TREASURE

D5.5: Materials recycling/recovery assessment report

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Technical References

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CO = Confidential, only for members of the consortium (including the Commission Services)

EXECUTIVE SUMMARY

The objective of Task 5.3, D5.5, is to assess the recycling performance as can be achieved by the application of existing metallurgical processes to recycle a range of different car electronics, which are also treated in the UNIVAQ process as developed in the TREASURE project.

Starting from a wide simulation of existing (well-advanced) metallurgical processes' sustainability performances, TREASURE will compare them with the already existing bio-hydrometallurgical process patented by UNIVAQ, which is reconfigured to treat car electronics. Here, a selected set of critical materials will be recovered through a lab-scaled version of UNIVAQ's process, which will be expanded to a pilot scale test in WP6.

The car parts as processed in the UNIVAQ process will be assessed in terms of recycling/recovery of critical materials, as well as for all other materials present in these parts when being processed in existing well-advanced metallurgical processes. The assessment of material recycling and recovery in existing processing routes is performed by the application of rigorous and physics-based process simulation models. This approach is based on the same approach as applied in Task 3.3 of this project, however the models and flowsheets have been developed in this Task 5.3 specifically for the recycling of the car electronic components as considered in WP5.

These models include the complex interlinkages of all functional materials in the car electronic parts as well as all chemical transformation processes in the reactors in the system model in versatile flowsheet simulation modules. These flowsheets as included in the model for the recycling of car electronics have been selected from the wide of range of industrial BAT (metallurgical) recycling infrastructures available. Successful accomplishment of such rigorous recycling assessment requires that detailed product data of the car (electronic) parts for which the recycling assessment is being performed, is available, i.e., in this case for the different car electronic parts and their build-up. The composition of the parts needs to be available in full compositional detail defined as compounds. Analyses on just an elemental basis are not providing enough information to assess recyclability. For example, the recycling of aluminium present as metallic Al is different from the recycling performance of aluminium present as Al_2O_3. Whereas metallic Al can be recovered, if separated from other materials and sent to aluminium recycling processing, Al_2O_3 will always go lost and cannot be recovered as Al.

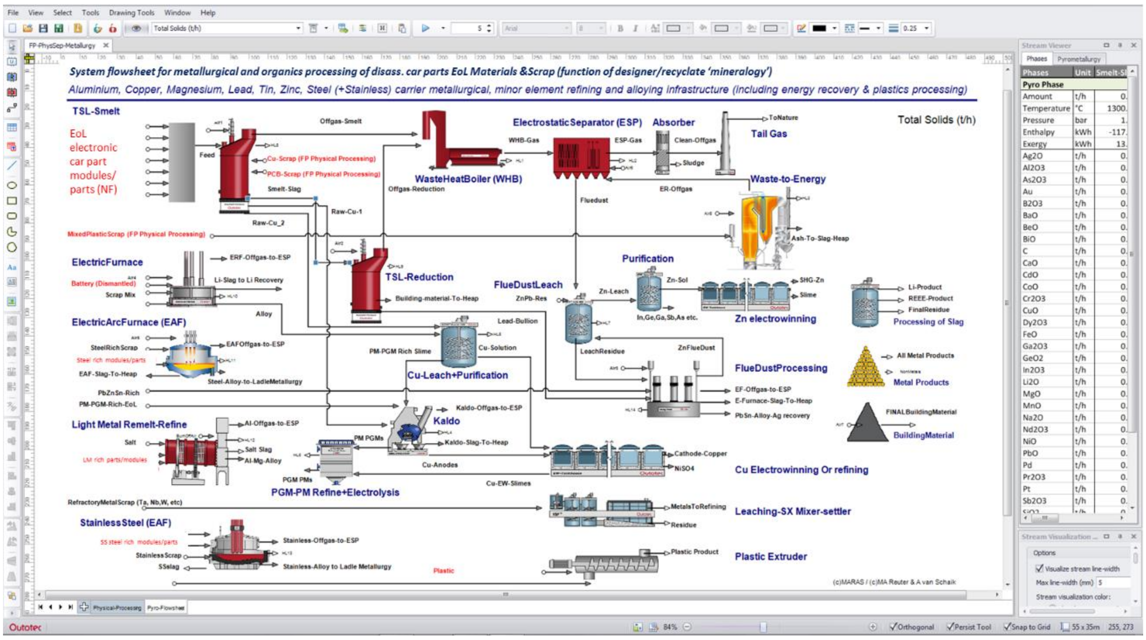
Data availability to be made available in sufficient details was defined to be crucial for completion of this Task in the DoA (not part of the work nor under the control of MARAS). For the IMSE detailed compositional data was made available TNO. For all other parts as processed in the UNIVAQ plant, only elemental analyses were available in WP5. As this does not provide enough depth to assess their recyclability, this limited the number of parts which could be assessed. However, MARAS has derived compositional data on the possible PCB composition(s) from the MISS data files as provided in WP3 by SEAT and performed the recycling assessment on this basis. The evaluation of different processing routes and applied approach to do so, remains however valid and provides useful insights. Hence, the following parts have been assessed for recycling performance in existing industrial metallurgical processing options:

- IMSE
- PCBs (including components)

Similar to the approach as applied in Task 3.3, the figure below is a visual summary of the simulation-based approach used to determine the recycling rate of the different electronic car

parts. It shows that each part is processed in a segment of the Metal Wheel for optimal recovery of materials and energy.

Depending on the composition of the part, either the best processing option have been selected upfront, or best options are selected based from the range of BAT processing options as available in industry (depicted in the Figure below and presented by the Metal Wheel where each segment in the Metal Wheel is representing a full metallurgical recycling infrastructure as included in the model). Selection and assessment have been based on the expert knowledge within MARAS.



The flowsheet model used for this simulation-based approach is based on industrial economically viable processing routes. Detailed flowsheets have been developed in this Task specifically for the processing of the different electronic car parts and are underlying this approach. It contains almost 190 unit operations for the ca. 310 materials and compounds in the car parts and produced by the flowsheet as well as over 840 streams for all phases including metals, molten flows, aqueous, dust, slimes, slags, calcine etc.

The recycling assessment, which incorporates the full compositional detail of the parts recovered through existing metallurgical processing and energy recovery flowsheets and calculated recycling rates for the total parts as well as all individual materials/elements, provides the physics-based quantification to compare and benchmark these existing recycling routes against the developed bio-hydro metallurgical pilot plant within TREASURE. The simulation-based approach, the detail as included in the assessment and the detailed results thereof provides the basis, together with the UNIVAQ lab-scale process data, for the level of detail on which the results of both existing processing and the UNIVAQ process are presented in this report. As the details of the bio-hydro plant were dependent on the completion of Task 5.4 by UNIVAQ, which was due at the same delivery date as this report, this caused a one and half month delay in Delivery data of D5.5.

The assessment of the recyclability of the various electronic (car) parts under consideration, as well as of all their composing materials, elements and compounds (so not just CRMs), is of importance to evaluate not only the recycling performance of these parts in terms of recovery of CRMs and other materials, but provides also the basis to compare the bio-hydrometallurgical plant with existing (metallurgical) processing options and position the UNIVAQ process in the market. The simulation-based recycling assessment also includes the assessment and quantification of produced by-products and their role and application in the Circular Economy. Similar data is presented for the UNIVAQ processes. These are crucial parameters to be included in the comparison. This implies that a true comparison of the performance of the bio-hydro plant and existing well-advanced industrial scale metallurgical processes in this Task as discussed in this report, is based on the comparison of recoveries as well as losses and residue creation, purity of produced metals and composition of residues, energy consumption and required addition of primary materials such as solvents, water and chemicals required to operate the processes. This detail will be produced by the recycling simulation models to assess recycling in existing (metallurgical) processing options and is presented in Chapter 4. The process description and results of the UNIVAQ processes are provided in Chapter 5 as presented in D5.4. On this basis and presented results, the comparison of the different processing options is performed in this work.

Hence, the comparison and benchmarking of the different recycling options has been performed based on the results as derived from the process simulations with comparable level of results of the bio-hydrometallurgical plant based on the assessment and processing of different electronic parts. As this detail of assessment includes all data relevant for CE, this is a rigorous basis to evaluate different processing options within the perspective of Circular Economy. The assessment has been based on the results of the lab-scale tests for the UNIVAQ plant. Optimized process results are expected from the pilot as performed in WP6 and will be reported on for this level for the UNIVAQ plant in D6.2.

The modelling, data processing and full recyclability analyses and interpretation of the results for the recycling of the different car electronic components have been performed by MARAS and are presented in this report. The data on the IMSE has been provided by TNO. The MISS data has been provided by SEAT in Task 3.3 and has been used and processed by MARAS to obtain data on the PCB part. The work as described in D5.5 on the recycling assessment as carried out by MARAS provides the rigorous basis for the comparison and benchmarking of the bio-hydro pilot plant. The description and results of the UNIVAQ processes for the different car parts are included by UNIVAQ in Chapter 5. The evaluation of the bio-hydro plant and existing processing routes as reported on in this deliverable is performed by MARAS.

Existing (metallurgical) processing options as shown, have proven recovery rates, purity of the produced metals, alloys, materials, slags and other output flows and residues created in the process. Their application can occur in terms of circular economy. On the other hand it can be conjectured that the UNIVAQ process, as tested on lab-scale based on different KPIs and parameters, may at this stage not provide products and materials that can all find an economic application in the circular economy when processing the IMSE as well as of the PCBs and components. This could be further optimised and refined in the pilot plant tests in WP6 and will be included in a follow up assessment.

The existing processing routes result in industrially and economically viable (generally also higher) recycling rates, much more materials/metals are recovered in these processes with a very high purity. This is something which cannot yet be fully achieved by the UNIVAQ process in which part of the metals are lost to residue streams (solid and waste-water). Plastics and organics are recovered in existing processing as energy and reductant, instead of becoming part of the residue flows of the process, as is the case for the UNIVAQ process. The UNIVAQ processes are characterised by a high need of input of other materials to run the process operable, such as water, chemicals and metal powders (for the GDR2 process). The process results in losses of valuable and other materials to the residue streams as well as the creation of high amounts of complex residues which have to be disposed of or have to be further processed as far as possible (something which is limited by the mix of metals/materials reporting to these residues). It is important to discuss how and to what extend these processes and their current high need of primary materials and water, combined with small quantities of (non LME grade) recovered metals and production of large amounts of waste water and solid residue, containing a mix of materials and non-recovered metals, can be justified from a Circular Economy and sustainability point of view. Based on the results and refinement of the UNIVAQ processes in the pilot scale tests, these points of importance for process improvement are recommended to be considered and can be included in the assessment within WP6. It is hence expected that the pilot tests will focus on these points and therefore will result in a more balanced and optimised presentation of the process and flows, and might solve several points of attention as discussed here.

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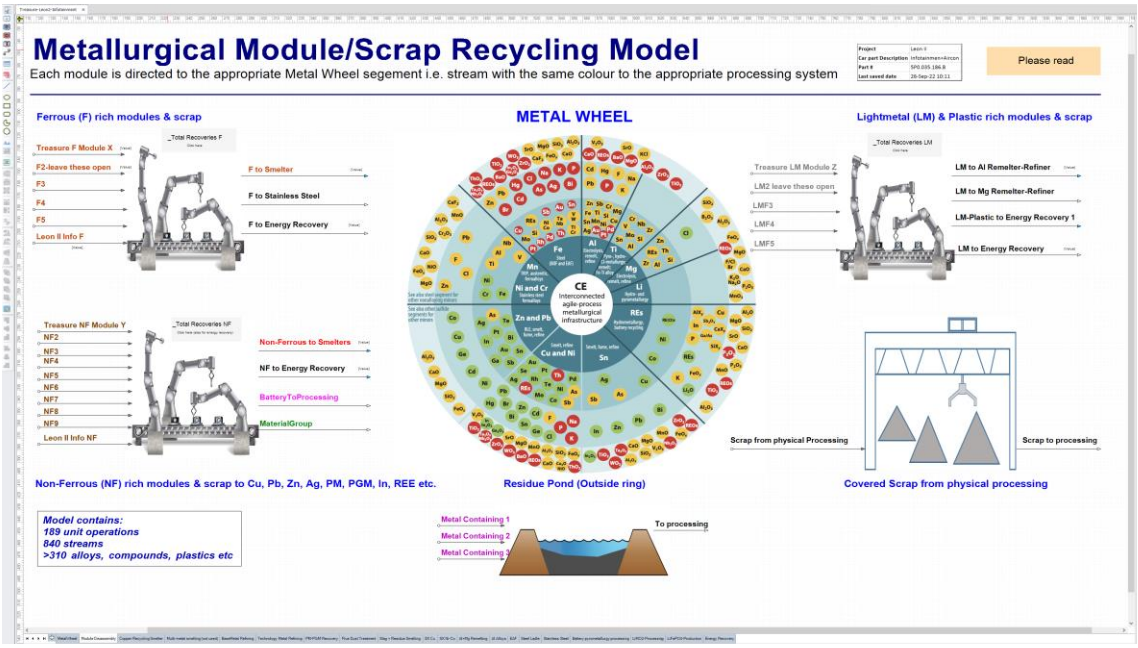
1. Introduction

1.1 Goals and purpose of the Material recycling and recovery assessment

Task 5.3 will assess the recycling performance of existing metallurgical and other final treatment processes for the different car electronic parts as are processed in the UNIVAQ process. In this task 5.3 innovative recycling system models are specifically developed for and applied to assess the recycling/recovery of these car electronic parts. These models simulate different existing metallurgical processing options suitable for the processing of these car parts in order to optimally recover the critical and other materials from it. Recycling performance of these different parts is assessed in this task to provide a comparison and existing benchmark for the developed bio-hydro pilot in the TREASURE project (lab-scale in this stage). The simulation models as developed and applied provide a digital twin of Best Available Techniques (BAT) in metallurgical recycling processing infrastructures as graphically depicted by the Metal Wheel (see Figure 1 below).

Figure 1 Digital twin of existing Best Available Techniques in metallurgical recycling options (new developments in technology can be included)



The material recycling and recovery assessment based on recycling process simulation models will provide the following:

- Material recycling and recovery rates of all materials, elements and compounds as contained in the different electronic (car) parts, will be calculated in the recycling assessment.
- The recycling assessment is based on the development and application of the developed recycling system models and includes processing flowsheets of the different existing well-advanced metallurgical and other final treatment processing options suitable for the recycling of the different electronic parts under consideration in WP5.
- In the assessment, all mass flows, recoveries and losses for all metals/materials and elements/compounds (both on physical as well as chemical level) will be revealed.

The research is following a Product Centric approach towards recycling as defined by Reuter and Van Schaik (Reuter and Van Schaik, 2013) and was also applied in Task 3.3 as presented in D3.3. This implies that the focus goes beyond only representing Critical Raw Materials (CRMs), as the combination of all materials/compounds/elements present interact during chemical and physical recycling and determine the recyclability and are crucial to quantify Circular Economy in the EoL stage of a product. The assessment and underlying calculations as performed by the application of the physics-based process simulation model, therefore include the complex interlinkages of functional materials in the car parts as well as all chemical transformation processes in the reactors in the system model in versatile flowsheet simulation modules. This approach permits the rigorous evaluation of the recyclability of a product within the circular economy, in which all materials/elements/compounds are included. This is required for a sound recycling assessment, as addressing only a selection of elements/materials will lead to erroneous results and conclusions.

This implicitly demands that full compositional data is available on the electronics parts' composition. This is similar as discussed in D3.3. Only elemental analyses are not sufficient to assess recycling performance. The number of the parts which could be assessed in this Task was determined by this data availability. Data was however not available for many of the parts in this level of detail. Hence, an important learning in this project as can be derived from the simulation model-based approach, is that compositional data in which the full compositional detail (mineralogy in chemical compounds) of the parts need to become available in order to assess and quantify recyclability. This also allows the quantification of the achieved results within a project such as TREASURE.

Crucial when comparing recycling performance of existing processing routes, as well as the UNIVAQ process as developed within the TREASURE project, is that not only recoveries, but also losses, residues created as well as input of (primary) resources such as solvents, water, fuel, etc as well as energy consumption and energy recovery are addressed, quantified and included. This aspect is crucial to truly assess the Circularity of the recycling solutions developed and investigated.

As the model based recycling assessment addresses all aspects of the in- and output of the parts processed, a comparison of the performance of existing processing routes, with that of the developed bio-hydro plant (UNIVAQ) process, demands that data on all in-and output flows, their masses, composition, energy consumption and recovery, use of (primary) resources etc is made available by UNIVAQ.

The process simulation model has been developed in the industrial software platform HSC Chemistry Sim® 10 (www.mogroup.com), providing a professional and industrial platform for process simulation tools and recycling as well as environmental impact calculations.

The material recycling and recovery analyses hence comprise of the following the activities:

- Advancement and application of recycling simulation models for recyclability analysis of the different electronic parts as processed in the UNIVAQ plant (lab-scale)
    - Recycling/recovery assessment based on most suitable industrially available BAT carrier metallurgical recycling infrastructures
    - Assessment based on full mass (& energy/exergy) balance for all materials/metals/elements/compounds of selected car parts

    - Definition of link between design data and chemical/metallurgical recycling: data interaction within TREASURE project of crucial importance (digitalization)

- Calculation of Recycling/recovery rates to quantify the recyclability of the various electronic parts
    - KPI's on recycling/recovery for whole parts/product as well as for individual elements/materials and energy recovery
    - Calculation of mass and composition of all produced output flows of the recycling system, recovery and dispersion of all materials over product and other output flows, energy balances (demand and recovery), purity of produced recyclates and CE application level of all outputs generated.

- Comparison of existing (well-advanced) metallurgical processes' sustainability and CE performances with that of the bio-hydrometallurgical process patented by UNIVAQ
    - The calculation of recycling KPI's for the processing of the various electronic car parts as processed in the UNIVAQ plant in existing metallurgical recycling processing options, including the calculation of all output flows and their composition, calculation of the purity of the recycling products as well as residues, dispersion of materials over the various output fractions, energy balances and required primary inputs, provides the basis to compare the performance of existing recycling processing routes with that of the UNIVAQ process considering all aspects playing a role in CE recycling.

1.2 Background of the work

The background of the work was already provided in D3.3. For completeness, a selection of references from high impact journals as well as industry applications of the recycling simulation models for recycling assessment, recycling rate calculations and Design for Recycling and Eco-design recommendations is provided revealing the basis for this work. The simulation model has evolved over the years as developed and explained in these publications (see various references by Van Schaik/Reuter/Ballester).

In task 3.3, D3.3, this simulation-based approach has been applied for the recycling assessment related to disassembly, at the same time resulting in forthcoming recycling system set up and DfR, design for modularity and disassembly recommendations. The approach as applied in Task 3.3 provides the basis for the Rec Module in the TREASURE platform and provides input to the ECO Module.

The guiding light in the simulation-based assessment of material recycling and recovery is to assess recycling systems maintaining high material quality, thus minimize exergy dissipation through low energy quality or dilution. The unit for this is kW, the same as energy flow. This therefore harmonises the circular and recycling performance in one unit, i.e., kW (Reuter et al. 2019). This goes beyond simpler foot printing methodologies, that lack this basis. This is also the basis for comparing existing processing routes with the developed bio-hydro pilot plant in this project and to draw learnings from this to increase and realise CE.

2. Electronic part compositional data availability and processing to link design data to thermodynamic recycling process simulators for recycling assessment

As already explained in D3.3, successful accomplishment of recycling assessment on a rigorous simulation basis requires that detailed product data of the car (electronic) parts for which the recycling assessment is being performed, is available. This equally applies for assessing the material recycling and recovery of car electronic parts. This implies in other words, that the complete "mineralogy" (compounds compositional build-up) of the parts must be available as is usual when simulating and optimizing metallurgical processes and flowsheets and applied as well in Task 3.3 in this project (see Reuter and Van Schaik, 2013; Van Schaik and Reuter, 2014 a & b; Ballester et al, 2017).

Therefore, the build-up of the parts to be assessed needs to be available in full compositional detail, i.e., all materials should be defined in their full stoichiometric formulas. Analyses on just an elemental basis are not providing enough information to assess recyclability. This is clearly explained by the example on recycling of Al versus the recyclability of Al_2O_3. The recycling of aluminium present as metallic Al is different from the recycling performance of aluminium present as Al_2O_3. Whereas metallic Al can be recovered, if separated from other materials and sent to aluminium recycling processing, Al_2O_3 will always go lost and cannot be recovered as Al.

In order to best create the potential value of this project, data availability, architecture, seamless integration of data structures and ontology would help to fully quantify the rarity and thermodynamic properties of all process streams, losses etc.

2.1 Electronics (car) parts included in the recycling assessment of existing metallurgical recycling options

In the UNIVAQ process, a range of different electronic car parts are processed, such as

- different IMSE samples (thermoformed PC IMSE, full silver area IMSE and the elongated IMSE)
- different PCBs originating from the combi-instrument of different SEAT models (Leon II, Leon III and Ibiza IV), from which different parts have been removed in order to be able to process the powders from them and
- different small electronic components originating from the PCBs and well as PBCs and components as provided by POLLINI.

For the IMSE, the composition is made available (by TNO) on a compound basis. For all other parts, only elemental analyses have been derived in D5.4, which is unfortunately not providing sufficient information to successfully assess recycling performance of these parts (the XRD analyses do show for Ag that this is present in metallic form). For this reason, these parts could not be included in the assessment and comparison of existing processing routes with the UNIVAQ process.

The value and applicability of the work as performed in this Task is however not affected by the data availability. The simulation-based approach and captured detail provides a clear demonstration of the basis on which newly developed processes can be compared to existing processes. A format of data that seamlessly communicates across various actors is suggested and proposed as a possible standard that permits a detailed rarity analysis of the CE system. The same applies for the type of information on the in- and outputs of the recycling processing routes, which is required to compare existing with newly developed processes for all different parts. This report presents and demonstrates on the performed cases, what type of information should be available from different processing options to compare their performance and select the most suitable and optimal processing route(s) for the parts under consideration. Hence, this work provides a rigorous full mass and energy balance based back-bone, including material quality (of product and residue streams), for assessment and definition of the most optimal and efficient processing option(s). The range of recycling flowsheets and processing routes included in the recycling simulation models as presented here, reveal the industrial existing options to process these types of complex electronics parts and demonstrates the performance of these processing routes, the possibility to combine them through assessment by process simulation, and results, which can be achieved when recycling these types of devices. The application of digital twins of metallurgical processing, captured in recycling simulation models, to benchmark new process development such as the UNIVAQ process, is clearly demonstrated in this Task.

Due to the unavailability of detailed and quantified compositional data, only the following car parts have been assessed in terms of recycling performance in existing industrial metallurgical processing options:

- IMSE (available from TNO)
- PCBs from combi-instrument from different SEAT models (derived from MISS data file(s))

Only for the IMSE detailed compositional data was available from TNO. For all other parts as processed in the UNIVAQ plant, only elemental analyses were available, which do not provide enough depth to assess their recyclability. Data availability was defined to be crucial for completion of this Task in the DoA, however it is not part of the field of influence of MARAS and is known to be a difficult issue in, e.g., PCB data availability (also from literature). Although additional XRD analyses have been performed to derive this information within D5.4 (and are presented there) on the PCB powders (obtained after removal of parts and grinding), these XRD analyses provided some indication of compounds present, however no quantified analyses on a full compound basis was derived from this. This limits the number of parts which could be assessed in Task 5.3.

In order not to be solely dependent on the data availability and perform this task as extensive as possible, MARAS has derived compositional data on the PCB composition of the combi-instrument of the different SEAT models, from the MISS data files and performed the recycling assessment on this basis.

2.2 Compositional build-up of the different electronic car parts

2.2.1 IMSE data

The data on the IMSE as made available by TNO, has been analysed and processed to be formatted into the structure matching the input required by process simulators, as well as to structure the input to recycling simulation models and to smoothen the integration of this data into HSC Sim, which is applied as the basis for the recycling assessment. All materials and parts have been converted into full stoichiometric formulas. This has been done for all materials, implying that metals, fillers, plastics, inks, etc have been defined in this format in order to be included in the assessment of the recyclability. Table 1 shows the composition of the IMSE as derived through data processing of the data, as provided by TNO in the format required for process simulation of recycling processing in the developed models. Masses have been normalised to 100% as the reference for the assessment. A consistent set of compounds is listed for all parts as assessed in this project. This is done based on the full compositional detail of all parts addressed for recyclability assessment within the TREASURE project and all compounds and phases that are/can be created during processing (this explains the blanks for a range of compounds in below Tables). This guarantees a consistent compound data base for the recycling assessment and allows to compare and combine different parts and processes in recycling assessment. This makes this approach rigorous and flexible.

