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Material Flow Analysis of the Recycling Pathways for Advanced (Nano)Materials

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1 INTERVIEW QUESTIONS FOR RECYCLING INDUSTRY

The goal of this questionnaire is to create scenarios of a Circular Economy (CE) based on the recycling point of view and the EU (waste management, environmental…) policy goals to understand what the flows of advanced nanomaterial could be when a CE wants to be implemented in EU27(CH, UK, NO). This interview will be kept informal, and it will be performed during the Global Methane Forum 2024 on 18 March, 2024, in Geneva, Switzerland. The questions were asked in the form of an interview and not all participants answered all the question.

1.1 Questionnaire

1. Introduction

Name: Profession: Company/Institute: Relevant experience: Questions for a direct recycler

- Confirming the recycling pathway they know/use the most
- Which recycling sector do you work in/ and at what scale do you operate?
- What are your input materials? Amounts?
- What are your final products $+$ wastes? Amounts?
- Do you perform a pre selection process? (in/out)
- Do you perform a pretreatment process?
- What is the main method/process you use for recycling (hydro. Pyro, incineration, mechanical…)?
- Do you perform any additional steps?
- What are the conditions of your processing?
- Main polluters of your product? Amounts?
- Main polluters to the environment? Amounts?
- What do you use as packaging for your product? Amounts?
- What do you do with it afterward?
- Is there a possibility that some of the material gets left in the packaging? Amounts?
- How do you deal with the waste of your process? Amounts?
- Does the process suffer loss of material? Amounts? Does this loss represent a hazard to the workers?
- Do you have local air emissions? (they then sediment to the floor?
- If yes, then how do you clean your facilities and where is it discarded?
- Do others in the industry follow the same or similar procedure to yours?
- To your knowledge, what are some differences between your process and others?
- Ask about the products (is the loop closing)
- Which of the products bring you revenue?
- Who do you mostly sell to? (types of producers/ not specific companies) real question is do you upcycle or downcycle, or reuse the material or do you just destroy?
- Which materials do you have to pay for to get rid of?
- Do you have products that you haven't decided what to do with yet?
- What do others do about it?
- Is there anything you export outside of the EU/EEA zone?
- To your knowledge, do others in the same sector export recyclable or recycled materials?

1.1.1 Question regarding nanomaterials

- Do you expect/Are you getting ready to receive nanomaterials in the recycling stream/ any other expectation?
- If there was a nanomaterial in your feed where is it most likely to end up?
- When do you expect nanomaterials to enter/increase in your recycling stream?
- Amount of nanomaterial expected in your material?
- Would it change anything in the procedure if nanomaterials are present in the feed?
- Do you think the addition of nanomaterial will help or worsen the recycling industry?
- Which advanced(nano) materials do you expect will be present the most?
- To your knowledge is anybody else from the sector doing anything regarding advanced nanomaterials?

1.1.2 Legislation questions

- What changes in the Eu waste legislation recently have changed the process/chain the most?
- Do you have knowledge of any future regulations that will represent big changes to the current operation cycles?

1.1.3 Questions for a remediator/landfiller

- Which are the main polluting substances from solid wastes that you encounter?
- Which of them come from the production process?
- Which of them come from the use phase?
- Which of them come from the EoL phase/ recycling phase?
- Which procedure do you use to treat these emissions?
- Would they work on nanomaterials?
- Are you getting ready for the possibility of treating nanomaterial emissions/materials that contain them?
- Which nanomaterials are you expecting to find most in your sector? What amounts are you expecting?
- To your knowledge, what is being done in the field, either in legislation or in industry?

1.1.4 Question on somebody overlooking the system

- Which recycling sector do you work with most?
- What is your opinion on the European collection and recycling targets for your sector? Are they achievable in that time scope in your industry? How much of it is achievable?
- Will the legislature evolve soon to take additives such as nanomaterials/advanced materials into account? How much of a priority are they, and for what sectors?
- Do you think that to adapt to the new materials the chain will see new additions or do you think the already existing facilities would adapt their processes?

2 EWL waste classification

Following the EU's List of Waste Categories, where waste is organized in 20 categories by generating source (European Commission 2015), the following were chosen as relevant for this study:

- 1. Chapter 03 wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard [Subchapters 02;03]
- 2. Chapter 04 wastes from the leather, fur and textile industries [Subchapters 02]
- 3. Chapter 08 wastes from manufacture, formulation, supply and use (MSFU) of coatings (paints, varnishes and vitreous enamels) adhesives, sealants and printing inks)
- 4. Chapter 09- wastes from photographic industry
- 5. Chapter 10 wastes from thermal processes
- 6. Chapter 11 wastes from chemical surface treatment and coating of metals and other materials, non-ferrous hydrometallurgy
- 7. Chapter 12 wastes from shaping and physical and mechanical surface treatment of metals and plastics
- 8. Chapter 15 waste packaging, absorbents, wiping sloths, filter materials and protective clothing not otherwise specified
- 9. Chapter 16 wastes otherwise not specified in the list
- 10. Chapter 17 construction and demolition wastes (including excavated soil from contaminated sites)
- 11. Chapter 18 Wastes from human or animal health care and/or related research (except kitchen and restaurant wastes not arising from immediate health care)
- 12. Chapter 19 Wastes from waste management facilities, off-site waste water treatment plants and the preparation of water intended for human consumption and water for industrial use
- 13. Chapter 20 municipal wastes (household waste and similar commercial, industrial and institutional waste) including separately collected fractions [Subchapters 01;03]

These categories were chosen as they originate from solid post-consumer waste. Post consumer waste is defined as material generated by households or by commercial, industrial and institutional facilities in their role as end-users of the product which can no longer be used for its intended purpose Hahladakis, J., & Iacovidou, E., 2019. This includes returns of material from the distribution chain. In line with this logic, wastes such as mining waste and sewage sludge have been excluded from the study.

