid 10 extractant was chosen for further tests since it was characterised by the highest stability under the process conditions and it showed the largest selectivity. The second stage of the SX research consisted of (1) determination of extraction isotherms at a defined pH level and different temperature levels; based on the obtained results, McCabe–Thiele diagrams were marked on the obtained isotherms; and (2) determination of the stripping isotherm together with a McCabe-Thiele diagram. The obtained results allowed us to present a schematic draft of the counter-current solvent extraction circuit.

As part of the research, ion-exchange (IX) tests were carried out as well from the H_2SO_4 solution (**PC4**) using selected ion-exchange resins. The IX tests were carried out under static and dynamic conditions at room temperature. Four series of static experiments were carried

out for each ionite, differing in the pH level of the feed solution and the ionite form. Ni and Mg sorption tests under dynamic conditions were carried out using a selected ionite. A laboratory ion-exchange column was used, containing ionite resin previously conditioned in mineral acid. Preliminary experiments show that a Ni selectivity of 93% can be obtained from **PC4**.

Hydroxide precipitation was initiated by adding an appropriate amount of Ca $(OH)_2$ or $CaCO_3$ to the chloride solutions – **PC5** and **PC3**. In the beginning, subsequent fractions of sediments were precipitated. Each fraction precipitated at a different pH level. The experiments were carried out at ambient temperature and at an elevated one (40 °C) to obtain concentrates of selected metals. The next stage of hydroxide precipitation was carried out to precipitate a Ni concentrate from the **PC5** solution and to regenerate HCl by gypsum precipitation (H_2SO_4 addition). After precipitating all metals, the obtained filtrate solution with a high content of Ca ions was tested for its ability to precipitate gypsum (calcium sulphate dihydrate).

The sulphide precipitations were performed at ambient temperature, using a solution of technical purity Na_2S and the sulphate solution **PC4,** after Fe and Al removal. Subsequent fractions of sediments precipitated. Each fraction precipitated with varying addition of Na_2S and/or at a different pH level. The experiments were carried out to demonstrate the possibility of precipitating NiS concentrates from the leached solutions.

All the tested technologies allow to separate nickel ions with an efficiency higher than 95%. However, the obtained results proved that, of all the tested ones, two technologies were the most promising: solvent extraction technique and hydroxide precipitation coupled with HCl regeneration. Solvent extraction allows a high Ni recovery selectivity (**PC4** > 95%) and despite the low selectivity for the precipitation of hydroxides (**PC5-3** < 5%), it was possible to obtain nickel concentrates with a Ni content exceeding 30% and low concentrations (< 5%) of the unwanted metals. Both will be tested as part of the upscaling work package (WP6). Especially the solvent extraction technology is promising. These two metal recovery technologies were chosen for one common reason. Both, the solvent extraction technique and the hydroxide precipitation from chloride solutions with HCl regeneration, have the potential to become nearly waste-free technologies. In the case of hydroxide precipitation, gypsum is a significant waste which can be a market product (if it meets the standards for construction materials). In the case of solvent extraction technology, the only waste will be a mixture of Mg and NH_4^+ sulphates. It can also be a product (e.g. fertilizer) when meeting purity standards.

Even though solvent extraction and hydroxide precipitation were selected as the best ones, it is planned to proceed as well with the IX tests to the first stage of upscaling (WP6). In addition to optimisation of the sorption process, the follow-up research, will include ionite regeneration, to produce a nickel solution with a concentration of Ni ions appropriate for recovery of that metal. Based on future results, a decision will be made whether to continue the IX research on an enlarged scale or not.