Table 1 Input definition of the IMSE as derived through processing of the data on the IMSE as made available by TNO – full compositional input to HSC Sim recycling simulation model (organics have been classified as defined in Task 3.3 in order to streamline the application of the models within the TREASURE project and allow for comparison and combined assessment when desired)

	IMSE including PC	IMSE PC dismantled		IMSE including PC	IMSE PC dismantled
Compounds (Chemical formulas)	**Mass% in part**	**Mass% in part**	**Compounds (Chemical formulas)**	**Mass% in part**	**Mass% in part**
***2CoO*TiO2**			Se		
*3MgO*4SiO2*H2O			Si		
Ag	0.06792922	0.308559763	Si(CH3)2O(g)		
Al			Si(OC2H5)4(l)		
Al(OH)3			SiN(g)		
Al2O3			SiO		
Al2O3*2SiO2			SiO2		
AlO			Sn		
As			SnO2		
As(CH3)3			SrFe12O19		
Au			SrO		
B			Ta		
B(OH)3			Tb		
B2O3			Te		
Ba			Ti		
BaO			TiO2	8.54773824	38.82700401
BaSO4			Ti(OC3H7)4(TTIPg)		
BaTiO3			V		
Be			W		
Bi			Zn		
Bi2O3			Zn(OH)2		
C	0.15060925	0.68412319	Zn5(OH)6(CO3)2		
CaCO3			ZnC2O4*H2O*CH3OH		
CaMg(CO3)2			ZnO		
CaHPO4*2H2O			ZnSO4		
CaO			ZrO2		
CaSO3			B(OCH3)3(l)		
CaZrO3			CH2(g)		
Cd			CH2ClO(CMRg)	7.18306E-05	0.000326281
Cl(g)			C10H10O4(DMT)		
Cl2(g)			C10H18O4(TESI)		
Co			C10H8O2(23DI)		
Co(NO3)2*6H2O			C10H8O4		
Co3O4			C11H30O3Si4		
CoO			C12H10(BPH)		
CoO*Al2O3			C12H11N(4AB)	2.371473747	10.77211516
Cr			C12H12O(1ENg)		

Cr(+3a)			C12H22N2O2		
Cr(OH)3			C12H22O4(DDA)		
Cr2O3			C13H30Si4O3		
CrMnNiO18Sb5Ti3			C14H14O(DBEg)		
Cr0.1Sb0.1Ti0.8O2			C14H28O2(TDA)	87.62367275	43.78212175
Cu			C15H12Br4O2(TBBPAg)		
Cu5FeS4			C15H16O2		
CuO			C15H21NO2S		
CuO*Cr2O3			C15H22O6		
CuSO4	0.002259139	0.010261848	C15H33N(1PAg)		
Dy			C16H16O3Cl2		
Fe			C16H32(UCP)	1.054867187	4.791598825
Fe2O3			C16H34OSn		
FeNiZnO			C18H15O4P		
FeO			C18H17Br4ClO3		
FeO*OH			C18H18O9		
Ga			C18H19N		
GaAs			C18H35O2Li		
I2(g)			C21H25ClO5		
In			C22H10N2O5	0.070936957	0.322222023
In2O3			C23H36N2S		
K2O			C2H4		
Mg			C2H6O(DMEg)		
Mg(OH)2			C32H16CuN6		
Mg3Si4O10(OH)2			C32H64O4Sn		
MgCO3			C33H42O9		
MgO			C3F6O(HFAg)		
Mn			C3H3Cl(1CPg)		
Mn3O4			C3H4O2		
MnO2			C3H6(PPYg)		
Mo			C3H8N2O		
N2(g)			C40H54O27		
Na2O			C4H10FO2P(Sg)		
Nb			C4H6O2		
Nd			C4H6O4(SUC)	0.050203083	0.228041063
Ni			C57H112O7Ti		
NiO			C5H8O2		
O(g)			C5H8O2(5PLl)		
O2(g)			C6H10O5(S)		
P			C6H11O6P		
H3PO4	0.015060925	0.068412319	C6H12O6(ADG)	0.045177668	0.205213758
Pb			C6H18OSi2(HMDl)		
PbO			C6H4O2(QUIg)		
PbO*TiO2			C6H5F(FBZg)		
PbO*ZrO2			C6H6S(BTHg)		
PbSiO3			C6H6S(BTHl)		
PC6H18N3(g)			C7H4F3NO2(3NIBg)		
Pd			C2H6O12Zn5 - C36H70O4Zn		
Pt			C7H6O2(BAC)		
Ru			C8H18O2S(DBSg)		
RuO2			C8H18OSi2		
S			C8H24O4Si4		
Sb			C8H8(COTl)		
Sb2O3			C9H16(2NOg)		
Sb2O5			**SUM**	**100**	**100**

2.2.2 PCB data

Table 2 shows for the PCB unit of the combi-instrument of the SEAT Leon II the full compositional detail as derived and processed from the MISS data into the format required for recycling assessment in a process simulator as HSC Sim. All materials and components are defined based on their full chemical composition and corresponding mass in the part. The list shows the mass normalised to 100%, as the input to the model. This mass distribution has been defined from all individual masses of each of the compounds in each part/sub part and component of the car part. This matches the level of detail as derived through data processing of the disassembled car parts assessed in D3.3 as derived from the MISS data files. For confidentiality reasons, this table only shows part of the full PCB composition, however data is available and applied for the full list of compounds. Similar data as presented in Table 2 for the SEAT Leon II has been derived for other PCB parts from the SEAT models and has been applied to assess PCB material recycling and recovery performance in selected best suitable processing routes.

This data processing provides the input data in a format suitable to recycling and recovery rate calculations using a process simulation platform.

Table 2 Input definition of the PCB part(s) of the combi-instrument from the SEAT LEON II as derived from and through processing of the data from MISS data file – full compositional input to HSC Sim recycling simulation model (after classification of organics)

PCB combi-instrument SEAT Leon II (including all components)			
Leon II			
Compounds (chemical formulas)	Mass % in car part	Compounds (chemical formulas)	Mass % in car part
*2CoO*TiO2		Si	0.202214
*3MgO*4SiO2*H2O		Si(CH3)2O(g)	
Ag	0.367077	Si(OC2H5)4(l)	
Al	5.409866	SiN(g)	
Al(OH)3		SiO	
Al2O3		SiO2	64.915165
Al2O3*2SiO2		Sn	2.542884
AlO	1.557354	SnO2	0.000261
As	0.000390	SrFe12O19	
As(CH3)3		SrO	0.521725
Au	0.252731	Ta	0.230738
B	0.027512	Tb	
B(OH)3		Te	
B2O3	0.549323	Ti	0.000009
Ba		TiO2	1.123890
BaO	0.425761	Ti(OC3H7)4(TTIPg)	
BaSO4		V	
BaTiO3	0.416079	W	0.000041
Be	0.000000	Zn	0.301814
Bi	0.001299	Zn(OH)2	
Bi2O3		Zn5(OH)6(CO3)2	
C	0.035066	ZnC2O4*H2O*CH3OH	
CaCO3		ZnO	0.000279
CaMg(CO3)2		ZnSO4	0.000538
CaHPO4*2H2O		ZrO2	
…	…	…	…
…	…	…	…
…	…	…	…
Pb	0.055399	C6H12O6(ADG)	
PbO	0.000009	C6H18OSi2(HMDI)	
PbO*TiO2		C6H4O2(QUIg)	
PbO*ZrO2		C6H5F(FBZg)	
PbSiO3	0.000030	C6H6S(BTHg)	
PC6H18N3(g)		C6H6S(BTHl)	
Pd	0.000001	C7H4F3NO2(3NIBg)	
Pt	0.006696	C2H6O12Zn5 - C36H70O4Zn	
Ru		C7H6O2(BAC)	
RuO2	0.000005	C8H18O2S(DBSg)	
S	0.005934	C8H18OSi2	
Sb	0.001307	C8H24O4Si4	
Sb2O3	0.087792	C8H8(COTl)	
Sb2O5		C9H16(2NOg)	
Se		**SUM**	100.000

3. Recycling system flowsheet simulation model for recycling assessment and included recycling processing infrastructures

The recycling of the various car electronic car parts as also recycled in the UNIVAQ pilot plant, has been assessed in T5.3 by the application of innovative recycling flowsheet simulation models. This chapter describes the further development and set up of the recycling system flowsheet simulation model, which has been advanced from past work and has been applied in T3.3 to assess the recyclability of different disassembled car parts, define BAT most optimal recycling routes, define the most optimal balance between disassembly and recycling as well as to define physics-based Design for Recycling recommendations.

It is important to keep in mind that recycling in the context of the circular economy is understood to produce the same quality of materials so that they can function at the same quality in the same product again.

The recycling flowsheet simulation models have been applied to assess and calculate the recycling/recovery rate of the electronic car parts as processed in the UNIVAQ plant. Many of the calculation units are based on Gibbs Free Energy Minimization, with activity coefficients estimated from thermochemical software such as FACT Sage, academic literature, adjustment of activity coefficient based on industrial reality and experience.

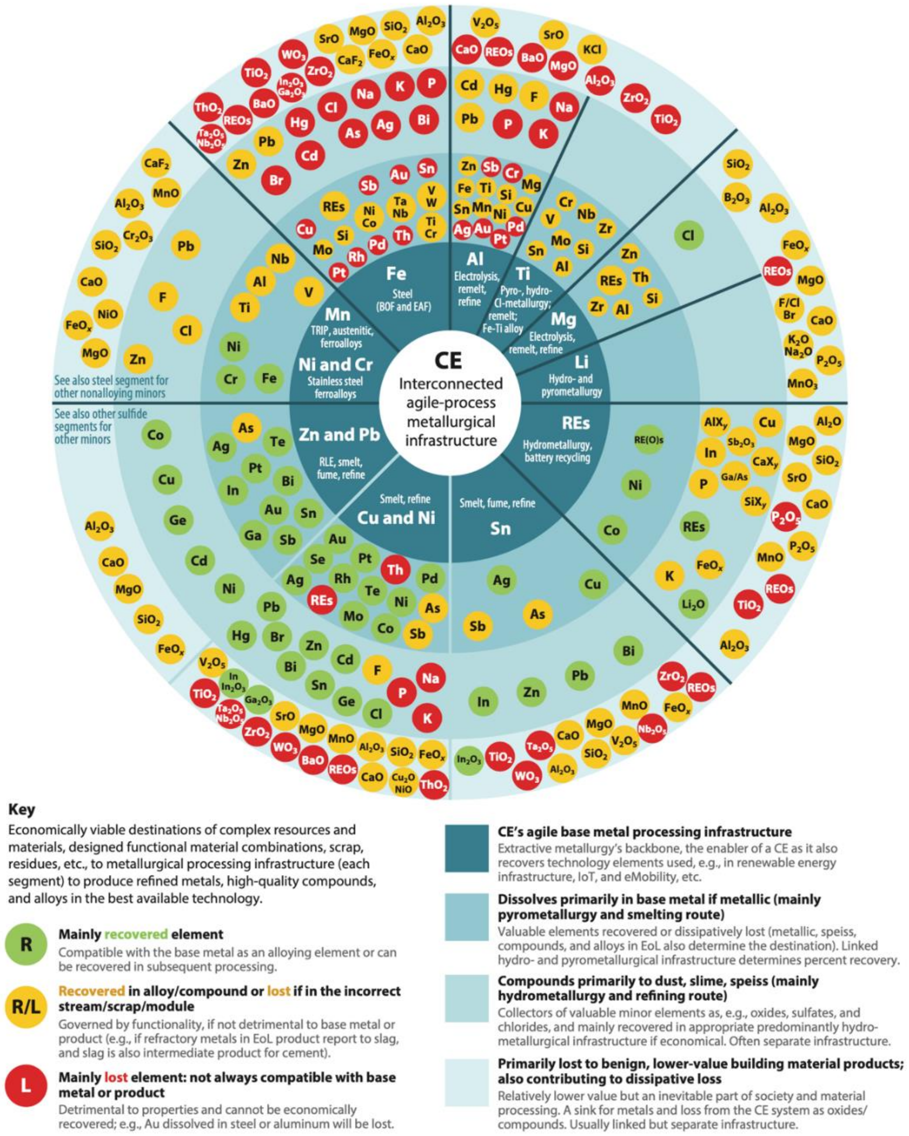
The recycling simulation models cover the entire recycling processing flowsheet for the optimal recycling of car (electronic) parts. These flowsheets are industrially realistic and economically viable for different processing routes. Recycling/recovery rates including energy recovery, are calculated, and different recycling processing options have been evaluated where possible for the recycling of the different car electronics. The assessment includes the energy flows within the recycling system. The work provides recycling KPI's, implying recycling/recovery rates for all materials/elements/compounds, a full overview.

3.1 Development of recycling simulation model and processing flowsheets in model

The (industrial) processing routes suitable and available for the recycling of the car electronic parts provides the basis for the calculation of the recycling rates. The Metal Wheel (Figure **2**) depicts the basic metallurgical infrastructure in the centre band, that makes the recovery of elements in each segment possible due to the refining and alloying infrastructure and compatible chemistry and material physics (Reuter and Van Schaik, 2013). This provides the basis for the assessment of existing recycling processing routes for the recycling of the car electronic parts under consideration in this work.

All these recycling routes have been captured in the simulation model in different full processing flowsheets for each processing infrastructure as available and included in the assessment for possible recycling of the parts under consideration. These processing flowsheet and models have been developed and extensively updated and advanced within TREASURE project based on existing background within MARAS (Reuter et al, 2018; Van Schaik and Reuter; 2016; Reuter et al; 2015; Van Schaik and Reuter, 2014). The flowsheets have been further developed and modelled in this Task, following up on the work performed in T3.3 for the processing of the different electronic car parts as tested in the UNIVAQ plant. It investigates and includes best suitable technologies for the processing of these parts and adopting and processing all materials/compounds/elements as present in these car parts.

Figure 2 The Metal Wheel, based on primary metallurgy but equally valid for metals recycling reflects the destination and hence recoverability or losses of different elements in a product/part for different interlinked metallurgical processes (Reuter and Van Schaik, 2013)



To allow for the assessment of recycling and the optimization of the industrial feasibility of the metallurgical recycling processing options, all materials and compounds present in the electronic car parts are included in the recycling assessment. Including all materials, elements and compounds in recycling assessment is crucial, as material combinations are affecting the mutual recovery rates in processing. Only including a selection of materials/compounds would lead to unreliable and erroneous recycling rate calculations, as all materials/compounds in the input are affecting each other and affect the recycling rate and losses resulting from the recycling processing of the car parts or any other product under consideration.

Similarly, to the work in Task 3.3, this implies that a Product Centric approach is followed (addressing all materials and compounds in a product and not just a selection of elements) as defined by Reuter and Van Schaik (Reuter and Van Schaik, 2013). When desired, materials of special interest (e.g. CRMs) can be given special focus where required, e.g. when selecting the most optimal or most suitable recycling route(s) for processing the different parts.

Hence, to be able to assess the recyclability of the (electronic) car parts and compare this to the performance of the bio-hydrometallurgical plant, a complete particle and thermochemistry-based flowsheet simulation model was developed, in which the existing BAT metallurgical recycling infrastructures as depicted by the Metal Wheel in Figure 1 as well as other applicable final treatment processes such as energy recovery processing as present in industry for the processing and recovery of all materials and compounds of the car electronic parts have been developed and included. The total flowsheet as included in the model is depicted by Figure 3. The separate flowsheets in Figure 4 to 12 in this report show the further expansion and details of the processing infrastructure flowsheet included in the model to cover all materials/elements/compounds as present in all the different parts under consideration. The flowsheet for steel, stainless steel, light metal recycling, etc are not presented in detail in this report, as these processing routes are not most suitable for the processing of the electronic parts as considered in WP5.

Each flowsheet is connected and links between different processing options have been defined in order to investigate the most suitable processing options for the various parts under consideration. These flowsheets have been defined and advanced specifically for the processing of the different electronic car parts, by considering their input compositional build-up based on the various materials and compounds (including organic materials, e.g., plastics) and have been adequately linked in this work to maximize recovery into the highest quality products. This allows not only to assess and compare different processing routes (including the UNIVAQ plant) but also allows to incorporate the (most beneficial) balance between disassembly (e.g., of the PC as present in the IMSE) and metallurgical and plastics processing as well as energy recovery.

While the calculation basis is Gibbs Free Energy minimization, the Metal Wheel reflects compatible metallurgy, which has its origins in the Ellingham Diagram (which can also be calculated in HSC 10.0). This, in fact, shows what can be recycled and what perhaps best goes to energy recovery. This will be discussed further below.

Note the metal wheel suggests also to fully realize the CE a fully integrated metal processing infrastructure must be available to fully realize the CE. The suggested process model digitally twins this for the car parts and surely new process routes, if producing economically viable products and less residues, can modify and enhance the performance of the system i.e. minimize the dissipation of exergy.

Figure 3 The metallurgical, energy and plastics processing flowsheet for (electronic) car parts and complex EoL products as industrially available to process the multitude of metals, alloys, functional materials, and plastics in these parts. It covers steel, stainless steel, copper, lead, tin zinc, aluminium and magnesium as carrier metal metallurgical infrastructure as well as plastics recycling and energy recovery

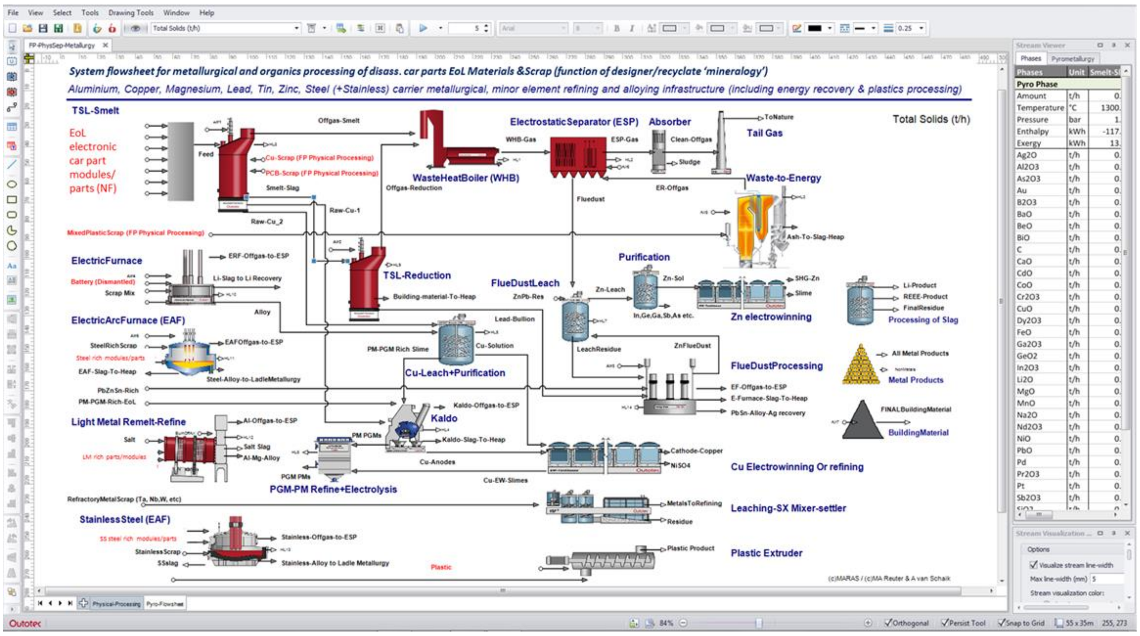


Figure 4 'Cu processing route' – Oxidative smelter (Cu Isasmelt™)), reduction of Pb bullion (Pb Isasmelt™ Reductive smelter) and Cu refining. The Isasmelt™ reactor (a Top Submerged Lance (TSL) reactor) can also be a proxy for a TBRC (Top Blown Rotary Convertor) type reactor, the metallurgy is determined by the partial oxygen pressure and temperature in the reactor. Also shown is the oxidative leach of raw copper and subsequent electrowinning of the copper

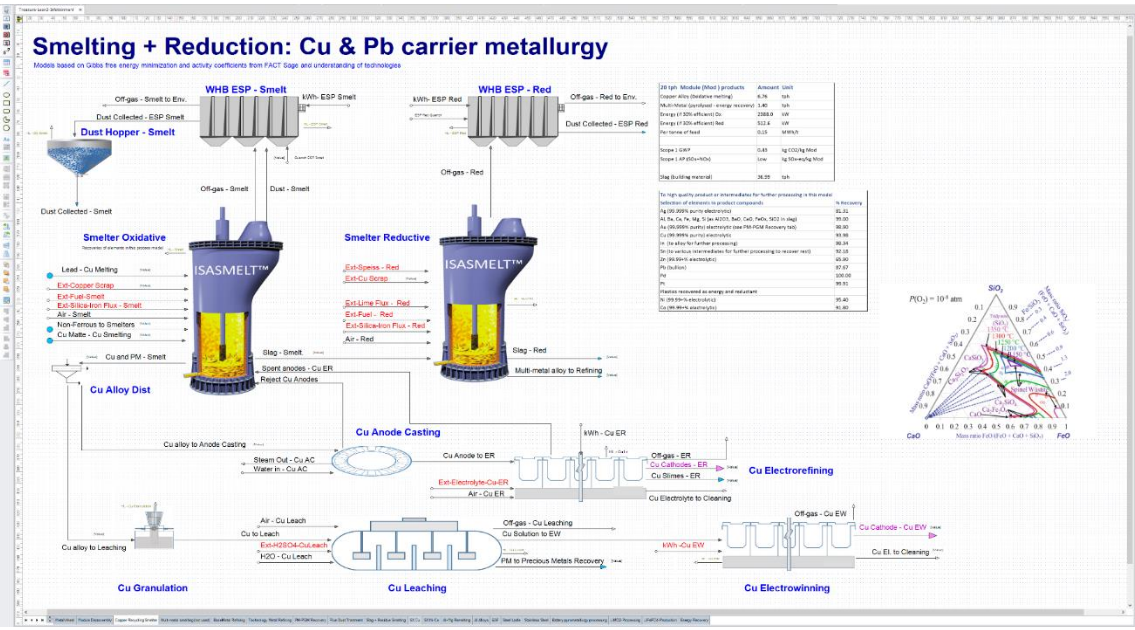


Figure 5 Detailed flowsheet of processes required for recovery of all recoverable (technology) elements (green bullets in the Cu segment of the Metal Wheel)

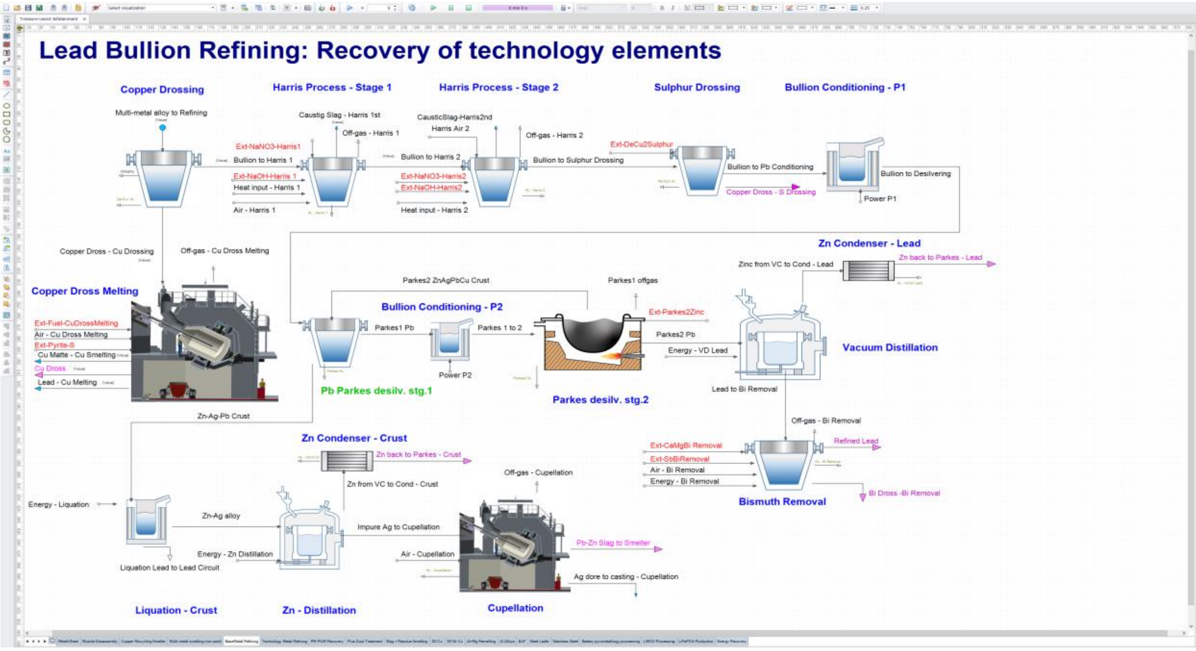


Figure 6 Detailed flowsheet of processes required for processing of slags to recover Sb, Sn, As, Te, In etc.