3 DPMFA report on the usage of an MCNM in cereal food packaging for food preservation

3.1 Introduction

The specific application refers to the multicomponent nanomaterial compromising of Bentonite (BNT) or Sepiolite (SEP) as a complex nanoclay and the addition of clove oil to form the multicomponent nanomaterial (MCNM). The system is encapsulated in a LDPE as a matrix which will be used as packaging material which extends shelf life for cereals, rice and legumes through a controlled release of the essential oil. The company expects the MCNM to take up anywhere from 1 to 2% of the total product, where clay would be the majority of the mass. Cereals encompass the following products: wheat, rye, corn, barley, oat, corn grits etc., while legumes include: dry peas, broad beans, soya, beans, lentils, chickpeas and others. The latter shows a good market growth due to the increase in the vegan, vegetarian and healthy diet recommendations. [1]

3.2 Methodology

The company estimated the year of market entry to be 2026. Although the company could not provide precise market size for the MCNM, the current study set the initial market size of MCNM to be 25 TPA in 2026 for a scenario analysis. Looking at the data provided by the EU's agricultural outlook (OECD-FAO 2021; European Commission 2023), cereal production is predicted to decrease 2.5% compared to 2021-2022 produce. Similarly, rice production is expected to decrease by 1.5% by 2030. Both of these are a consequence of new agricultural policies and climate patterns. In contrast, the legume market is forecasted with growth of 6%, with a promising demand both within and outside the EU. It can be therefore concluded that the market demand projected by the company won't vary further by 2030.

An important factor to consider during the MFA is the export value. All three types of products have a relatively small annual export rate outside the EU's borders. Since the system boundary for the study is EU27(+NO+CH+UK), the numbers stand at 9% for cereal, while for legumes and rice it ranges from 5 to 10%.[5] That gives an overall of 8% yearly export rate, which corresponds to the overall agricultural export number for 2023.[5]

The company had also provided the duration of the use phase of the product ranging for 3-12 months. As the computations are done yearly, a life span of one year is assumed.

During this time a lot of the essential oil will go to air emissions, as part of its controlled release. Since the company stated that there is a 30% loss during 4 months, a 90% emission is considered during the use phase.

The MCNM is incorporated into its matrix, Low-Density Polyethylene (LDPE) during the manufacturing process. Consequently, in subsequent phases such as Use and End of Life (EoL), the product is treated in accordance with its LDPE matrix. After the use phase, the product enters the EoL stage through mixed waste collection. Once collected, LDPE materials can be landfilled, recycled or incinerated. The current recycling rate of LDPE is around 31% [3], however, in order to take into account the temporal dynamics and EU's plastic recycling targets, the recycling rate increases over time until it reaches 55% in 2030 [4]. The number for landfilled waste would have to decrease from its current 25% to 10%, which also aligns with the EU targets [4]. The remaining outflows from mixed waste, aside from recycling and the landfilling, are directed to incineration. An error margin of 15% is considered for the computation for each of the estimated transfer coefficients.

Lastly, the segment of mass which is sent to recycling can also be either exported (around 50 %) for cheaper recycling outside the EU or undergo either mechanical or chemical recycling.

So far, mechanical recycling stands well above chemical recycling, where only 11% [6] of the mass would go. Mechanical recycling consists mainly of separation techniques (ex. floatation) and extrusion, resulting in new LDPE pellets, later on used for piping, sheeting, films and trash bags for composite lumber, building and agricultural applications. [2] This form of recycling will make sure to eliminate the rest of the essential oil while the nanoclay would stay in place. However, during chemical recycling, whilst the essential oil will once again be eliminated, the nanoclay would be segregated as an impurity. Chemical recycling involves processes such as hydrolysis, glycolysis, methanolysis, hydrocracking, gasification, pyrolysis, and combustion that break down polymers into their components [7], and the obtained products are usually high-value monomers, feedstocks for chemicals/materials/fuels production, lubricants, waxes, and gaseous and liquid hydrocarbons that can be used as fuel in various industries. [8] After chemical recycling, one of the byproducts that can be obtained is char. Char typically contains fillers, pigments, and ash, therefore the nanoclay will end up here. [9] There are possible uses for char after its production, such as an absorbent of lead present in aqueous media [10] or filler, however the estimation of the transfer coefficients for its usage are uncertain.

