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Detritus - Multidisciplinary Journal for Waste Resources and Residues - is aimed at extending the “waste” concept by opening up the field to other waste-related disciplines (e.g. earth science, applied microbiology, environmental science, architecture, art, law, etc.) welcoming strategic, review and opinion papers. **Detritus is indexed in Emerging Sources Citation Index (ESCI) Web of Science, Scopus, Elsevier, DOAJ Directory of Open Access Journals and Google Scholar**. Detritus is an official journal of IWWG (International Waste Working Group), a non-profit organisation established in 2002 to serve as a forum for the scientific and professional community and to respond to a need for the international promotion and dissemination of new developments in the waste management industry.

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Editorial

ENERGY, A MAJOR OVERSIGHT IN THE CIRCULAR ECONOMY AND RESOURCE MANAGEMENT?

With the threat of resource depletion, the idea of "Circular Economy" has virally spread in recent years as a "buzzword" with a positive symbolic charge. It has become essential in order to define modern waste management, not only in Europe but also abroad, such as in China. However, there is no single and commonly accepted definition of this concept. This one always seems simple and attractive with the image of an eternal cycle or a closed loop of our resources in a perfect circle.

Many questions then arise around this almost miraculous idea: "Is it really a closed circle?", "How large is the circle of the circular economy?", "How to transform this concept into a concrete, scientific and measurable project?", "What are the essential raw materials on which we depend?", "How can we keep the circular economy clean?", and finally, "Where is the energy to make this "wheel" turn smoothly and is this energy circular? ». Energy is the fundamental "detail" not to be forgotten, because there are no resources, no economy, not even life without energy! Perpetual motion does not exist, just like infinite recycling or zero waste. Leonardo da Vinci's beautiful inventions such as the helicopter remained motionless for more than 4 centuries in the absence of the energy source able to animate them.

Before sketching out some answers to these questions, let's start with the origins of the concept of circular economy. It surprisingly is a Chinese invention from the early 2000s. First identified in the Chinese scientific literature in 2003 (Bartl, 2019), the principle of circular economy was firstly adopted at the regulatory and legislative level by China. Its national strategy for the management of its resources and waste is based on this notion. It first appeared in its 11th five-year plan in 2006, then in its "Law for the Promotion of the Circular Economy" in 2008. Articles 2 and 15 of this law give a definition of the “generic term of circular economy describing the activities of reducing, recycling and resource recovery in production, circulation and consumption” and above all ask to "*recycle those wastes articles if possible, or otherwise make harmless treatment if they cannot be reused due to economic or technical restrictions*". The result of this policy has been the rapid and significant development of non-recyclable Waste-to-Energy (WtE) plants in this country as a fundamental pillar of China's Circular Economy law. The installed capacity in China in just over a decade has now exceeded that of Europe built in more than a century (Hanwei-Zhang, 2019).

In the same state of mind, due to the lack of some natural resources, Japan has also adopted similar legislation called “*3R (Reduce, Reuse, Recycle) for a sound material cycle society in Japan*”. The separate collection of large number of material streams for recycling is taken there to the extreme. Nevertheless, as in China, the final outlet for the treatment of residual and non-recyclable waste is based on energy recovery with a thousand WtE facilities. Ten years after China, the concept of circular economy was introduced in Europe in the 2018 European directive on waste (EUR-Lex, 2018) which defines it as: *"Improving the efficiency of resource use and ensuring that waste is valued as a resource can contribute to reducing the Union’s dependence on the import of raw materials and facilitate the transition to more sustainable material management and to a circular economy model"*. After these definitions, let's come back to our questions.

"Is this a perfect closed circle?"

The ideal of a cyclic system, while desirable, is unrealistic for many reasons. The different materials are intentionally mixed in the production phase of the products or unintentionally mixed as waste. This leads to an inevitable decline in their quality for each additional use. There is no such thing as infinite recycling. Moreover, every step involves leakage and therefore residues to be treated. Anthropogenic stocks are also an important underestimated topic in circular economy discussions. Approximately 50% of all extracted resources are used to build up new anthropogenic stocks. (Mavropoulos, 2020). Finally, the circular economy narrative focuses explicitly on raw materials and ignores the growing energy demands for the development of closed loops. Yet 15-20% of the extracted resources are energy carrier resources which cannot be replaced by secondary materials. This is why the more precise concept of use cascades was introduced (ISWA, 2015). But it has not been as attractive as that of the circular economy.

"How large is the circle of circular economy?"

A major ambiguity is hidden here. The territorial dimension of the circular economy is indeed one of the crucial issues to be considered. On the one hand, we hear about a very micro and local vision, of circular cities or dwellings. Some are dreaming of autonomous cities able to feed their inhabitants with the promotion of urban gardening supported by domestic compost of our kitchen waste in front of each building. The principle of proximity is indeed a good tool for obtaining solutions adapted to the metabolism of

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cities, especially regarding waste management. On the other hand, the macro and worldwide vision corresponds more to the reality of our globalised economy. The value chains of most consumer products have long since been globalised with resources and industries relocated beyond our national or European borders. Europe is now the continent with the fewest sovereign resources, especially for non-renewable ones. For resources, materials, energy carriers or raw secondary materials, the circular economy cannot therefore be well designed either locally or globally. With 2018's "China ban", Europe and USA have experienced the rejection of materials that are recyclable according to us but considered of poor quality by Asian countries. It has also shown that these recycled materials must find an outlet within the continent which produced them. The European directive's objective of reducing the Union's dependence on the import of raw materials shows us that the sovereignty of a country or continent like Europe is the right dimension of the "circle" of the circular economy. This 'national' approach is very much in line with the vision of the circular economy of countries such as China.

"How to transform this concept into a concrete, scientific and measurable project?"

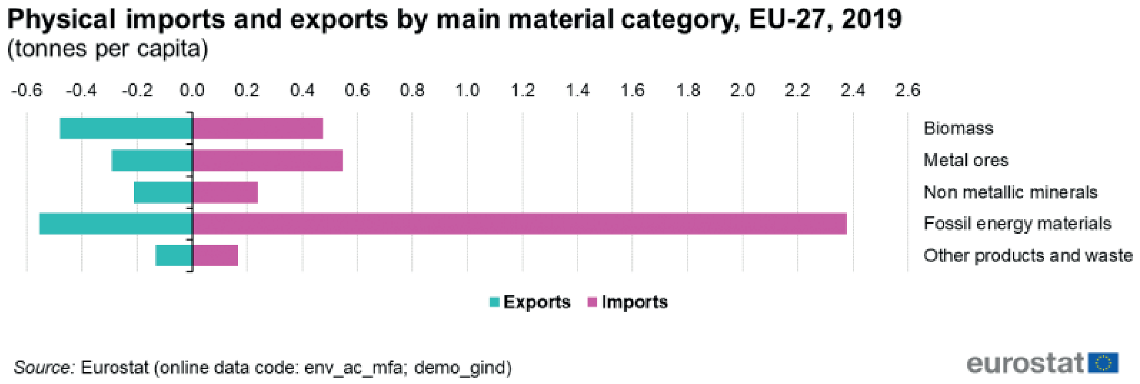
Measurement and progress indicators are essential and the recycling rate, which is the focus of attention in Europe, is not sufficient on its own. In addition to this one, some others have been implemented in China and Japan, such as resource productivity (GDP/natural resource input) and the amount of waste in final disposal in landfills. So-called Sankei diagrams provide a vision of the different involved flows and the circularity of the economy of each country or of the European Union. It shows for example for metals the EU's net important dependence on imports of metals ores, but also its mitigation through a high recycling rate (Mayer, 2019). One should not forget that one of the main drivers of circular economy should be economy! This should be also an efficient tool to measure progress.

"What are the essential raw materials on which we depend most?"

While the EU's economy is almost self-sufficient in the supply of non-metallic minerals (construction materials) and biomass, an examination of EU's trade reveals a clear asymmetry between physical imports and exports for the 2 other main categories of materials (see Figure 1 - EUROSTAT, 2019). We have seen above that imports assigned to the category of metal ores amount to around 0.5 tonnes per capita and are almost twice as large as their exports. But this is nothing compared to European extreme dependence on fossil primary energy sources. Imports of fossil energy materials are both the most important (with more than 2 tonnes per capita) and the most unbalanced (as physical imports are about four times larger than exports). Therefore, it doesn't make sense, for the EU to import its fossil fuels and then export oil in the form of recycled plastic when it could be used for productive purposes. It makes even less sense to landfill plastics or metals when they could at least be respectively converted into energy or recovered after the Waste-to-Energy process. This WtE treatment method relieves this deficit balance with local, mostly renewable and non-intermittent energy.

"How to keep the circular economy clean?"

Quality recycling means protecting the circular economy from hazardous substances and keeping it clean. Non-recyclable waste contains contaminated materials and substances that are health and safety hazards. They must be safely removed from circulation. These materials can be safely destroyed by combustion while recovering energy. WtE has a crucial and unique role in the complete destruction of organic hazardous materials, in the reduction of risks due to pathogenic microorganisms and viruses and in the concentration of valuable metals as well as toxic metals in certain fractions. This is its role as a safe and final sink for pollution mitigation (Brunner, 2015). Combustion of contaminated streams in large (hazardous or clinical waste) or more diffuse (municipal waste) quantities in well-equipped facilities is the best available solution thanks to the advanced pollution control technologies of state-of-the-art flue gas cleaning systems. This avoids the contamination of the circular economy by avoiding the recycling of pollution that could have an impact on both the environment and the human health. Indeed, this issue has motivated the moratorium of Asian countries on our so-called recyclable materials exported to Asia. Their mediocre quality in relation to their standards could not allow their insertion in their circular economy, therefore leading them to requalify them as waste.



Source: Eurostat (online data code: env_ac_mfa; demo_gind)

FIGURE 1: Physical imports and exports by main material category in EU 27, 2019 (tonnes per capita).

"Where is the energy to make this "wheel" turn smoothly and is it circular?"

Due to the current abundance of chemical and thermal energy sources represented by fossil fuels, we are no longer aware of our dependence and the super-powers that this concentrated and cheap energy affords us. The mechanical energy that a man can develop with his muscles alone is very limited and very expensive (Jancovici, 2020) Indeed, the average daily muscular work capacity of a man is limited to about 0.25kWh/day (FAO, 2021), i.e. about 100kWh/year with an estimated marginal cost in Europe of around 200EUR/kWh. 1 litre of fuel oil contains 10kWh of thermal energy, i.e. the equivalent in mechanical energy of the daily work of about ten men. However, each European consumes an average of 10 litres per day (average primary energy consumption per European people 100kWh/day - 3toe/capita/year). (Eurostat, 2020). Thanks to this cheap energy, all the machines often used unconsciously by everyone every day thus provide us with the equivalent of the muscular work of a hundred men at the service of each European inhabitant with a marginal cost per mechanical kWh of around 500 times cheaper with these machines. This energy has given us “inexpensive” super-powers that are obviously ephemeral!