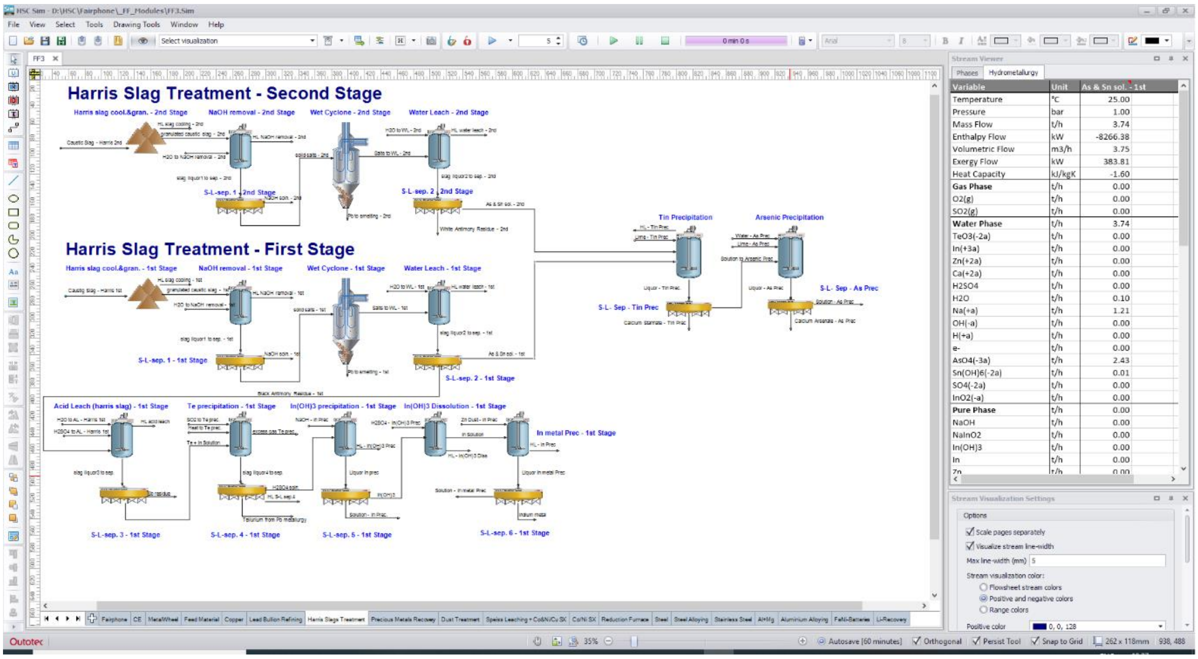


Figure 7 Precious metal recovery as part of the refining in the Cu processing/refining route

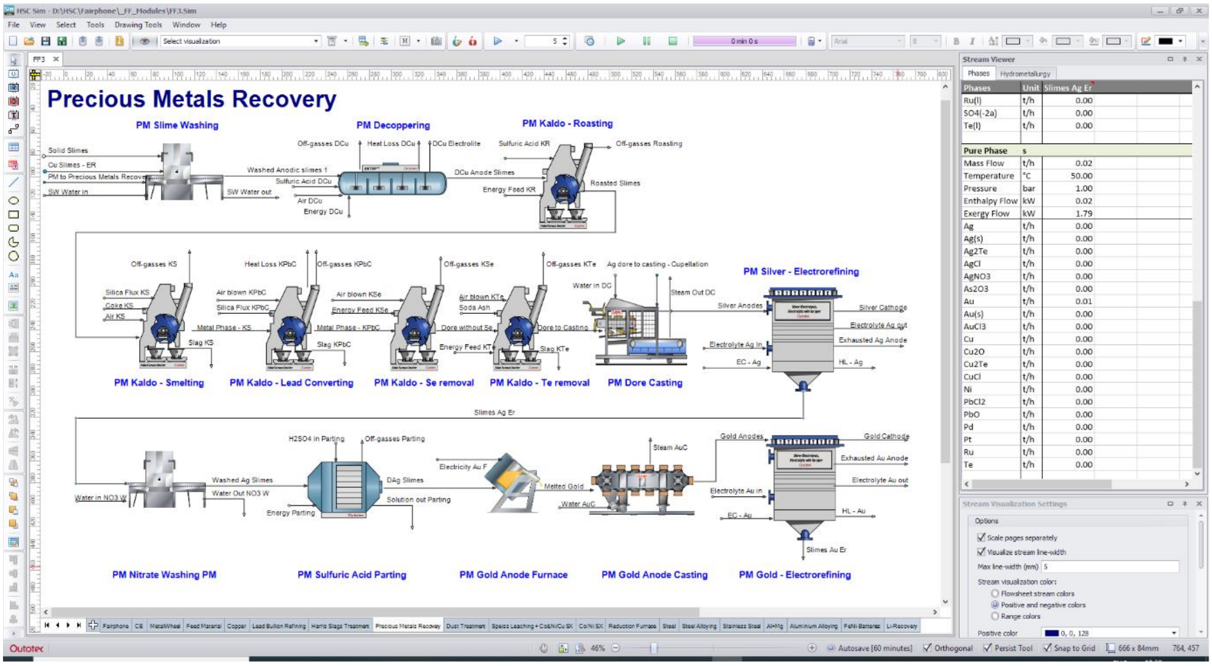


Figure 8 Detailed flowsheet for Zn, Pb, Zn, Mn etc. recovery

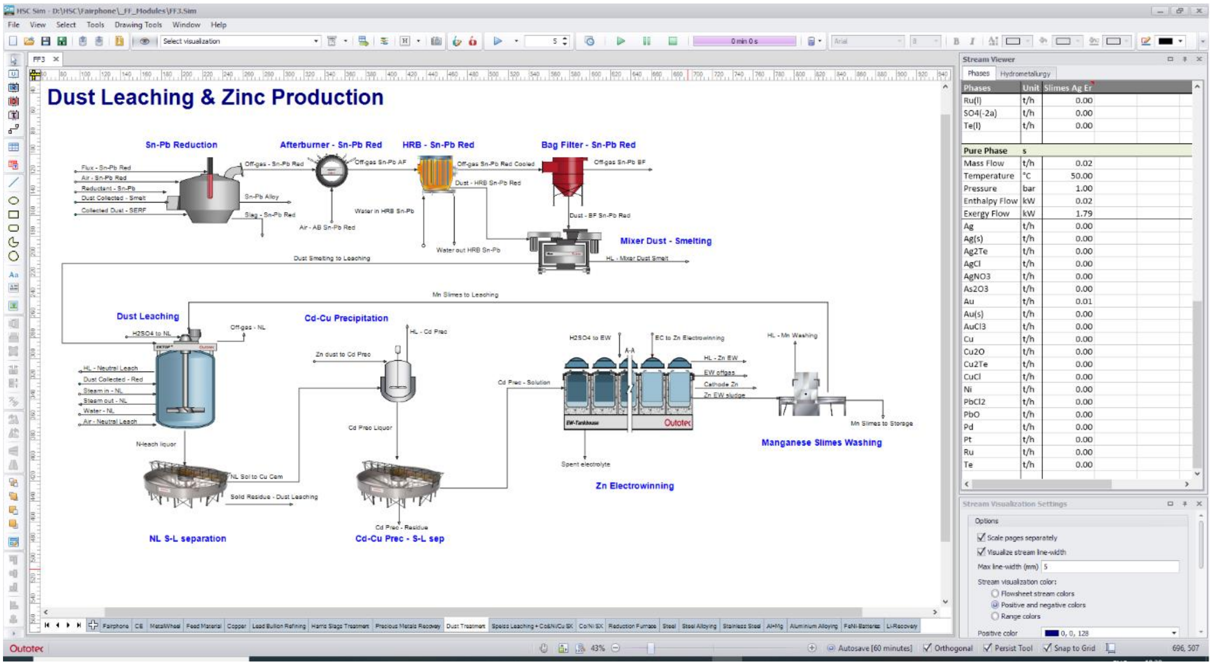


Figure 9 Co, Ni, Cu recovery by solvent extraction and electrowinning

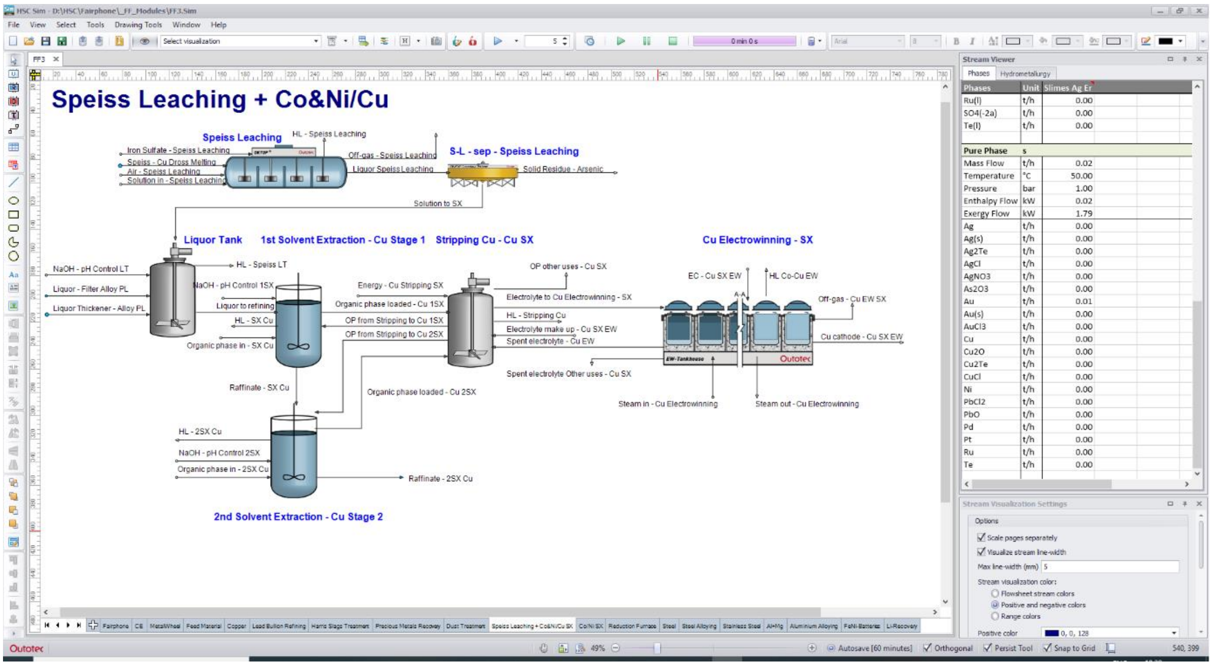


Figure 10 Co, Ni, Cu recovery by solvent extraction and electrowinning

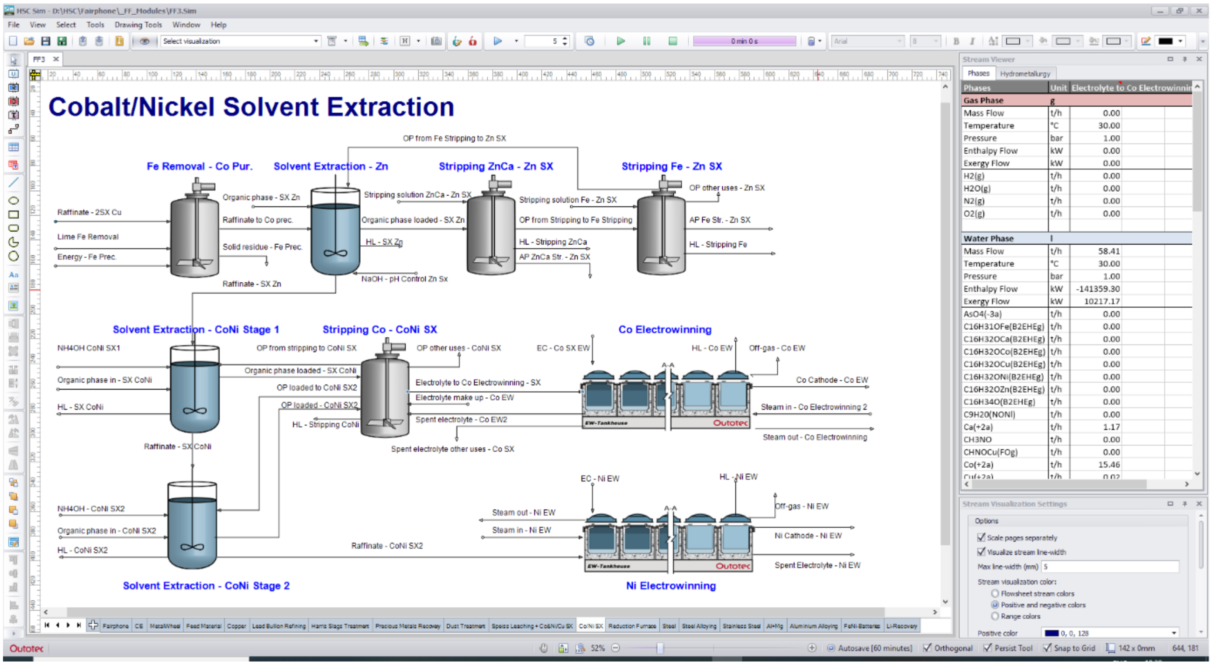


Figure 11 Slag cleaning and alloy production, which is further processed for the electronic parts

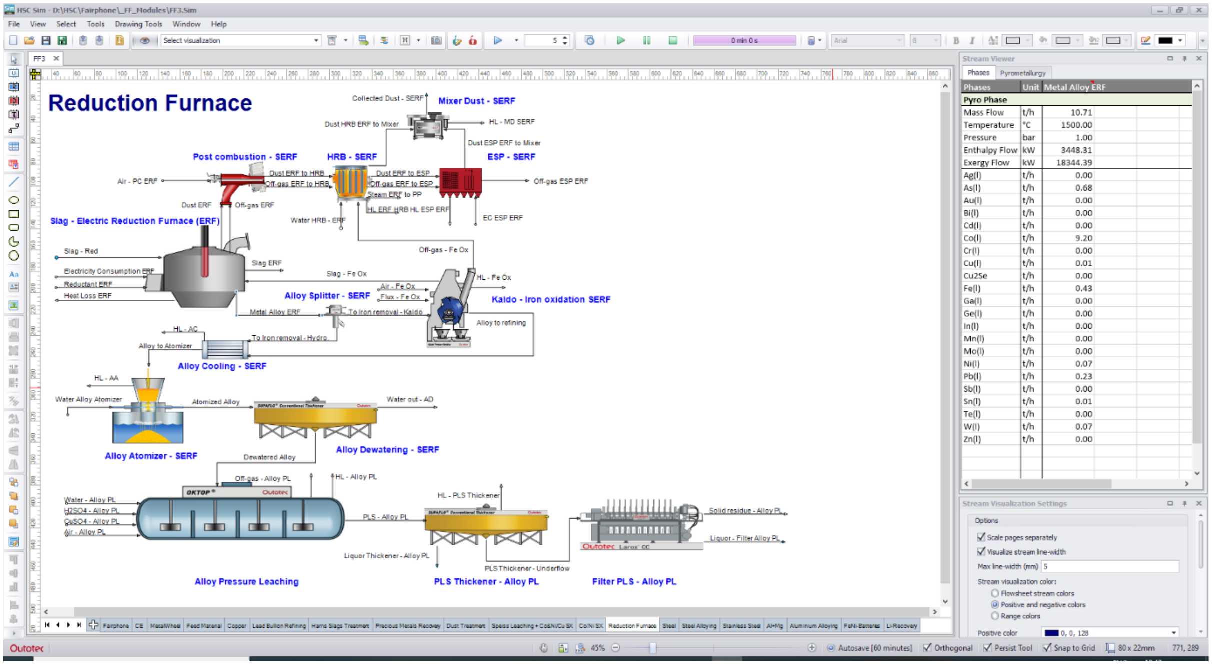
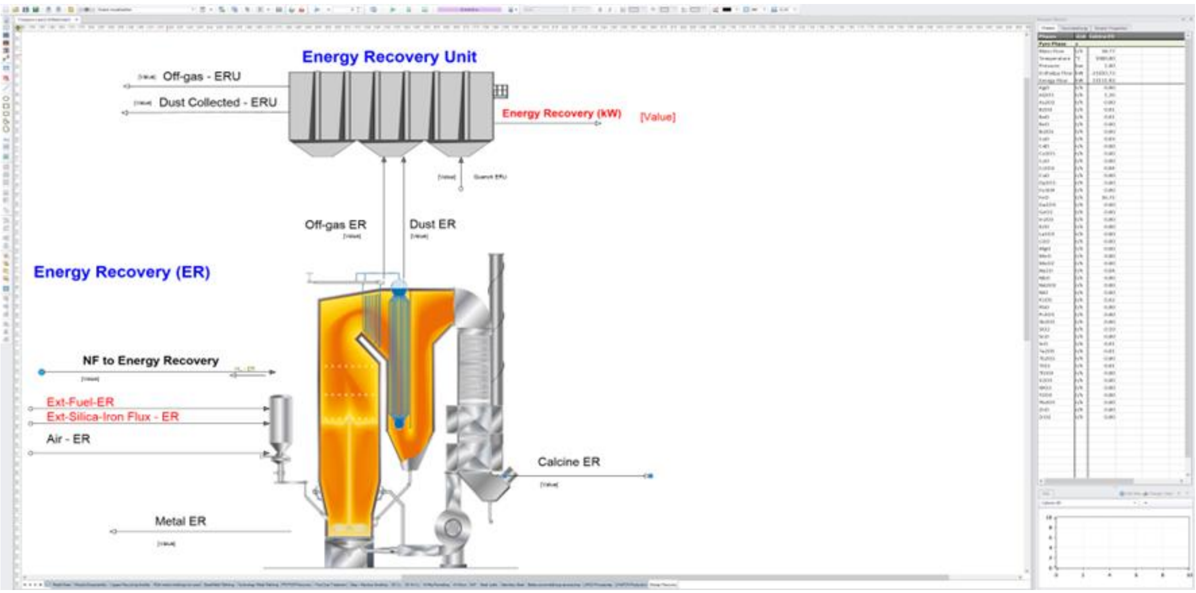


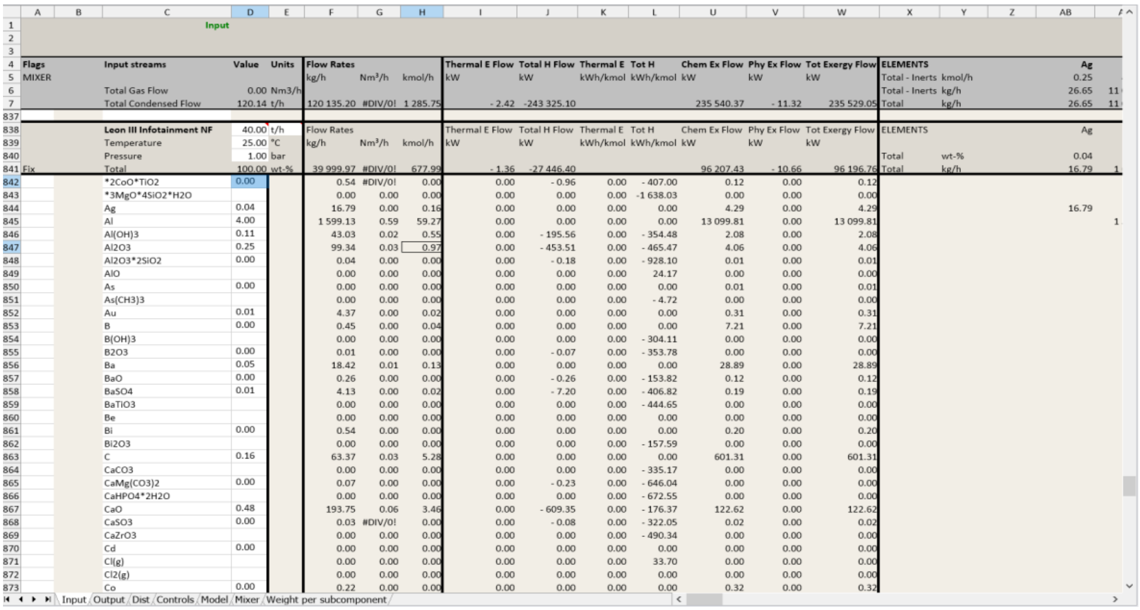
Figure 12 Energy recovery processing to create calcine (oxidized elements as well as some highly alloyed and low value metal alloy and energy from all car parts



3.2 Integration of part compositional data in recycling simulation models for material recycling and recovery assessment performance linked to thermochemical databases

All compositional data of the IMSE and PCB part(s) as described in Chapter 2 is integrated into the simulation models. An example is given in Figure 13 by showing a screen capture of the recycling model input definition. Figure 13 shows directly that HSC Chemistry Sim 10 calculation modules automatically utilize extensive thermochemical databases, which contains enthalpy (H), entropy (S) and heat capacity (C) data for all materials and compounds included, allowing not only recycling rate calculations, but at the same time environmental analysis including exergy assessment (not part of this deliverable). This quantifies therefore also each stream not only in kg/h units but also in MJ/h or kW. This allows analysing the true losses also in terms of thermodynamics of all materials, i.e., in terms of exergetic dissipation or losses in line with the second law of thermodynamics.

Figure 13 Screen capture of recycling model input definition in HSC Sim showing the car part compositional input of Table 2 integrated in HSC Sim (left column). The figure also reveals all other parameters (next to mass % of input) such as flow rates (kg/h) and energy thermodynamic parameters (in kW) (the input to the model has been simulated for 20 ton/h in order to render the process industrially realistic)



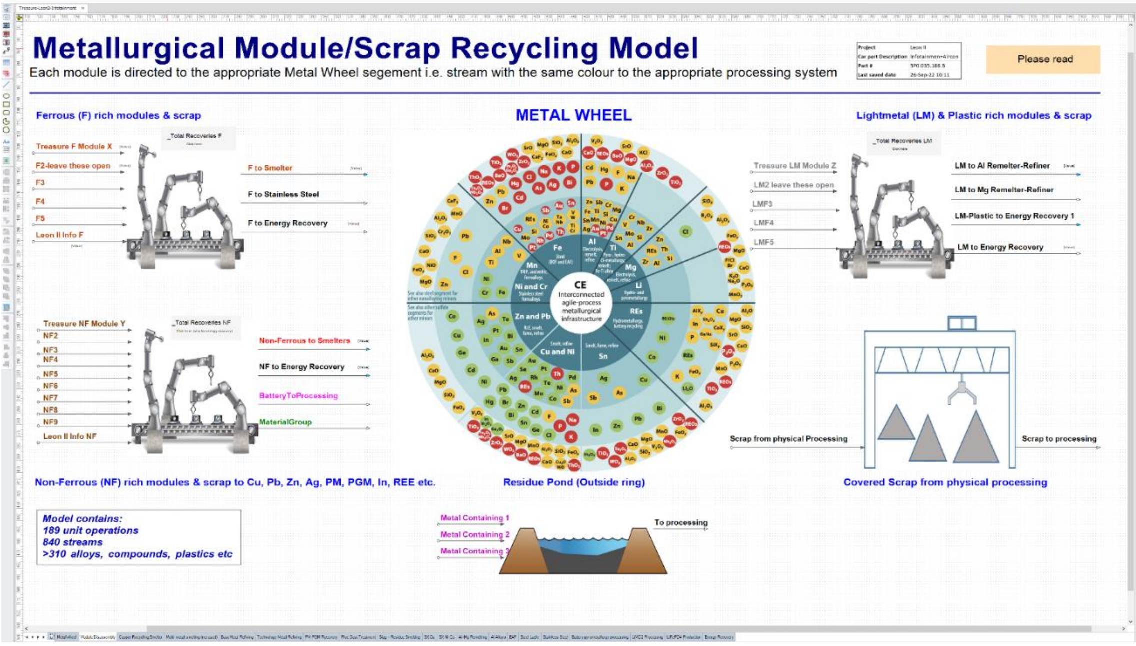
	A	B	C	D	E	F	G	H	I	J	K	L	U	V	W	X	Y	Z	AB	
1			Input																	
2																				
3																				
4	Flags		Input streams	Value	Units	Flow Rates			Thermal E Flow	Total H Flow	Thermal E	Tot H	Chem Ex Flow	Phy Ex Flow	Tot Exergy Flow	ELEMENTS			Ag	
5	MIXER					kg/h	Nm³/h	kmol/h	kW	kW	kWh/kmol	kWh/kmol	kW	kW	kW	Total - Inerts	kmol/h		0.25	
6			Total Gas Flow	0.00	Nm3/h											Total - Inerts	kg/h		26.65	11
7			Total Condensed Flow	120.14	t/h	120 135.20	#DIV/0!	1 285.75	-2.42	-243 325.10			235 540.37	-11.32	235 529.05	Total	kg/h		26.65	11
837																				
838			Leon III Infotainment NF	40.00	t/h	Flow Rates			Thermal E Flow	Total H Flow	Thermal E	Tot H	Chem Ex Flow	Phy Ex Flow	Tot Exergy Flow	ELEMENTS			Ag	
839			Temperature	25.00	°C	kg/h	Nm³/h	kmol/h	kW	kW	kWh/kmol	kWh/kmol	kW	kW	kW					
840			Pressure	1.00	bar											Total	wt-%		0.04	
841	Fix		Total	100.00	wt-%	39 999.97	#DIV/0!	677.99	-1.36	-27 446.40			96 207.43	-10.66	96 196.76	Total	kg/h		16.79	1
842			*2CoO*TiO2	0.00		0.54	#DIV/0!	0.00	0.00	-0.96	0.00	-407.00	0.12	0.00	0.12					
843			*3MgO*4SiO2*H2O			0.00	0.00	0.00	0.00	0.00	0.00	-1 638.03	0.00	0.00	0.00					
844			Ag	0.04		16.79	0.00	0.16	0.00	0.00	0.00	0.00	4.29	0.00	4.29				16.79	
845			Al	4.00		1 599.13	0.59	59.27	0.00	0.00	0.00	0.00	13 099.81	0.00	13 099.81					1
846			Al(OH)3	0.11		43.03	0.02	0.55	0.00	-195.56	0.00	-354.48	2.08	0.00	2.08					
847			Al2O3	0.25		99.34	0.03	0.97	0.00	-453.51	0.00	-465.47	4.06	0.00	4.06					
848			Al2O3*2SiO2	0.00		0.04	0.00	0.00	0.00	-0.18	0.00	-928.10	0.01	0.00	0.01					
849			AlO			0.00	0.00	0.00	0.00	0.00	0.00	24.17	0.00	0.00	0.00					
850			As	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01					
851			As(CH3)3			0.00	0.00	0.00	0.00	0.00	0.00	-4.72	0.00	0.00	0.00					
852			Au	0.01		4.37	0.00	0.02	0.00	0.00	0.00	0.00	0.31	0.00	0.31					
853			B	0.00		0.45	0.00	0.04	0.00	0.00	0.00	0.00	7.21	0.00	7.21					
854			B(OH)3			0.00	0.00	0.00	0.00	0.00	0.00	-304.11	0.00	0.00	0.00					
855			B2O3	0.00		0.01	0.00	0.00	0.00	-0.07	0.00	-353.78	0.00	0.00	0.00					
856			Ba	0.05		18.42	0.01	0.13	0.00	0.00	0.00	0.00	28.89	0.00	28.89					
857			BaO	0.00		0.26	0.00	0.00	0.00	-0.26	0.00	-153.82	0.12	0.00	0.12					
858			BaSO4	0.01		4.13	0.00	0.02	0.00	-7.20	0.00	-406.82	0.19	0.00	0.19					
859			BaTiO3			0.00	0.00	0.00	0.00	0.00	0.00	-444.65	0.00	0.00	0.00					
860			Be			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
861			Bi	0.00		0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.20					
862			Bi2O3			0.00	0.00	0.00	0.00	0.00	0.00	-157.59	0.00	0.00	0.00					
863			C	0.16		63.37	0.03	5.28	0.00	0.00	0.00	0.00	601.31	0.00	601.31					
864			CaCO3			0.00	0.00	0.00	0.00	0.00	0.00	-335.17	0.00	0.00	0.00					
865			CaMg(CO3)2	0.00		0.07	0.00	0.00	0.00	-0.23	0.00	-646.04	0.00	0.00	0.00					
866			CaHPO4*2H2O			0.00	0.00	0.00	0.00	0.00	0.00	-672.55	0.00	0.00	0.00					
867			CaO	0.48		193.75	0.06	3.46	0.00	-609.35	0.00	-176.37	122.62	0.00	122.62					
868			CaSO3	0.00		0.03	#DIV/0!	0.00	0.00	-0.08	0.00	-322.05	0.02	0.00	0.02					
869			CaZrO3			0.00	0.00	0.00	0.00	0.00	0.00	-490.34	0.00	0.00	0.00					
870			Cd	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
871			Cl(g)			0.00	0.00	0.00	0.00	0.00	0.00	33.70	0.00	0.00	0.00					
872			Cl2(g)			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
873			Co	0.00		0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.00	0.32					

3.3 Recycling assessment of electronic parts and process of selection/definition of most suitable processing routes for assessment

In the assessment of the recyclability, the most suitable recycling route(s) and/or combination of processes are defined for the recycling of the different electronic parts, by considering the composition of these different parts linked to the processing and recovery options of all processes as available and included in the recycling flowsheet simulation model. In other words, the different electronic parts are assessed based on their compositional build-up and directed (by application of expert knowledge as present in MARAS on the processes) into the most suitable recycling flowsheet/combination of processes. In fact, the parts follow the segments in the Metal Wheel, which is covered in the simulation models by the complete flowsheets and range of reactors composing the different (metallurgical) processing infrastructures (as displayed in the 'Feeds' sheet of Figure 1 and 14). Most suitable routes imply the recycling processing infrastructure in which the compounds of the module are most optimally recycled with a minimum of losses and emissions. This will differ per electronic part, due to its specific material composition as defined in the design. For some parts, different options in processing are considered and compared, depending on which of the materials is preferred to recycle from the car part's material content.