Nanoclay				
From	To	Transfer coefficient	Reference	
Inflow	Nanoclay inflow	0.98 to 0.99	Company	
Nanoclay inflow	Production & Manufacturing	1	Company	
Production & Manufacturing	In Use	0.92	Company	
Production & Manufacturing	Export	0.08	Eurostat. (2023, November 6). Extra-EU trade in agricultural goods.	
In Use	Mixed waste collection	1	Ioannis Antonopoulos, Giorgia Faraca, Davide Tonini, Recycling of post-consumer plastic packaging waste in the EU: Recovery rates, material flows, and barriers, Waste Management, Volume 126, 2021, Pages 694-705,	
Mixed waste collection	Recycling	0.55	European Parliament. (2018, December 12). Plastic waste and recycling in the EU: Facts and figures	
Mixed waste collection	WIP	0.35	Calculated	
Mixed waste collection	Landfill	0.1	European Parliament. (2018, December 12). Plastic waste and recycling in the EU: Facts and figures	
Recycling	Mechanical Recycling	0.39	European Recycling Industries' Confederation. (2021). Plastic recycling fact sheet.	
Recycling	Chemical Recycling	0.11	European Recycling Industries' Confederation. (2021). Plastic recycling fact sheet.	
Recycling	Export	0.5	European Recycling Industries' Confederation. (2021). Plastic recycling fact sheet.	

Table 1. Transfer coefficients in the DPMFA study on nanoclay at year 2030

Mechanical Recycling	LDPE Pellets	EDL Packaging Engineers. (2021, May 28). How is LDPE film recycling after it's used for secondary packaging?
Chemical Recycling	Char	Martín-Lara MA, Piñar A, Ligero A, Blázquez G, Calero M. Characterization and Use of Char Produced from Pyrolysis of Post-Consumer Mixed Plastic Waste. Water. 2021; 13(9):1188. https://doi.org/10.3390/w13091188

Table 2. Transfer coefficients in the DPMFA study on essential oil at year 2030

Table 3. Reorganized table (from HH) of table 1 and 2

3.3 Results and Discussion

Results are presented in Figure 1 in the final year of the study- 2030. In that timeline both components act very differently from each other and will therefore end up in different final sinks. From the final sinks only Export contains both components, with 88% belonging to

nanoclays and the left over 12% to essential oil. Afterwards, most of the essential oil is excreted during its use-phase, with a value of 90% yearly. Even if the product is landfilled or just stored for recycling earlier, the emissions would still go to the same sinks.

The technical sinks contain only nanoclays, where the highest amount will end up in the Landfill, while new LDPE pellets are a close second. Even though recycled LDPE products aren't used for high-end applications, some testing should be done on how the presence of nanoclay as an impurity could affect the system and how much nanoclay will end up in a single pellet.

On the other hand, the environmental sinks with larger mass values contain only essential oil, the larger of the two being natural and urban soils. The form that the oil is in wouldn't be harmful for the environment. Further, the amount of nanoclays is negligible in the environmental sinks that do contain it. For example, barely anything will enter the Waste water system in the timeframe explored.

Another sink which is outside the system scope is Elimination. This means that the product will change chemical composition. The only component eliminated is the essential oil due to the temperatures used in the processes of incineration and both types of recycling included in the study. Li et al. (2022) claims that clove oil decomposes at temperatures around 200°C. The process of mechanical recycling has the lowest temperatures out of the three, which specifically for LDPE will vary between 120 and 190°C. Therefore, the elimination for this segment is an assumption and possibly further testing should be done to prove or disprove this claim. Chemical recycling temperatures can reach up to 1500°C, which guarantee the decomposition of the oil.Waste incineration plants operate between 590°C and 650°C and at 980°C to 1200°C if the waste is considered hazardous. Both of these temperature ranges ensure the elimination of clove oil in that form.

Figure 1. PDMFA of the nanoclay-essential oil system in cereal packaging

3.4 Conclusion

The DPMFA report underscores the potential of multicomponent nanomaterial (MCNM) in cereal food packaging. Integrating Bentonite or Sepiolite nanoclay with clove oil in an LDPE matrix aligns with market trends favoring healthier and sustainable packaging solutions with an extended life.

The report notes that most of the essential oil will be released to Air, since the controlled release will continue no matter where the product is. That is not the case for nanoclay, which stays inert and in the same chemical form throughout all the processes the LDPE matrix could be subjected to. Therefore, this material will appear in later products and its significance should be explored further.

3.5 Literature

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4 DPMFA report on the usage of an MCNM as a mortar additive to aid NOx capture

4.1 Introduction

The proposed product is a mortar additive which could improve air quality by reacting and capturing NOx from air. The substance in question is a nanomaterial composed of $SiO₂$ and ZnO, where the latter is said to react with the nitrogen oxides and trap them in the mortar, whilst the SiO2's job is to keep these compounds inside by dissolution and connection to the mortar itself. For the sake of this MFA the SiO2-ZnO system will be considered as one material and the additional possible mass from the nitrogen oxides won't be considered. Moreover, the company could also distinguish the mass ratio of the two oxides in the system, however since both would behave similarly only the total inflow will be considered.

4.2 Methodology

The company had set the goal of special mortar production to 1.000.000 TPA, where the additive would have a mass of 20.000 TPA. It had also estimated the life span of their product to be anywhere between 15 and 25 years. They have also specifically stated that there is no loss during production and manufacturing and therefore the study considers that to be true.Additionally, according to market data, the mortar market is predicted to grow by 0.66% each year until 2030[4]. This value was found in multiple sources, even extending a couple of years, and therefore is also taken into account.

Accordingly, the first outflows of the system would be during the use phase, where 1% of material will be lost to natural and urban soils due to weathering. This information is obtained from Azimzada et al. (2020), who tested outside weathering effects on stains and paints that included TiO₂. In this case TiO₂ could be considered as a reference material since the SiO₂-ZnO MCNM is expected to behave in the same way.