We are not aware of all this energy involved in the creation and distribution of products as well as in the treatment of our waste, which will always hinder the achievement of total Circular Economy. Most of this energy is doomed to be linear as shown in the attached diagram (see Figure 2). The idea of transforming all waste into materials comes back, so to speak, to the alchemy of transmuting lead into gold, which is impossible just as perpetual motion without energy. We could face a bottleneck on production even with plenty of capital or work if we have a bottleneck on energy. Same for biodiversity. Nothing will be fished even with plenty of boats and fishermen if no gasoline (energy) or no fish (biodiversity). No production without energy and biodiversity. Bottlenecks are where we don’t look at.

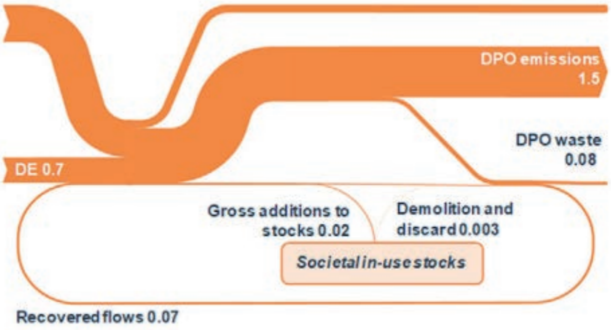


FIGURE 2: Fossil energy materials flows through the EU28 economy. In this Sankey diagram, the width of the arrows is proportional to the size of material flows; the numbers show the size of the material flows in Gt/yr. (DE = domestic extraction, DPO = domestic processed output) - Source: (Mayer, 2019).

The pandemic and situations of lockdown and scarcity have recently and cruelly reminded us of the importance of these principles of sovereignty over our resources and of proximity of tools to meet our vital needs. This crisis has shown how essential the continuity of public waste management services is, as a basic human need, part of the "metabolism" of cities. Waste contains resources rich in materials and energy. In each kg of residual waste that each European produces every day, there is about 2.5kWh of thermal energy available that WtE facilities recover safely while eliminating the pollution resulting from the mixture of materials we consume. Here is found circular energy which keeps circular economy clean!

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REFERENCES

Bartl. (2019). The eu circular economy package: Are new paths being taken or is it an old story? Sardinia 2019.

Brunner. (2014). Waste to energy , key element for sustainable waste management. Waste management.

European Parliament. (2018). Directive (EU) 2018/851 of the European Parliament on waste. Retrieved from https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.150.01.0109.01.ENG

EUROSTAT. (2019). Physical_imports_and_exports. Retrieved from https://ec.europa.eu/eurostat/statistics-explained/index.php/Physical_imports_and_exports#Import_dependency

Eurostat. (2020). Energie primaire . Retrieved from https://ec.europa.eu/eurostat/databrowser/view/t2020_33/default/table?lang=fr

FAO. (2021). Force motrice humaine. Retrieved from http://www.fao.org/3/ah810f/AH810F08.htm#:~:text=Les%20besoins%20%C3%A9nerg%C3%A9tiques%20alimentaires%20s,200%20%C3%A0%20300%20Wh%2Fjour

Hanwei-Zhang. (2019). World Waste to Energy and Resources London. World Waste to Energy and Resources London. London.

ISWA Task force. (2015). Report 5: CIRCULAR ECONOMY : Energy and fuels. ISWA

Jancovici. (2012). How to Improve Energy Efficiency with Circular Economy. Retrieved from University of Bradford: https://www.youtube.com/watch?v=lRAMA4mT0z0

Mavropoulos, A. (2020). Industry 4.0 and circular economy. ISWA

Mayer. (2019). Measuring Progress towards a Circular Economy (jiec.12809)

Ministry of the Environment of Japan. (2006). Japan's experience in promotion of the 3R's .

Republic of China. (2008). Circular Economy Promotion Law of the People’s Republic of China. Retrieved from http://english.mep.gov.cn/Resources/laws/envir_elatedlaws/201712/t20171212_427823.shtml

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HAZARDOUS WASTE CLASSIFICATION: REVIEW OF WORST CASE TO LESS WORST CASE METAL SPECIES WITH A WORKED EXAMPLE FOR A CONTAMINATED SOIL

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ABSTRACT

The classification of waste as either hazardous or non-hazardous, especially for mixtures such as contaminated soils, ashes, filter cakes and sludges, is not straight forward. In particular, as the laboratories can only measure total metal concentrations, both the European and the UK technical guidance state that if the classifier doesn't know exactly which metal species is in their waste, then they should start from a worst case species and use lines of evidence to work towards a more reasonable (less hazardous) species. However, the guidance doesn't define or list worst case nor less worst case species. While some authors have documented worst case species, this is only in relation to documenting the concentrations at which each hazard property is triggered for a given worst case species. This paper addresses this gap. It documents how to define both the worst case species and more importantly, lists less worst case species for 32 elements and 204 metal species; species based on those listed in the European legislation but also supplemented by species that haven't (yet) been included in this legislation but are significant nevertheless. For each species, the paper tabulates the hazard property that triggers first, metal concentrations, conversion factors and other metadata, species by species, in descending order of hazard. Finally, to demonstrate how to use the data, either manually or by utilizing commercial software, the paper will give a worked example for a contaminated soil, showing how classifiers can use the list to help move from a worst case to a less worst case species.

1. INTRODUCTION

The classification of waste, in particular mixtures such as contaminated soils, ashes, filter cakes and sludges, as either hazardous or non-hazardous, is not a simple process. Whilst the European legislation allows two approaches, chemical testing and direct testing (also called effects-based testing or toxicity testing) (Concawe 2020), to assess the both the fifteen hazard properties and the persistent organic pollutants (POPs) content, neither is straight forward.

This paper reviews one of the biggest stumbling blocks for classifiers using the chemical testing approach, namely metal speciation. When a classifier asks a chemical test laboratory to characterize a particular waste, they will ask the laboratory to test their waste for a set of mainly heavy metals, for example, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium and zinc. They will also ask for other determinands such as petroleum hydrocarbons, polyaromatic hydrocarbons (PAHs), selected anions, pH and moisture etc.; the actual selection being based on the findings of a desktop study. The challenge with the inorganic compounds is that a laboratory can only measure total metal concentrations (e.g. total zinc) while classification requires the use of metal compounds or species (e.g. zinc chromate) for hazardous waste classification. This is a different approach to the landfill legislation's simpler Waste Acceptance Criteria (WAC) defined in Council Decision 2003/33/EC, as amended (EU 2003), where the leaching concentration of twelve specific metals has to be less than a defined threshold for a particular class of landfill. For WAC, knowledge about the metal species is not required.

For a given metal, both the European Commission's and the UK's technical guidance (EU 2018, WM3 2018) state that where there is any doubt about which inorganic compounds are present, the classifier should start with worst case metal species and then work towards more reasonable case species, for a given metal, based on a combina-

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tion of lines of evidence and expert judgement. However, neither guidance document:

- lists worst case metal species, or
- lists other metal species in decreasing (less) worst case order.

As many workers still classify their waste by hand, or in spreadsheets, earlier papers (Hennebert 2019, INERIS, 2015) published tables detailing just the worst case species for a given metal (they use the term element), along with the relevant thresholds for each hazard property that applied to that metal species, under the regulations in place at the time the paper was written.

Utilising worst case species is fine especially if you are manually classifying your waste and a worst case outcome is acceptable. However, especially with the advent of comprehensive waste classification software that manages all the substances and the calculations, a manual approach leaves the classifier more likely to report a hazardous outcome, which increases transport and disposal costs and sends more waste to landfill. The manual approach also ignores the time savings, accuracy and reporting benefits of the on-line software.

This paper tabulates worst case to less worst case species for 32 elements and 204 metal species, covering commonly encountered alkali metals, alkaline earth metals, transition metals, metalloids and reactive non-metals from the periodic table. It also gives an example of how the classifier can work from worst case to a more reasonable case using lines of evidence and expert judgement.

2. LEGISLATION

Since the introduction of the Waste Framework Directive 2008/98/EC (EU 2008a) (WFD) and its enactment in each member state's national legislation, most domestic, commercial and industrial waste in Europe has to be classified as either hazardous or non-hazardous and given the appropriate six digit code from Decision 2014/955/EU (EU 2014a). This document is known both as the European Waste Catalogue (EWC) and the List of Waste (LoW). While many of the codes in the LoW are either absolute hazardous entries (AH, e.g. 03 07 01* fuel oil and diesel) or absolute non-hazardous entries (AN, e.g. 03 01 01 waste bark and cork), codes applicable to many mixtures are called mirror entries. These entries are typically a pair of codes, one mirror hazardous (MH), the other mirror non-hazardous (MN). For example, the mirror entries for a contaminated soil are:

- 17 05 03* Soil and stones containing hazardous substances (MH)
- 17 05 04 Soil and stones other than those mentioned in 17 05 03* (MN)

The selection of which mirror entry code applies to the waste and goes on the disposal paperwork, depends on whether the waste has any hazardous properties or certain POPs.

A hazardous waste is a waste that due to its (intrinsic) chemical or other properties, displays one or more of the fifteen hazard properties listed in Annex III of the WFD or any of the POPs (above a given concentration limit or threshold) listed in EU (2014a). All the hazard properties and POPs are summarised in Table 1.

The WFD was amended further by Regulation (EU) No. 1357/2014, known as the Annex III amendment (EU 2014b), and the later Regulation (EU) 2017/997 (EU 2017), known as the HP 14 amendment. These state that the classification of waste as hazardous is based on the European Union legislation for classifying chemicals; the current European chemical legislation being Regulation (EC) No. 1272/2008 for the Classification, Labelling and Packaging of substances and mixtures (EU 2008b), known as the CLP, and Regulation (EC) No 1907/2006 Registration, Evaluation, Authorisation and restriction of Chemicals (EU 2006), known as REACH, plus some other subsidiary legislation covering cosmetics, pesticides, biocides and pharmaceuticals.

Annex VI, Table 3 of the CLP (CLP Table 3) contains more than 4,250 substances, known as harmonized entries. For each entry, it tabulates one or more hazard statements that together define which hazard properties are known to apply to that entry. These hazard statements, along with the thresholds and tests defined in both the Annex III amendment and the later HP 14 amendment, determine whether one or more substances in a waste, at given concentrations, a) makes the waste hazardous and b) for which hazard properties.