Subtask 4.1.2 Selective metal recovery using supported liquid membrane - based separation technology (IDENER) – Pre-concentrates PC6, PC7, PC13 and P14

The target metal in supported liquid membrane experiments was Zn, which was the most concentrated metal in **PC6** and **PC13**, and Cu, Ni and Co as secondary metals. Hollow fibre supported liquid membranes (HFSLM), flat sheet supported liquid membranes (FSSLM) and emulsion liquid membranes (ELM) were first tested under the same experimental conditions to compare their efficiency in metal recovery, by using the commercial extractant LIX 84-IC diluted in kerosene, specific for Cu, Ni, Zn and Co. The behaviour of metal recovery was studied at different times. HFSLM showed the best efficiency, reaching 100% of Cu recovery in the stripping solution after 1 h, so it was selected for subsequent experiments with synthetic **PC6** and **PC13** solutions and real **PC6** and **PC13** solutions. The technology was also tested with leachates obtained in the same conditions as **PC6** and **PC13** but with the materials being roasted first (**PC7** and **PC14**).

In experiments with synthetic solutions of **PC6** and **PC13**, it was found that although Zn was extracted at 40-50% from the feed solutions, it did not pass to the stripping solution. Cu recovery in the stripping solution remained at 100% in all cases.

To obtain Zn recovery in the strip solutions with real leachates, the molarity of the H_2SO_4 stripping solution was increased one order of magnitude. Also, the concentration of LIX84-IC was increased to 40%, and an additional experiment was performed by using Cyphos IL 101 as extractant at 20%. Results showed that Cyphos IL 101 at 20% concentration had more affinity for Zn than LIX84-IC at 40%, and Zn and Cu were recovered in the stripping solution, while leaving behind the unwanted metals. Due to this reason, experiments with pre-concentrates were performed using Cyphos IL 101 as extractant diluted in kerosene at a higher extractant concentration (40%). Although Zn was recovered in the strip solution after 1 h, the recovered concentration was very low comparing to the leachates concentration. To test the influence of the time on the recovery, samples were withdrawn from feed and strip solutions after 24 h.

The obtained results showed that 40% Cyphos IL 101 was very selective for Zn extraction (99.9% of recovery). Fe was also extracted more than 44%. The recovery percentage in the strip solutions considerably increased in relation to the previous experiments, being Zn recovery of around 20%, and Fe recovery around 4%. It is important to note that the initial Zn concentration in e.g. **PC16** was around 6-fold higher than the Fe concentration, which means that the stripping solution was composed of 76% of Zn.

Subtask 4.1.3 Recovery of metal values from aqueous and non-aqueous leachates by supported ionic liquid phases (SILPs) (KULeuven) – Pre-concentrates PC4 and PC8

A goethite leachate (**PC8**) was produced and investigated by KULeuven using the supported ionic liquid phase (SILP) technique. First, the [A336][Cl] SILP was employed to investigate the

selective recovery of Ge from a synthetic goethite leachate that mimics the composition of the pre-concentrate **PC8**. Since Ge^{4+} would not be extracted as such to the SILP, citrate anions were added to the aqueous phase. This way, negatively charged Ge-citrate complexes are formed, which are extracted to [A336][Cl]. Given that Fe^{3+} forms more stable citrate complexes than Ge^{4+}, the reduction of Fe^{3+} with iron powder to Fe^{2+} was crucial. The affinity of Ge^{4+} for citrate is higher than that of Fe^{2+}, thus significantly improving selectivity for the former. Ti^{4+} would form very stable citrate complexes too, but it was observed that an additional benefit of adding the iron powder to the goethite leachate was that it precipitated titanium, thus efficiently removing this contaminant from solution. The Ge adsorption percentage from the simulated goethite leachate was 99%. A relatively pure Ge solution was obtained, with a Ge/Fe ratio = 9, which corresponds ton enrichment factor = 15,152 (selectivity = 100.0%) for this process. Therefore, the presented method is considered very selective, especially when comparing these values to the respective concentrations in the original leachate.

The [A336][I] SILP was synthesised and studied for its potential to selectively recover In from the real pre-concentrate **PC8**. The added value of the iodide system compared to the chloride system arises from the fact that, by addition of iodide ions to the aqueous solution, extractable $[InI_4]^-$ complexes can be formed, whereas iron does not form negatively charged iodide complexes and is therefore not extracted to the [A336][I] SILP. Reduction of Fe^{3+} to Fe^{2+} by addition of iron powder was again required, here to avoid oxidation of I^- to I_3^-. Despite quantitative results on a synthetic binary Fe-In solution (with iron in large excess compared to indium), the In adsorption percentage from the actual goethite leachate was only 66%. Nevertheless, a relatively pure In solution was obtained, with an In/Fe ratio = 8, which corresponds to an enrichment factor = 5,400 (selectivity = 100.0%) for this process.