As also discussed in Task 3.3, but equally valid in this work, it is important to be aware that all technologies as included in the recycling assessment are industrial operations running at economy of scale. In the simulations/calculations, only the selected parts under consideration are assessed in terms of their recyclability and are fed as the only secondary input to the simulations in order to be able to assess the true recyclability of the specific car part. In normal operation conditions, different input types will be mixed and integrated on site by the operator, to create the most optimal input to the furnace. This is creating the economy of scale to also feed different car part types (as part of the other input flows) to these industrial plants. It is considered in the simulations that all fractions/parts lie within the acceptable ranges of the selected processing route/plant and all materials are taken care of technologically as well as economically in the selected and/or most suitable processing route(s). In the simulations, the effects of only simulating the recycling performance of the car part are included in the setting of the processing conditions and input, in order to address the normal operation conditions and input integration. Where applicable this is discussed in the presentation of the results in the next chapter and where needed, constraints to the recycling specific car parts are included in the discussion of the results. Usually processing of these parts will be integrated and mixed with other metal recyclate (and/or primary) flows and processed together to render processing economic. This is the basis of the HSC Sim simulations of the recycling assessment for all parts and processing routes assessed. This allows simulating normal operating conditions, while still being able to address the specific recycling rate, losses and emissions of the car part under consideration.

Figure 14 In the process model, the "Feeds" sheet is of importance as it shows in which metallurgical processing infrastructure (according to the segments of the Metal Wheel in the middle) the car parts and possible disassembled sub-parts are processed



3.4 Results of material recycling and recovery assessment from process simulation models

The recycling assessment does not only provide recycling rates for the car electronic parts but provides a quantified basis for comparison of different industrial processing options and process combinations with that of the UNIVAQ process and provides the rigorous framework to define the best suitable recycling flowsheet system architecture to most optimally process the different electronic parts, not only looking at CRM recovery, but including all in- and output flows (including losses/residues) and their quality. To accomplish this, the recycling and processing flowsheets have been extensively integrated in the model within this project in order to facilitate this and reflect state of the art industrial processing options for recycling.

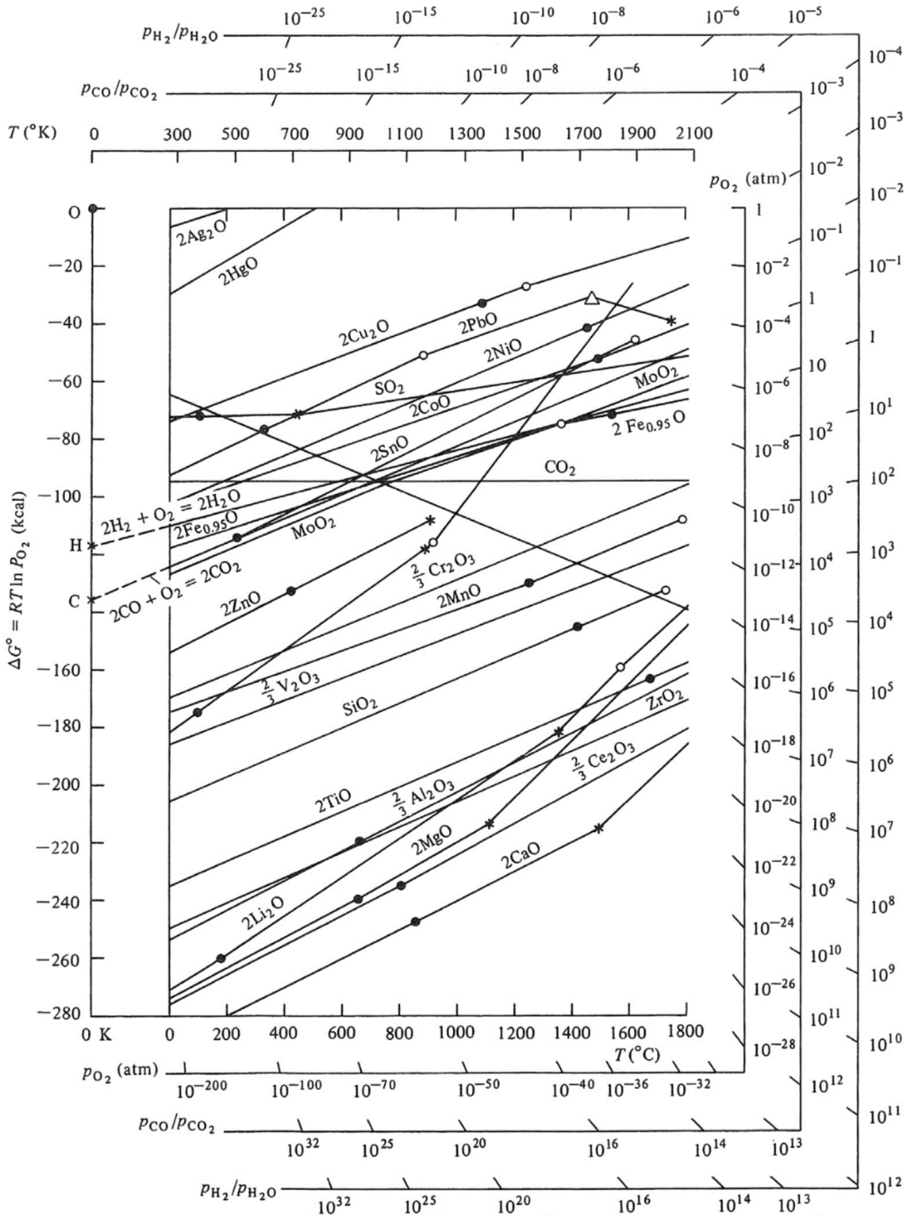
Hence, the assessment cases generate insight on the Best Available Technique (BAT) industrial (and hence economic viable) recycling processing routes and hence plants to be applied to derive the most optimal treatment for the different parts and objectives of recycling (either focussing on optimal total recovery or optimal recovery of specific elements).

The basic idea behind Figure 14 is the Ellingham diagram in Figure 15, that directs metals to segments where these can be processed under suitable partial oxygen and temperature conditions. A similar diagram for hydrometallurgy exists, i.e., the Eh-pH diagramme, all at specific conditions, concentrations etc.

From Figure 15 it would be clear when it would be useful to calcine/pyrolyse to produce on the one hand metal and oxides on the other hand. The challenge is then to separate the calcine from metal, but there are techniques for this. The metals can then return to metallurgical processing without the refractory oxides such as oxides of Al, Ca, Mg, Ti etc., which are situated more at the lower side of the diagram, i.e., with a very negative Gibbs free energy.

In the simulation model, Gibbs minimization is calculated for all the many elements and resulting compounds as shown above, which makes the simulation model rather powerful and realistic, i.e., the partial oxygen pressure to remove O from the element, from which it is clear which elements will oxidize and what are easily reduced to metal (Handbook of Recycling, Worrell & Reuter 2014, Elsevier)

Figure 15 The Ellingham Diagram of a selection of elements for different reduction potentials, i.e., the partial oxygen pressure to remove O from the element, from which it is clear which elements will oxidize and what are easily reduced to metal (Handbook of Recycling, Worrell & Reuter 2014, Elsevier)



4. Results of recycling assessment of processing car electronic components in existing (metallurgical) processing routes

This chapter will present and discuss the results of the recycling assessment as performed on the basis of the process and methodology as described in the previous Chapter.

The following parts have been assessed in terms of recyclability dependent on their compositional data availability from the project. The results of the recycling assessment for each of these parts, is presented and discussed in this chapter.

- IMSE
- PCB (from Combi-instrument and Infotainment Unit)

4.1 Model definitions and set up for recycling assessment of (electronic) parts as also processed in the UNIVAQ pilot plant

As pointed out in Chapter 2, the data of the different electronic parts as provided by TNO and data derived, analysed and processed by MARAS (from the TNO data and the MISS data file of the combi-instrument panel as earlier provided in WP3 this project by SEAT), have been integrated as input into the HSC Sim 10.0 simulation models. This has been done by including the required detailed description of materials in terms of needs to functionally describe metallurgical processing using a thermochemical based process simulator.

The HSC Sim simulation model as applied for the assessment of the recycling of the electronic parts has (see Figure 2):

- 189 reactors/unit operations,
- 840 streams, and
- over 310 alloys, compounds, organics, etc being processed.

From the 310 alloys, organic and inorganic compounds, elements, etc. originate 182 compounds/elements/materials from the range of electronic and car disassembled parts as input to the recycling processes (this includes the compounds from the disassembled parts as addressed in WP3). The other compounds, alloys, etc are the phases created during the processing of the car parts, either as intermediate and/or end products.

4.2 Determination of most suitable recycling routes for recycling of car electronics

The feed sheet, i.e., the 'cover' of the model, shows how flows of different electronic parts can be directed to the most suitable combination of (i.e., with the highest recovery and lowest amount of losses/emissions) metallurgical processing. This is done based on the composition of the electronic part and the processing abilities of the different flowsheets and processing routes. To achieve to most optimal recycling result, the recycling analyses include the assessment of different recycling infrastructures when applicable (depending on the type of component) and/or assesses and determines the best combination of metallurgical recycling infrastructures as depicted by the Metal Wheel, as some parts cannot be optimally processed in just one recycling infrastructure due to their varying material combinations, which can best be recovered through a combination of processes. This is done based on the extensive expert knowledge within MARAS, based on careful study of the part compositional analyses linked to the range of processing options.

The work results in not only assessment of recyclability, but also in the definition of the most optimal combination of processes for recycling of the part under consideration. This can then be compared to the performance of the UNIVAQ plant performance.

In the next sections, the results of the material (and energy) recycling and recovery assessment for the different electronic parts will be discussed and elaborated on.

It is important to understand in the context of this project, and in analogy with the recycling assessment in Task 3.3, is that the recycling of a product within the circular economy implies creating the same material quality after recycling so that it can be applied in the same product. This approach is favoured in the selection of most suitable processing routes, hence in the assessment of material (and energy) recycling and recovery. This definition of CE recycling levels is taken into account when presenting the recycling results (where applicable). Energy recovery from feed is also included in the results, as use of organic materials in the smelting process(es) both as reductant as well as energy carrier, replacing the addition of (part) of the primary resources is usual industrial practice to achieve the required thermodynamic, kinetic and processing conditions for processing. This differs however per type of recycling route as is shown in the results below. Including this is also important in order to assess the balance with disassembly options (e.g., as for the case of PC (encapsulant and/or substrate) dismantling/removal from the IMSE).

As recycling efficiency is not only determined by the recovered metals and product flows created, but is affected by the full in- and output balance, including the creation of residues, their composition and destination/application in the CE, the dispersion and losses of valuable elements to other flows than the produced metal fractions, the required input of primaries and the purity/quality of the recovered metals, these results are presented for the different parts assessed. As explained above, this level of detail and information should be(come) equally available from the UNIVAQ process, to allow for a sound and realistic comparison of the different recycling options as already established in industry and developed within this project.

4.3 Results recycling assessment electronic car parts

In this section, the results of the performed recycling assessment of the assessed parts are provided and discussed. The major findings and results are included in this section and provide the basis for comparison with the UNIVAQ process.

4.3.1 IMSE recyclability calculations and assessment

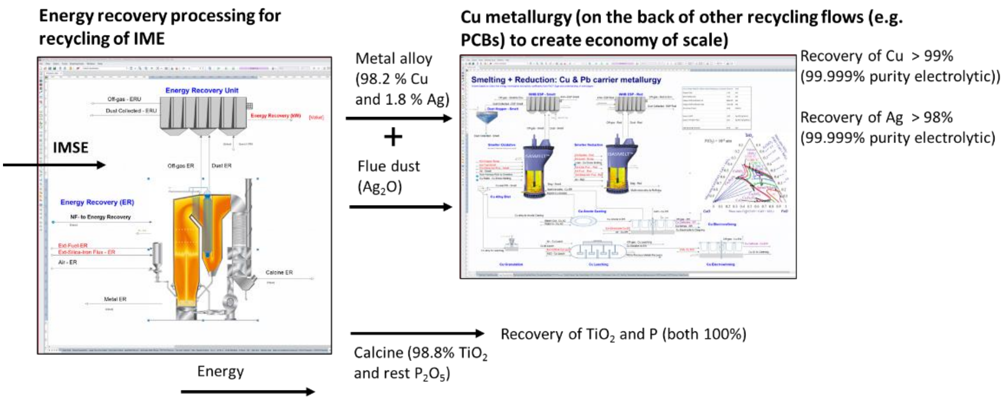
Table 1 shows the composing materials/compounds of the IMSE. Based on its composition, a combination of different recycling processes has been selected from the entire processing flowsheet and recyclability and recycling results have been assessed for this route. The composition, as provided by TNO and applied as the basis for the material recycling and recovery model-based assessment, matches most with what is called the ‘thermoformed PC’ IMSE as processed in the UNIVAQ plant.

Considering the complexity of the IMSE composition and build-up and the filler (TiO_2 contained in the white) the combination of processing infrastructures, which proves to be the most suitable and optimal combination for the processing of the IMSE to most optimally recover both the contained (valuable) metals as well as the energy contained in the PC encapsulant and substrate as present in the IMSE is:

- Energy recovery processing: recovery of energy in the first process step to reach an economy of scale and to concentrate the different (valuable) metals in the output fractions produced from the energy recovery process
- Cu processing route: the flue dust and the metal, as created during the energy processing route, are recycled in the Cu processing route. This is done on the back of other inputs (such as the PCB from the combi-instrument to create a sufficient economy of scale).
- Recovery of TiO_2 and P in dedicated recycling processes: the calcine from the energy recovery process containing TiO_2 and P_2O_5 are further recycled for the recovery of TiO_2 and P (fully recovered).

Figure 16 visualises this combination of processes applied and assessed for best recycling performance and the produced and recovered flows.

Figure 16 Recycling system flowsheet/configuration for optimal processing and recycling of IMSE in existing processing routes with major products and composition of output flows visualised



The major products of recycling the IMSE by in this flowsheet configuration of processes are:

- Energy (see Table 3)
- Metal alloy/phase due to reducing gases: ca. 98.2 % Cu and ca. 1.8% Ag, which is recycled to the reductive (Cu) smelter (see Figures 3&4).
- Flue dust: Essentially pure Ag_2O which is recycled to the reductive (Cu) smelter (see Figure 4).
- Synthesis gas if not oxidized for energy recovery (ca. 52.9 % N_2; 3% CO_2; 4.6% H_2O; 20.7% CO; 18.7% H_2 and rest, which can be used as fuel or reductant).
- Calcine, which is basically pure, i.e., ca. 98.8% TiO_2 and rest P_2O_5. This can then be recycled for TiO_2 and recovery of P (Table 3 below).

Table 3 Products from IMSE recycling processing in energy recovery processing (step 1, Fig. 15)

Products from IMSE processing in energy recovery processing (simulated for 20 tph IMSE feed)	Composition	Amount	Unit
Metal phase (recycled to other units in flowsheet)	98.2 % Cu and 1.8% Ag	0.01	tph
Flue dust phase (recycled to other units in flowsheet)	Ag_2O	0.0042	tph
Energy (if 100% efficient boiler)	52.9 % N_2; 3.0 % CO_2; 4.6% H_2O; 20.7% CO; 18.7% H_2 and rest	95965.24	kW
Total part feed tph		20	tph
Energy recovery per tonne of feed		4.8	MWh/t
Calcine	98.8% TiO_2, 1.2% P_2O_5	1.71	tph

Table 4 reveals both the recovery rates of the different metals/compounds as achieved through this route for the combination of processes as depicted in Figure 16 and listed above, as well as the quality/purity of the different recycled metals. This is crucial to guarantee true circularity by producing high quality metal products.

In the Table 4 it is clear that the Cu and Ag are recovered ca. 99.1% and 98.4% respectively at the purity shown, which is LME grade (marked green in the Table 4). The recycled metals from the IMSE match the CE level 1 recycling performance (high quality, no further processing required). The other elements shown in the Table 4 are not relevant for the IMSE case, but it shows that in reality material never get processed on economy of scale individually (see explanation in Chapter 3).

Table 4 Results of recycling processing of the IMSE (including PC) through the combination of energy recovery processing, Cu processing (reductive smelter) and TiO_2 and P (all process steps)

Recovered metals to high quality product or intermediates for further processing (selection of elements in product compounds)	% Recovery
Ag (99.999% purity electrolytic)	98.42
Al, Ba, Ca, Fe, Mg, Si (as Al2O3, BaO, CaO, FeOx, SiO2 in slag)	99.00
Au (99.999% purity) electrolytic (see PM-PGM Recovery)	99.00
Cu (99.999% purity) electrolytic	99.06
In (to alloy for further processing)	2.91 (low due to low level in IMSE)
Sn (to various intermediates for further processing to recover rest)	77.99
Zn (99.99+% electrolytic)	33.92 (low due to low level in IMSE)
Pb (bullion)	96.46
Pd	100.00
Pt	Not present in IMSE
Plastics (PC) recovered as energy and reductant	(see Table 3)
Ni (99.99+% purity electrolytic)	96.65
Co (99.99+% purity electrolytic)	92.56
P	100
TiO_2	100

As HSC Sim is intrinsically linked to LCA simulation software and the inventory can be directly obtained from the process simulation based on true performance, material and energy flows and qualities as created during recycling (rather than relying on general and non-applicable LCA databases which do not cover product unique recycling inventories) scope 1 impacts are calculated for the performed recycling assessment. Results are shown in the Table 5. It should however be realised that as the processing of the material would be one of many materials in an industrial plant, it makes little sense to footprint the complete flowsheet. Only basically the allocation for Scope 2 and 3 should be the electrolysis, which would constitute the major footprint.

Table 5 A selection of LCA indicators (scope 1) for the recycling of the IMSE in the processing route as depicted in Figure 14

EoL LCA for processing IMSE	Amount	Unit
Total kg CO2	46942.00	kg
Scope 1 GWP	2.35	kg CO2/kg Mod
Scope 1 AP (SOx+NOx)	Low	kg SOx-eq/kg Mod

The above results are showing the recycling performance of the IMSE from which the PC encapsulant and substrate has not been removed by dismantling (matching the 'thermoformed PC' IMSE as discussed in D5.4). However, TNO is investigating options to selectively remove the PC encapsulant and/or to recover the polycarbonate from it. Recycling of the IMSE after disassembly of the PC encapsulant and/or substrate will obviously lead to different results than presented above. The major difference with the presented results will be the difference in the amount of energy recovered, which will be lower with decreasing organics content. Also, the amount of CO_2 created (and related scope 1 GWP) will be lower. Therefore, it would be desirable to design the part in such a way that the PC encapsulant and/or substrate are pure PC and when separating only a small part of it goes together with the valuable elements to ensure also that the footprint is low. Note the PC has around 0.69 tonne C per tonne of part. As demonstrated, this can be processed in calcination/pyrolysis to recover the energy content from it, or processed in the Cu route, where it is applied as reductant and energy carrier.

How much organics/plastics must be in a part before it can go to calcination/pyrolysis is determined by:

- the technology and the energy balance, i.e., can it deal with the large amount of energy set free
- if it is around 50% it can easily go straight to copper production for example, obviously is there is copper in the part, as well as Au and Ag so that it can be economic
- if the plastics % in the part becomes too large and the plastics complexly functionally joined, energy recovery is well suited and the calcine can be further processed
- if the plastics is passed through hydrometallurgy, the leaching recovery is never 100%, fillers will stay locked up in the plastic, rendering this a waste, which will then become uneconomic to process, thus becomes a (toxic) waste that needs to be dumped

Balancing existing processing options, with disassembly options of the PC contained in the IMSE is a worthwhile exercise. Important is to investigate and assess the quality of the PC, which can be recovery through additional disassembly (or other removal technique as investigated by

TNO), so ensure that the recovered PC can be applied in a high-quality material application. It should also be checked that the amount of valuable metals/materials are not separated from the IMSE together with the PC and will then go lost for recovery while decreasing the quality of the PC. Environmental impact, including energy consumption as well as use of, e.g., solvents have to be included when investigation these options. When a high enough quality of PC can be recovered, material recycling has the preference over energy recovery. The level of PC removal from the IMSE can be balanced with processing in existing (metallurgical) recycling options of the remaining IMSE.

4.3.2 PCB recyclability calculations and assessment

Figure 17 shows the major composing materials/compounds of two different PCB types from the SEAT Leon II as derived from the MISS data file and depicted detail in Table 2. Two types have been included in the assessment in order to show the variance in recycling results when PCB composition is changing. This is done to provide a more rigorous basis for the comparison with the recycling results of PCBs as performed in the UNIVAQ plant. Due to data issues, it is not possible to make a one-on-one comparison on what the PCBs as processed in the UNIVAQ are exactly composed of. Thus, assessing different PCB types (from a compositional point of view) allows for a better comparison and insight in the spread in results. It should also be noted that from the PCBs as processed in the UNIVAQ plant, different electronic components have been removed. The grinded PCBs and removed components are processed in two different recycling routes to optimise the metal extraction yields by UNIVAQ (see description of processes in Chapter 5). The PCBs as assessed for the existing processing routes, do not require grinding and/or removal of electronic components, but can be processed in their full composition.

As the recycling simulation models provide detailed insight not only into materials recovered, but also into materials lost (or recovered in a lower CE application level), this can provide feedback on what materials/compounds should better be removed from the PCBs and processed separately, in order to optimise recycling. This is an interesting link to be explored to the disassembly activities as performed by POLIMI. Insight into the compositional (compound detail) of different electronic components as can be removed by POLIMI, is essential to make this work in practice. This reveals once again the importance of sound data management, detail and data availability.

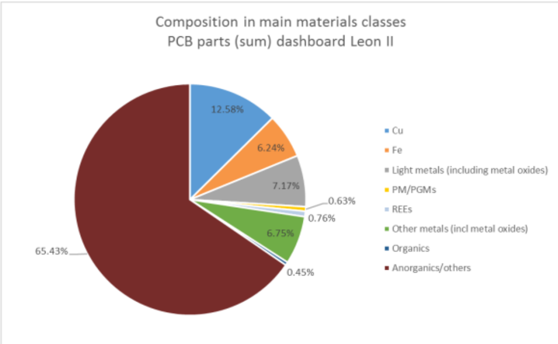
In order to be able to present an easy to interpretate overview of the compositional similarities and differences for the different parts (also providing input to the TREASURE platform in this manner, rather than presenting long tables and protect confidentiality of data), the composition of all car parts is given in this report in classified form in various pie-charts. This also provide an easy-to-understand basis to reveal the link to the compositional requirements and suitability of the various (metallurgical) recycling processing infrastructures as assessed. It is important to be aware, that in order to assess the compatibility with the processing routes and assess the recyclability, the full compositional detail, of which a section is illustrated in Tables 1 and 2, is required and always included in this work as the basis for the simulations.