There are further challenges for classifiers (and technical publications, including this one), which can change the resultant classification.

1. CLP Table 3 is regularly updated by Adaptations to Technical and scientific Progress (ATPs). At the time of writing, there were 15 ATPs to the CLP. These, with respect to waste classification, can be divided into two general types; those that:
   1.1. Modify CLP Table 3 by deleting existing harmonised entries, modifying the data for existing entries or adding new entries; typically these are published on an annual basis. ATP 1 (EU 2009) for example updated some 500 harmonised entries.
   1.2. Change the rules, for example by adding a new hazard property, modifying calculation methods or defining new hazard statements. This type of ATP occurs every two years and is related to revisions of the United Nations' Global Harmonised System (GHS 2019). If the changes are waste related (as opposed to labelling or packaging of products for example), this would initiate a revised version of the technical guidance some months later.

2. The CLP, unlike the older European chemical legislation phased out in 2015 (EEC 1967, EU 1999) considers every entry in CLP Table 3 as potentially incomplete, i.e. a harmonized entry can be missing one or more hazard classes (e.g. carcinogenic, flammable liquid) and the classifier is meant to "self-classify" and identify any missing hazard classes. Whilst this is a challenge for the manufactures of chemical products, who know exactly which chemicals go into their products, it is much

more of a challenge for waste classifiers dealing with mixtures, who potentially have to deal with many hundreds of (often unknown) compounds and tend not to have toxicologists or chemists on their staff.

2.1 UK: Retained EU legislation

Following the exit of the United Kingdom of Great Britain (GB) and Northern Ireland from the EU, the CLP Regulation as amended, is retained in UK law by the European Union (Withdrawal) Act 2018 (UK 2018) and subsequent exit regulations (UK 2019, 2020). All existing EU harmonised classification and labelling in force on 31 December 2020, are retained by the GB CLP Regulation in a data set known as the GB mandatory classification and labelling list or GB MCL list (UK 2020). Waste that is classified for disposal or recovery in GB is now required to use the mandatory entries in the GB MCL list, while waste classified for disposal or recovery in Northern Ireland (or rest of the EU) continues to use the harmonised entries in the EU CLP Regulation (EU 2008b). As the mandatory entries in the GB MCL list and the harmonised entries in CLP Table 3 are currently the same, this paper will just refer to the harmonised entries in CLP Table 3. In the future, while the entries in these two data sets may diverge slightly, the approach detailed in this paper can still be used to identify worst case and less worst case substances.

3. TECHNICAL GUIDANCE

Waste classification and with that an understanding of the European chemical legislation is daunting to most waste producers. Various national regulators have published varying levels of technical guidance over the last ten years, some as short as a couple of pages. Classifiers in the UK have had comprehensive, up-to-date, technical guidance throughout. The current version, WM3 v1.1 (WM3 2018), reflects the requirements of the most recent legislative changes, namely the HP 14 amendment.

Following publication of the HP 14 amendment in 2017, which came after a European Commission review of four different approaches for the calculation of HP 14 (Hennebert et al., 2016), the European Commission published the first Europe-wide technical guidance, Notice 2018/C 124 (EU 2018). Both WM3 (2018) and EU (2018) give a step by step (manual) approach to the whole waste classification process focusing on the chemical testing approach. The basic steps are:

Step 1. confirming the waste falls under the remit of the WFD (refer also to enacting national legislation),
Step 2. selecting the correct LoW code or mirror entry pair of LoW codes, and
Step 3. for mirror entries:
  Step 3.1 identifying hazardous substances that may be or are in the waste,
  Step 3.2 undertaking chemistry laboratory testing,
  Step 3.3 assessing measured concentrations against a series of tests and thresholds,
  Step 3.4 based on the outcome of Step 3.3, selecting the hazardous mirror entry code if the waste has one or more hazardous properties (or POPs); the non-hazardous mirror entry code if the waste does not have any hazardous properties (or POPs).

Both documents have a chapter for assessing each hazard property (and one for POPs), including flow diagrams and relevant calculations, plus guidance on finding data for either incomplete entries or for substances that are not in CLP Table 3. There are also chapters on assigning the correct LoW code(s) and an introduction to sampling and in WM3 (2018), a chapter on statistics.

While the two documents have exactly the same assessment methodologies for the assessment of the fifteen hazard properties and the POPs, there are a few differences between them. In particular:

- Differences in the entry type designation (AH, AN, MH, MN) for 87 of the 843 LoW codes. For example, 01 05 05* oil-containing drilling muds and wastes is (MH) in EU (2018) and (AH) in WM3 (2018).
- Unlike WM3 (2018), EU (2018) offers no support for unknown oils (hydrocarbons) in a waste such as oil contamination in a soil, sludge or a filter cake. The reason is that terms like “unknown oil”, “TPH” and “mineral oil” are not recognized as group entries in the CLP. However, classifiers still have to deal with unknown oil contamination in their wastes so WM3 (2018) provides a practical set of hazard statements to help classifiers assess unknown oils.
- WM3 (2018) also provides sets of hazard statements for a number of Petroleum Groups; specifically; petrol (gasoline), diesel, heavy fuel oils and crude oil. The commercial software, HazWasteOnline™ (www.hazwasteonline.com) has added two further Petroleum Groups for kerosene and bitumen. The creation of these Petroleum Groups is to aid the classifier in the assessment of oils, in particular oil contaminated mixtures such as soils, sludges and filter cakes. The reason for creating these Petroleum Groups is that the vast majority of the oils (specifically oils resulting from the refining of crude oil) in CLP Table 3 are incomplete; generally they only have a single hazard statement, typically for HP 7 carcinogenic, HP 11 mutagenic or HP 5 single target organ toxicity (STOT). This means that they are missing one or more hazard statements such as those for HP 14 ecotoxic or HP 3 flammable. It is worth noting that up until ATP 2 (2011), all the refined oils (and other entries such as coal tars) in CLP Table 3 were designated “Note H” which indicated a known, incomplete entry. As only a few of these oils have been updated since ATP 2 (2011), they remain incomplete. Therefore, classifiers should not use the entry in CLP Table 3 but should instead consult WM3 (2018) or REACH compliant Safety Data Sheets (SDS) from oil companies, to identify the missing hazard statements / hazard properties. A summary table of the hazard statement codes for different petroleum groups can also be found in Concawe (2020).

It is outside the scope of this paper to describe the mathematical steps, the tests or rules, or the assignment of the different hazard properties when assessing a waste, as these, if classifying by hand, are clearly described in the guidance. If the classifier is using the commercial software, then all the data, tests, exceptions, notes and calculations are embedded in the classification engine, letting the classifier focus on what is in the waste, rather than how to do the calculations.

4. HAZARD PROPERTIES

The fifteen hazard properties and their hazard statements, along with the relevant cut-offs[1], thresholds and whether the hazard statements are additive[2] or individual[3] are summarized in Table 1. The table also lists the POPs and their thresholds.

The hazard properties are split into three groups.

1. H200s; Physical hazards (HP 1 Explosive, HP 2 Oxidising and HP 3 Flammable and HP 15). Generally, the thresholds for these hazard statements can only be ascertained by physical testing. Table 1 references some of the physical tests which are detailed in the testing regulation (EC 2008c) and explained further in the European Chemical Agency's guidance to the application of the CLP (ECHA 2017). WM3 (2018) and EU (2018) do provide thresholds for some flammable substances that, in contact with water, may release flammable gases or which may ignite spontaneously (hazard codes H260 & H261)
2. H300s; Health hazards (HP 4 Irritant to HP 13 Sensitising)
3. H400s; Environmental hazards (HP 14 Ecotoxic)

Note that:

- the table contains additional hazard statements, defined in the CLP, that are not yet defined in the GHS; these are of the form EUH0xx, such as "EUH001 Explosive when dry" and are only included in a classification where another hazard property is present or if the guidance has defined a calculation method.
- for "HP 12 Release of an acute toxic gas", the technical guidance also details the methodology for calculating substance specific thresholds for substances assigned the following additional hazard statements: EUH029, EUH031 and EUH032.

TABLE 1: Summary of the fifteen hazard properties and POPs, their hazard statements and thresholds..

Hazard Property	Hazard	Hazard Statements (code, class & category)	Cut-offs [1]	Threshold [2, 3]
Physical Hazards				
HP 1	Explosive	H200, H201, H202, H203, H204, H240, H241	-	Testing (mainly EU 2008c, A.14) or experience
HP 2	Oxidising	H270, H271, H272	-	Testing (mainly EU 2008c, A.17) or experience
HP 3	Flammable	H220 to H226, H228, H240, H241, H242, H250, H251, H252 H260, H261	-	Testing (mainly EU 2008c, A.10) or experience Examples of substance specific thresholds documented in WM3 (2018), Table C3.2, duplicated in EU (2018), Table 11.
Health Hazards				
HP 4	Irritant (Skin irritation and eye damage)	H314 Skin Corr. 1A H318 Eye Dam. 1 H315 Skin Irrit. 2 H319 Eye Irrit. 2	1%	Σ H314 1A ≥ 1% Σ H318 ≥ 10% Σ (H315 and H319) ≥ 20%
HP 5	Specific Target Organ Toxicity (STOT) Aspiration Toxicity	H370 STOT SE 1 H371 STOT SE 2 H335 STOT SE 3 H372 STOT RE 1 H373 STOT RE 2 H304 Asp. Tox. 1	-	Ind. H370 ≥ 1% Ind. H371 ≥ 10% Ind. H335 ≥ 20% Ind. H372 ≥ 1% Ind. H373 ≥ 10% Ind. H304 ≥ 10% Σ H304 ≥ 10% and overall kinematic viscosity (at 40°C), is less than 20.5 mm²/s
HP 6	Acute Toxicity	H300 Acute Tox.1 (Oral) H300 Acute Tox. 2 (Oral H301 Acute Tox. 3 (Oral) H302 Acute Tox 4 (Oral) H310 Acute Tox.1 (Dermal) H310 Acute Tox.2 (Dermal) H311 Acute Tox. 3 (Dermal) H312 Acute Tox 4 (Dermal) H330 Acute Tox 1 (Inhal.) H330 Acute Tox.2 (Inhal.) H331 Acute Tox. 3 (Inhal.) H332 Acute Tox. 4 (Inhal.)	Cat. 1, 2 or 3: 0.1% Cat. 4: 1%	Σ H300 1 ≥ 0.1% Σ H300 2 ≥ 0.25% Σ H301 ≥ 5% Σ H302 ≥ 25% Σ H310 1 ≥ 0.25% Σ H310 2 ≥ 2.5% Σ H311 ≥ 15% Σ H312 ≥ 55% Σ H330 1 ≥ 0.1% Σ H330 2 ≥ 0.5% Σ H331 ≥ 3.5% Σ H332 ≥ 22.5%
HP 7	Carcinogenic	H350 Carc. 1A , 1B H351 Carc. 2	-	Ind. H350 ≥ 0.1% Ind. H351 ≥ 1%
HP 8	Corrosive	H314 Skin Corr. 1A, 1B , 1C	1%	Σ H314 ≥ 5%
HP 9	Infectious	-	-	Rules laid down in reference documents or legislation in Member States – WM3 (2018), Appendix C9, EU (2018), Section 3.9
HP 10	Toxic for reproduction	H360 Repr. 1A, 1B H361 Repr. 2	-	Ind. H360 ≥ 0.3% Ind. H361 ≥ 3%
HP 11	Mutagenic	H340 Muta. 1A, 1B H341 Muta. 2	-	Ind. H340 ≥ 0.1% Ind. H341 ≥ 1%