When the material reaches the end of life stage, it is segmented by the collection of waste by the construction and demolition waste management and the rest is assumed to go to landfill. According to EU targets, the amount of collected and recycled construction and demolition waste has to reach 70% by 2030 [2][3]. This target should be reached by the end of the lifespan of the mortar.

Furthermore, the majority of the recycled products from this type of waste would mostly end up as road filler, while a small fraction would be used as construction materials again, either as filler or new concrete/mortar[5]. Since the second group will have the same final destination - a new building, they are considered as one category. Numbers here are uncertain, however there is an active push to reach a scenario where 50% of the collected waste is used as construction materials again.[6] That being the case, the MFA calculates a range of values for these 2 placements varying from 10 to 50% that could go to new building materials or 50 to 90% that would be used as road filler. [6]

The MFA for the chosen year of 2046, which is 20 years after the assumed market penetration in 2026. This year was chosen since the C&C waste management could have been receiving the material for 5 years already.

4.3 Results

The results from Figure 1 shows the mass flows and sinks at year 20 since the material's breach of the market in 2026. Since the lifespan of the material is 15 to 25 years, within 20 years there are enough flows towards the end-of-life stage to assess the final destination of the nanomaterial system. It can be observed that most of the mass is still in the use phase, and that once it reaches its end of life a good part will still end up in the Landfill sink. However, the values for Road filler almost rival the masses accumulated in landfills, with the sink of Construction materials reuse holding approximately half of the other two technical sinks. Therefore, it can be concluded that more of the material will go toward reuse or downcycling rather than landfilling. There is also promise that the construction and demolition waste management sector could succeed with greater collection than anticipated and proper guidance of the material to the recycling sector.

The only environmental sink of interest is the before mentioned Natural & Urban Soil sink, to which the material comes through weathering. As the material is mostly inert and hard to separate from the matrix, it won't pose a hazard for the environment more than the usual construction material.

Also worth mentioning is that the release to the environment isn't guaranteed to be that value because opinions vary. The study that was chosen as a reference, written by Azimzada, A et al. (2020) did their experiment outdoors and within the timeframe of a year, but on the other hand, a study that was done in a laboratory with artificial weathering cycles and used the same material (TiO₂) for their experiment showed a release rate of 0.007% [7] as opposed to the 1%

from before. The first was chosen because of the experiment being done under more realistic conditions.

Figure 2. PDMFA of the SiO2-ZnO system as a mortar additive

4.4 Conclusion

The multicomponent nanomaterial will be in use for a long period. By 2046, which is the middle of the inspected timeframe, most of the MCNM mass will remain in use, with significant portions destined for landfills and road fillers. The push towards using recycled materials in new construction will continue, but current trends suggest that a larger share of the material will be used as road filler.

As the SiO2-ZnO system is of similar nature to its encapsulant - in this case mortar, it will behave in accordance with the matrix. Therefore, there is little concern that it would add to environmental emissions or that it would bring about unwanted effects of recycled products.

4.5 Literature

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5 WEEE mini case studies

5.1 Tetra Pak

Out of the presented composite structures, the plastic segments often end up being used or disposed of for energy recovery. Tetra Pak Is a layered structure consisting of multiple polymers, aluminum, and paper, meaning it contains paper-plastic, plastic-plastic, and metalplastic relations, leaving out only glass-plastic composites as found in packaging, as shown in Figure X. Therefore, it is an interesting structure to look deeper into, and it would require the coverage of almost all types of composites from packaging.

Figure 1. Tetra Pak structure (Source: Jamnicki, Tatjana & Jamnicki Hanzer, Sonja. (2010))

Currently, only paper is successfully recycled via a process called hydro-pulping. The rest of the composite, which consists of plastic and aluminum, is disposed of or used for energy recovery. Promising processes have been studied to address this issue, and multiple solutions have been proposed.

One solution suggests the use of a molten metal pyrolysis reactor. Pyrolysis has been suggested multiple times so far, almost every time a plastic composite is mentioned. The aluminium is recovered as a metal but needs further cleaning from carbon residues. The polyethylene is recovered as waxes. The study also highlights that this procedure is calculated to be economically viable. The second solution found suggests that after hydro pulping is performed for paper, a selective dissolution-precipitation (SDP) process should follow and, in this way, recover both LDPE and aluminum. Lastly, an innovative mechanical method called solid-state shear milling (SM) pulverizes the material and disperses its components at ambient conditions. This increases the processibility of the thermoplastic polymer. The authors claim a promising industrial application for the process. More solvent-based techniques, such as delamination, hydrolysis, glycolysis, aminolysis, methanolysis, and catalytic depolymerization, are presented by P. Tamizhdurai et al. (2024) in their review of multi-layer packaging. They also suggest a biochemical method of separation.

5.2 Printed Circuit Boards (PCB)

PCBs are the most economically viable segment to recycle from most WEEEs since it contains a lot of precious metals like gold. It's also a complex composite whose matrix is comprised of either:

(1) an epoxy resin-based plastic reinforced with glass fibres coated with a copper layer (FR-4 type PCB) or

(2) a single layer of fiberglass or cellulose paper and phenolic resins coated with a copper layer (FR-2 type PCB).