The high contribution of Cu and other valuable metals, and the focus to recover as many of these metals as possible from the PCB parts, makes the Cu route (as depicted in Figure 4) the most suitable processing option for this type of parts.

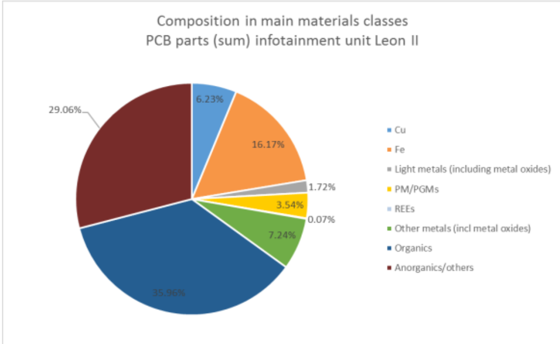
The recycling results are presented below and can be compared to that of the processing of this part type in the UNIVAQ plant (*to be done*).

Figure 17 Composition in main material classes of two different PCB 'types' from the SEAT Leon II

PCB type 1

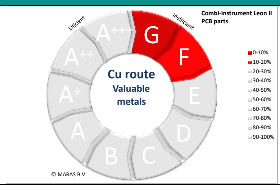
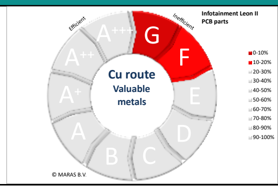
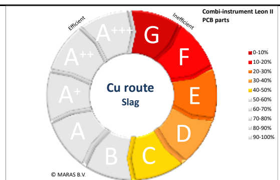


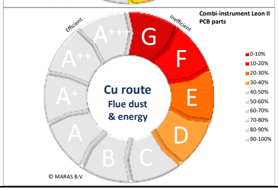
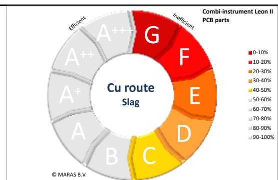
PCB type 2



The overall recycling rate for the different PCB parts for the assessed most optimal recycling route is given in Figure 18 by the Recycling Index (RI) for the three different CE levels

Figure 18 Recycling Index/recycling rates for closed and open loop CE products and energy recovery as a result of the processing of the different PCB types in the most suitable recycling route (Cu processing route)

<table>
<tr><th>Recycling in terms of CE recycling products</th><th>Recycling of PCB type 1 parts in Cu processing route</th><th>Recycling of PCB type 2 parts in Cu processing route</th></tr>
<tr><td>1. Closed loop CE – high quality products which can go straight back into part or product</td><td>
</td><td>
</td></tr>
<tr><td>2. Open loop CE to be processed into closed loop CE – intermediate products</td><td>Not produced</td><td>Not produced</td></tr>
<tr><td>3. Open loop CE – (intermediate) products for repurposing, e.g., as building / construction material etc.</td><td>


</td><td>

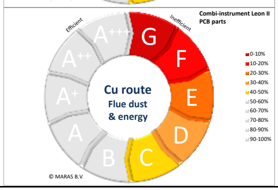

</td></tr>
<tr><td>4.Energy recovery from feed</td><td>0.009 kWh/t feed (this strongly depends on the amount of organics in the PCBs and could therefore differ)</td><td>0.13 kWh/t feed (this strongly depends on the amount of organics in the PCBs and could therefore differ)</td></tr>
</table>

Table 6 presents the results of the recycling processing of the different PCB types and the obtained quality. It is clear, that the metals are recovered at very high rates, respectively at the purity shown, which match the CE level 1 recycling performance (high quality, no further processing required). (Table 6 also indicates which metals will go to further processing to recover rest).

Table 6 Results of recycling processing of different PCB types in the Cu processing route

Recovered metals from full PCBs from SEAT parts to high quality product or intermediates for further processing (selection of elements in product compounds)	PCB type 1 % Recovery	PCB type 2 % Recovery
Ag (99.999% purity electrolytic)	98.77	95.79
Al, Ba, Ca, Fe, Mg, Si (as Al2O3, BaO, CaO, FeOx, SiO2 in slag)	99.00	99.00
Au (99.999% purity) electrolytic (see PM-PGM Recovery tab)	99.00	99.00
Cu (99.999% purity) electrolytic	97.95	99.03
In (to alloy for further processing)	3.12	0.00
Sn (to various intermediates for further processing to recover rest)	74.80	77.95
Zn (99.99+% electrolytic)	62.39	33.93
Pb (bullion)	95.65	96.11
Pd	100.00	100.00
Pt	99.91	Not present in feed
Plastics recovered as energy and reductant	see Table 7	see Table 7
Ni (99.99+% electrolytic)	96.62	96.13
Co (99.99+% electrolytic)	93.12	92.57

Figure 19 shows the material recycling rates for a selection of elements/materials visualised by the Material Recycling Flower.

Figure 19 Individual material recycling rates for different PCB types presented by the Material Recycling Flower (as presented in Table 7)

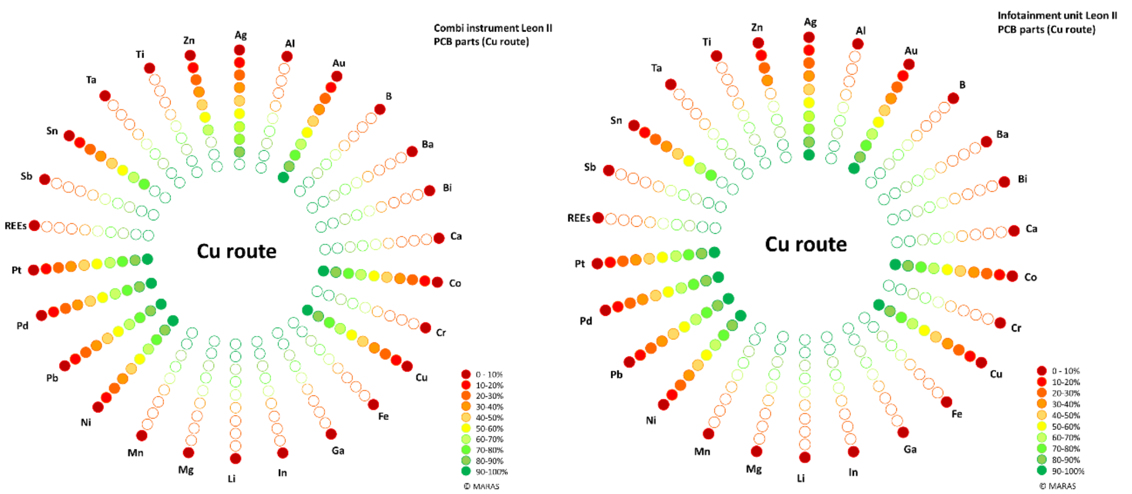


Table 6 shows and overview of all recycling products as created during the processing of the PCB parts in the Cu recycling route. This provides, separate from recycling rates and achieved purity of recycled materials, the basis to compare these existing processing options with the bio-hydrometallurgical plant.

Table 7 Products from PCB recycling processing in Cu recycling route

Products from PCB processing in Cu processing route (simulated for 20 tph PCB feed)	PCB type 1 Amount	PCB type 2 Amount	Unit
Copper Alloy (Oxidative melting)	9.54	8.73	tph
Energy (if 30% efficient) Ox	0.00	2368.34	kW
Energy (if 30% efficient) Red	175.72	163.86	kW
Per tonne of feed	8.79	126.61	kWh/t
Slag (building material)	0.68	0.59	tonne / total feed
Total recovery of materials from input into valuable products	52.3%	48.5%	%

As discussed for the results of the IMSE assessment, environmental impact calculations are directly linked in HSC Sim. This implies that LCA indicators and assessment on the EoL environmental performance can be calculated from this. Scope 1 results are presented here for the processing of the PCBs as discussed in this work. Table 8 illustrates, that environmental indicators (as well as exergy assessment - not shown here) could be included in the selection of the most suitable and optimal recycling processing route. These are Scope 1 and directly calculated by the simulator, which shows economy of scale processing infrastructure.

The simulation model, i.e., metal wheel, also show nicely and simply also considering the full composition, what needs to be processed where, using the Ellingham diagram/Metal Wheel as first design decision criteria.

Table 8 A selection of LCA indicators (scope 1) for the recycling of the PCB in the Cu processing route

EoL LCA for processing PCB	PCB type 1 Amount	PCB type 2 Amount	Unit
Scope 1 GWP	0.01	0.67	kg CO2/kg Mod
Scope 1 AP (SOx+NOx)	Low	Low	kg SOx-eq/kg Mod

5. Recycling of different car (electronic) parts in the UNIVAQ plant

The following hydrometallurgical recycling processes, developed and optimized by UNIVAQ during T5.3 and T5.4, are considered:

a. PCBs recycling
b. In-mold electronics recycling

The present section shows the developed flowsheets, the characterization of the input, the achieved extraction yields, and the characterization of all the outputs such as product and wastewater. Also, the distribution of the main elements in the outputs is shown. In addition, chemical and energy consumptions are described.

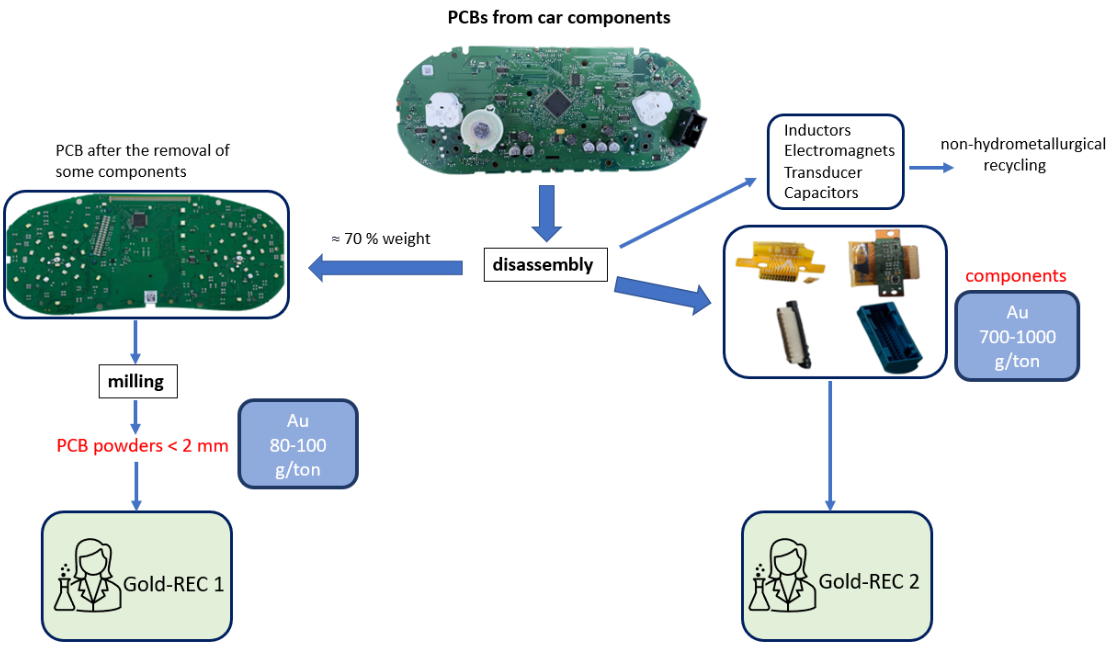
5.1 PCBs UNIVAQ recycling process

For the treatment of PCBs, two hydrometallurgical recycling routes were defined. A disassembly stage is necessary to obtain the input of the two recycling processes. The sample preparation occurred according to the following steps:

a. Remove specific components that inhibit the recycling rates.
b. Remove specific components to be treated with Gold-REC 2 hydrometallurgical process.
c. Grind the remaining components with the board to be treated with Gold-REC 1 hydrometallurgical process.

In Figure 20, the scheme of the two hydrometallurgical routes for the recovery of base and precious metals from PCBs is shown.

Figure 20 PCBs hydrometallurgical recycling routes



5.1.1 GDR1 process for the treatment of grinded boards

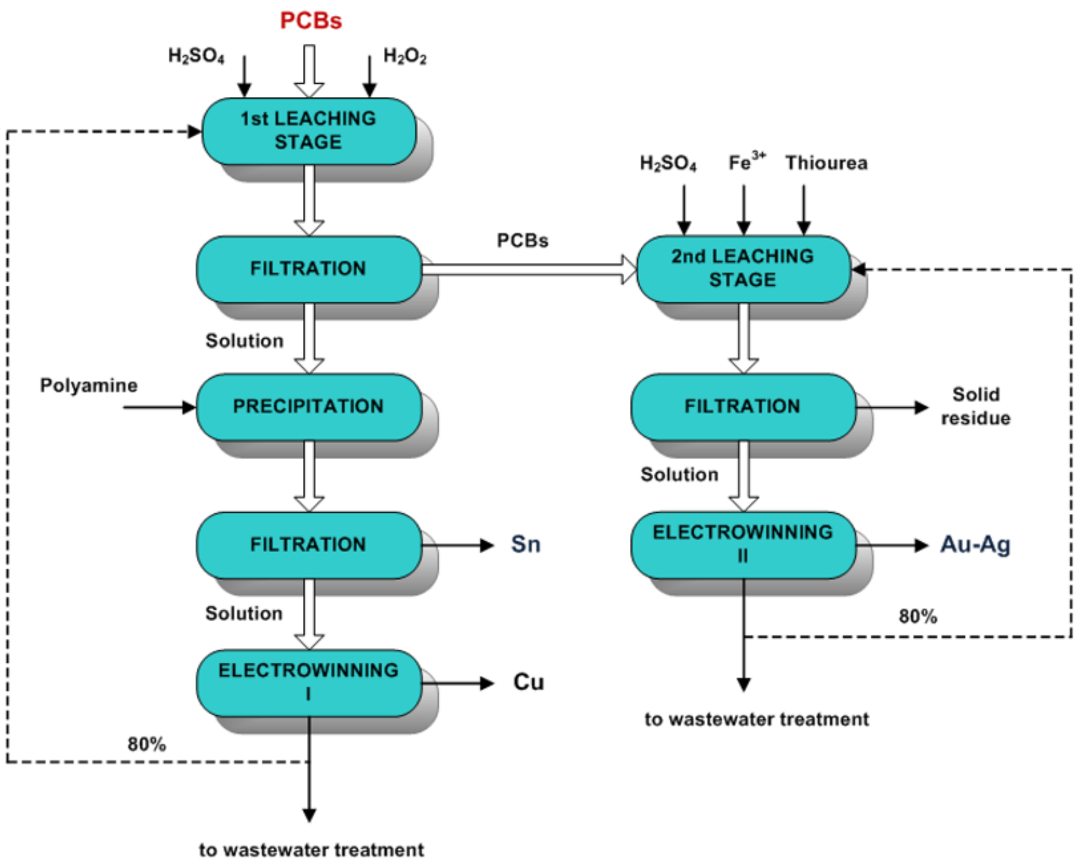
The following process was developed starting from the GDR1 (Gold-REC 1) UNIVAQ patent and optimizing it based on the characteristics of the input materials, the combi-instruments' PCBs of cars (SEAT). The optimization purposes were related to the reduction of wastewater production and chemical consumption, in addition to maximising metal extraction yields.

5.1.1.1 Process description

The board with the remaining components has been grinded to obtain a powder with a particle size below to 2 mm. The energy consumption for grinding, by considering the adopted lab-scale equipment, was 330 kWh/ton.

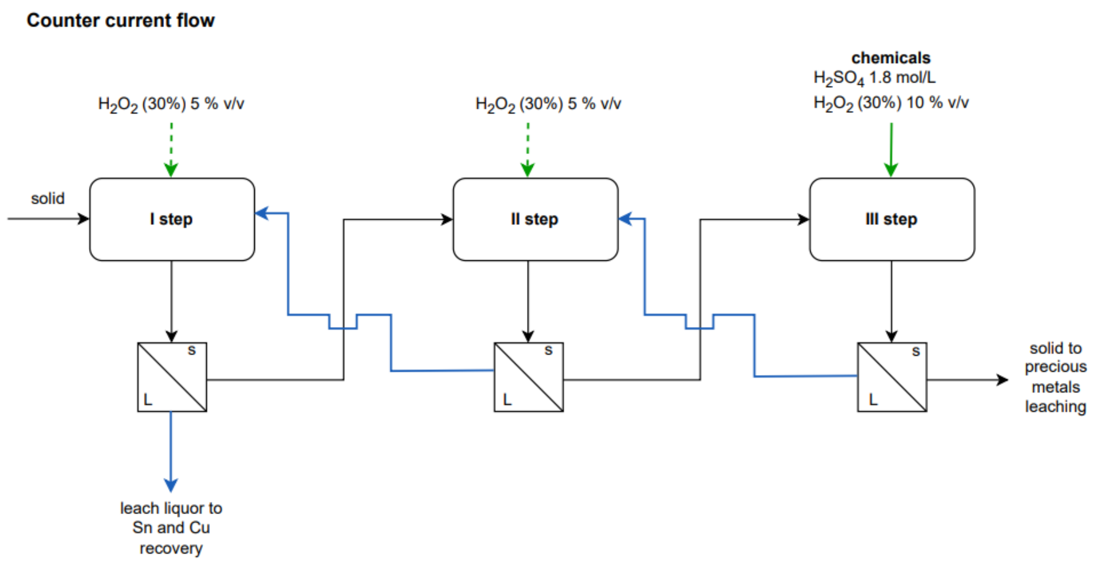
This process, as shown in Figure 21, is composed of two-stage leaching sections: in the first, containing three counter-current stages of leaching, the dissolution of base metals, and in the second, the dissolution of precious metals such as gold and silver, occur. This selective leaching is very helpful in separating metals already in the leaching section, allowing their efficient recovery. Tin is precipitated by flocculation with the aim of polyamine in the form of metastannic acid that can be thermally treated to obtain tin oxide as a final product. Copper remains in the solution after filtration and is recovered by electrodeposition. The second pregnant solution after the thiourea leaching undergoes the recovery of gold and silver by electrodeposition, which based on the experimental tests, cannot take place selectively. Therefore, is to be considered a refining step aimed at dissolving silver from the gold-silver alloy to increase gold purity. Silver can be recovered from the acid solution as chloride.

Figure 21 GDR1 hydrometallurgical recycling process flowsheet for the treatment of PCBs powders



In addition, it should be considered that with the aim of minimizing wastewater production and chemical consumption, the first step of leaching of base metals, which includes three leaching steps by hydrogen peroxide and sulfuric acid, was studied to be conducted by a counter-current scheme (Figure 22).

Figure 22 Counter current multistage base metals leaching scheme



Concerning with the input materials, PCBs powders are obtained after removing some components, the full list has been reported in D5.4, and subsequent grinding up to 2 mm. PCBs powders' input characterization is shown in Table 9.

Table 9 Solid input characterization

Input – PCBs powders (below to 2 mm after removal of some components)			
Metals (ICP-OES analysis)		C-H-N-S analysis	
Cu, wt. %	19.1	Carbon wt. %	22.62
Al, wt. %	2.46	Hydrogen wt. %	1.62
Sn, wt. %	1.01	Nitrogen wt. %	0.34
Ni, wt. %	0.29	Sulfur wt. %	0.30
Fe, wt. %	0.28		
Ti, wt. %	0.18		
Zn, wt. %	0.11		
Ag, g/t	273.3		
Au, g/t	94.2		
Zr, g/t	33.7		
Pd, g/t	27.5		

5.1.1.2 Results

In this section the results obtained by the treatment of PCBs powders have been fully described, more in detail concerning with the following points:

a. Summary of the metal extraction yields
b. Characterization of the process outputs

c. Distribution of the elements in the process outputs
d. Mass balance
e. Chemical consumptions
f. Energy consumptions

A summary of the experimental results has been reported in Table 10.

Table 10 Summary of the obtained results for the treatment of PCBs powders

stage	Recoveries for each stage			
	Au	Ag	Cu	Sn
1st leaching stage			95%	96%
2nd leaching stage	70%	89%		
Sn precipitation				89%
Cu electrowinning			97%	
Au-Ag electrowinning	85%	55%		

The process outputs have been characterized to evaluate their management in case of disposal or treatment and to define the selling price in the case of products of industrial interest. The outputs are below listed:

I. final dry solid residue
II. wastewater 1 (from the base metals leaching stages) 20 % v/v
III. wastewater 2 (from the precious metals leaching stage) 20 % v/v
IV. tin oxide
V. copper
VI. gold-silver

The final dry solid residue is the powder of PCBs subjected to the leaching operations to dissolve base and precious metals. The obtained amount is 783 kg for 1 ton of treatment; the residual metal fraction is about 4-5% wt., detected by the solid residue chemical attack. In Table 11, the residual metal contents were reported.

Table 11 Final dry solid residue metal characterization

Final dry solid residue metal characterization	
Al, wt. %	2.57
Cu, wt. %	1.07
Ti, wt. %	0.23
Fe, wt. %	0.15
Sn, g/t	464
Ni, g/t	729
Zn, g/t	435
Zr, g/t	70.3

Ag, g/t	34.9
Au, g/t	20.4
Pd, g/t	5.3

During the leaching operations, the metal fraction is essentially affected, while the residual parts of the PCBs, such as fiberglass and plastic, remain in the solid residue.

Wastewater 1 (see Table 12 for composition) is the spent solution that, according to Figure 19, is obtained from the leaching system composed of sulfuric acid and hydrogen peroxide to dissolve base metals.

Table 12 Wastewater 1 composition

Wastewater 1 composition	
Sulfuric acid	1.58 mol/L
pH	< 0.5
Cu	819 mg/L
Al	378 mg/L
Fe	227 mg/L
Ni	205 mg/L
Sn	110 mg/L
Zn	12 mg/L
Ti	< 5 mg/L

Wastewater 2 (see Table 13 for composition) is the spent solution that, according to Figure 21, is obtained from the leaching system composed of thiourea, ferric sulphate and a low concentration of sulfuric acid, to dissolve precious metals. After the leaching operation, the leach liquor solution is subjected to gold and silver recovery by electrodeposition.

Table 13 Wastewater 2 composition

Wastewater 2 composition	
thiourea	19 g/L
sulfuric acid	0.2 mol/L
pH	1.0
Fe	4.7 g/L
Cu	118 mg/L
Al	78 mg/L
Ti	18 mg/L
Ag	16 mg/L
Sn	8 mg/L
Ni	5 mg/L

Tin oxide product was obtained after recovery of tin from the first leach liquor solution by precipitation with the use of polyamine. After filtration, metastannic acid is obtained. This product is thermally treated at 650 °C to obtain tin oxide with the following composition, as shown in Table 14.

Table 14 Tin oxide composition

Product	SnO_2 %	CuO %	traces
Tin-oxide	97.4	2.3	Polyamine, Zn, Ni, Al

Copper was obtained by electrodeposition, after that tin was recovered from leach liquor solution obtained by the first leaching step of PCBs powder, the base metals dissolution. The grade of obtained copper was about 99 % with different metal impurities as shown in Table 15.

Table 15 Copper composition

Product	Cu %	Fe %	Ni %	Zn %	Al %
Copper	98.7	0.55	0.37	0.32	0.22

The sum of the content of the elements consisting of the copper product slightly exceeds 100 % wt. due to experimental errors.

Based on the small quantities treated at the lab-scale, the composition of the gold-silver product was not determined. However, the gold and silver content was estimated by considering the decrease in their concentrations in the solution at the end of the electrodeposition. The product estimation composition is 29 % of gold grade and 71 % of silver grade. It is a typical composition of a product named 'dorè'.

Selective separation of gold from silver can be obtained by performing a nitric acid leaching stage that aims at dissolving only silver. Although the use of nitric acid is not environmentally sustainable due to the production of NOx gaseous emissions, in this case, given the very low quantities to be treated, 0.189 kg of gold-silver product per ton of PCBs powders, is a route that can be followed. Then, silver is recovered from the solution in the form of chlorides by adding hydrochloric acid or sodium chloride, while a gold concentrate remains in the solid residue of nitric acid leaching.

Table 16 summarizes the distribution of various elements for each process output. The most present elements in the initial sample are considered.

Table 16 Distribution of the main elements in process outputs

Items	Cu, %	Sn, %	Al, %	Fe, %	Ti, %	Ni, %	Zn, %
Solid input	100	100	100	100	100	100	100
Tin oxide	< 1	89	1	0	0	8	10
Copper	92	< 0.5	2	35	0	23	52
Wastewater 1	3	7	12	23	1	47	7
Wastewater 2	< 1	< 0.5	3	0	1	2	0
Dry solid residue	4	4	82	42	98	20	31

In Table 17, based on the experimental lab-scale tests, a mass balance was described considering all the inputs and outputs of the GDR1 hydrometallurgical process; the mass balance is referred to the treatment of 1 ton of PCBs.