For the laterite pre-concentrate **PC4**, a very selective pre-concentration step was successfully performed by dropwise addition of a 10 M NaOH solution. It appeared that, by increasing the pH of the laterite leachate to a value of 5.6, the interfering elements Fe, Al and Cr could be quantitatively removed from solution (down to 0 ppm) without affecting the Co concentration (100% recovery). This can be explained because the precipitation-pH zones of the matrix metals do not overlap with the one of Co. The very efficient hydrolysis-precipitation pre-concentration step was followed by adsorption on the Cyanex 272 impregnated Amberlite beads (Cya272 SIR). The Co adsorption percentage from the laterite leachate could be increased up to 75%. Although co-adsorption of Ni was very low, also Mn and Mg appeared to be adsorbed by the SIR, in addition to Co. Given the very high Mg concentration, saturation of the sorbent readily occurred, which is why a relatively high amount of SILP particles was required to achieve sufficient recovery of Co. Optimisation experiments to avoid Mg contamination of the SIR would be interesting in this respect. Then, only the valuable metal Mn must be separated from adsorbed Co, which may be easily achieved by performing a selective stripping step with an inorganic acid.

Subtask 4.2.1. Biosorption (UGent, RISE) – Pre-concentrates PC9, PC10, PC11, PC12, PC13, PC14 and PC15

UGent has studied the biosorption of metals from the selected streams PC9, PC10, PC11, PC12, PC13, PC14 and PC15. The high metal concentrations of most of the leachates (several g/L) are typically not suitable for the biosorption process. Thus, chemical precipitation was performed prior to biosorption in PC9, PC10, PC12, PC13 and PC14 to generate lower metal concentration solutions for the subsequent application of biosorption. Because of limited availability of pre-concentrates from WP3 (either in volume or in time), the work started with synthetic leachates that mimicked these pre-concentrates, before validating the tests with the real streams.

The chemical precipitation was performed sequentially at increasing pH values (typically 4, 6, and 8) using a protocol provided by VTT. $Ca(OH)_2$ was used for precipitation at pH 4 and NaOH for precipitation at higher pH values. Zn was effectively (93%) and selectively precipitated from PC9 at pH 8. Minor amounts of Zn (< 4%) were lost in the precipitation at pH 4 and 6. Pb was effectively (99%) precipitated from PC10 at pH 8; however, Pb and Zn were not effectively separated, possibly because the final pH was slightly higher than 8.0 (pH 8.2). This indicates the need to finely control the process conditions in order to obtain selective precipitation. The target metal was highly enriched in the precipitate (42% Zn for PC9 and 53% Pb for PC10) and other impurities accounted for less than 1%. For PC15, a significant amount of Zn (21%) co-precipitated with Fe at pH 4, thus only 79% of the initial Zn precipitated at pH 8.

As tested in a synthetic leachate, the precipitation at pH 6 was not effective to remove impurities from PC14. Thus, the precipitation of the real leachate PC14 was performed only at pH 8. At this pH value, 97% Zn was precipitated with high selectivity against Ca (98%). Although the selectivity against other metals was poor (<85%), the amount of Zn in the precipitate (24%) was much larger than other impurities (e.g. 0.2% Al). This contrasts with PC13, a similar pre-concentrate obtained from AcH/AcNa heap leaching of Zn-rich sludge without thermal treatment. PC13 contains a large amount of Fe (several g/L) that is problematic for the selective recovery of Zn. A first precipitation step at pH 7 removed 97% Fe, but 23% Zn co-precipitated as well. Thus, only 72% of the initial Zn was selectively precipitated (> 80%, except against Mn) at pH 8.

After precipitation, significant amounts of metals remained in the solutions. Moreover, other non-targeted, hazardous metals may be present as well. Biosorption is an attractive option for the recovery of these lower metal concentrations and/or depollution of the solution.