HP 12	Release of an acute toxic gas	EUH029, EUH031, EUH032	-	Testing (ECHA 2017 section 2.12 or 1M HCl for EUH031 or EUH032) or experience Examples of substance specific thresholds documented in WM3 (2018), Table C12.2, duplicated in EU (2018), Table 21
HP 13	Sensitising	H317 Skin Sens. 1, 1A, 1B H334 Resp. Sens. 1, 1A, 1B	-	Ind. H317 ≥ 10% Ind. H334 ≥ 10%
Environmental Hazards				
HP 14	Ecotoxic	H400 Aquatic Acute 1 H410 Aquatic Chronic 1 H411 Aquatic Chronic 2 H412 Aquatic Chronic 3 H413 Aquatic Chronic 4 H420 Ozone	H400, H410: 0.1% H411, H412, H413: 1%	Σ H400 ≥ 25% Σ [(100*H410) + (10*H411) + (H412)] ≥ 25% Σ (H410 + H411 + H412 + H413) ≥ 25% Σ H420 ≥ 0.1% Alternative: Direct Testing
Physical, Health and Environmental Hazards				
HP15	Waste capable of exhibiting a hazardous property not displayed by the original waste	H205 Expl. 1.5 EUH001; EUH019, EUH044	-	Testing, (ECHA 2017 section 2.1 provides guidance on EUH001, EUH044 and H205) or experience Norden (2015) reports hazard property is not generally applied; limits can be defined by individual member states
Health and Environmental hazards				
Persistent Organic Pollutants (POPs)	Waste containing one or more POPs; the POPs being those listed in EU (2014a), thresholds defined in EU (2014c)	Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF); Polychlorobiphenyls (PCBs) Pesticides: DDT; chlordane; dieldrin; endrin hexachlorocyclohexanes, including lindane; heptachlor; chlordecone; hexachlorobenzene; aldrin; pentachlorobenzene; mirex; toxaphene Brominated flame retardants: hexabromobiphenyl	-	PCDD/PCDF: $\Sigma(C_i \times TEF_i) \geq 15$ μg/kg (where TEF_i is the toxic equivalency factor and C_i the concentration of an individual PCDD or PCDF substance i) Rest: ≥ 50 mg/kg

Note : Annex IV of Regulation No. 850/2004 as amended (EU 2004) contains a larger list of POPs that have specific disposal requirements when found in a waste:

- *Pesticides*: endosulfan, dicofol (candidate POP)
- *Brominated flame retardants*: tetra-, penta-, hexa-, hepta- and decabromodiphenylether; hexabromocyclododecane (HBCDD)
- *Chlorinated compounds*: polychlorinated naphthalene; short-chain chlorinated paraffins (SCCPs); hexachlorobutadiene
- *Fluorinated compounds*: perfluorooctane sulfonic acid and its derivatives (PFOS); perfluorooctanoic acid (PFAS) and perfluorohexane sulfonic acid (PFHxS) and their derivatives (candidate POPs)

These POPs are not listed in the current waste regulations so do not make the waste hazardous at the threshold concentration of 50 mg/kg.

5. WASTE CLASSIFICATION METHODOLOGY

Assuming that the correct chemistry data have been collected for the classification step (Hennebert et al. 2013, AFNOR XP X30-489 2013), some practitioners (Hennebert 2019, INERIS 2015, Norden 2016) discuss a tiered approach to assessing whether the waste, in particular mixtures, has any hazardous properties. The approach is essentially a manual methodology, aimed at paper or spreadsheet based assessment:

- Tier 1: is confirming that the material is a waste and identifying the correct LoW code for absolute entries (AH, AN) or pair of codes (MH, MN) for mirror entries.

For the assessment of hazardous properties:

- Tier 2: Screening at high level to exclude non-relevant hazardous properties from further assessment. For example, it is likely that HP 1 Explosive, HP 2 Oxidising, HP 3 Flammable[4], HP 9 Infectious can all be excluded for incinerator bottom ash (IBA) or fly ash, based partly on the nature of feed stock but also because the minimum incinerator temperature is 850°C.
- Tier 3 a: Assessment of hazardous properties not eliminated in Tier 2 by determining the chemical composition of the waste.
- Tier 3 b: It may be necessary to undertake physical testing for some hazard properties not eliminated in earlier tiers. This step is mainly relevant for HP 1, HP 2 and HP 3. Note that HP 9 Infectious, which isn't assessed using the chemical analysis approach, also needs to be considered and either discounted at the desktop study stage or, other suitable (non-chemical) testing undertaken. Weight of evidence and expert judgement are often used in this step of the assessment.
- Tier 3 c: For some wastes it may be possible to assess hazardous properties based on the principle of bridging; assuming that the waste has the same LoW code as the waste from another process and is similar or identical to waste generated from that process. For example, in the UK, incinerator bottom ash (IBA) from the incineration or pyrolysis of municipal waste (19 01 11* / 19 01 12) is generally disposed of under 19 01 12 based on the ESA sampling and testing protocol (ESA, 2018) but bottom ash from the co-incineration of waste wood (10 01 14* / 10 01 15) cannot use, or bridge using this protocol and the earlier findings of ESA's original baseline characterisation.
- Tier 4: for some waste streams, based on a positive, cost benefit analysis, more specialized chemical analysis and modelling may be advisable. For example, this might be considered for IBA from a waste wood co-incinerator that generates 10,000 tonnes of IBA every year.

The rest of this paper will focus primarily on the Tier 3a step and assessing metal species.

5.1 Classification of Safety Data Sheets

The classifier can use the information in a product's SDS when the product remains un-altered in the resulting waste stream. The use of the data in a SDS for waste classification can generate a different classification to the original product classification. Some hazardous products are re-classified as non-hazardous wastes and vice-a-versa. In particular, HP 4, HP 6, HP 8, HP 13 and HP 14 show major differences to their counterparts in the CLP regulation (INERIS 2016). The biggest discrepancies are caused by:

- In the case of products, classifiers have to use the Specific Concentration Limits and M factors[5] where stated in Table 3 of the CLP, whereas their use is not required in waste classification.
- Any hazard statements published in Section 2 of the SDS can reflect additive calculations; calculations based on the actual concentrations of the ingredients in the mixture (Section 3); these additive calculations and hence the result, differ from those calculations utilized in waste classification.
- In Section 3 of the SDS, manufacturers disguise the exact composition of hazardous ingredients in their products by using ranges of concentrations (e.g. 5 to 10%) or maximum concentrations (e.g. <10%); the waste classifier has to use the maximum concentrations.

6. WASTE CLASSIFICATION

Some of the most difficult wastes to characterize and classify are mixtures such as contaminated soils, filter cakes, ashes and sludges. This is because the classifier does not know exactly what is in the waste, combined with the knowledge that the standard laboratory test suites can't tell us everything we would like to know about the chemical composition of our particular waste.

For waste characterisation, many classifiers have a "minimum" chemical test suite that they will use as a starting point. With respect to the metals and considering waste soils, this minimum suite often includes antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium and zinc. Following a review of the processes that created and/or contaminated the waste, the classifier may then add extra metals to their minimum suite to better characterize the waste.

As an example, during work to determine whether a filter cake generated during the production of a firefighting foam has any hazardous properties (Bishop and Gill 2018), both calcium and iron were added to the suite of tests. The metals were identified because this industrial process entails the alkaline hydrolysis of a hoof and horn meal to release polypeptides. The process uses significant quantities of lime (calcium hydroxide, CaO) to create the alkaline conditions and iron(II) sulphate ($FeSO_4$) and carbon dioxide (CO_2) after the hydrolysis. These metals were included, not because the resulting calcium and iron compounds in the filter cake were likely to be hazardous, but more to confirm that a) the hydrolysis and hence the filter cake contained what was expected and b) would help demonstrate a better mass balance calculation.

This requirement to identify all compounds that may be at sufficient concentration to trigger a hazardous property is in contrast to the WAC approach (EU 2003), where (with respect to inorganic compounds):

- WAC only requires the testing of the eluate for twelve specific metals (and three anions); these are therefore not total metal concentrations but only the soluble (leachable) metal fraction (WAC testing ignores the insoluble compounds), and
- Depending on the class of landfill (hazardous, inert etc.) the WAC assessment simply compares the concentrations against a defined concentration threshold; a simple pass fail approach.

A few actors offer a simple, spreadsheet-based, worst case type classification for contaminated soils whereby they undertake a "no extra knowledge" classification; to put it simply, they assume worst case substances for the metals and simply process the chemical analysis as is. However, there is much confusion over what is worst case, with a number of these actors incorrectly assuming that the compounds in the contaminated soil example in WM3 (2018) are worst case, which is incorrect; these compounds were chosen for a specific industrial contamination scenario and five of the seven quoted species are not worst case.

6.1 Metal species

The challenge is that the laboratory results for the metals only give you the total metal concentrations and not the specific species (or species[6]) concentrations for each metal. This species knowledge is critical in waste classification because:

- for each metal, we have to use the concentration of a metal species in a classification, not the total metal concentration (There are exceptions known as Note 1 compounds that are discussed later), and
- the standard laboratory tests can only estimate the total concentrations of individual metals e.g. total arsenic, copper or zinc and are not able to identify which specific species of metal is present in the waste.