Table 17 Mass balances for the treatment of 1 ton of PCBs powders (GDR1 process)

Input	kg	Output	kg
Solid (more details in Table 33)	1000.0	Dry solid residue	783.0
H_2SO_4 (50 % w/v)	2719.4	Wastewater 1	6899.3
H_2O_2 (30 % w/v)	1477.9	Wastewater 2	8375.2
Thiourea	164.4	Tin oxide	11.24
Ferric sulphate	184.8	Copper	178.3
Polyamine (10 % w/v)	19.1	Gold-Silver	0.189
Water for 1st leaching stage	4280.0	Humidity	511.2
Water for 2nd leaching stage	7764.8	-	-
Total input	17610.4	**Total output**	16758.4
Experimental error 4.8%			

Concerning the outputs, the humidity is referred to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the products. Wastewater 1 is the sulfuric acid solution after the base metals counter-current leaching, from which tin and copper have been recovered. Wastewater 2 instead is the thiourea solution from which gold and silver have been recovered by electrodeposition. Wastewater densities were 1.15 g/cm^3 and 1.07 g/cm^3, respectively. About the products, 11.24 kg of tin oxide is recovered after metastannic acid oxidation at 650 °C, 178.3 kg of copper is recovered by electrodeposition, and the mixture of gold-silver alloy, also named dorè, is recovered after electrodeposition. A leaching stage can be performed by using nitric acid to dissolve silver and leave gold metal as a solid residue to separate gold and silver. Then, adding hydrochloric acid or sodium chloride can precipitate silver nitrates as silver chlorides.

Table 18 shows the chemical costs for the treatment of 1 ton of PCBs powders.

Table 18 Chemical consumption and costs for the treatment of 1 ton of PCBs powders

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
H_2SO_4 (50 % w/v)	2719.4	0.13	353.5
H_2O_2 (30 % w/v)	1477.9	0.40	591.2
Thiourea	164.4	1.00	164.4
Ferric sulphate	184.8	0.30	55.4
Polyamine	19.1	1.00	19.1
Water	12084.8	0.0015	18.1
			1201.7€

The total cost of chemicals is 1201.7 €.

Regarding energy consumption, the GDR1 process for the treatment of PCBs powders can be developed in a plant that requires the following energy consumptions: stirring for the leaching operations and for the preparation of the solutions, pumps to discharge the chemical reactors and to separate the leach liquor from the solid residue, the furnace to oxidize the metastannic acid that needs to be conducted at 650 °C for 1 h, and the energy consumption for the electrodepositions, that was 2.1 kWh/kg for the copper and 10 kWh/kg for the precious metals. Table 19 shows the energy consumption for each specific operation.

Table 19 Energy consumption

Operation	kWh
PCBs grinding	**330** to be evaluated at industrial scale
Stirring	27
Pumps	32
Furnace for tin refining	123
Cu electrowinning (2.1 kWh/kg)	374
Au-Ag electrowinning (10 kWh/kg)	1.9
	557.9 kWh

5.1.2 GDR2 process for the treatment of PCBs specific components

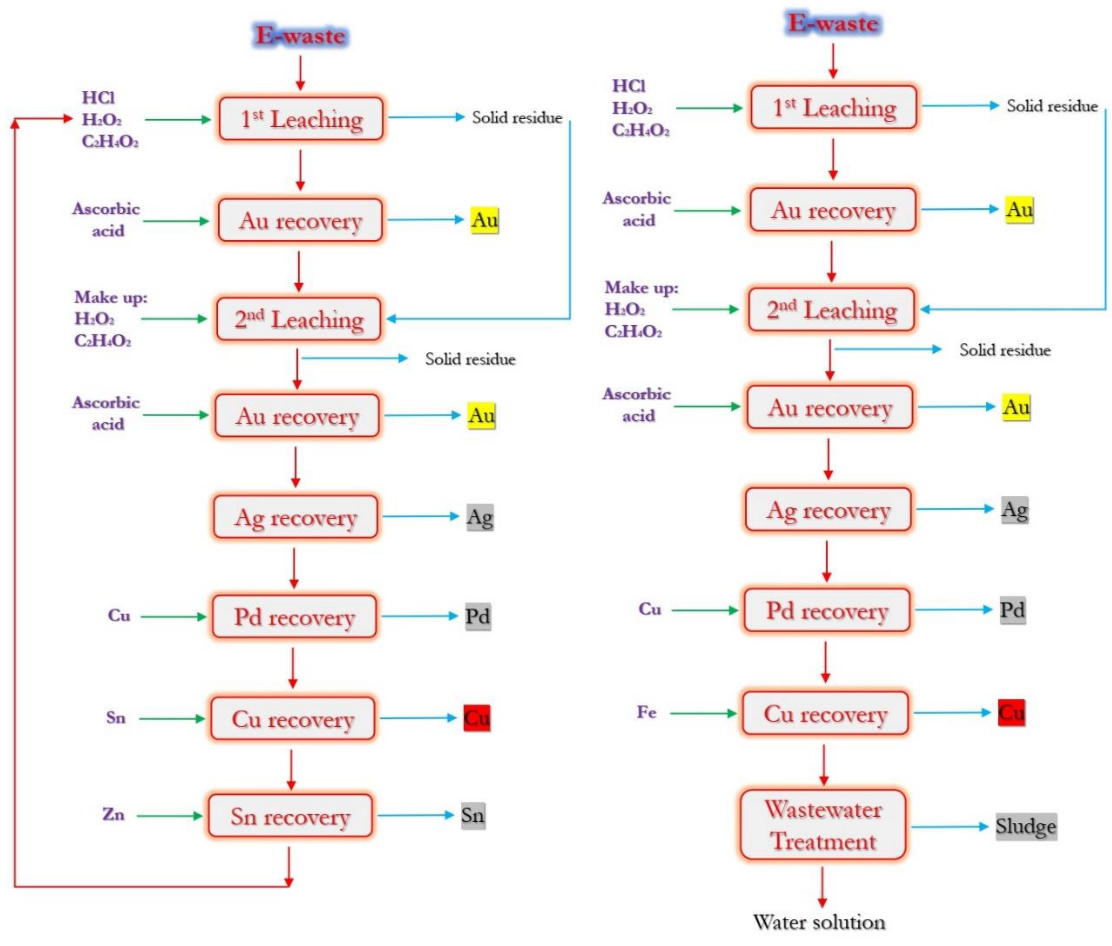
In this section GDR2 process is employed for the recovery of precious metals from a mixture of different components detached from of the main board (POLLINI). The following process was developed starting from the GDR2 (Gold-REC 2) UNIVAQ patent and optimizing it based on the characteristics of the input materials. The low extraction yields showed that further refinement would be necessary. The lack of additional input materials made it impossible to further optimize the process. Probably a low energy consumption size reduction such as a shredder operation could be useful to increase the metal extraction yields.

5.1.2.1 Process description

The process includes two steps of leaching, which were performed according to the conditions stated in GDR2 to have high leaching efficiency for all elements. Leaching experiments were performed in a solution containing 30% HCl (37%), 20% H_2O_2 (30%) and 10% $C_2H_4O_2$ (99%) with a pulp density of 15-20% for most of the experiments, for 5 hours at room temperature without stirring. 100% for hydrogen peroxide and 50% for HCl was made up before second leaching. Figure 23 shows the scheme of the process.

A selective gold recovery stage should be performed on the leaching solution before going to the second stage of leaching, with a reduction with ascorbic acid (5 g/L). Ascorbic acid is added to reduce Au into metallic state in the form of precipitates, which is separated by filtration. After second leaching, gold recovery is performed again, by reduction with ascorbic acid. Silver recovery is performed by mixing the washing water (30% of leaching liquor) and the primary solution, and colling down the solution to 5 °C immediately, after Au recovery stage. Palladium, copper, and tin are recovered by cementation using metallic powders of Cu, Sn, and Zn, respectively (Figure 23).

Figure 23 Two flowcharts for selective recovery of metals of interest in two possible routs: a) with the possibility of recirculation of solution, b) for disposal purposes in which, final solution is sent to wastewater treatment stage.



(a) (b)

Chemical characterization of the mixture of different components detached from of the main board (POLLINI) is shown in Table 20.

Table 20 Chemical characterization of the mixture of different components of the main board

		Mixture: Display connector, large and small Golden wires, CPU
g/ton	Ag	913
	Au	248
	Pd	63
	Ti	9593
	Zn	3015
	Pb	55
	Cr	1359
	Fe	6338
%wt.	Cu	38.06
	Ni	1.70
	Sn	2.49

The obtained mixture of the components was treated by GR2 process with two stages of leaching.

5.1.2.1 Results

In this section the results obtained by the treatment of a mixture of PCBs components have been fully described, more in detail concerning with the following points:

a. Summary of the metal extraction yields (leaching and precipitation stages)
b. Distribution of the elements in the different stages of the process
c. Output characterization
d. Mass balance
e. Chemical consumptions

The results are shown in Table 21.

Table 21 Metal recovery (%) in each stage of leaching for the mixture of different components of the main board

Groups of components	Elements	Extraction yield (%) 1st stage of leaching	Extraction yield (%) 2nd stage of leaching	% Remained value in solid residue	Total
Mixture: Display connector, large and small Golden wires, CPU	Ag	64.08	12.20	23.72	100
	Au	34.94	12.43	52.63	100
	Pd	37.46	23.33	39.21	100
	Ti	3.98	3.49	92.53	100
	Zn	34.90	21.99	43.11	100
	Pb	15.61	4.04	80.35	100
	Cr	31.78	9.73	58.49	100
	Fe	31.06	9.57	59.28	100
	Cu	36.15	23.19	40.66	100
	Ni	49.41	6.37	44.22	100
	Sn	92.09	0	7.91	100

Weight percentage of solid residue after chemical attack was calculated for the mixture of components. As can be seen, after complete dissolution of metals about 53% of initial weight of waste is remained.

Selective metal recovery was carried out on the pregnant leaching solution obtained in previous leaching section. Based on GR2 process Au, Ag, Pd, Cu and Sn can be recovered selectively in different stages. It should be mentioned, due to low concentration of Pd in solutions, Pd recovery stage was omitted. Sn recovery was performed in two steps (Table 22).

Table 22 Selective metal recovery results (%) in different stages for the obtained solution of second leaching process

Recovery tests	Elements	Recovery yield in each recovery stage (%)								
		Au recovery stage	Ag recovery stage	Pd recovery stage	Cu recovery stage	1st Sn recovery stage	2nd Sn recovery stage	Total recovery (%)	Initial conc. (mg/l)	Final conc. (mg/l)
Solution of optimization leaching test of mixed components (POLLINI)	Ag	3.30	0	-	87.07	2.90	5.07	98.34	72.23	0.96
	Au	64.67	14.64	-	19.36	0.59	0.73	100	5.91	0
	Pd	10.29	2.95	-	83.87	2.89	0	100	3.78	0
	Ti	33.25	5.12	-	1.91	5.24	5.09	50.61	72	28
	Zn	67.60	0	-	6.37	0	0	73.97**	169	26083
	Pb	47.20	0	-	0	0	0	47.20	2	1.3
	Cr	0	0	-	2.89	7.49	9.29	19.68	54	35
	Fe	0	0	-	4.08	7.85	7.48	19.42	247	160
	Cu	5.24	6.24	-	83.42	0	5.09	99.99	22552	0.92
	Ni	6.57	6.61	-	2.96	14.75	8.41	39.31	90244	43947
	Sn	0	3.68	-	0	38.37	37.60	75.98*	2316	3878

*Total recovery value calculated based on the concentration of the metal in solution, after added value of Sn for Cu recovery.

** Total recovery value calculated based on the concentration of zinc in solution, before adding Zn for Sn recovery.

Table 23 shows the distribution of the elements in all outputs. It should be noted, the mass balance for Sn and Zn is somehow different, because some amounts of Sn and Zn are added in Cu recovery and two stages of Sn recovery, respectively. So, recovery percentages for Sn are considered respect to initial value of Sn in e-waste, till the Cu recovery stage, and then it has been calculated respect to the added value of Sn, during and after Cu recovery stage. Accordingly, the same method of calculation was applied for Zn. Thus, Zn recovery percentages are considered respect to initial Zn content till the Sn recovery stages, and afterwards it has been calculated based on the added value of Zn in Sn recovery stages. Therefore, considering this aspect regarding the added values of Sn and Zn, and considering the remained values of Sn and Zn respect to initial values in e-waste, the total mass in final solution is calculated based on treatment of 1000 kg of e-waste, which is presented in Table 23 (sum of added values of Sn and Zn and remained values in solution). According to mass balance calculations and input values, it is estimated that the final volume of solution is about 8667 liters. Therefore, the mass values in Table 23 should be considered in this volume.

Table 23 Distribution of the elements for the whole process for the mixture of components

	Elements	Recovery yield of elements in each output respect to initial value in the e-waste (%) Au recovery between 2 leaching stages	Final solid residue	Au recovery stage (Au concentrate)	Ag recovery stage (Ag concentrate)	Cu recovery stage (Cu concentrate)	1st Sn recovery stage (Sn concentrate)	2nd Sn recovery stage (Sn concentrate)	Final solution	Total value (%)
Solution of optimization leaching test of mixed components (POLLINI)	Ag	3.2	23.7	2.4	0	63.6	5	3.7	0	101.6
	Au	23.7	52.6	15.3	3.5	4.6	0.8	0.2	0	100.7
	Pd	1.3	39.2	6.1	1.7	49.9	2	0	0	100.2
	Cu	0.6	40.7	3.1	3.7	49	2.1	3	0	102.2
	Sn	0	7.9	0	3.4	11.8*	38.4*	37.6*	88.7**	100
	Fe	0.8	59.3	0	0	1.6	0.6	3	34.7	100
	Ni	0.2	44.2	3.6	3.7	1.6	4	4.7	38	100
	Zn	1	43.1	37.8	0	3.6	0.2*	0*	14.5**	100
	Cr	0.7	58.5	0	0	1.2	0.2	3.8	35.6	100
	Pb	0	80.4	9.3	0	0	0	0	10.3	100
	Ti	0.1	92.5	2.5	0.4	0.1	0.2	0.4	3.8	100

*Respect to the added value of Sn (or Zn)
** respect to initial value in the e-waste

The characterized process outputs are below listed:

I. wastewater
II. Au concentrate from the 1st leaching stage
III. Au concentrate after the 2nd leaching stage
IV. Ag concentrate
V. Cu concentrate
VI. Sn concentrates

The wastewater solution characterization after the recovery stages has been reported in Table 24. Anyway, this solution ca be reused for the treatment of a new cycle with a specific make-up of chemicals.

Table 24 Total mass of elements in final wastewater after recovery stages for the treatment of 1 ton of components

Ag (kg)	Au (kg)	Pd (kg)	Cu (kg)	Sn (kg)	Fe (kg)	Ni (kg)	Zn (kg)	Cr (kg)	Pb (kg)	Ti (kg)
0	0	0	0	50.21	2.20	12.87	299.90	0.48	0.006	0.37

Chemical analysis of recovered solids after each stage was carried out by chemical attack and doing mass balance. The results are presented in Table 25. For Ag and Au concentrates, the chemical composition was calculated based on a mass balance in solution, before and after recovery process, due to very low value of recovered solids. But for Cu and Sn concentrates a few amounts of solid was dissolved in aqua regia. As it can be seen, gold and silver percentages are very low in Ag and Au concentrates and copper is the dominant element in the composition (Table 25).

Table 25 Chemical composition of solids after selective recovery stages.

	Wt. %										
	Ag	Au	Pd	Cu	Sn	Fe	Ni	Zn	Cr	Pb	Ti
Au concentrate (between 1st and 2nd leaching)	1.09	2.20	0.03	90.12	0	1.83	2.92	1.17	0.37	0	0.27
Au concentrate (after 2nd leaching)	0.15	0.26	0.03	81.36	0	0	8.61	7.91	0	0.04	1.64
Ag concentrate	0	0.05	0.01	86.70	5.24	0	7.77	0	0	0	0.23
Cu concentrate	0.37	0.01	0.01	84.48	14.68	0.05	0.27	0.11	0.01	0	0
1st Sn concentrate	0.06	0	0	10.40	79.60	0.05	1.77	0.76	0	0	0.2
2nd Sn concentrate	0	0	0	0.02	87.64	0.03	0.40	0.92	0.01	0	0.01

Considering 1 ton of E-waste and having a pulp density of 15 % wt./v, the required reagents can be estimated as Table 26, considering the lab results. The mass balance for input and output streams are calculated according to the process (Figure 19-a), with two leaching stages and make-up of some chemicals. In addition to solid outputs, some portion of elements remained in the final solution, which their total value was calculated based on the data in Table 25 and represented above, in Table 26. Therefore, final solution should be treated suitably to remove these elements, before reusing for leaching or disposal purposes. It can be seen, there is a 2% difference (235.43 kg) between total input mass and total output mass, which is probably, due to the error in calculations and analysis.

Table 26 Mass balances for the treatment of 1 ton of mixed components

Input, kg		Output, kg	
Solid	1000	1st Au concentrate	2.64
Water	2666	2nd Au concentrate	13.76
HCl (37%)	2400	Ag concentrate	15.45
H_2O_2 (30%)	1480	Cu concentrate	187.54
$C_2H_4O_2$ (99%)	700	1st Sn concentrate	89.84
Wash water after Au recovery	2000	2nd Sn concentrate	98.87
Sn powder	230	Final solid residue (plastic?)	526.88
Zn Powder	300	Final solution	9246
		Remaining elements in final solution	359.59
Total input	**10776**	**Total output**	**10540.57**
Experimental error (%)			2.2

According to Table 26 it is possible to estimate the cost of chemicals which are used for treatment of 1 ton of E-waste. The results are shown in Table 27.

Table 27 Chemical consumptions and costs for treatment of 1 ton of e-waste

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
Water	2666	0.0015	4
HCl (37%)	2400	0.18	432
H_2O_2 (30%)	1480	0.35	518
$C_2H_4O_2$ (99%)	700	0.4	280
Sn powder	230	1.5	345
Zn Powder	300	2	600
			2179€

Therefore, the total cost of chemicals for treating 1 ton of e-waste (detached components) is 2179 €.

Considering the impure products achieved in different stages of selective metal recovery (Table 25), it is not possible to calculate the revenues at this stage. Hence, some optimizations stages should be taken to increase metal recovery and the purity of final products.

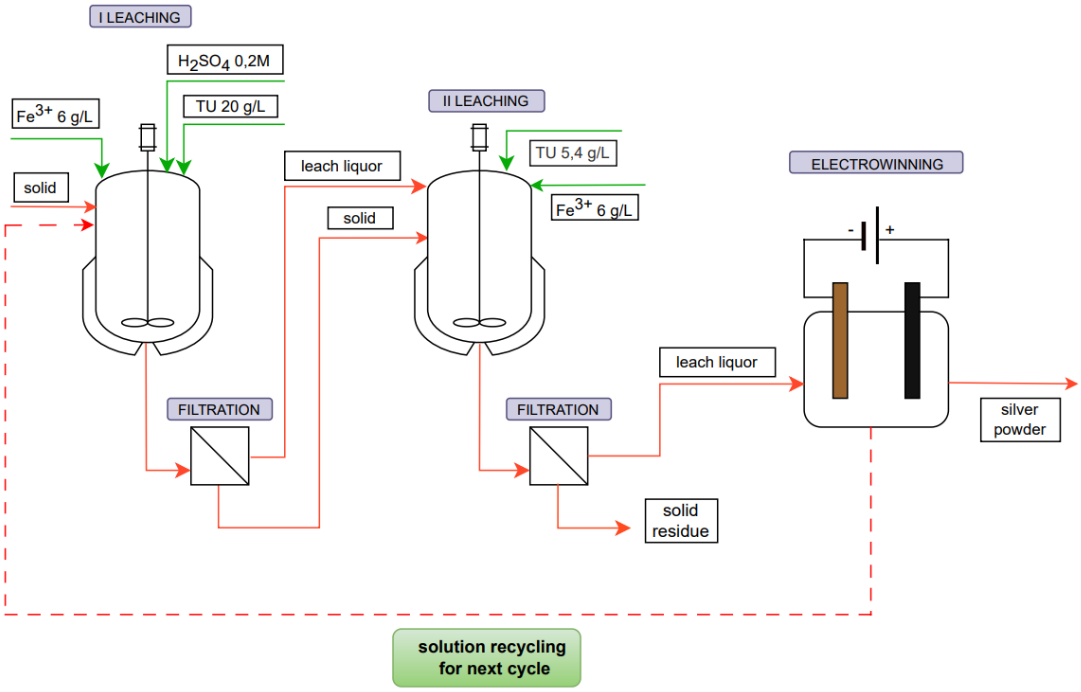
5.2 In-mold electronics UNIVAQ recycling process

UNIVAQ developed a hydrometallurgical process for the recycling of silver from IMSEs provided by TNO Holst Centre. More in detail, this process was tested on different types of samples like thermoformed, full silver area, elongated and on a mixture of different samples always with silver ink on the surface.

5.2.1 Process description

In Figure 24 is shown the flowsheet for the recycling process of in-mold electronics aimed at recovering silver. The process includes two stages of leaching for the dissolution of silver and electrowinning to recover the silver from the solution in which was dissolved. The second stage was performed on the same solid by using as a leaching solution the leach liquor obtained from the first leaching performing a make-up of chemicals based on the quantities consumed. In addition, the discharged silver solution can be recycled to carry out a second cycle on a new solid. This results in a reduction in water use and a decrease in the consumption of chemicals, also exploiting a partial regeneration of thiourea that occurs during the electrowinning operation. Solution recycling has been studied for three cycles, thus achieving a scenario that allows a significantly reduced wastewater production according to an MLD approach. It is not excluded that additional cycles can also be carried out before purging for wastewater treatment.

Figure 24 Silver recycling process scheme with the reuse of the solution for the next cycle



ICP-OES quantitative results and their standard deviations are reported in Table 28.

Table 28 Quantitative characterization of the input material (thermoformed-PC)

Thermoformed-PC sample: quantitative analysis (ICP-OES analysis)		
Element	**concentration wt %**	**standard deviation wt %**
Ag	0.931	0.091
Fe	0.865	0.012
Element	**concentration g/t**	**standard deviation g/t**
Pb	462	78
Ca	207	27
Mn	193	32
Cu	170	17
Ti	21.4	3
Si	not determined	-

The quantitative analysis shows a silver content with an average of 0.94 wt % and a standard deviation of 0.09 %. Among the other elements 0.87 wt % of iron is determined. Lower concentrations are detected for lead, calcium, manganese, and copper. Silicon was not quantitatively determined by ICP-OES.

The sample was also subjected to XRD analysis to identify the form of the previously identified elements and, eventually, other phases. XRD patterns, more in detail, showed the presence of metallic silver with a higher intensity of the peaks than the others, highlighting how this metal is the most present in the investigated materials. A manganese silicate hydrate phase and iron oxide were detected regarding the other elements. Moreover, was identified an amorphous phase, probably quartz.

5.2.2 Results

In this section, the results obtained by the treatment of IMSEs have been fully described, more in detail concerning with the following points:

a. Summary of the silver extraction yields
b. Distribution of the elements in the different stages of the process
c. Output characterization
d. Mass balance
e. Chemical consumptions
f. Energy consumptions

In Table 29, the results in terms of silver recoveries are reported for each step of the process.

Table 29 Summary of the obtained results in terms of silver recovery for each stage

Process step	Ag, %
First leaching	69.5
Second leaching	85.0
Electrowinning	87.5

Adopting the proposal process to thermoformed IMSE samples with a silver content of 0.93 wt. % and operating at a solid concentration of 10 % w/v, a silver dissolution of 85.0 % can be achieved after two steps of leaching, calculated as the average value for the three treatment cycles. It should be noted that the recovery of silver obtained by electrowinning is closely linked to the equipment used. Generally, industrial-scale electrowinning achieves recoveries of more than 95 %.

In addition, Table 30 summarizes the distribution of various elements for each process output. The most present elements in the initial sample are considered.

Table 30 Distribution of various elements in the process outputs

Process output	Ag, %	Fe, %	Cu, %	Mn, %	Ti, %	Si, %
Solid residue	15.0	9.9	30.2	25.7	44.6	100.0
EW - Silver powder	74.4	-	-	0.0	0.0	0.0
Wastewater	10.6	-	-	74.3	55.4	0.0

The table shows that silver dissolution is 85.0 %, then after electrowinning, 87.4 % is deposited on the cathode and recovered in the form of metal powder, the remaining is in the wastewater. With respect to iron and copper, their dissolution yields are 90.1 % and 69.8 %. It is impossible to establish their distribution among the silver powder and the wastewater because they are found in the recovered powder, but this may also be due to other sources. For example, iron was added in high amounts during the leaching operations, and the cathode material is of copper, and since the powder is recovered from the electrode by manually scraping the impurity could also depend on this. Manganese and titanium during the leaching operations are dissolved with a yield of 74.3 % and 55.4 %, respectively; during the electrowinning, they remain in the wastewater. Silicon, instead, was not dissolved and thus remains in the solid output.