The biosorption work was performed until now using synthetic leachates mimicking those produced by WP3 partners. Validation with real pre-concentrates will be done for the most successful cases in the following months. Biosorption was tested from the synthetic leachates with and without a previous precipitation step. A few biosorbents were effective for adsorbing target metals from the leachates. Chitosan (CTS) was effective for the adsorption of Ni and Zn.

Other materials such as microalgae (MaB), macroalgae (GT, SM), biochars (SSBC, RHBC) and phosphorylated biosorbents (pSD, pMWBC) were also effective to a different extent for Zn sorption. In most cases, a precipitation step was needed prior to biosorption and biosorption was used as a polishing step. Nevertheless, CTS reached high sorption efficiencies (97% Ni, 97% Zn, 75% Pb) from the original high metal concentration leachates too (**PC10**, **PC11**).

CTS was selective for Ni over Ca (100%) in **PC11** and for Zn over Mg (100%) and Mn (94-100%) in **PC9**, **PC15** and **PC14**. However, Zn sorption was not selective compared to Cd (0%) in **PC9** or Pb (23-62%) in **PC10**. The Zn selectivity over Cd in **PC9** was very poor (< 6%) with all biosorbents. Although this is a negative result for the aim of Zn recovery, it may be an opportunity if biosorption is to be used as a polishing step. Taking as reference the metal discharge limits imposed by the Flemish regulations (VLAREM II), CTS and GT removed Cd to below the discharge limit (0.2-0.6 mg/L) and CTS, MaB, GT, pSD and pMWBC removed Zn to below the discharge limit (3 mg/L) when used after chemical precipitation in **PC9**. Moreover, it could be explored whether the metal-loaded biomaterials collected in this polishing step could be recycled to another extractive technology (e.g. pyrometallurgy), possibly if the metal concentrations in the loaded biomaterials are high and the cost of the material is low.

The metal targets of **PC12** were Cr and Ni, which were present in solution in combination with Fe. Because of the low pH, Ni and Cr biosorption was not effective (< 50%). However, Fe was very effectively adsorbed (> 90%) with several sorbents (CTS, MaB, pSD, pMWBC). In the case of phosphorylated biosorbents (pSD, pMWBC), the selectivity of Fe over Cr and Ni was high (> 85%), which shows a potential route to remove Fe without removing Cr (metals that are difficult to separate by chemical precipitation). The biochar SSBC also showed high selectivity for Fe (> 99%) and, although the sorption efficiency was lower (79%), it could be a cheaper option for this strategy. Moreover, RISE will support a further development of the biosorption process by means modelling tools.

Subtask 4.2.2 Bioprecipitation (UGent, RISE, VTT) – Pre-concentrates PC2, PC9, PC10, PC16 and PC17

Indirect bioprecipitation

Indirect sulphide bioprecipitation has been applied by VTT for the treatment of **PC2**, **PC9**, **PC10**. Such technique utilises sulphate-reducing microorganisms which reduce sulphate to sulphide in anaerobic conditions utilizing an external energy (carbon and electron) source. The produced sulphide is used to precipitate metals from different leachates as metal sulphides.

In a possible continuous process, the high concentrations of ferric Fe, Al and sulphate in the pre-concentrates is first reduced with the use of lime or calcium carbonate. Then the bioreactor effluent containing sulphide is used to precipitate the remaining metals in a specific order so that all the metals can be recovered selectively. The resulting metal-free solution is fed to the bioreactor and the remaining sulphate is reduced to sulphide, which is recycled back

to the metal precipitation stage together with bicarbonate (alkalinity). Additional pH control may be needed in the metal precipitation units.

The sulphate-reducing bioreactors utilised in this study produced suitable amounts of effluents with sulphide concentrations high enough to be used for sulphide precipitation. The main metals of interest were Ni and Co in the laterite leachate (PC2) and zinc in the jarosite leachate (PC9, PC10).