There is a complementary technique, X-Ray Diffraction (XRD) (alongside X-Ray Fluorescence (XRF)), that can be used to analyse the mineral composition of naturally existing or manufactured crystalline materials. Unfortunately, XRD cannot identify compounds in complicated mixtures such as a soil where there are hundreds of amorphous compounds, with no crystalline form, disseminated throughout the material, typically with concentrations < 1%.

The guidance states that where the classifier doesn't know which metal species is present in a waste, the classifier must start with the worst case and then work towards a more reasonable case, based on lines of evidence. The evidence that can be considered will depend on the nature of the waste stream and knowledge of some basic chemistry.

For example, to assess an industrial filter cake, a desktop study would include:

- a review of the entire process that generates the filter cake; what are the input materials, which chemicals are added, what is the composition of the product and what substances might be expected in the filter cake based on the design of the process,
- examining what could be added by accident to the process due for example to equipment malfunction or contamination of the feed stock,
- collecting REACH compliant SDS for chemicals utilised,
- understanding the chemical reactions – how substance X reacts with substance Y to create substance Z, and
- a review of any existing chemical data; data typically collected for a different purpose such as assays or the annual monitoring specified in an environmental permit.

For a contaminated soil, this desktop study would include:

- a review of the historical industrial uses of the site and surrounds – this would have been covered in a Phase 1 desktop type study,
- a review of any Phase 2 site investigation work, including the re-assessment of any chemical data gathered during that investigation to identify contaminated soils,
- a walk over to identify evidence of contamination such as burning, staining and fly tipping and any relevant issues that may have occurred post the site investigation,
- review of the construction drawings and materials management plan to identify a) where excavated soils would come from and b) what volume of soils are planned for disposal[7].

Following the review, the classifier would have also:

- designed the laboratory testing suite,
  - including expanding the chemical analysis to help identify / rule out certain metal species and the type(s) of hydrocarbon contamination.
- designed the sampling plan,
- collected the samples, and
- commissioned a suitable chemical test laboratory.

6.2 Worst case

WM3 (2018) introduces the term "Worst case substance" (Step 4, page 7) following an introduction stating that chemical analysis, with respect to mainly inorganic substances, does not always identify specific components but rather the individual cations (i.e. the metals) and anions (e.g. sulphates, phosphates, chlorides etc.). It makes it clear that if there is any doubt about which substance is in a waste, then "*the worst case substance should be considered present*". This term is further explained in Step 5 (page 8) which tells the classifier that they have to identify the 'worst case' substances, giving only lead chromate as an example for lead. The guidance then states that these worst case substances have to be identified separately for each hazard property.

EU (2018) uses the term "*Realistic worst case substance*" (section 4.2.1) and states that "*Worse case compounds should be determined taking into consideration which substances reasonably could exist in the waste (e.g. based on the substances used in the process generating the waste and its associated chemistry)*". It has a footnote to further define the term "reasonable" and defers to the definition in WM3 (2018) which states that "*reasonable indicates that the substances cannot exist within the waste because, for example, of their physical and chemical properties can be excluded*". The footnote does go further and refers readers to the INERIS (2015) technical guidance document which "*contains a collection of 'realistic worst case' substances by elements for each hazard property*".

This is as far as the guidance documents go as neither WM3 (2018) or EU (2018) reference or publish a list of either worst case compounds, or less worst case compounds, nor describe how to deal with some of the exceptions encountered when trying to compile such lists. Some authors (INERIS 2015) have published lists of worst case compounds, by element and hazard property, or have proposed a "worst case with information" list (Hennebert 2019) but none have published a comprehensive list of less worst case compounds focusing on compounds, rather than just hazard properties. This is partly because these approaches assume a manual analysis, which if you were to add more variables, such as less worst case, makes the classification process even more onerous.

The alternative approach to the manual, step by step identification of hazard properties for every substance in a waste, is to start with worst case species for all relevant metals (and all the other determinands such as the PAHs, hydrocarbons, pH, moisture etc.), import the chemical results directly from the laboratory and classify using commercial software like HazWasteOnline™. This tells the classifier in seconds whether any of the determinands have any hazardous properties. If one or more determinands flag up as hazardous, the classifier can prioritise these for further work. If nothing flags up as hazardous, the classifier could stop at this point.

Typically most classifiers want to fine tune their classification further, either based on additional (analytical) knowledge of some of the inorganic compounds in the waste and/or because of other information in the chemical results which can help rule out certain inorganic compounds. For example, if there isn't any chromium(VI) in the waste (EN 15192), all the metal chromates can be swapped to the next (less) worst case species. However, the question then raised is what is the next less worst case metal species. Classifiers need a list that:

- goes from worst case to less worst case for each metal,
- documents the metadata that first triggers a hazard property for each metal species, and
- details the assumptions and limitations used to compile the list.

It must be noted that both approaches, manual or software, still requires a thorough desktop study to both identify what to physically test for and for the metals, evidence for using more reasonable (less worst case) metal species. Both methods rely on the premise that the classifier has identified all potentially hazardous compounds in the waste.

6.3 Conversion Factors, Group Entries and Note 1

For a given metal, once the classifier has identified the metal species that they want to use, they have to perform one further step; converting the total metal concentration to the species concentration using a Conversion Factor (see note[8] for worked example). The resulting species concentration is the number that has to be used in the waste classification.

There is one special case and one exception to this requirement: Group Entries and Note 1 entries.

- Group Entries (see Table 3 for examples) are of the form "*metal X compounds with the exception of those specified elsewhere in this Annex*", the Annex being CLP Table 3. So as long as the metal X compound you suspect is in your waste (e.g. lead sulphate) is not listed in CLP Table 3, the classifier can use the metal's Group Entry instead. However, the classifier still has to apply a Conversion Factor for a hypothetical species; a species not already listed in CLP Table 3.
- Some entries in CLP Table 3 are marked as Note 1. The CLP's definition of Note 1 is "*The concentration stated or, in the absence of such concentrations, the generic concentrations of this Regulation are the percentages by weight of the metallic element calculated with reference to the total weight of the mixture*"; effectively this means that the classifier can use the total metal concentration in the classification and not worry about applying a Conversion Factor for a hypothetical metal species.

About half of the Group Entries in CLP Table 3 (e.g. lead compounds) are also Note 1; this simplifies the exercise even further as for these entries, the classifier doesn't have to work out a Conversion Factor for any particular metal species. However, for those Group Entries that are not Note 1; beryllium, chromium(VI), selenium, thallium and uranium, the classifier has to utilise a Conversion Factor for a suitable metal compound and herein lies the challenge. There is no guidance or legislation that dictates how such a compound should be chosen and thus a suitable Conversion Factor defined. One practice is to go worst case and try and identify a worst case metal compound that is 1) not already listed in CLP Table 3 and 2) could be a reasonable source of contamination in the waste. Hennebert (2019) suggested the metal oxide where the oxide was not already a harmonised entry in CLP Table 3.

Apart from Group Entry "arsenic acid and its salts..." where arsenic acid is a logical selection, this paper utilises oxides for the Group Entries for selenium, thallium and uranium (plus an alternative chromate for thallium). However, where the oxides are present, both beryllium chloride and beryllium hydroxide and chromic acid (H2CrO4) have been listed. Note that where the classifier has evidence for a different compound for one of these Group Entries, then they should use the Conversion Factor for that compound, which in turn, might affect the relative position of the Group Entry in Table 3.

6.4 What is worst case?

The approach to assessing worst case inorganic compounds is to calculate how much of the metal, for a given metal species, is required to create a hazardous outcome. For most species, this outcome is based on:

- the size of the Conversion Factor (note that a larger conversion factor does necessarily equate to a more hazardous species), and
- which hazard statements a given compound has and by correlation, the thresholds defined in the LoW.

Other factors that could influence the outcome include:

- Whether the compounds is a Note 1 substance e.g. lead chromate.
- Whether the compound has a threshold defined at technical guidance level e.g. HP 12: (EUH031, EUH032) and HP 3 (fifth indent).
- Whether the harmonized entry is an incomplete entry and missing one or more hazard classes (e.g. barium salts).
- Whether the harmonised entry is a minimum entry[9]. For example, mercury dichloride has "H300 Acute Tox. 2*", threshold0.25%butitcouldbeAcuteTox.1,threshold0.1%.

The approach also has two important caveats that cannot be factored into a worst case assessment:

- With a few exceptions, the assessment doesn't assess the contribution of the physical hazards, HP 1, HP 2 and HP 3 and HP 12 (and related hazard statement's category code marked ****). This is because a) there are no published thresholds and b) it depends on synergistic/antagonistic effects with other components in the waste; some components may increase the physical hazard while others may mitigate the hazard. There are calculation methods for HP 3 flammable: fifth indent (Water-react. 1; H260 and also H261) and HP 12 (EUH031, EUH032), detailed in WM3 (2018) & EU (2018), which have been included in this review.
- The assessment does not take into account additivity of the selected species with other additive substances present in the same waste. HP 4, HP 5, HP 6, HP 8 and HP 14 all have one or more additive hazard statements. Additivity can therefore make a waste hazardous at lower concentrations than that of the individual concentration of the substance alone.

It must also be noted that the CLP considers that all the harmonized entries in CLP Table 3 may be incomplete with respect to hazard classes that are not listed for given entry.

For substances that are known to be incomplete (for example all the refined petroleum hydrocarbon entries) and haven't been amended since the publication of ATP 2 (EU 2011), when Note H[10] was removed, or for the millions of substances that are not listed in CLP Table 3, the classifier is responsible for self-classification; this means checking other sources including ECHA's C&L Inventory (C&L 2020), REACH compliant SDS and other sources such as IARC (2020). With respect to the self-classifications for a given non-harmonized substance in the C&L Inventory, the guidance recommends assessing those hazard statements having the higher number of notifiers.

One further example of an incomplete entry (that was also not marked as Note H) is the Group Entry for barium salts mentioned above. Two Group Entries need to be reviewed:

- *barium salts, with the exception of barium sulphate, salts of 1-azo-2-hydroxynaphthalenyl aryl sulphonic acid, and of salts specified elsewhere in this Annex, and*
- *chromium (VI) compounds, with the exception of barium chromate and of compounds specified elsewhere in this Annex.*

Both would imply that you would expect barium chromate to be a harmonized entry in CLP Table 3 as all chromates are carcinogenic (threshold 0.1%, HP 7). However, barium chromate is missing from CLP Table 3 and the unwary classifier could easily use the barium salts Group Entry (threshold 22.5%, HP 6) and thus seriously misclassify their waste. Indeed, as barium salts is a Note 1 entry (i.e. you can use the total barium concentration only in the calculations; threshold 22.5%), you could actually have a barium chromate concentration of 41.5% in the waste if the Conversion Factor (1.845) for barium to barium chromate were to be applied.