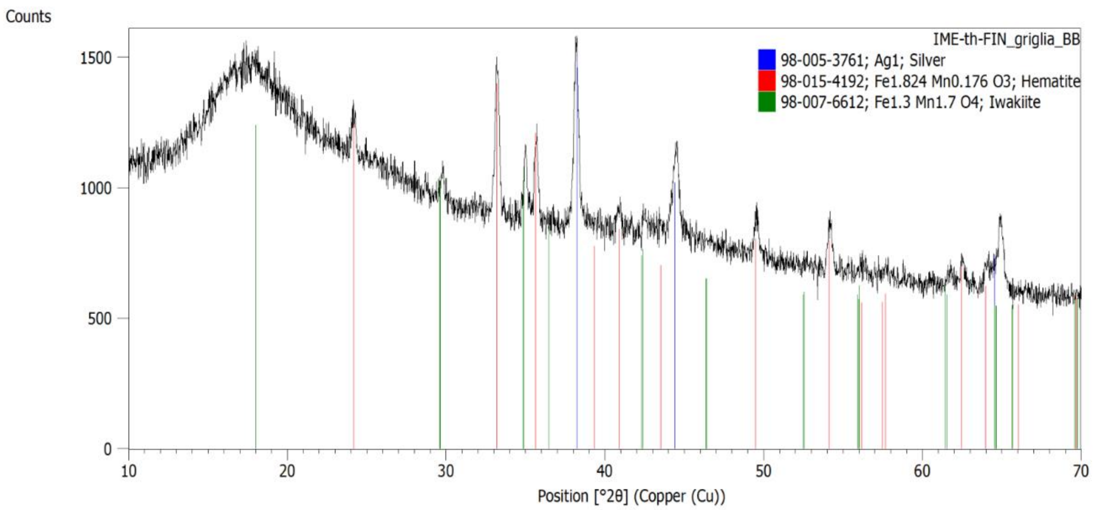
The following outputs were characterized to evaluate their management better:

I. solid residue
II. powders from the electrowinning
III. wastewater

The management of the solid residue, based on the high amount, is a crucial point of the developed process. The aim is to evaluate if the plastic substrate is affected by the leaching operations for silver recycling.

The Figure 25 shows how visually the silver ink's rows have become white after leaching operations. In addition, the striped part has been analysed via XRD to evaluate possible changes in the phases. The XRD pattern is shown in Figure 23.

Figure 25 XRD pattern of the solid process output



The spectrum shows the presence of a hump in the range of 10-25 degrees, indicating an amorphous phase in the material. This result could be due to decreased intensity of the silver peaks since it is recovered or even a possible effect of hydrometallurgical treatment. With the aim of carrying out further evaluations on the quality of the polycarbonate substrate, some samples were sent to TNO Holst Centre.

Regarding the recovered powder from electrowinning, the grade of silver is the main aspect to evaluate the economic sustainability of the process. In Table 31, the compositions of the powder after electrodeposition and after a 600 °C thermal treatment are reported.

Table 31 Composition of the powder recovered after electrowinning

Elements	powders wt %	After 600°C thermal treatment wt %
Silver	47.4	86.5
Copper	5.2	9.5
Iron	2.2	4.0
Non-metallic fractions (organic compounds, graphite)	45.2	0.0

First, it is necessary to consider that given the small quantities obtainable on the laboratory scale, powder composition could be affected by experimental errors. Therefore, for more assessments, it is necessary to consider the powder obtainable on a pilot scale.

Based on the lab-scale experimental results, a silver grade of 47.4 % ± 8.2 % was determined. The metallic impurities were copper and iron. Copper maybe because the powder is recovered by the copper cathode manually, and therefore, there may be contamination with some copper particles removed unintentionally from the cathode. Iron impurity, on the other hand, could be due to the contamination of the solution in contact with the powder on the cathode when the current supply ends before removing the cathode from the electrolysis cell. This could therefore be an impurity closely related to the equipment used on a lab scale. Non-metallic fraction is composed of organic compounds resulting from the degradation of thiourea that occurs during the electrowinning operation, such as free sulphur, or graphite from the anode.

The non-metallic fraction can be removed after a 600 °C thermal treatment to increase the purity of silver in the final product of the process, but also the other metallic fractions. A silver grade of 86.5 % could be theoretically obtained based on the composition of the powders; the experimental test allowed us to closely match this value, with a result of about 84 %. XRD analysis on the powder confirmed that silver is mainly in its metallic form, but from the spectrum are also visible less intense peaks of silver oxide, this would make the other metallic impurities would be lower. In any case, if such metallic impurities remain, given the melting point of the silver lower than that of copper and iron, thermal refining that guarantees high purity of silver could be achieved.

Wastewater composition after three cycles of IMSE treatment is reported in Table 32.

Table 32 Composition of process wastewater

Elements	Concentration, mg/L
Fe	19682
Cu	222.7
Ti	209.5
Mn	123.1
Ag	60.59

The main element present in wastewater is iron, with a concentration of almost 20 g/L, obviously derived from the reagents used during the leaching phase; in fact, it is added as ferric sulphate at each leaching step. The other elements that compose the wastewater have concentrations lower than 250 mg/L, they derive from elements present in the initial IMSE solid that were dissolved during leaching operations.

A pH value of around 1 is measured in the wastewater, with a sulfuric acid concentration of about 0.2 mol/L, sulphates, thiourea, and formamidine disulphides are detected.

Two different routes for wastewater treatment can be conducted: the first by neutralizing the acid solution with lime hydroxide up to a pH of about 9, thus ensuring the precipitation of metals; the second one through the advanced oxidation processes like the Fenton one. In the present case, it has been hypothesized the wastewater disposal to an external company, but for the construction of a plant, it would be considered also to include a wastewater treatment section to decrease operating costs.

Based on the experimental results, mass balances referred to the hydrometallurgical process of 1 ton of IMSE are reported in Table 33. The mass balances are calculated according to the process with three cycles of treatment with the recycling of solution and make-up of some chemicals.

Table 33 Mass balances for the treatment of 1 ton of thermoformed IMSE

Input, kg		Output, kg	
solid	1000.0	dry solid	991.2
water	3239.8	humidity	70.7
thiourea	127.8	powder from EW	14.6
ferric sulphate	441.2	wastewater	3863.2
sulfuric acid, 50 %	130.9	-	-
total	**4939.7**	total	**4939.7**

Concerning the outputs, the humidity is referred to the water that remains on the solid after separating the leach liquor solution from the solid and to the water associated with the powder recovered from the cathode after electrowinning; based on the experimental results are equal to 6.1 % and 40 %, respectively. By focusing on the dry solid quantities, you can see that almost all the solid input comes out as the output of the process; therefore, managing this solid is crucial for environmental sustainability analysis. The powder amount recovered from the cathode is not referred only to the silver but also the impurities. The silver amount in the powder is 6.9 kg, while the metallic fraction is 8.0 kg. Finally, wastewater output is 3863.2 kg with a density of 1.15 g/cm^3.

Table 34 shows the chemical costs for the treatment of 1 ton of IMSE.

Table 34 Chemical consumptions and costs for the treatment of 1 ton of IMSE

Chemical	Amount, kg	Cost per unit, €/kg	Cost, €
water	3239.8	0.0015	4.9
thiourea	127.8	1.00	127.8
ferric sulphate	441.2	0.30	132.4
sulfuric acid, 50 %	130.9	0.13	17.0
			282.1

The total cost of chemicals is 282.1 €.

Regarding energy consumption, a proposed process can be developed in a plant that requires the following equipment: two chemical reactors, one cartridge filter, one electrolysis cell, and three pumps, in addition to the pump for the recirculation of the solution during the electrowinning operation. It is also necessary to consider the heating of an oven for the removal of organic compounds from the powder obtained by the electrowinning operation. Then a scrubber for acid gas extraction and neutralization is necessary, so that it is also included the energy cost related to the gas suction from the fan and the recirculation pump for the soda bath used for neutralization. In Table 35, OPEX is reported for treating 1 ton of IMSE.

Table 35 OPEX for the treatment of 1 ton of IMSE

Item			Cost, €/ton of IMSE
Chemicals	details are reported in Table 19		282.1
Energy consumption	kWh	€/kWh	51.5
	143	0.36	
Wastewater	m^3	€/m^3	436.8
	3.36	130	
Solid residue	kg	€/kg	-
	991.2	to be evaluated	
			770.4

Further economic evaluations are described in D5.4

6. The UNIVAQ bio-hydrometallurgical plant for the recycling of car electronic components: a possible alternative to present practice?

This chapter provides an objective discussion of the strengths, potential and weaknesses of the proposed UNIVAQ process and also provides some recommendations to optimise this process compared to options available from existing processing routes and point of attention for the next pilot stage, which could be beneficial to refine the process. Of importance should always be the analysis of not only the products' quality but especially all the exergy dissipation into residues and/or the further processing and cleaning of these. In the end this affects the CAPEX and OPEX of technological solutions.

6.1 Recycling of In Mold Structural Electronics (IMSE)

Before starting to discuss the comparison of the processing of IMSE in existing and UNIVAQ process, it is important to be aware that the analyses of the IMSE according to the data as provided by TNO (see Chapter 2) and the quantitative analyses of the thermoformed PC sample, shows some significant differences (see Chapter 5). Important difference is the high presence of Fe in the sample according to the ICP-OES analyses, which cannot be declared based on the TNO data. Also, the presence of Mn, Ca and Pb cannot be derived from the TNO data. The presence of P (in the form of H_3PO_4) is not reported on in the ICP-OES analyses and has hence not been included in the assessment of the UNIVAQ plant. As can be seen from the analysis, the composition is provided as elements, while for the proper assessment of the recycling performance in existing processing routes, a compositional detail on compound level is required as provided in Chapter 2.

6.1.1 Recycling rates/yields and purity of recovered metals/materials are possible for different processing options

Table 36 shows the recycling rates of the different metals/materials as contained in the IMSE for both the existing and the bio-hydrometallurgical (lab-scale) plant. Table 36 makes clear that the recycling rates as obtained by the existing processing routes are much higher than achieved by the UNIVAQ process. The silver can be recovered for 98.4 % compared to 74.4% in the UNIVAQ (lab scale) plant. In addition, the polycarbonate can be recovered in the existing processing routes as energy and reductant. The PC is not recovered in the UNIVAQ process, where this ends up in the solid residue. The UNIVAQ process in applied to IMSE samples in which Ag is made accessible on the surface, by preceding dismantling/removal of the PC encapsulant. Moreover, the TiO_2 and P are fully recovered in the existing processing route, while these are not recovered in the UNIVAQ plant.

Table 36 Possible recycling rates for the recycling of IMSE as achieved by existing processing and the UNIVAQ process for a selection of metals

Elements/metals/compounds of the IMSE	Recycling in existing processing options	Recycling in UNIVAQ bio-hydrometallurgical plant (lab scale)
	Recovery [%]	Recovery [%]
Ag	98.42	74.4
Fe	Not present in IMSE according to TNO data – if present 99.00% recovered (as FeOx in slag)	0.00 (9.9% lost to solid residue, to EW metal powder (contaminant) and as contaminant in waste water)
Si	99.00 (as SiO_2 in slag)	0.00 (100% to solid residue)
Ca	99.00 - recovered in slag as CaO	Not reported on
Cu	99.06	Not reported on (30.2% to solid residue)
Plastics (PC)	Recovered as energy and reductant	To solid residue with metal contamination
P	100	Not included in assessment
Pb (in bullion)	96.46	Not reported on
TiO_2	100	Ends up in wastewater (dissolved with a yield of 55.4% during leaching)
Mn	Not present in IMSE based on TNO data	Ends up in wastewater (dissolved with a yield of 74.3% during leaching)

In addition to the recycling rates which can be achieved for the different materials present in the IMSE, is the purity of the recovered silver an important factor when evaluating and comparing processing options for the recycling of IMSEs. Table 37 shows the achieved purity of different metals as reported on for the existing versus UNIVAQ processing of IMSEs. It is clear that the existing processing route produces directly a LME grade (market green) quality of the silver of 99.999% purity, which realises true circularity and can directly be applied in the production of new IMSE. This is not the case for the UNIVAQ process. The purity of the silver powder can be upgraded by thermal treatment of the powder to 86.5% (within reported bandwidth) and needs further processing to be separated from the other metals/materials which are also contained in the produced powder.

Table 37 Purity of recovered metals for the recycling of IMSE as achieved by existing processing and the UNIVAQ process for a selection of metals

Recovered metals	Existing processing options (see flowsheet in Figure 15)	UNIVAQ bio-hydrometallurgical plant (lab scale)	
	Purity %	Purity % in powder*	Purity after 600°C thermal treatment*
Ag	99.999 (electrolytic)	47.4	86.5
Cu	99.999 (electrolytic)	5.2	9.5

*it is important to note that the silver and copper (and other metals and materials) are all present in the powder before and after thermal treatment and **not** in separate fractions as is the case for existing processing routes. Further processing on the powder obtained through the UNIVAQ process is hence required to separate the different metals from each other. This is not needed for the metals as recovered by the application of existing processing routes. A standard deviation of ± 8.2 % on the silver composition was reported on in D5.4 (see Table 31)

6.1.2 Reagents required input of primary materials and produced output flows and CE application

Based on the experimental results, mass balances referred to the hydrometallurgical process of 1 ton of IMSE are reported in Table 38. The mass balances are calculated according to the process with three cycles of treatment with the recycling of solution and make-up of some chemicals.

Table 38 Mass balances for the treatment of 1 ton of thermoformed IMSE

Input, kg		**Output, kg**	
Solid	1000.0	Dry solid	991.2
Water	3239.8	Humidity	70.7
Thiourea	127.8	Powder from EW	14.6
Ferric sulphate	441.2	Wastewater	3863.2
Sulfuric acid, 50 %	130.9	-	-
Total	**4939.7**	Total	**4939.7**

Table 39 shows the results of the existing recycling processing and the produced output streams. All output flows, i.e., the metal phase, flue dust phase and calcine are being processed in a subsequent part of the flowsheet as depicted in Figure 15 from which the metals (fully composing the flows listed in Table 39) are being recovered. This implies that all output flows of the processing of the IMSE can be recovered as materials with a very high quality which can be applied for the production of the same or similar products.

Table 39 Products from IMSE recycling processing in energy recovery processing (step 1, Fig. 15) (note that the processing has been simulated and is performed at a larger scale of 20 tph)

Mass balance/products from IMSE recycling in energy recovery processing per 1000 kg of IMSE feed	**Composition**	**Amount**	**Unit**
Total part feed tph		1000	kg
Metal phase (recycled to other units in flowsheet)	98.2 % Cu and 1.8% Ag	0.5	kg
Flue dust phase (recycled to other units in flowsheet)	Ag_2O	0.21	kg
Energy (if 100% efficient boiler)	52.9 % N_2; 3.0 % CO_2; 4.6% H_2O; 20.7% CO; 18.7% H_2 and rest	4798.26	kW
Energy recovery per tonne of feed		0.24	MWh/t
Calcine (to recovery process of TiO2 and P)	98.8% TiO_2, 1.2% P_2O_5	85.5	kg

Considering the results and mass balances of the existing (metallurgical) processing with the processing of the IMSE in the UNIVAQ plant, reveals that for the UNIVAQ plant, for the lab-scale stage, large emission flows of solid residue and wastewater are created. The solid residue created in the UNIVAQ process makes up the largest part of the output (over 99% of the IMSE input mass). As indicated under the description of the UNIVAQ process above, the management of the solid residue, based on the high amount, is a crucial point of the developed UNIVAQ process. The aim is to evaluate if the plastic substrate is affected by the leaching operations for silver recycling. Important is to consider the effect of the presence of different metals (including the silver) which report to this stream as shown in Table 30. These might contaminate the polycarbonate substrate remaining after the leaching process. This implies not only that metals could go lost in the process to this stream, but at the same time, that the quality of the solid residue and polycarbonate could be significantly affected, and could hence limit the reapplication of this fraction in terms of CE. In this stage, the polycarbonate and the included metals have to be considered a residue stream and loss of materials from the Circular Economy of the IMSE. In the existing metallurgical processing options, the polycarbonate fraction is recovered based on its energy content and as reductant. Further development of the UNIVAQ plant and investigation of processing options of the solid residue will be considered in the pilot and could reveal possible alternative processing routes (whether or not combined with removal of polycarbonate), which will be very interesting to evaluate to define the most optimal combination of processing steps for the IMSE.

Currentlyhigh amount of water has to be added to the process (over 3 times more than the IMSE input) as well as all chemicals, such as the Thiourea, Ferric sulphate and Sulfuric acid. Many metals dissolve in the wastewater, according to Table 32. Although two different options to process the wastewater are considered, these should be further investigated and tested to include and evaluate the results thereof. In the present case, it has been hypothesized that the wastewater is disposed of to an external company implying loss of the various metals contained as well as an economic and environmental burden related to it. For the construction of a plant, it would be considered also to include a wastewater treatment section to decrease operating costs. This would benefit to the viability of this processing route.

6.1.3 Evaluation of energy requirement and costs associated with the processing of IMSE

In Chapter 5, the energy consumption and costs for the UNIVAQ plant for the treatment of IMSE are presented. What is evident, is that the amount of water required and produced solid residue and wastewater, is increasing costs and energy requirement per ton material (which increase due to the large amount of water adding to the input). This might be reduced by additional processing of the residue and/or recirculation or treatment options for wastewater and can be included in a next step after the pilot.

As the input of the IMSE into the existing processing routes, will only compose a very small part of the input and will be processed together with other input fractions to create sufficient economy of scale, it makes no sense to allocate the energy consumption of the process range specifically to the IMSE as the process energy balance is determined by the total mix of inputs, which is normal plant operation. For this reason, the comparison of the energy requirement is not included in this discussion. However interesting in the evaluation of different processing options is the fact that the polycarbonate (and other organics contained in the IMSE) are recovered as energy and reductant, which positively contributes to the energy balance of the process as well as the reduction of the input of primary materials for reducing and are not resulting in the creation of a residue fraction, which is in the current status of development, the case for the UNIVAQ process.

6.1.4 Conclusions on different processing options for recycling IMSE

The evaluation of the different processing options available to recover IMSE based on different KPIs and parameters, such as recovery rates, purity of the produced metals, other output flows created in the process and their application level in terms of circular economy (can the material be applied in the same product and quality as originally applied) as well as consumption of primary resources and energy leads to the following conclusions for this stage of the project and development of the bio-hydrometallurgical plant:

- The recovery rates of the various metals when recycling the IMSE in existing processing options (see Figure 16) are higher than the recovery rates which can currently be achieved by the lab-scale UNIVAQ process, obviously this can possibly be improved
- The entire range of metals present in the IMSE, including the Ag, Cu (although present in a very low percentage from the $CuSO_4$ in the IMSE according to TNO data), also the metals present as fillers and additives (TiO_2, P, etc) can be recovered to high quality metals and final products. In the UNIVAQ process, these metals are mostly reporting to the solid residue and wastewater fraction in a complex mixture of materials which need to be ponded. Further treatment options will be considered in next steps and will change this.
- The metals are recovered in separate, high quality metal fractions, i.e., Ag, Cu, TiO_2 and P are produced as very pure separate metal products (see Table 36), when recycling the IMSE in existing recycling infrastructures. Ag, Cu and other metals are recovered at 99.999% purity via electrolysis, which allows direct use in the production of IMSE, compared to a purity of 86.5% for Ag and 9.5% for Cu for the bio-hydrometallurgical processing route (after thermal treatment of the EW powder at 600°C). In the UNIVAQ process, the Ag, Cu and other metals/materials (such as Fe, organics) are ending up in one product fraction, which therefore requires further processing to separate the different metals and increase quality.
- In the UNIVAQ process a large solid residue fraction is created in which the polycarbonate is ending up. To this fraction, also a range of metals are reporting and could contaminate the PC. Processing options for this solid residue fraction are point of attention in the next stage of the project and will be interesting to evaluate, also combined possible separation of PC and metals as investigated by TNO. The polycarbonate (and other organics) are recovered as energy and reductant in the existing processing routes, not creating a residue fraction. This could also be balanced with PC removal. Defining the most optimal flowsheet from these initiatives and options will be an interesting development in the project.
- A wastewater fraction, containing different metals such as Fe, Cu, Ti, Mn and Ag is a residue fraction of the UNIVAQ process to which metals are lost instead of being recovered (such as Ti). This is subject to further investigation in this processing route.
- The UNIVAQ process has a significant water footprint requiring a rigorous water balance and requirement of chemicals. Treatment options for the wastewater have to be investigated. Possible reuse of the wastewater and contained chemicals is an option which is indicated by UNIVAQ to reduce the amount of water and chemicals required in the process. In order to include this in the assessment of the process and comparison, this reduction has to be quantified.

At this stage of development of the UNIVAQ process it appears that the processing of the IMSE should happen in existing (metallurgical) processing routes considered within a Circular Economy point of view. Existing (metallurgical) processing, in the flowsheet set up as investigated in this Task (see Figure 16) allow for the recovery of a wide range of metals as reflected by the Metal Wheel at very high rates (>98% for Ag) and with very high purity, production of (intermediate) products such as slag, which can find application in open loop CE applications such as construction, cement, bricks and the recovery of PC content as energy and reductant. Further refinement and optimisation of the UNIVAQ process in the pilot plant will be interesting to include in a follow up evaluation to define different options and results from the range of processes available and achievable results for the recycling of these type of components.

6.2 Recycling of PCBs

The recycling of PCBs can be performed in the existing processing routes in the Cu recycling infrastructure as described in Chapter 4. No pre-treatment or disassembly is required to process the different PCB types in this processing infrastructure.

For the treatment of PCBs in the UNIVAQ process, two hydrometallurgical recycling routes were defined. A disassembly stage is necessary to obtain the input of the two recycling processes. The sample preparation is performed according to the following steps as described in Chapter 5 and D5.4:

a. Remove specific components that inhibit the recycling rates.
b. Remove specific components to be treated with Gold-REC 2 hydrometallurgical process.
c. Grind the remaining components with the board to be treated with Gold-REC 1 hydrometallurgical process.

The PCBs can be processed in existing processing routes without any further pre-treatment.

In the recycling comparison of PCBs is an open point the data of removed components. Now this is included in the assessment of the total PCB part as the data of the removed components was not detailed enough to assess these separately (separate from the economy of scale required to process these small devices).

This implies that the comparison cannot be performed one-on-one, due to the fact that the full PCB is processed in the existing infrastructure in comparison to the disassembled PCBs from which (i) specific components have been removed to allow for processing in the UNIVAQ plant and which (ii) are processed in two different routes, from which the results are not combined to predict the recycling performance for the full PCB, but are reported separately.

However, the comparison will be performed on the basis and results as presented.

6.2.1 Recycling rates/yields and purity of recovered metals/materials at a glance

Table 40 shows the recycling rates of the different metals/materials as contained in the PCBs for both the existing and the 2 different bio-hydrometallurgical (lab-scale) routes (GDR1 and GDR2). Table 40 makes clear that the recycling rates as obtained by the existing processing routes are significantly higher than can be achieved in this stage of development of the bio-hydro plant for both the GDR1 and the GDR2 process. The Sn is recovered to a higher percentage in the GDR1 route. This is not recovered as Sn metal but as SnO_2, and requires further processing as this still contains some CuO and traces of polyamine, Zn, Ni and Al. In the GDR2 process, a small range of metal fractions are produced from the process, i.e., Au concentrates, Ag concentrate, Cu concentrate and Sn concentrate. Table 40 reveals that the recovery rates for the GDR 2 process are at this moment still quite low. This is also discussed in Chapter 5 and D5.4 for this process, and needs further refinement as indicated. Point of attention is that the process retrieves only a small selection of metal concentrates (Au, Ag, Pd, Cu and Sn), implying that all other metals and materials in the input of this process route, will go lost. It is recommended to investigate if this can be optimised.

From the presented results of the UNIVAQ process, it must be concluded that less metals/materials as contained in PCBs and components can be recovered to usable end products, compared to the existing metallurgical processing of PCBs and included components, in which a wide suite of metals/materials is recovered. The plastics and organics are recovered in the existing processing route as energy and reductant, in the UNIVAQ process, these end up in the solid residue which is not further processed. Fibre glass is, e.g., recovered in the existing processing route in the slag fraction as SiO_2. This fraction can be applied as building or construction material. In the UNIVAQ GDR1 process, the fibre glass ends up in the solid residue. This implies that with the existing processing options, not only the recycling rate of the different (valuable) metals is higher, as well as the total recycling rate of the part is higher than what can be achieved with the UNIVAQ process (due to the fact that not only more metals are recovered in higher percentages, but also that the organics/plastics are recovered as energy and reductant). Separate from the higher recycling performance, the purity of the metals obtained from recycling processing, is higher for the existing processing routes.

Table 40 Results of recycling processing of different PCB types in the Cu processing route and in two UNIVAQ processes (GDR1 and GDR2)

	Existing processing - Cu recycling infrastructure		UNIVAQ process	
Elements/metals/compounds of different types of PCB	PCB type 1 % Recovery	PCB type 2 % Recovery	GDR1 % Recovery	GDR2 %Recovery
Ag (99.999% purity electrolytic)	98.8	95.8	49.0 (89.0 in leaching, 55.0 in EW)	75.01
Al, Ba, Ca, Fe, Mg, Si (as Al2O3, BaO, CaO, FeOx, SiO2 in slag)	99.0	99.0	Not reported on	0.00
Au	99.0	99.0	60.0 (70.0 in leaching, 85.0 in EW)	47.37
Cu (99.999% purity) electrolytic	98.0	99.0	92.2 (95.0 in leaching, 97.0 in EW)	59.33
In (to alloy for further processing)	3.12	0.00	Not reported on	Not reported on
Sn (to various intermediates for further processing to recover rest)	74.8	78.0	85.4 (96.0 in leaching, 89. in precipitate)	69.97
Zn (99.99+% electrolytic)	62.4	33.9	Not reported on	0.00
Pb	95.7	96.1	Not reported on	0.00
Pd	100.0	100.0	Not reported on	0.00 Not recovered due to low concentration of Pd in solutions
Pt	99.9	Not present in feed	Not reported on	0.00
Plastics / organics	recovered as energy and reductant	recovered as energy and reductant	Not recovered, reports to solid residue	Not recovered, reports to solid residue
Ni (99.99+% electrolytic)	96.6	96.1	Not reported on	0.00
Co (99.99+% electrolytic)	93.1	92.6	Not reported on	Not reported on

As discussed for the IMSE, not only the recycling rate of the different materials is important in the comparison of the processes, however the purity of the recovered metals is an important factor when evaluating and comparing processing options for the recycling and in terms of CE. Table 41 summarises for a selection of the metals as reported for the UNIVAQ plant, the purity obtained by both existing and UNIVAQ processing. In existing processing route a LME grade (market green) quality of the Ag, Cu and Au of 99.999% purity is produced, which realises true circularity and can directly be applied in the production of new products/parts. This is not (yet) the case in the UNIVAQ process. The Ag and Au are recovered in a doré fraction, composed of 71% Ag and 29% Au that requires further refining per a route as shown in the flowsheet in Chapter 3 for the processing of PCBs. The Cu produced from the UNIVAQ process still contains Fe, Ni, Zn, and Al, compared to a 99.999% LME (market green) purity as obtained by the existing processing route.