The resin board is overlaid with microelectronic components such as semiconductor chips and capacitors plus solder, which is a Pb-Sn alloy (Zeng, Li, Xie, & Liu, 2013; Zhu et al., 2012c). Since its one of the most important parts of electronic equipment there is a lot of research on how to further advance this segment, making it susceptible to the implementation of new AdMa. Nevertheless, other than the metals a lot of the other fractions are usually discarded in landfills or to incineration (Hadi et al., 2015).

The recycling of PCBs follows the general outlook for the rest of the WEEE. It first goes through mechanical recycling which is sorting and size reduction such as shredding and pulverization, the latter of which is singled out as essential for the pseudo-homogeneity of materials, which aids in subsequent recycling stages. Since it is a composite, a lot of the treatment's possibilities are similar to the ones mentioned above in the wind turbine section, as well as hydrometallurgical methods, using a variety of progressive (like ionic liquids) or classical solvents (acids and bases). It is advised to target base metals first and precious metals later on to be able to leach them without them hindering each other. On the other hand, this could in fact result with less precious metals recovered since they aren't the first target, which isn't economically optimal. Some innovative technologies also suggest the generation of advanced (nano) materials from the materials obtained such as high-value copper oxide nanoparticles or gold nanoclusters to improve profit.

An interesting segment for PCBs is the option to perform early-gold leaching via hydrometallurgical methods, explained by Latacz D. et al. (2020). This means that mechanical treatment of the PCBs would be minimal or none and the PCBs are just submerged in the appropriate solvent, for which multiple options are present. The solvent used for gold ore is cyanide and great effort is being put into finding a solvent which is more environmentally friendly and one of the best possibilities found were thiosulfate, thiourea and sodium metal complexes (Birich A. (2020)). Results show that better leaching is performed if copper was removed before hand since it also reacts with the solvents. This process is used when the PCB wastes obtained come from manual sorting rather than a shredder fraction. This is an extremely time-consuming process, counting from a day to several weeks to finish.

5.3 Cables and power supply

Cables are usually collected separately and treated in a different facility or line than the rest of the WEEE. That is because they contain high purity and a big amount of copper and it's easier to separate them from the beginning. The energy required to recycle copper is significantly lower than the energy needed to extract and refine new copper from ore, making recycling a more sustainable option. This is why copper was also chosen to be studies in depth for its

procedure. Other than copper, materials that are used in cables can also be aluminum on the conductive core, insulating layers made of polyvinyl chloride (PVC), polyethylene (PE), or crosslinked polyethylene (XLPE). Other thermoplastics like polycarbonate (PC) and polypropylene (PP) may also be present in specific parts, such as connectors or sheathing. In addition to these primary materials, cables may contain auxiliary components like silicone rubber for extra insulation and fillers such as calcium carbonate (CaCO3) to add strength. Some cables include metal shields or reinforcements like polyester foil and cotton cords.

For larger cables with uniform thickness this top insulation layer can be removed manually by a special cutting machine, also called the cable stripping machine, leaving the core bare. The cables that aren't susceptible to this machine have to pass through the separation & sorting treatment as explained above. Like for other waste types, here there is also the option of other pretreatment such as chemical or thermal methods. Chemical methods include PVC swelling which involves the use of organic solvents to swell the PVC, making it easier to separate from the copper core. The PVC is then processed into smaller particles through rod milling . Pyrolysis is also used to break down the polymers, however there are strict regulations on this because of the presence of chloride in PVC. Sometimes the cables have a coating that can't be removed by the current process and the EU legislatives don't allow for the treatment of these materials in a way that is economic for the company, so more often than not the cables are shipped to countries like Morocco where they burn these protective layers on the cables. Otherwise, the plastics can be used as fuel in the smelters.

The recycling of copper is a very good example for the combination of pyrometallurgical and hydrometallurgical methods. Granules aren't suitable for the process because of their small size so they have to bracketed. The process begins by imputing the scrap material into a continuous smelting and refining furnace at high temperatures. Here, oxygen is introduced to the process so that the unwanted materials form oxides, as that makes that lighter, they float on top as slags. The melted liquid is then deslaged. The slags are also being dealt with by selling them to another smelter-recycler. Iron mostly coming from automative scrap is removed in slag from blast furnace but high levels of iron can greatly influence the recovery of copper. Then comes the poling furnace and the final part is the casting wheels. The pooling furnace uses natural gas to remove the oxygen that bonded with copper. The last part of this step is to remove impurities such as arsenic in the third furnace (anode furnace).

Zinc is one of the main contaminants removed in the process. Zinc removed in the blast furnace as a fume or in a separate reduction furnace which separates zinc oxide as fumes and gives a lean and tin alloy, which are also major contaminants. Metals other than copper stay is what is called anode slime. This consistency is put through a filter press and then sold to other plants that are interested in extracting the nickel, gold, silver and PGMs. These metals also require a mix of pyro- and hydrometallurgy such as leaching and fire refining. Slags from the reduction furnace are sent as aggregates for concrete while the lead can be sent to a refinery. Umicore, a major e-waste recycler in Europe, does this process. It also takes the residues from lead, copper and nickel refineries and separates precious and special metals in their proper refineries. Additionally, the separation of copper and nickel can be done via evaporation and crystallization to obtain copper and electrowinning, evaporation and again crystallization to get nickel. It is worthy to note that even with this applied technology the nickel product isn't of the highest quality. Utilizing this technology, the copper sulphate and sulfuric acid can also be recovered.