For both laterite and jarosite leachates, the sulphide precipitation experiments were successful in terms of reaction kinetics, pH and redox potential observation and visual inspection of the formed precipitates. Recoveries of 43% for Ni and 79% for Co were obtained for the laterite leachate. Despite the relatively low recoveries, the selectivity for Ni and Co over other metals was as high as 97%. For the jarosite leachate PC9, a recovery of 98% was achieved for Zn with a corresponding selectivity of 23% over other metals. The low selectivity was caused by the precipitation of Cu alongside Zn; however, the concentration of Cu was low in the leachate and the purity of the final ZnS product was 98%, being high enough for a feasible process. The study will be performed as well with preconcentrate PC10.

A kinetic-growth model and a flowsheet model of the indirect sulphide bioprecipitation process, *i.e.* SRB (sulphate reducing bacteria) process, have been developed by RISE and simulated in the software tools MATLAB and SuperPro Designer®, respectively. The models estimated the sensitivity of the process against sulphate and pH alterations and assessed the excess of sulphate or sulphide in respect to metal concentration, factors important for the feasibility of the process in a METGROW+ flowsheet context. Performing a similar assessment experimentally would imply an extensive and laborious work because of the slow growth of the microorganisms. The simulation allows the formulation of predictions that can be verified experimentally, reducing the number of experiments needed. The models showed how the SRB process is affected by the relevant sulphate concentrations in the METGROW+ effluents after chemical and biological leaching with sulfuric acid. This information is critical for the design of the process and has been useful for developing strategies for the experimental design of the upcoming trials. In addition, the models have shown how the METGROW+ effluents from WP3 have an imbalance of low metal concentrations in respect to sulphate concentration which will create an excess of either sulphide concentration or incomplete sulphate conversion. These factors will be considered for process optimisation.

Direct bioprecipitation

UGent developed direct microbial reduction and precipitation using viable bacterial cells for the recovery of metals from pre-concentrates PC16 and PC17. For this purpose, novel microbial-electrochemical systems (MES) have been developed as novel reactor systems for metal recovery, allowing the use of cathodes as sustainable, clean, economical electron donors (energy source) for microbial respiration and metal recovery.

The primary metals targeted from METGROW+ streams where Cr from Cr-rich sludges (via Cr^{6+} reduction to $Cr(OH)_3(s)$) and Cu from automotive shredder residues (via reduction/precipitation of Cu^{2+} to CuO and/or Cu^0). As for "Subtask 4.2.1. Biosorption", high metal concentrations (several g/L) are not suitable for application of direct bioprecipitation because of the high toxicity of metal ions to viable microbial cells. However, the application of direct microbial bioprecipitation after chemical precipitation or dilution (mg/L) of concentrated streams could provide routes for their application in METGROW+. As part of this subtask, the aim was not only the metal removal via bioprecipitation, but also the potential valorisation from waste streams by synthesis of nano and/or microscale metal precipitates with the vast potential application as functional materials.

Cr^{6+} and Cu^{2+} recovery was tested with the archetypal dissimilative metal reducing bacterium (DMRB) *Shewanella oneidensis* MR1 and the novel strain *Serratia marcescens*. Additional experiments were conducted with *Cupriavidus metallidurans* CH34 and *Pseudomonas putida*, highlighted in the literature for high resistance to heavy metal toxicity. In addition to their ability to take up and accumulate metals, these strains have been applied mainly from metal remediation perspectives. Therefore, their application for metal recovery here is prudent and worthy for further exploration. Based on an extensive literature survey of key factors that influence metal bioprecipitation, experiments were conducted with synthetic solutions for a range of parameters (pH, temperature, metal and bacterial concentration, oxic/anoxic conditions, etc.).

Based on the results from microbial tests, a proof of principal MES was developed and further tested. The conditions selected from the optimised experimentation with microbial species were mimicked in the MES.