7. RANKING PROTOCOL

The paper focusses primarily on the harmonized entries for simple inorganics compounds published in CLP Table 3. However, this paper's Table 3 also contains a number of extra entries from HazWasteOnline™, which are not harmonised entries. Non-harmonised entries are required to:

- help assess mixtures such as contaminated soils where non-CLP substances like chromium(III) oxide need to be managed; [they are also needed for many organic compounds such as unknown oil and several of the standard PAHs e.g. anthracene, pyrene].
- accommodate non-CLP substances that are named or implied in Group Entries, such as barium chromate.

The ranking process is quite straight forward; it is primarily based on which hazard statements a compound has and, with a few exceptions (like Note 1), on its compound concentration.

For a given metal, only the simpler inorganic compounds, published in CLP Table 3 (plus a number of non-harmonized species) have been assessed. There are many CLP compounds (such as chemical industry intermediates) that are not included in this assessment. If the classifier suspects that such a compound or a non-harmonised compound could be present in their waste, then they should add that compound to their assessment and include lines of evidence to discount the more hazardous compounds where necessary.

The exercise encountered a number of issues that required a further methodology for deciding some species' ranking. These were:

- As discussed in section 6.3, out of the thirteen Group Entries detailed in Table 3, six of them (arsenic salts, beryllium, chromium(VI), selenium, thallium and uranium) are not marked Note 1 and need a suitable Conversion Factor. Conversion Factors for other (non-harmonised) species have been documented but the classifier should adjust accordingly if they have evidence for a different species.
- Where a number of metal species (primarily for species of cadmium, cobalt and lead) are both Note 1 and have the same hazard statement (so the same threshold), the species are ordered using the following approach;
  1. For a given class e.g. carcinogenic, the higher category code is listed first – e.g. Carc. 1A; H350, before Carc. 1B; H350, and then
  2. For two or more species with the same category code e.g. Carc. 1B, the species with the higher Conversion Factor (CF) is listed first. For example, a species with a CF of 1.6 ranks higher than one with a CF of 1.5.

  Other factors that have a bearing:

- M factors[5] defined in CLP Table 3 are currently not implemented in the waste legislation, so are not considered in this paper.
- The concentration limits in the Annex III amendment (EU 2014b) do not apply to metal alloys in their massive form (assuming they are not contaminated with hazardous substances). The only exception to this rule (at the time of writing) is amalgam waste from dental care, 18 01 10*. An alloy is a mixture of two or more metallic elements, so for example, steel (17 04 05) is an alloy of iron and carbon and copper (as in pipe, 17 04 01), while a minimum of 99.9% copper, can be alloyed with up to 0.04% phosphorous. The term "massive", while not defined in the waste legislation, is generally accepted to be particles ≥ 1mm; a size used to differentiate between nickel powders in ATP 1 (EU 2009) and lead powders in ATP 9 (EU 2016). However, ATP 15 (EU 2020) recently added granulated copper to CLP Table 3 for particle lengths of 0.9 to 6.0 mm and width 0.494 to 0.949 mm.
- Whether a metal species is hazardous at a particular metal concentration is also dependent on whether a given metal concentration is reported as a dry weight or an as-received (wet weight) metal concentration. Laboratory analysis of metals (typically aqua regia extraction and ICP-OES[11]) is done on the dried material and reported in dry weight terms. Unlike the WAC assessment however, water is an integral component of the waste, so any dry weight concentrations should be converted back to their as-received equivalent before a waste classification is undertaken.
- The analysis has not considered hydrated forms where the hydrous form is not listed in CLP Table 3.

7.1 Anhydrous and hydrous forms

Out of the 204 entries in Table 3, only copper and zinc have defined entries for both the anhydrous and one or more hydrated forms. The CLP makes it clear that where the hydrated form is not present in CLP Table 3, the classifier can use the hazard statements from the anhydrous form. However, in this case, the classifier also has to apply a suitable Conversion Factor to account for one or more water molecules; a Conversion Factor that will be larger than that for the anhydrous molecule (i.e. the hydrated molecule will be hazardous at lower cation concentrations than the anhydrous molecule). If the classifier is considering a metal species that has hydrous forms (and also not listed in Table 3), then they will have to consider applying a suitable Conversion Factor.

7.2 Most characteristic metal

One other lesser known but useful fact can be discerned from the first three digits of the CLP index number in CLP Table 3. The CLP states that "*Entries in Part 3 [i.e. Table 3] are listed according to the atomic number of the element most characteristic of the properties of the substance*". So the first three digits of the index number indicate either the atomic number of the key element or if in the 600s, the organic group that is most characteristic with respect to the hazard properties. For example:

- 082-011-00-0 lead hydrogen arsenate, $\mathbf{Pb}HAsO_4$: 082 refers to lead and not arsenic
- 024-007-00-3 zinc chromate, $Zn\mathbf{Cr}0_4$: 024 refers to chromium and not zinc
- 615-017-00-4 calcium cyanamide, $Ca\mathbf{CN}_2$: 615 refers to cyanamide anion

This information has been included in Table 2 and later in Table 3, where the most characteristic element or organic group, where defined by a CLP index number, is emboldened in the chemical formula.

7.3 Metal species containing two metals

A potential conflict arrives in the listings when a species contains more than one hazardous metal, for example, lead hydrogen arsenate, selenium compounds like nickel selenite and all the chromates. Considering the chromates, should a chromate be listed under the cation (e.g. zinc for zinc chromate) or under chromium, as a given species can be hazardous by either metal but at different concentrations. Practically, this is also an important consideration for classifiers when assessing whether a particular species can be present or not.

To explore this conflict further, it is also helpful to be able to refer to the metal with the highest concentration that triggers a hazardous outcome, defined here as the primary metal (effectively the element with the largest relative atomic mass), the other(s) being referred to as the secondary metal(s). For example, 361 mg/kg of zinc, in the form of zinc chromate, would trigger HP 7 at 1,000 mg/kg. Within this total, 361 mg/kg is zinc while only 287 mg/kg is chromium (VI)[12]. Here, zinc is the primary metal, and chromium the secondary metal.

Calculating the concentration of the secondary metal (sometimes referred to as the limiting concentration) is useful because if the laboratory reports significantly[13] lower concentrations of the secondary metal, the classifier can make the case that there isn't enough chromium(VI) to make hazardous concentrations of zinc chromate and then move on to the next less worst case species.

To highlight the issues around ordering by either the cation or in the case of chromates, by chromium(VI) and to examine the distribution of the primary and secondary metals, Table 2 shows a selection of metal chromates ordered from worst case cation to less worst case; Table 2a in terms of the cation and Table 2b in terms of chromium. With one exception (lead chromate, Note 1), the tables list the relative concentrations of both the metal cation and of chromium(VI) relative to the hazardous threshold of 1,000 mg/kg for HP 7. Clearly, one table is simply the reverse of the other (Note 1 excepted) as we are dealing with the same atomic ratios.

Both the orders shown in Table 2 have their uses depending on whether you are considering the cation concentration or the concentration of chromium(VI). It is also clear that chromium is the primary metal for calcium and sodium chromate, and the dichromates, but for all the other chromates, the cation is the primary metal. So, for metals species containing two metals, knowledge about which is the primary metal doesn't help us pick one ordering system over another.

Finally determining which is the primary metal is more important where the compound is marked Note 1, such as in the case of lead chromate above or lead hydrogen arsenate, where the lead is primary and arsenic is secondary. The determination is more critical because in these cases, more of both the primary and secondary metals can be present before a hazardous threshold is reached.

7.4 Ranking protocol decision

The result of reviewing both the primary/secondary metals and the most characteristic metal confirms that there is no simple method for worst case listing by either the primary metal or the characteristic metal. In reality, workers test a) for a subset of metals, which rarely include tests for many potentially primary elements such as Ca, Na, K, S, P, O, N, Cl etc. and b) most workers see their heavy metals as the key reference point, so for example, will intuitively look at a list of zinc compounds when considering zinc and not necessarily consider the chromium in zinc chromate on the first pass.

So in this paper we have compromised and listed primarily by the cation but with a few examples of some compounds listed twice (e.g. lead hydrogen arsenate (where arsenic is secondary) or nickel selenite (where selenium is primary) to try and remind the classifier that they should consider both the primary metal and the secondary metal in their work.

Table 3 contains 32 elements and 204 metal species, listed from worst case to less worst case for each metal. For each entry, the table documents (by column number):

1. Which hazard property triggers first.
2. Whether the substance has one or more additive hazard statements (Σ).
3. Which hazard property hasn't been or can't be evaluated e.g. HP 3.
4. Which hazard statement caused the trigger.
5. The threshold concentration for that hazard statement, in %. (For reference 0.1% = 1,000 mg/kg).
6. Except for the rows highlighted in green, the name of the entry as published in CLP Table 3.
7. The molecular formula, with the characteristic element

TABLE 2: List of worst case to less worst case for the CLP Table 3 chromates ordered from worst case to less worst case. In Table 2a the order is defined by the concentration of the cation. In Table 2b the order is defined by the concentration of chromium. The primary metal for each compound is shown in red while the secondary remains in black. (Barium chromate is not a harmonised entry and is self-classified (refer Table 3).) Embolden text in the chemical formula shows most characteristic element as defined by the entry's index number in CLP Table 3.