When a very high purity of copper is required, there is a system Aurubis employs called Umicast system where they put the copper in a furnace of 3 parts, one of which is made with graphite. Graphite is added in a form of flakes on top, which seals the entrance to the furnace preventing oxygen from coming in but also reacts with the copper itself. At the bottom of the furnace there is a die to suck out the copper as also serves as a cooling tool. This process can't be continuous because it can make surface finish problems. Even as a batch process, the utilization of the die makes the copper wire have a type of bamboo surface.

 \Box Refuse-Derived Fuel (RDF) is defined as "a fuel produced from various types of waste, including non-recyclable plastics, paper, textiles, and other combustible materials. RDF is processed to remove non-combustibles and then converted into a fuel that can be used in industrial processes or energy generation" (Cimpan et al., 2015).

 $\sqrt{2}$ The backlight of choice for LCD manufacturers prior to 2009 were mercury-containing cold cathode fluorescent lightbulbs (CCFLs). In about 2009, the shift towards light emitting diodes (LEDs) began, and by 2013 LEDs largely displaced CCFLs as backlights.

5.4 LCD

Researched by Boundy, Thomas & Taylor, Patrick. (2018), the recycling of LCDs is crucial as they constitute up to 90% of the indium-bearing components in WEEE. As mentioned above, the EU is striving to recover most of the CRMs, and indium is part of that list. Therefore, most procedures revolve around obtaining indium while other integral materials like glass and plastics, which make up significant portions of LCD panels, receive less attention. The polarizer foils in LCDs, primarily composed of cellulose acetate, are valuable and can be sold. However, the glass substrate, which constitutes the highest mass share in LCDs, poses challenges for end-of-life treatment due to potential contaminants added during production and is usually discarded. A methodology was suggested by Uaberschaar M. et al. (2017), to first remove the polarizer foils from the glass substrate. Then, apply one of the methods explained below to separate the ITO from the glass substrate.

The recovery itself, although largely researched, hasn't begun in full scale. The EU mandates the separate collection and disposal of LCD screens, creating favorable conditions for indium recovery. There is also a government-sponsored pilot plant which has begun operating, but no commercial recycling ventures have yet emerged. The researched processes can be physical/mechanical or chemical. Physical/mechanical methods are generally low-cost and environmentally friendly, while chemical processes, though more expensive, can achieve higher concentrations of valuable materials. Chemical methods are commonly used in indium recovery from LCDs, with nitric acid, sulfuric acid, and hydrochloric acid being effective leachates, and even counter-current leaching is suggested. However, these techniques are often economically unfeasible for low-grade indium feedstocks due to high acid costs and low indium concentrations.

Additionally, high-temperature processes like carbothermal reduction and vaporization under vacuum have been explored, leveraging the volatility of certain indium species, reaching recoveries exceeding 80% at 400°C. Nonetheless, the economic feasibility of these methods is also not established.

Mechanical and physical processes for indium beneficiation from LCDs are less studied. Some researchers suggest that abrasive techniques could be effective due to the surface confinement of indium on the glass. Electrical disintegration and autogenous attrition scrubbing have been investigated, with the latter producing an indium concentrate of approximately 2000 mg/kg. Another method involves mechanical stripping, where whole LCD screens are ground with a roller brush to remove indium as fine particulate, which is then separated and further refined.

Recent research, done by Zhang K. et al. (2017), has demonstrated that crushing the ITO glass may not be necessary. A non-crushing leaching method using ultrasonic waves has shown that indium can be efficiently leached with low concentrations of hydrochloric acid without additional heating. Approximately 96.8% of indium can be recovered within an hour. This process is more efficient and simplifies the indium leaching process, yet its economic achievability is still unclear.

5.5 LED

Similarly to LCDs for indium, the recycling of LEDs is essential for recovering valuable metals such as gallium (Ga), indium (In), and rare earth elements (REEs), but especially gallium. Various recycling technologies are employed to achieve this, and they can be broadly categorized into physical, pyrometallurgical, and hydrometallurgical processes. It can be argued that recovering indium from LCDs is actually a lot easier than recovering in from LEDs, due to their increasingly complex structure and presence of a plethora of elements, many of which are considered hazardous.

In addition, there are multiple types of LED versions on the market including Quantum-dot LED, MicroLED and Organic LED, all varying slightly in structure and composition. For example, the OLED has its organic layer which should be sent to chemical recycling. Further, MicroLEDs are placed directly onto a substrate so it will need delicate abrasive methods like chemical etching to remove them from the substrate.

As pretreatment, other than familiar dismantling, size reduction and sorting here some methods are specifically preferred or advanced technologies can be included. Electrostatic separation, for example, is particularly effective as it isolates non-conductive LED chips from metallic components, which not only reduces the acid consumption in subsequent chemical treatments but also increases the concentration of valuable metals like Ga. Further, an advanced technology in the form of supercritical and solvothermal treatments utilize supercritical fluids like ethanol to dissolve and degrade organic materials, simplifying the separation of critical metals from other components. Like for other types of waste pyrolysis and incineration also work as a pretreatment to recover metals. On top of that, for LEDs specifically other pyrometallurgical methods are an option. Vacuum metallurgy is one, where the materials are heated in a vacuum, allowing for the selective condensation of metals like Ga, In, and others at different temperatures. Another process is chlorination, where GaN powder is treated with chlorinating agents like NH4Cl at 500°C to form soluble GaCl3, which can then be separated and recovered. This method also enables the spatial separation of Ga and In due to differences in their chloride vapor pressures.