For Cu^{2+} solutions, bioprecipitation of microscale copper oxide was achieved using strains of *P. putida* and *S. marcescens*. Further experiments for these strains will aim to optimise and validate Cu bioprecipitation for METGROW+ leachate streams from automotive shredder residues. For Cr^{6+} solutions, high reduction (> 50%) and removal (> 54%) was obtained with *S. oneidensis* MR-1. Based on the optimal conditions of the initial tests, a proof of principal MES was developed consisting of ion-exchange membranes, with the application of cathodes as sustainable electron donors for microbial bioprecipitation. High Cr^{6+} reduction and removal were achieved in the MES, with maximum reduction (as Cr^{3+}) and removal of Cr by 83% and 61%, respectively, after 24 hours of incubation time. Further experiments will aim to optimise and validate Cr^{6+} microbial and microbial-electrochemical bioprecipitation with METGROW+ leachate streams from Cr-rich sludges.

Subtask 4.2.3. Assessment of cost-effective environmental energy sources for biorecovery processes (RISE, UGent)

The energy source of the SRB process significantly contributes to the operational cost of the process. The price of carbon source and electron source is assessed with respect to the amount of ZnS that can be potentially produced from sulphate reduction to sulphide in the biological process and where the sulphide reacts with Zn^{2+} as a model ion in WP3 leachate. The price is approximately 130-260€ for acetate, ethanol, molasses and methanol, 100-400€ for hydrogen and 660 and 2000€ for lactate and formate, respectively. These calculations are based on a total conversion of the substrate into bicarbonate. In the case of hydrogen, it is hydrogen and carbon dioxide that are used as gases (the price of carbon dioxide not included in the assessment). This process needs additional process equipment to provide gas for liquid mass transfer. However, it is commonly seen that ethanol is only partly converted to acetate, which makes ethanol three folds more expensive than acetate. A similar observation can be done with molasses, which availability is limited to central parts of Europe. Moreover, if the carbon source is not completely converted, it becomes a water management problem of the process as it contributes to water pollution through the increase of chemical oxygen demand (COD). In the assessment of carbon sources, RISE has considered both the cost and the zero-waste criterion where the metallurgical process should recover the water used in the process. Acetate was chosen as the most promising carbon and energy source based on i) the price per recovered metal sulphide, ii) a growth kinetic survey of literature data, iii) the production of by-products contributing to water pollution, iv) the availability all over Europe, v) avoiding the use of hazardous/explosive chemicals and additional process equipment and vi) the fact that acetic acid is used in some of the leaching processes in WP3. Although acetate was not the carbon source that promoted the fastest microbial conversion efficiency there was no clear trend favouring any other industrial relevant carbon source based on specified criteria. Efforts will be done to improve the conversion rate on acetate while reducing the water requirement of the process. The cost of the acetate is approximately 20% of the potential revenue of Zn concentrate assuming 85% purity (~ 1270€/ton ZnS).

Subtask 4.3.1 Metal electrodeposition from Deep Eutectic Solvents (IDENER, IMN) – Pre-concentrates PC18, PC19, PC20, PC21 and PC22

IDENER has set up a process for the electrodeposition of metals from pre-concentrates produced by ionometallurgical extraction using Deep Eutectic Solvents (DES).

Generally, the electrodeposition of metals and alloys from aqueous electrolytes is limited by the narrow electrochemical window and hydrogen evolution. Ionic liquids are a promising alternative to surpass these disadvantages. Choline chloride (ChCl), a quaternary ammonium salt, can form deep eutectics by mixing with numerous organic compounds and it has been shown that DES has good electrical conductivity. For that reason, pre-concentrates obtained

using DES made of choline chloride and malonic acid (ChCl: MA (1:1)) from five different materials treated in the project (**PC18**, **PC19**, **PC20**, **PC21**, **PC22**) will be tested using the best operational conditions obtained in this report. For this purpose, ChCl:MA (1:1) DES has been characterised using a three-electrode cell as set up where the current electrode (CE) and reference electrode (RE) were platinum and Ag/AgCl respectively and two different working electrodes (WE) were tested (platinum and glassy carbon). The objective of this characterisation is to study ChCl: MA (1:1) DES cyclic voltammograms (CV) under different operational conditions.