	First HP		Triggering hazard statement	**Threshold %**
chromates				
	HP7		Carc 1A/1B; H350	0.1

Table 2a Ordered in terms of the cation

Species	**Compound Conc. mg/kg**		**↓ mg/kg**	**CF**	**mg/kg**	**CF**
		Formula	**cation**		**chromium(VI)**	
ammonium dichromate	1,000	$(NH_4)_2\mathbf{Cr}_2O_7$	143	6.987	413	2.424
sodium dichromate	1,000	$Na_2\mathbf{Cr}_2O_7$	176	5.697	397	2.519
nickel dichromate	1,000	$\mathbf{Ni}Cr_2O_7$	214	4.680	379	2.641
calcium chromate	1,000	$Ca\mathbf{Cr}O_4$	257	3.894	333	3.002
potassium dichromate	1,000	$K_2\mathbf{Cr}_2O_7$	266	3.762	353	2.829
sodium chromate	1,000	$Na_2\mathbf{Cr}O_4$	284	3.523	321	3.115
nickel chromate	1,000	$\mathbf{Ni}CrO_4$	336	2.976	298	3.360
zinc chromate	1,000	$Zn\mathbf{Cr}O_4$	361	2.774	287	3.488
potassium chromate	1,000	$K_2\mathbf{Cr}O_4$	403	2.483	268	3.735
strontium chromate	1,000	$Sr\mathbf{Cr}O_4$	430	2.324	255	3.916
barium chromate	1,000	$BaCrO_4$	543	1.845	205	4.872
lead chromate	1,000	$\mathbf{Pb}CrO_4$	641	1.560	161	6.216
lead chromate (Note 1)	1,560	$\mathbf{Pb}$	1,000	1.000	251	6.216

Table 2b Ordered in terms of chromium

Species	**Compound Conc. mg/kg**		**mg/kg**	**CF**	**↓ mg/kg**	**CF**
		Formula	**cation**		**chromium(VI)**	
lead chromate	1,000	$\mathbf{Pb}CrO_4$	641	1.560	161	6.216
barium chromate	1,000	$BaCrO_4$	543	1.845	205	4.872
lead chromate (Note 1)	1,560	$\mathbf{Pb}$	1,000	1.000	251	6.216
strontium chromate	1,000	$Sr\mathbf{Cr}O_4$	430	2.324	255	3.916
potassium chromate	1,000	$K_2\mathbf{Cr}O_4$	403	2.483	268	3.735
zinc chromate	1,000	$Zn\mathbf{Cr}O_4$	361	2.774	287	3.488
nickel chromate	1,000	$\mathbf{Ni}CrO_4$	336	2.976	298	3.360
sodium chromate	1,000	$Na_2\mathbf{Cr}O_4$	284	3.523	321	3.115
calcium chromate	1,000	$Ca\mathbf{Cr}O_4$	257	3.894	333	3.002
potassium dichromate	1,000	$K_2\mathbf{Cr}_2O_7$	266	3.762	353	2.829
nickel dichromate	1,000	$\mathbf{Ni}Cr_2O_7$	214	4.680	379	2.641
sodium dichromate	1,000	$Na_2\mathbf{Cr}_2O_7$	176	5.697	397	2.519
ammonium dichromate	1,000	$(NH_4)_2\mathbf{Cr}_2O_7$	143	6.987	413	2.424

shown in bold and where applicable, Note 1 shown to indicate that the metal concentration should be used in the calculations.

8. The substance's CAS registry number.
9. The concentration of the metal in mg/kg, required to trigger the hazardous outcome.
10. The conversion factor[14].

It is also interesting to note that of the 204 species in Table 3, the vast majority (94%) are additive, having one or more additive hazard statements. The remaining 6% are dominated by entries with only a single (non-additive) hazard statement.

8. EXAMPLE: WORKING FROM WORST CASE TO LESS WORST CASE

So the next critical question is how does the classifier work from worst case to a more reasonable case. The guidance advises the use of lines of evidence to achieve this.

TABLE 3: List of worst case to less worst case metal species, grouped by element, listed worst case to less worst case.

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
Al 013	HP 6	Σ		Acute Tox.1; H330 [A, B]	0.1	aluminium phosphide	$\mathrm{Al}\mathbf{P}$	20859-73-8	466	2.148
	HP 3		HP3(ii)	Water-react. 2; H261 [A]	0.1	aluminium powder	$\mathbf{Al}$	7429-90-5	1000	1.000
	HP 8	Σ		Skin Corr. 1B; H314	5.0	aluminium chloride	$\mathbf{Al}\mathrm{Cl}_3$	7446-70-0	10,118	4.942
Sb 051	HP 7			Carc. 2; H351	1.0	antimony trioxide	$\mathbf{Sb}_2\mathrm{O}_3$	1309-64-4	8,354	1.197
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	antimony pentachloride	$\mathbf{Sb}\mathrm{Cl}_5$	7647-18-9	10,180	2.456
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	antimony trichloride	$\mathbf{Sb}\mathrm{Cl}_3$	10025-91-9	13,344	1.874
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	antimony trifluoride	$\mathbf{Sb}\mathrm{F}_3$	7783-56-4	17,029	1.468
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	antimony compounds with the exception of tetroxide ...	**Sb** (Note 1)	-	25,000	1.000
As 033	HP 7	Σ		Carc. 1A; H350	0.1	lead hydrogen arsenate	$\mathbf{Pb}\mathrm{HAs0}_4$ (Note 1)	7784-40-9	see lead	
	HP 7	Σ		Carc. 1A; H350	0.1	arsenic acid and its salts with the exception of those ...	as $\mathrm{H}_3\mathbf{As}\mathrm{O}_4$	-	528	1.895
	HP 7	Σ		Carc. 1A; H350	0.1	arsenic pentoxide	$\mathbf{As}_2\mathrm{O}_5$	1303-28-2	652	1.534
	HP 7	Σ		Carc. 1A; H350	0.1	arsenic trioxide	$\mathbf{As}_2\mathrm{O}_3$	1327-53-3	758	1.320
	HP 7	Σ		Carc. 1A; H350 [C]	0.1	arsenic	$\mathbf{As}$	7440-38-2	1000	1.000
	HP 7	Σ		Carc. 1A; H350 [C]	0.1	arsenic compounds, with the exception of those ...	**As** (Note 1)	-	1000	1.000
Ba 056	HP 7	Σ	HP 2	Carc. 1B; H350	0.1	barium chromate [F]	$\mathbf{Ba}\mathrm{Cr0}_4$	10294-40-3	543	1.845
	HP 12	Σ		EUH031 [B]	0.8	barium sulphide	$\mathrm{Ba}\mathbf{S}$	21109-95-5	6,486	1.233
	HP 14	Σ	HP 2	Aquatic Chronic 2; H411	2.5	barium chlorate	$\mathrm{Ba}(\mathbf{Cl}\mathrm{O}_3)_2$	13477-00-4	11,285	2.215
	HP 6	Σ		Acute Tox. 3; H301	5.0	barium chloride	$\mathbf{Ba}\mathrm{Cl}_2$	10361-37-2	32,975	1.516
	HP 6 HP 8	Σ		Acute Tox. 3; H301 Skin Corr. 1B; H314	5.0	barium oxide [G]	$\mathbf{Ba}\mathrm{O}$	1304-28-5	44,783	1.117
	HP 6	Σ		Acute Tox 4; H302	25.0	barium carbonate	BaCO_3	513-77-9	173,977	1.437
	HP 6	Σ		Acute Tox 4; H332	22.5	barium salts, with the exception of barium sulphate, and those ...	**Ba** (Note 1)	-	225,000	1.000
	-	-		-	-	barium sulfate [H]	BaSO_4	7727-43-7	-	1.700
Be 004	HP 7	Σ		Carc. 1B; H350 [D]	0.1	aluminium beryllium silicates	as $\mathrm{Al}_2\mathrm{Be}_3\mathrm{Si}_6\mathrm{O}_{18}$ as $\mathrm{Al}_2\mathrm{Be}_2\mathrm{Si}_5\mathrm{O}_{15}$	1302-52-9 37220-37-4	51 40	19.880 25.099
	HP 7	Σ		Carc. 1B; H350	0.1	beryllium chloride [I]	BeCl_2	7787-47-5	113	8.868
	HP 7	Σ		Carc. 1B; H350	0.1	beryllium compounds with the exception of aluminium beryllium silicates, and those ...	**Be** as BeCl_2 as $\mathrm{Be(OH)}_2$	-	113 210	8.868 4.774
	HP 7	Σ		Carc. 1B; H350	0.1	beryllium oxide	$\mathbf{Be}\mathrm{O}$	1304-56-9	361	2.775
	HP 7	Σ		Carc. 1B; H350	0.1	beryllium	$\mathbf{Be}$	7440-41-7	1,000	1.000
B 005	HP 6	Σ		Acute Tox. 2; H300	0.25	boron tribromide	$\mathbf{B}\mathrm{Br}_3$	10294-33-4	108	23.173
	HP 6	Σ		Acute Tox. 2; H300	0.25	boron trichloride	$\mathbf{B}\mathrm{Cl}_3$	10294-34-5	231	10.838
	HP 10			Repr. 1B; H360	0.3	boric acid	$\mathrm{H}_3\mathbf{B}\mathrm{O}_3$	10043-35-3 11113-50-1	525	5.719
	HP 6	Σ		Acute Tox. 2; H330	0.5	boron trifluoride	$\mathbf{B}\mathrm{F}_3$	7637-07-2	798	6.272
	HP 10			Repr. 1B; H360	0.3	diboron trioxide; boric oxide	$\mathbf{B}_2\mathrm{O}_3$	1303-86-2	932	3.220
Cd 048	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium sulphate	$\mathbf{Cd}\mathrm{SO}_4$	10124-36-4	540	1.855
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium chloride	$\mathbf{Cd}\mathrm{Cl}_2$	10108-64-2	614	1.631