Regarding hydrometallurgical techniques, other than subsequent leaching of different metals using strong acids or using bacteria, here a **n**ano/ultra-filtration is another technique employed to recover Ga from leach solutions, with nanofiltration proving more effective at lower pH

levels. Both of these treatments separate gallium based on particle size and are very dependent on the pH of the solution because it influences how much of the gallium compounds precipitate.

A study done by Mir S. et al. (2022) has shared market value calculations, which demand highlight the importance of recycling gallium, indium and other valuable elements such as Au, Ag, and REEs also for an overall economic benefit. The same study also underlines that reutilization of LEDs isn't considered; however, they predict that that will change in the near future.

5.6 Photovoltaic panels

Generally, EU as a whole has been pushing for the recycling of PV panels on its manufacturers. Currently 13 000 tons of PVs are discarder every year but predictions say that it will reach 100 000 tons by 2025 and continue to 1.7 million tons by 2030, 90% of which are silicon-based. A lot of the second-had modules that are deemed intact go to a second-hand market outside of the EU. Otherwise, there are multiple recyclers who can take care of the panels however the efficiency and cost effectiveness of the process is a current issue. Germany specifically has been assigning large sums of investments for developing processes to recycle PVs and no uniform process has been established. Normally, each of the components are sent to its own recycling channel once separated, which in a lot of cases means a different facility. Out of these aluminum and silver are the most valuable whilst glass seems to be the most problematic because of high costs for collection and reprocessing. In spite of that, all the recovered materials can be used in the manufacturing of new products other than the foils. The foils i.e. plastics are usually incinerated. In most cases, only aluminum, glass and copper have properly taken part in the recycling economy whilst the metals from the silicon cell are going to waste, however the main efforts are being done in recovering the silicon wafer.

Delamination is mainly done to separate glass from the silicon cell. This can be done both chemically, thermally and even by some mechanical methods. Chemical methods tend to perform well but the main challenge is to determine the correct composition, concentration and temperature. Usually etching is performed, using potent acids and bases. In thermal recycling, the PV module is heated in a high-temperature furnace, causing the plastic materials to evaporate, which separates the PV cells from the glass. Another thermal technique uses the laser surface cleaning method, already installed by a company in Germany. A study done by Dávid Strachala et al. did experimental texting to compare chemical etching with the laser method using a neodymium laser. They report that the laser method is much slower and more expensive than chemical etching.

An additional technique suggested is supercritical carbon dioxide. This process would seamlessly dissolve the plastic junction in the cell effectively separating the different materials.

5.7 Wind turbines

When discussing wind turbine recycling, Rathore N. and Panwar N. L. (2023) explain that the focus mostly falls on the turbine blades. These are also a huge contender matrix to add AdMa to. Wind turbine blades are primarily made of composite materials such as glass fiberreinforced polymers (GFRP) and carbon fiber-reinforced polymers (CFRP), with the latter wasting the most energy during recycling (Hardik k. et al. (2022). Other materials include epoxy resins, steel, aluminum, and various polymers. Presently, they aren't recycled but only stored underground, although Khalid M.Y.et al. (2023) states that 80-85% of the materials can be recycled, with the potential to reach 100%. There is ample research being done in the fields of technological and policy making sense, to figure out how to deal with these blades. The choice of a recycling method depends on the desired quality of the recovered material, the economic considerations, and the environmental impact. An argument by Chen J. et al. (2019) calls attention to the need for eco-design in these materials specifically, which would give a better remanufacturing option for the turbine blades

The composite fibers present one of the main target's materials for the recycling research, since the magnets, steel and other segments already have established recycling streams. Treatment suggests mechanical methods of size reduction and separation like the one used for the rest of the WEEEs, but this method significantly reduces the mechanical properties of the fibers, limiting their reuse in high-strength applications. The recycled materials are often used in lower-grade applications such as construction fillers. Thermal methods like pyrolysis, fluidized bed processes and microwave pyrolysis are also an option. There, the composite would be heated up at high temperatures, enough to decompose the resin matrix and recover the fibers, which can then be used to make new composites. Pyrolysis is mostly discussed in the Battery segment, but its important for this segment because it can recover fibers with properties comparable to virgin materials, but the process can be energy-intensive and may produce toxic byproducts. Microwave pyrolysis is a better option because the heat comes as microwaves, making the process faster and the recovery cleaner. The third option – fluidized bed reactor uses hot air around 450-550°C to decompose the resin. Although it can produce clean fibers, the process often results in a significant loss of mechanical properties, particularly for glass fibers. A different route is chemical recycling. The use of supercritical fluids is an option worth entertaining. This method can effectively recover both the fibers and the matrix materials. Two processes that can incorporate it are solvolysis and supercritical fluid recycling. Solvolysis uses alcohols, ketons or glycols to break down the resin matrix, and the addition of high temperature and pressure make the process results better. This process can also be conducted under subcritical conditions or low mild temperatures, with the latter requiring stronger acids. A negative argument for the solvolysis process is that the choice of solvent, temperature and pressure differs depending on how the composite material is constructed. For example, higher temperatures and pressures must be used for components made of epoxy resin rather than if they are made of polyester resin fabric (Paulsen E.B. & Enevoldsen P. (2021)). A different fluid that can be used for supercritical fluid recycling is water, which results in the fibers retaining most of their mechanical properties. Generally, chemical methods it is more expensive and technically complex compared to mechanical and thermal methods. Additionally, hybrid processes are being explored such as microwave-assisted chemical recycling is emerging as a promising approach to enhance efficiency and reduce processing time.