CV allows the study of the relationship between the potential applied to a WE and the resulting current flow. In a solution with metals of interest, the correct application of this technique allows for important information regarding the electrochemical process to be derived including thermodynamics, interfacial kinetics, identification of mass-transfer regime and rate-limiting processes. To study and understand the behaviour of the selected DES when working as an electrolyte, this technique was applied to the DES without metals. Information regarding the operational window of ChCl: MA (1:1) DES using different WE helped to select the best operational conditions to improve the further recovery of metals.

Different operational windows were possible depending on the WE used. Glassy carbon WE offered a wider operational window and current densities were lower than on Pt. The increasing influence of the scanning rate to reduce current of oxidation current was monotonous, but it appeared that the behaviour of the system suffered from fewer variations when using a glassy carbon WE. After determination of the values of electrochemical windows using these two different WE, it could be concluded that glassy carbon offered a wider operational window and more stable conditions for the recovery of metals previously extracted with ChCl: MA (1:1) DES using electrodeposition techniques. The experiments will proceed during the following months to study the electrodeposition of metals from the pre-concentrates **PC18**, **PC19**, **PC20**, **PC21** and **PC22**.

Subtask 4.3.2 Recovery of copper from dilute solutions (HCM) – Pre-concentrates PC23, PC24, PC25 and PC26

HCM tested the recovery of Cu from actual acidic leachates collected from 4 abandoned open-pit copper mines (pre-concentrates **PC23**, **PC24**, **PC25**, **PC26**) in Cyprus by Solvent Extraction (SX) and Electrowinning (EW) processes. The recovery of Cu was achieved using a laboratory SX pilot plant and the electrolysis of the copper electrolyte took place in a laboratory scale EW cell. Approximately 30 m^3 of Cu containing leachates were transferred from the pit of each mine to the premises of HCM for all the tests.

Several chemicals analyse and preliminary tests (including copper solubilities) were performed on the collected samples. A number of SX laboratory experiments were carried out to find the optimum parameters and the optimum stages of SX and stripping through the isotherm

curves. Following the preliminary tests and based on the obtained results, copper extraction tests were performed with a pilot Solvent Extraction plant. The pilot plant was operated with each pre-concentrate for 27 days and the solution was fed into the plant with a flow rate of 12 L/h. Two stages of extraction (E1, E2) and one stage of stripping (S1) were selected. The experiments were carried out by using 2% and 4% of the extraction agent ACORGA M.5640 with an O/A ratio = 1:1. The loaded organic phase was agitated with stripping solutions with O/A ratio 1:1. During the experiment samples of pre-concentrate, raffinate, organic solution, electrolyte was taken for Cu analysis every 2 h. The aqueous and organic solutions were analysed for copper concentration by atomic absorption spectrometer (AAS). The electrolyte solutions were analysed for Cu by iodometric titration and the acid concentration was analysed by caustic titration. It was observed that the recoveries of Cu in all samples were higher than 20 g/L after 27 days.

The electrolyte produced by the solvent extraction pilot plant was transferred in the mini EW plant for electrolysis. Copper cathodes were produced using the Electrowinning method. The Cu content in the copper cathodes was measured with a portable XRF instrument and it was found to be 99.9% Cu. Further experiments will be developed during the next months to further optimise the metal recovery.

III.   Conclusions

In WP4 of METGROW+, the recovery of metals from several pre-concentrates produced from low-grade ores or wastes from the European industry was studied through a broad range of technologies.

The most promising technologies selected for further testing in "metallurgical system validation" work package (WP6) were solvent extraction, ion exchange and (hydroxide) precipitation. Each of these technologies allow to separate Ni ions with an efficiency higher than 95%, producing Ni concentrates with Ni content exceeding 30% and low concentration of unwanted metals.

Although some of the tasks have still not fully finished, the current information shows the potential of some of the most innovative techniques such as SILPs, biosorption and bioprecipitation for the coupling with more established techniques (such as precipitation) for the recovery of valuable metals present in very low concentrations from complex mixtures. The experimental work within the biosorption, bioprecipitation and electrowinning activities will be continued during the next months to validate the developed techniques with pre-concentrates from WP3.