Table 41 Purity of recovered materials for the recycling of different PCB types in the Cu processing route and in two UNIVAQ processes (GDR1 and GDR2)

Recovered metals	Existing processing options	UNIVAQ bio-hydrometallurgical plant (lab scale)	
	Purity %	GDR1	GDR2
Ag	99.999	71 (in dore with 29% Au)	0
Au	99.999	29 (in dore with 71% Ag)	0.26
Cu	99.999	98.7	84.48
Sn	to various intermediates for further processing to recover Sn	97.4 as SnO_2	87.64
Zn	99.999		Not recovered
Ni	99.999		Not recovered
Co	99.999		Not recovered

6.2.2 Comparison of required input of primary materials and produced output flows and CE application

The GDR 1 process outputs have been characterized to evaluate their management in case of disposal or treatment and to define the selling price in the case of products of industrial interest. The outputs are below listed:

I. final dry solid residue
II. wastewater 1 (from the base metals leaching stages) 20 % v/v
III. wastewater 2 (from the precious metals leaching stage) 20 % v/v
IV. tin oxide
V. copper
VI. gold-silver

The final dry solid residue is the powder of PCBs resulting from the leaching operations in the UNIVAQ process. The remaining amount of this fraction is 783 kg for 1 ton of treatment; the residual metal fraction in the solid residue is about 4-5% wt. A complex mix of metals are composing this residue, such as Al, Cu, Ti, Fe, Sn, Ni, Zn, Zr, Ag, Au, Pd (quantities reported in Chapter 5). Materials such as the fibre glass and plastics from the PCBs are also reporting to this fraction. As no further treatment options are discussed for this residue, this implies that more than 78% of the input of the PCBs are lost through this fraction.

The GDR2 output flows have been reported on in Chapter 5. The created and characterized process outputs are listed below:

I. wastewater
II. Au concentrate from the 1st leaching stage
III. Au concentrate after the 2nd leaching stage
IV. Ag concentrate
V. Cu concentrate
VI. Sn concentrates

The wastewater solution characterization after the recovery stages has been reported in Chapter 5. However, it is mentioned that this solution can be reused for the treatment of a new cycle, requiring a specific make-up of chemicals. The composition of the wastewater shows that many metals are reporting to and hence currently being lost to this fraction such as Sn, Fe, Ni, Zn, Cr, Pb, Ti. Table 42 shows that relatively high percentages of the input of the GDR2 process, report to the solid residue fraction, hence being a direct loss of materials from the CE cycle and creating a residue with a complex build-up of materials, which has to be disposed of.

Table 42 Distribution of elements in input GDR2 process to solid residue

Distribution of elements in each output respect to solid residue (%)	
Elements	Solid residue
Ag	23.7
Au	52.6
Pd	39.2
Cu	40.7
Sn	7.9
Fe	59.3
Ni	44.2
Zn	43.1
Cr	58.5
Pb	80.4
Ti	92.5

Table 43 shows the mass balance (based on experimental lab-scale tests) was described considering all the inputs and outputs of the GDR1 hydrometallurgical process referring to the treatment of 1 ton of PCBs. This mass balance reveals the high input of chemicals and water to operate this process. Relative to 1 ton of PCB input, 16.6 ton of chemicals and water is required to run the process from which only 0.19 ton of metal products can be derived and from which 0.78 ton of solid residue is produced as residual fraction next to the large amount of wastewater (and materials dissolved in this) created in the process. This is a high demand of resources resulting in ahigh production of residues for the recovery of relatively small quantities of materials. Considering these figures, a serious and rigorous reflection on the reduction of water and chemical demand and/or recirculation of wastewater and processing of solid residue is recommended to take place to position this process as a feasible option in the range of processes available to realise CE by recycling PCB parts and components. It should be evaluated under which conditions this type of processing can contribute to recycling from a CE point of view. Currently a high amount of residues is created, exceedingthe amount of material which can be recovered through the process.

Table 43 Mass balances for the treatment of 1 ton of PCBs powders (GDR1 process)

Input	kg	Output	kg
Solid (more details in Table 33)	1000.0	Dry solid residue	783.0
H_2SO_4 (50 % w/v)	2719.4	Wastewater 1	6899.3
H_2O_2 (30 % w/v)	1477.9	Wastewater 2	8375.2
Thiourea	164.4	Tin oxide	11.24
Ferric sulphate	184.8	Copper	178.3
Polyamine (10 % w/v)	19.1	Gold-Silver	0.189
Water for 1st leaching stage	4280.0	Humidity	511.2
Water for 2nd leaching stage	7764.8	-	-
Total input	17610.4	**Total output**	16758.4
Experimental error 4.8%			

The mass balance for input and output streams of the GDR2 process are calculated according to the process as given in Chapter 5, with two leaching stages and make-up of some chemicals. The mass balance of in- and outputs is summarised in Table 44 and discussed in detail in Chapter 5. This table shows that similar to the GDR1 process, a high input of chemicals, water and for metal powders for cementation is required to run this process operable. For 1 ton of input (components), almost 10 ton of input of chemicals, water and metal powders is required. From the total input of 1 ton components, 0.4 ton of metal concentrates are produced. Only the Cu and Sn concentrates are of relatively high purities (85 and 88% respectively, but still not matching LME market green grades). In addition, it should be considered that this input however excludes the 0.53 ton primary metal input of Sn and Zn powder as added to the process. Table 44 is showing, is that 0.35 ton of elements are remaining in the final solution. When comparing Sn input as powder added to the process and output reported as Sn concentrate, it is remarkable that from the total of 230 kg added Sn powder (and about 25 kg Sn in the input as reported in Chapter 5), only 199 kg of Sn is recovered as (impure) Sn concentrate, implying that Sn is lost relative to the Sn powder added. It is recommended to include this as a point of attention in the pilot test.

From this, it has to be considered, similar as for the GDR1 process, under what conditions this process can contribute to the goal of Circular Economy as a high input of materials is needed to run the process, compared the amount and quality of recovered materials resulting from it and the amount of residues (solid and waste water) created from the process, which should be optimised and refined in the next steps in this project

Table 44 Mass balances for the treatment of 1 ton of mixed components in the UNIVAQ GDR2 process

Input, kg		Output, kg	
Solid	1000	1st Au concentrate	2.64
Water	2666	2nd Au concentrate	13.76
HCl (37%)	2400	Ag concentrate	15.45
H_2O_2 (30%)	1480	Cu concentrate	187.54

$C_2H_4O_2$ (99%)	700	1st Sn concentrate	89.84
Wash water after Au recovery	2000	2nd Sn concentrate	98.87
Sn powder	230	Final solid residue	526.88
Zn Powder	300	Final solution	9246
		Remaining elements in final solution	359.59
Total input	**10776**	**Total output**	**10540.57**
Experimental error (%)			2.2

Table 45 shows the results of the existing processing route (Cu route) for the recycling of PCBs. It shows that from the input, depending on the PCB type, around 50% can be recovered as valuable materials and that the plastics and organics are recovered as energy (and reductant) in this processing route, hence no residue of this input material is created. Metal, slag and flue dust as created through this process can be applied either as closed loop CE recycling products (metal phase) or as open loop CE – (intermediate) products for repurposing e.g. as building / construction material etc. rendering this type of processing effective in the realisation of CE and recovery of materials and contained energy, while minimising the amount of input needed and residues and emissions created.

Table 45 Products from 1 ton PCB input recycling processing in Cu recycling route

Products from PCB processing in Cu processing route (per ton of PCB)	PCB type 1 Amount	PCB type 2 Amount	Unit
Copper Alloy (Oxidative melting)	477	436.5	kg
Energy (if 30% efficient) Ox (recovered)	*0*	*118.42*	*kW*
Energy (if 30% efficient) Red (recovered)	*8.79*	*8.19*	*kW*
Energy recovered per tonne of feed (summarised Ox+Red)	8.79	126.61	kWh/t
Slag (building material)	34	29.5	kg
Total recovery of materials from input into valuable products	**52.3%**	**48.5%**	**%**

6.2.3 Evaluation of energy requirement and costs associated with different processing routes for the recycling of PCBs and components

In Chapter 5, energy requirements and cost associated to the input of chemicals, water and metal powders (for GDR2) for the two different processes are presented. the results show that there is in the current stage of development of this processing route a high need for water and additional input materials of respectively 10 to 16 tonnes for processing of 1 ton of input material. This will obviously be of influence of the energy demand and costs to operate this process. As presented, additional energy is required for pre-processing (grinding) of the PCBs for the GDR1 process. This step is not required when processing the PCBs in existing processing routes. In the existing processing route, the plastic and organics are contributing positively to the energy balance of the process, as energy is recovered from these materials, as well as reducing the amount of reductant required, as these materials also function as reductant in the process. This also prevents the creation of contaminated solid residue fractions and related costs. The same applies for the creation of wastewater (in which part of the metals are dissolved). The output flows of the existing processing routes (such as slag and flue dust) can be applied as open loop CE products, hence contributing to the benefits of the process and minimisation of residue creation.

6.2.4 Conclusions on recycling PCBs in different processing routes

The evaluation of different processing options for the recycling of PCBs and components based on different KPIs and parameters, such as recovery rates, purity of the produced metals, other output flows and residues created in the process and their application level in terms of circular economy (can the material be applied in the same product and quality as originally applied) as well as consumption of primary resources and energy leads to the following conclusions:

- The recovery rates of the various metals when recycling the PCB and PCB components in existing processing options are higher than the recovery rates which can be achieved by the lab-scale UNIVAQ process, obviously this can possibly be improved
- The range of metals present in the PCBs and components can be recovered to high quality metals in existing processing routes. In the UNIVAQ process, for the moment, only a selection of these metals is recovered. Various other metals, including also some valuable metals, are partially still reporting to the solid residue and wastewater fraction in a complex mixture of materials. Further treatment and reuse has to be investigated and considered in next stage of evaluation of processing options based on the pilot scale results.
- The metals are recovered in high purity in existing processing routes. Ag, Au, Cu and other metals are recovered at 99.999% purity, which allows the use in the same level of high-quality products. In the UNIVAQ process, lower qualities of metals are obtained, and/or metals are recovered in mixed fractions which require further processing and separation (such as the dore fraction in the GDR1 process which can be processed in existing flowsheet as depicted in Chapter 3). In the GDR2 process, the qualities of both Ag and Au are still very low, as these metals mainly report to the Cu fraction, together with other elements. Further processing and recovery of materials from these fractions is recommended.
- In the UNIVAQ process a large solid residue fraction is created for the GDR 1 and GDR 2 processes. For the GDR1 process, the plastics, glass fibre together with non-recovered metals are ending up in the solid residue. In the GDR2 process, metals are lost to this fraction. Output fractions such as slag and flue dust created in existing processing options can be applied as open loop CE products. The plastics (and other organics) are recovered as energy and reductant in the existing processing routes, avoiding the creating a residue fraction
- Due to the high consumption of the UNIVAQ GDR1 and GDR2 processes, a large wastewater fraction, containing different metals and materials, is created as residue fraction of the UNIVAQ process. The analyses of the wastewater fractions show that a range of different metals are reporting to and contaminate these fractions. The planned optimisation of recirculation of the wastewater as well as investigation of possible treatment options of this, will contribute to optimise the process. In the existing processing routes, no wastewater fraction is created. The UNIVAQ GDR1 and GDR2 processes demand in this stage of development ahigh input of water and chemicals to run the process. It is important to discuss how and to what extend these processes and their current high need of primary materials and water, combined with relatively small quantities of recovered metals and production of large amounts of wastewater and solid residue, containing a mix of materials and non-recovered metals, can be justified from a Circular Economy and sustainability point of view. It is also expected that the pilot tests will focus on these points and therefore will

result in a more balanced and optimised presentation of the process and flows, and might solve several points of attention as discussed here.

In summary, existing (metallurgical) processing options as shown, have proven recovery rates, purity of the produced metals, alloys, materials, slags and other output flows and residues created in the process. Their application can occur in terms of circular economy. On the other hand it can be conjectured that the UNIVAQ process, as tested on lab-scale based on different KPIs and parameters, may at this stage not provide products and materials that can all find an economic application in the circular economy when processing the IMSE as well as of the PCBs and components. It is interesting to keep in mind, that the pilot tests will provide more optimised results of the UNIVAQ route. The evaluation and points as discussed in this Task, could help to define the issues to be included and assessed in the pilot tests in WP6

7. Conclusions and further work

7.1 Material recycling and recovery of electronic parts in different existing and alternative processing routes

This report presents the assessment of the material recycling and recovery from IMSE and PCBs and components in the existing (metallurgical) recycling processes. By application of process simulation models as developed by MARAS, the most suitable and optimal processing options for the recycling of both IMSE and PCBs (including components) from existing processing options have been defined and recycling performance has been assessed. This can be combined with the results of the UNIVAQ process, in order to investigate the range of existing and newly developed processing options. Recycling flowsheets and recycling results, mass balances, obtained material purities/grade and application and use of recovered metals and materials, energy recoveries and application of other output fraction in terms of CE for the processing of different car electronics have been discussed in this report. Based on the description and results of different existing and developed alternative processing options (i.e. the UNIVAQ processes developed and applied on lab-scale in this stage of the work, recycling performance and applicability of different processing options and alternatives as developed in this project are being evaluated and discussed to determine the most preferred and optimal recycling options for the processing of car electronics components and to identify options and challanges for refinement in the development of the UNIVAQ process to provide an alternative to or combined with existing processing options

7.2 Data availability and digitalisation and linking of data sources and needs

Due to the fact that only for some parts, full compositional data was available (data on just elemental basis is not sufficient for reliable recycling analyses), the comparison of processes could only be performed for these parts. This is also the case for the disassembled components from the PCBs. If data on these components will become available in more compositional detail, the benefits of disassembly with respect to optimisation of recycling (i.e., by separating incompatible materials during recycling) could also be assessed. This would allow to define the most optimal balance between disassembly and processing of the PCBs. This also points out the link which would be very interesting to be made between MISS data files on PCB data (as applied to collect data for the model-based material recycling and recovery assessment) and the removed components through selective dismantling as performed by POLLINI (and POLIMI by use of the cobot). Being able to make this link in data sources, would allow on the one side for a more detailed recycling assessment linked to the disassembly activities on the electronics part as assess their effect when processed in existing recycling routes. On the other hand, this would be a big step ahead in the data digitalisation as favoured and required in this project and the TREASURE platform.

7.3 Approach/methodology for evaluation of processing options for the recycling of car electronic components

The recycling simulation models provide a rigorous and physics based back bone for truthful industry-based recycling assessment and provide the basis for the evaluation of different recycling options and their most optimal combination to recycle the different electronic car parts as considered in this project on a full CE focussed basis. All output flows are calculated and reported on and included in this evaluation, both from a mass as well as compositional point of view, energy recovery and consumption are taken into account. The starting point of the recycling (and simulations) should always be to create material and metal products, alloys, compounds etc. of a functional quality so that these can be used in the same product these have originated from. This is true circularity and provides the basis to assess and combine processes from a circularity point of view including quality of produced recycling and outflow flows.

7.4 Conclusions on recycling IMSEs and PCBs and components in existing and UNIVAQ recycling processing routes

Existing (metallurgical) processing options as shown, have proven recovery rates, purity of the produced metals, alloys, materials, slags and other output flows and residues created in the process. Their application can occur in terms of circular economy. On the other hand it can be conjectured that the UNIVAQ process, as tested on lab-scale based on different KPIs and parameters, may at this stage not provide products and materials that can all find an economic application in the circular economy when processing the IMSE as well as of the PCBs and components.

The UNIVAQ processes are in this stage of development characterised by a high need of input of other materials to run the process operable, such as water, chemicals and metal powders (for the GDR1 process). This will however be further investigated and reuse of the water in more cycles will be tested in the pilot plant tests. The bio-hydrometallurgical process results in this stage in losses of valuable and other materials to the residue streams as well as the creation of complex residues which have to be disposed of. Investigation of options for further processing of these streams will be included in the next steps and are recommended on based on this performed evaluation in this Task, with the objective to optimise this process in order to provide an feasible alternative to existing processing options or become part of a combined processing route (for some streams options might be limited due the mix of metals/materials reporting to these residues). Interesting and important to discuss is under which conditions these alternative processes and their high need of primary materials and water, combined with relatively small quantities of (non-LME grade) recovered metals and production of considerable amounts of wastewater and solid residue, which containing a mix of materials and non-recovered metals, can contribute to Circular Economy supporting a sustainable alternative to existing options. It is expected that the pilot tests will focus on refining the process as well as on the reduction of residues/wastewater and therefore will most likely lead to a more optimised balance of process and flows, and might solve several points of attention as discussed here. This will provide an interesting basis to continue the evaluation and assessment of various existing and alternative processing routes.

The energy consumption and costs of the processing routes are not fully included in the compared, due to the fact that the input of the IMSE, PCBs and components into the existing processing routes, will only compose a very small part of the input and will be processed together with other input fractions to create sufficient economy of scale. For this reason, it makes no sense to allocate the energy consumption of the process range specifically to the car electronic components as processed, as the process energy balance is determined by the total mix of inputs, which is normal plant operation. However important in the comparison is that the polycarbonate (and other organics contained in the car electronics both for IMSE and PCBs and components) are recovered as energy and reductant, which positively contributes to the energy balance of the process as well as the reduction of the input of primary materials for reducing. Investigation of processing options for the created solid residue i.e. for IMSE together with TNO, while at the same time including other pre-processing options for PC removal are very interesting developments to be included in the investigation of defining most optimal processing options. Expanding this evaluation by including energy consumption and costs per ton of processed material for existing processing options, could contribute to this. It is recommended to include this in WP6 evaluation However, it will not change the more optimal performance in terms of CE of existing processing options but could provide another KPI to evaluate the different processing routes.

7.5 Further work and future comparison based on pilot scale operation and results and refinement of the UNIVAQ process (WP6)

In WP6, the UNIVAQ process will be tested and refined on pilot scale. It is recommended, as also discussed in D5.4, that specific attention is paid to optimisation of both recovery and purity, and the treatment options for the residue fractions created (solid and wastewater) (as is to an extend indicated in the process description of the UNIVAQ process in Chapter 5). Due to the high demand of input of water, chemicals and other materials, focus should be given to process optimisation which would lead to significant reduction thereof.

Evaluation of existing processing options for the recycling of car electronic parts and the developed processing alternative of the UNIVAQ plant based on the pilot plant results, can be performed within WP6 on the basis as discussed and demonstrated in this Task 5.3.

When more detailed compositional data on the other car electronic parts becomes available, the material recycling and recovery assessment by the use of recycling simulation models can be performed for these parts as well (i.e., for ITO glass), expanding the work as discussed in this Task.

8. Abbreviations

CE	Circular Economy
EoL	End-of-Life
ELV	End-of-Life Vehicle
MISS	Material Information Systems
LCA	Life Cycle Assessment
EAF	Electric Arc Furnace
DRI	Direct Reduced Iron
RI	Recycling Index
MFA	Material Flow Analysis
TSL	Top Submerged Lance
TBRC	Top Blown Rotary Convertor
AI	Artificial Intelligence
CRMs	Critical Raw Material(s)
DfR	Design for Recycling

9. Definitions

Recycling for Circular Economy: Recycling of a product within the circular economy implies creating the same material quality after recycling so that it can be applied in the same product.

Compound: Material defined in its stoichiometric chemical composition, i.e. aluminium as Al, Al_2O_3, etc.

Design for Recycling: Designing a product or part with the objective to optimise its recyclability into high quality recycling products

Disassembly: Includes dismantling and implies taking selected car parts from the entire EoL car as well as understanding if the disassembled car parts can be further selectively disassembled into smaller parts that can be channelled into the correct processing for optimal recycling.

Energy recovery: Plastic compounds are used as an energy source as well as for feedstock recycling e.g. using C and H as reductants.

Feed composition: The simulation model requires a full description of the compounds as input to the model, which must add up to 100% in weight.

Flowsheet: A logical sequence of reactors that convert the input into among others high quality materials, compounds, alloys, metals, building materials, energy as well as residues and intermediates that can be ponded or used in further processes. These flowsheets are industrially realistic and economically viable for different processing routes.

Flows: All the flows of materials, solution, mixture, phases, gases, dust (among others) are quantified in terms of enthalpy and entropy (kWh/h) values in addition to the mass flows (both total mass flows and mass flows per compound) in kg/h or tonnes/h.

Car part: The selected cars part for disassembly from the EoL car.

Sub-parts: Specific parts on the car part that can possibly be removed and sent to more dedicated processing.

Plastic compounds: Full composition of all organic molecules of C, H, O, N, Br, Cl, metals atoms etc. in addition to fillers within the plastic. These are complex functional materials that are difficult to recycle to produce the same quality as for the original plastic compound.

Product data: This is the complete composition of the product, thus all compounds, functional materials, alloys, plastics etc. and their spatial position on the modules. This means aluminium in Al, an alloy of aluminium, Al_2O_3 as an oxidized/anodized layer on the aluminium, or a filler etc.

Reactor: A unit in which the input of material is converted to a product, energy, off gas, solution or similar.

Recycling rate: Within the circular economy paradigm this means producing the same quality material, alloy, metal, or compound that can be used within the different car parts. The recycling rate of each element thus implies the recycling into high quality products that can go back into the same part or product.

Simulation: Predicting the flows of all compounds and phases throughout the complete flowsheet on a thermochemical basis including the detail of the different reactor types in the system.

Metal Wheel: Depicting the paths of recycling of materials into different processing infrastructures.

10. References

Ballester, M., van Schaik, A. & Reuter, M.A. (2017). Fairphone's Report on Recyclability – Does modularity contribute to better recovery of materials? – https://www.fairphone.com/en/2017/02/27/recyclable- fairphone-2/ and https://www.fairphone.com/en/2017/08/08/examining-the-environmental-footprint-of-electronics-recycling/

Handbook of Recycling (Eds. E. Worrel, M.A. Reuter), Elsevier BV, Amsterdam, 595p, (ISBN 978-0-12-396459-5), pp 307-378.

HSC Chemistry Sim® 10, www.mogroup.com

Reuter, M.A., Schaik, A. van and Ballester, M. (2018). Limits of the Circular Economy: Fairphone Modular Design Pushing the Limits. World of Metallurgy – ERZMETALL 71 (2018) No. 2, p. 68-79.

Reuter, M.A., A. van Schaik, J. Gediga (2015): Simulation-based design for resource efficiency of metal production and recycling systems, Cases: Copper production and recycling, eWaste (LED Lamps), Nickel pig iron, International Journal of Life Cycle Assessment, 20(5), 671-693.

Reuter, M.A., Hudson, C., Van Schaik, A., Heiskanen, K., Meskers, C. and Hagelüken, C. Metal recycling: Opportunities, limits, infrastructure, A Report of the Working Group on the Global Metal Flows to the International Resource Panel (2013). http://www.resourcepanel.org/reports/metal-recycling

Schaik, A. van and Reuter, M.A. (2016) Recycling indices visualizing the performance of the circular economy, World of Metallurgy – ERZMETALL, 69(4), 201-216

Schaik, A. van and M.A. Reuter (2014a), Chapter 22: Material-Centric (Aluminium and Copper) and Product-Centric (Cars, WEEE, TV, Lamps, Batteries, Catalysts) Recycling and DfR Rules. In: Handbook of Recycling (Eds. E. Worrel, M.A. Reuter), Elsevier BV, Amsterdam, 595p, (ISBN 978-0-12-396459-5), pp 307-378.

Schaik, A. van and Reuter, M.A. (2014b). Product centric design for recycling: Predicting recycling rates – An example on LED lamp recycling. – Proceedings, Going Green – Care Innovation 2014, November 17-20, 2014, Vienna.

Schaik, A. van and Reuter, M.A. (2013). Product Centric Simulation Based Design for Recycling (DfR), 10 Fundamental Rules & General Guidelines for Design for Recycling &Resource Efficiency. Report in commission of NVMP, The Netherlands. https://www.nvmp.nl/uploads/pdf/nieuws/2013/2013%2010%2011%20Summary%20MARAS%20def3.pdf

Schaik A. van and Reuter M.A. (2010) Dynamic modelling of E-waste recycling system performance based on product design. Miner Eng 23: 192–210.

Schaik, A. van and Reuter, M.A. (2007). The use of fuzzy rule models to link automotive design to recycling rate calculation. Minerals Engineering 20(9) : 875-890. DOI:10.1016/j.mineng.2007.03.016

Schaik. A. van, Reuter, M.A., Boin, U.M.J., Dalmijn, W.L. (2002). Dynamic modelling and optimisation of the resource cycle of passenger vehicles. Minerals Engineering 15(11):1001. DOI:10.1016/S0892-6875(02)00080-8