Paulsen E.B. & Enevoldsen P. (2021) concluded that recycling through co-processing to produce cement as the most suitable method for handling WTBs based on the current TRL of the various recycling methods. The co-processing involves a hybrid process between mechanical methods and pyrolysis, which is compatible with future and current composites in the turbine blades. The methods and routes discussed here apply for most composite materials of this nature and the process would be used for matearials also coming from packaging waste, ELV or other WEEEs.

5.8 Toners

Toner cartridges, which can be remanufactured 2–3 times, significantly reduce the volume of waste that is left untreated. The primary components of toners are polymer resin and pigments, with additional substances like charge control agents, flow agents, and waxes. Waste Toner Powder (WTP), leftover from the ink, mainly consists of toxic organic compounds such as polystyrene, styrene acrylate copolymers, polyesters, epoxy resins, and urethanes (Fernández B. et al. (2022)). Additionally, WTP contains AdMa nanoparticles of iron oxides, SiO2, and TiO2. Due to its composition, WTP is classified as hazardous waste, posing risks of ignition and explosion. To recover it the size reduction should be done in an eclosed space with appropriate dust collectors as explained by Ruan J., Li J. and Xu Z. (2011).

Research has explored various methods to repurpose WTP. Some ideas include its uses as a colorant in synthetic rubber (retaining its color even after the vulcanization process at 180°C), use in bituminous products, cement, and concrete as strengthening filler and colorants, use in energy storage as an anode or conversion into nanocomposites.

Lastly, WTP has shown potential as an adsorbent for removing heavy metals from wastewater, similar to other nanomaterials like carbon-based nanomaterials, zero-valence metals, metal oxide-based nanomaterials, and nanocomposites.

Literature

1. Hadi, P., Ning, C., Ouyang, W., Xu, M., Lin, C.S.K., & McKay, G. (2015). Toward environmentally-benign utilization of non-metallic fraction of waste printed circuit boards as modifier and precursor. Waste Management, 35, 236-246. <https://doi.org/10.1016/j.wasman.2014.09.020>.

2.

6 Case studies with graphene

6.1 Graphene in tires

Table 5. Dynamic transfer coefficients for tires

6.2 Graphene in batteries

Table 6. Dynamic transfer coefficients for batteries

7 Techno-Economic Analysis (TEA) for AMANDA

7.1 Step 1: Problem and Objectives Definition

Problem: Evaluate the financial viability of AMANDA.

Objectives:

- Calculate Technical Viability
- Cost and Revenue Calculations
- Market Demand Potential
- Determine Financial Allure
- Risk Identification

7.2 Step 2: Data Collection

- 1. Cost Analysis:
	- o Software Capital Expenditure: Software development investment required, hardware costs, office fit out, marketing, and consulting tools.
	- o Operational Expenditure: Salaries, software and hardware maintenance, overheads, recurring marketing expenses, and client acquisition costs.
- 2. Market Research:
	- o Industry trends
	- o Different consulting/competitor pricing
	- o Competitor analysis and market share analysis
- 3. Revenue Projections:
	- o Income from consulting fees, software licensing, and subscription models.

7.3 Step 3: Cost Analysis

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7.4 Step 4: Revenue Analysis

7.5 Step 5: Financial Viability Calculation

Assumptions:

- Capital Initial Investment: ϵ 1,692,500 (midpoint)
- Yearly Operational Costs: €627,500 (midpoint)
- Yearly Revenue Estimation: €1,425,000 (midpoint)
- Project Timeframe: 5 years
- Discount Rate: 8% (consulting industry standard rate)
- Tax Rate: 25% (assumed rate)

1. Net Present Value (NPV)

Year-by-year Present Values:

2. Internal Rate of Return (IRR)

Assumptions:

- Capital Initial Investment: $\epsilon 1,692,500$
- Annual Net Profit: ϵ 797,500 for 5 years

This IRR is quite high and represents a good ROI and an alluring investment possibility.

3. Payback Period

This return period is in excess of the industry expectation of 3-5 years and represents a good investment opportunity

7.6 Step 6: Sensitivity Analysis

To guarantee a robust model further test should be conducted to include:

- 1. Cost Volatility:
	- o To analyze the effect of shifting costs both operational, technical, and repair on profitability
- 2. Revenue Shifts:
	- o An analysis of how shifting client interest/subscriptions will affect profit and whether our company is more susceptible to profit decrease due to cost hikes or revenue drops.
- 3. Market Conditions:
	- o Illustrate how demand and increased competition, change our revenue and costs predictions.

7.7 Step 7: Decision-Making

AMANDAS decisions based on TEA is to proceed with the venture as it displays low risk, with good potential for financial feasibility and the likelihood of becoming a market leader with substantial m