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium fluoride	CdF_2	7790-79-6	748	1.338
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	cadmium iodide	CdI_2	7790-80-9	768	3.258
	HP 7	Σ		Carc. 1B; H350	0.1	cadmium oxide	CdO	1306-19-0	876	1.142
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium nitrate	$Cd(NO_3)_2$ (Note 1)	10325-94-7	1,000	2.103
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium carbonate	$\mathbf{Cd}CO_3$ (Note 1)	513-78-0	1,000	1.534
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	cadmium hydroxide	$\mathbf{Cd}(OH)_2$ (Note 1)	21041-95-2	1,000	1.303
	HP 7	Σ		Carc. 1B; H350	0.1	cadmium sulfide	$\mathbf{Cd}S$ (Note 1)	1306-23-6	1,000	1.285
	HP 7	Σ	HP 3	Carc. 1B; H350	0.1	cadmium	$\mathbf{Cd}$	7440-43-9	1,000	1.000
	HP 7	Σ		Carc. 1B; H350 ^{D}	0.1	cadmium compounds with the exception of cadmium sulphoselenide… and …	$\mathbf{Cd}$ (Note 1)	-	1,000	1.000
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	cadmium hexafluorosilicate	$\mathbf{Cd}F_6Si$	17010-21-8	1,105	2.264
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	cadmium diformate	$\mathbf{Cd}C_2H_2O_4$	4464-23-7	1,389	1.801
	HP 6 HP 14	Σ		Acute Tox. 2; H300 Acute Tox. 1; H310 Aquatic Chronic 1; H410	0.25	cadmium cyanide	$\mathbf{Cd}(CN)_2$	542-83-6	1,709	1.463
	HP 4 HP 5	Σ		Skin Irrit. 2; H315 STOT SE 3; H335	20.0	cadmium sulfoselenide red ^{E}	$\mathbf{Cd}_2SSe$	58339-34-7	133,869	1.494
Ca 020	HP 7	Σ		Carc. 1B; H350	0.1	calcium chromate	$Ca\mathbf{Cr}O_4$	13765-19-0	257	3.894
	HP 6	Σ	HP 12	Acute Tox. 1; H330	0.1	calcium phosphide	$Ca_3\mathbf{P}_2$	1305-99-3	660	1.515
	HP 12	Σ		EUH032 ^{B}	0.2	calcium cyanide	$\mathbf{Ca}(CN)_2$	592-01-8	871	2.298
	HP 3			Water-react. 1; H260 ^{A}	0.1	calcium hydride	$Ca\mathbf{H}_2$	7789-78-8	953	1.050
	HP 12	Σ		EUH031 ^{B}	0.3	calcium sulphide	$Ca\mathbf{S}$	20548-54-3	1,667	1.800
	HP 12	Σ	HP 2	EUH031 ^{B}	0.6	calcium hypochlorite	$Ca(O\mathbf{Cl})_2$	7778-54-3	1,682	3.568
	HP 3			Water-react. 1; H260 ^{A}	0.3	calcium carbide	$Ca\mathbf{C}_2$	75-20-7	1,876	1.599
	HP 3			Water-react. 2; H261 ^{A}	0.2	calcium	$\mathbf{Ca}$	7440-70-2	2,000	1.000
	HP 4	Σ		Eye Dam. 1; H318	10.0	calcium cyanamide	$Ca\mathbf{CN}_2$	156-62-7	50,034	1.999
	HP 4	Σ		Eye Dam. 1; H318	10.0	calcium hydroxide ^{J}	$Ca(OH)_2$	1305-62-0	54,094	1.849
	HP 4	Σ		Eye Dam. 1; H318	10.0	calcium oxide ^{K}	CaO	1305-78-8	71,470	1.399
	HP4	Σ		Eye Irrit. 2; H319	20.0	calcium chloride	$Ca\mathbf{Cl}_2$	10043-52-4	72,224	2.769
Cr 024	HP 7 HP 11	Σ	HP 2	Carc. 1B; H350 Muta. 1B; H340	0.1	ammonium dichromate	$(NH_4)_2\mathbf{Cr}_2O_7$	7789-09-5	143	6.987
	HP 7	Σ		Carc. 1B; H350	0.1	chromium(VI) compounds, with the exception of barium chromate and …	$\mathbf{Cr}$ as H_2CrO_4	-	441	2.270
	HP 7 HP 11	Σ	HP 2	Carc. 1A; H350 Muta. 1B; H340	0.1	chromium(VI) oxide	$\mathbf{Cr}O_3$	1333-82-0	520	1.923
	HP 13	Σ		Skin Sens. 1; H317	10.0	chromium(III) oxide ^{E}	Cr_2O_3	1308-38-9	68,421	1.462
Co 027	HP 7	Σ		Carc. 1B; H350	0.1	cobalt dinitrate	$\mathbf{Co}(NO_2)_2$ (Note 1)	10141-05-6	1,000	3.104
	HP 7	Σ		Carc. 1B; H350	0.1	cobalt di(acetate)	$\mathbf{Co}(C_2H_3O_2)_2$ (Note 1)	71-48-7	1,000	3.004
	HP 7	Σ		Carc. 1B; H350	0.1	cobalt sulfate	$\mathbf{Co}S0_4$ (Note 1)	10124-43-3	1,000	2.630
	HP 7	Σ		Carc. 1B; H350	0.1	cobalt dichloride	$\mathbf{Co}Cl_2$ (Note 1)	7646-79-9	1,000	2.203

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
	HP 7	Σ		Carc. 1B; H350	0.1	cobalt carbonate	$\mathbf{Co}CO_3$ (Note 1)	513-79-1	1,000	2.018
	HP 7	Σ		Carc. 1B; H350	0.1	cobalt	$\mathbf{Co}$	7440-48-4	1,000	1.000
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	cobalt sulfide	$\mathbf{Co}S$	1317-42-6	1,620	1.544
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	cobalt oxide	$\mathbf{Co}O$	1307-96-6	1,967	1.271
Cu 029	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper sulphate pentahydrate	$\mathbf{Cu}SO_4.5H_2O$	7758-99-8	637	3.929
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(II) chloride dihydrate [L]	$CuCl_2.2H_2O$	10125-13-0	932	2.683
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper sulphate	$\mathbf{Cu}SO_4$	7758-98-7	996	2.512
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(II) chloride [M]	$CuCl_2$	7447-39-4	1,182	2.116
	HP 14	Σ	HP 12	Aquatic Chronic 1; H410	0.25	copper thiocyanate	$\mathbf{Cu}SCN$	1111-67-7	1,307	1.914
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	tetracopper hexahydroxide sulphate	$\mathbf{Cu}_4(OH)_6SO_4$	1333-22-8	1,405	1.779
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(II) carbonate - copper(II) hydroxide (1:1)	$\mathbf{Cu}CO_3{\cdot}Cu(OH)_2$	12069-69-1	1,437	1.740
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	dicopper chloride trihydroxide	$\mathbf{Cu}_2(OH)_3Cl$	1332-65-6	1,488	1.680
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(I) chloride	$\mathbf{Cu}Cl$	7758-89-6	1,605	1.558
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(II) hydroxide	$\mathbf{Cu}(OH)2$	20427-59-2	1,629	1.535
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(II) oxide	$\mathbf{Cu}O$	1317-38-0	1,998	1.252
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	copper(I) oxide	$\mathbf{Cu}_2O$	1317-39-1	2,221	1.126
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	granulated copper	$\mathbf{Cu}$	7440-50-8	25,000	1.000
Fe 026	HP 4	Σ		Skin Irrit. 2; H315 Eye Irrit. 2; H319	20.0	iron(II) sulfate heptahydrate	$\mathbf{Fe}SO_4.7H_2O$	7782-63-0	40,177	4.978
	HP 4	Σ		Skin Irrit. 2; H315 Eye Irrit. 2; H319	20.0	iron(II) sulfate	$\mathbf{Fe}SO_4$	7720-78-7	73,525	2.72
Pb 082	HP 7	Σ		Carc. 1A; H350	0.1	lead hydrogen arsenate	$\mathbf{Pb}HAs0_4$ (Note 1)	7784-40-9	1,000	1.675
	HP 7	Σ		Carc. 1B; H350	0.1	lead chromate molybdate sulfate; C.I. Pigment Red 104	$\mathbf{Pb}CrO_4$, $\mathbf{Pb}MoO_4$, $\mathbf{Pb}SO_4$ (Note 1)	12656-85-8	1,000	1.560
	HP 7	Σ		Carc. 1B; H350	0.1	lead chromate	$\mathbf{Pb}CrO_4$ (Note 1)	7758-97-6	1,000	1.560
	HP 7	Σ		Carc. 1B; H350	0.1	lead sulfochromate; C.I. Pigment Yellow 34	$\mathbf{Pb}CrO_4$, $\mathbf{Pb}SO_4$ (Note 1)	1344-37-2	1,000	1.511
	HP 7	Σ		Carc. 1B; H350	0.1	lead compounds with the exception of … (worst case) [N]	$\mathbf{Pb}$ (Note 1)	-	1,000	1.000
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	lead di(acetate) [N]	$\mathbf{Pb}(C_2H_3O_2)_2$ (Note1)	301-04-2	2,500	1.570
	HP 14	Σ	HP 1	Aquatic Chronic 1; H410	0.25	lead azide [N]	$\mathbf{Pb}(N_3)_2$ (Note 1)	13424-46-9	2,500	1.406
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	trilead bis(orthophosphate) [N]	$\mathbf{Pb}_3(PO_4)_2$ (Note 1)	7446-27-7	2,500	1.306
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	lead compounds with the exception of those … [N]	$\mathbf{Pb}$ (Note 1)	-	2,500	1.000
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	lead powder; <1mm [O]	$\mathbf{Pb}$	7439-92-1	2,500	1.000
	HP 10			Repr. 1A; H360	0.30	lead powder; ≥1mm	$\mathbf{Pb}$	7439-92-1	3,000	1.000
Li 003	HP 7	Σ		Carc. 1A; H350	0.1	cobalt lithium nickel oxide	$Li\mathbf{Ni}_{0.8}Co_{0.2}O_2$ [P]	-	72	14.066
	HP 3	Σ		Water-react. 1; H260 [A]	0.1	aluminium lithium hydride	$LiAl\mathbf{H}_4$	16853-85-3	183	5.469
	HP 3	Σ		Water-react. 1; H260 [A]	0.1	lithium	$\mathbf{Li}$	7439-93-2	1,000	1.000
Mg 012	HP 6	Σ		Acute Tox. 1; H330	0.1	magnesium phosphide	$Mg_3\mathbf{P}_2$	12057-74-8	541	1.850
	HP 3		HP3(ii)	Water-react. 1; H260 [A]	0.1	magnesium	$\mathbf{Mg}$	7439-95-4	1,000	1.000

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
	HP 3		HP3(iii)	Water-react. 2; H261 [A]	0.1	magnesium, powder or turnings	$\mathbf{Mg}$	7439-95-4	1,000	1.000
	HP 6	Σ		Acute Tox. 3; H301	5.0	magnesium hexafluorosilicate	$MgSi\mathbf{F}_6$	16949-65-8	7,305	6.845
Mn 025	HP 14		HP 2	Aquatic Chronic 1; H410	0.25	potassium permanganate	$K\mathbf{Mn}O_4$	7722-64-7	869	2.877
	HP 14	Σ		Aquatic Chronic 2; H411	2.50	manganese sulphate	$\mathbf{Mn}SO_4$	7785-87-7	9,096	2.749
	HP 14	Σ		Aquatic Chronic 1; H411	2.50	manganese(II) chloride [Q]	$MnCl_2$	7773-01-5	10,914	2.291
	HP 6	Σ		Acute Tox. 4; H332	22.5	manganese dioxide	$\mathbf{Mn}O_2$	1313-13-9	142,185	1.582
Hg 080	HP 14	Σ	HP 1	Aquatic Chronic 1; H410	0.25	mercury difulminate	$\mathbf{Hg}(CNO)_2$	628-86-4	1,762	1.419
	HP 14 HP 6	Σ		Aquatic Chronic 1; H410 Acute Tox. 2*; H300 [R]	0.25	mercury dichloride	$\mathbf{Hg}Cl_2$	7487-94-7	1,848	1.353
	HP 14 HP 6	Σ		Aquatic Chronic 1; H410 Acute Tox. 2*; H300 Acute Tox. 1; H310	0.25	inorganic compounds of mercury with the exception of mercuric sulphide and....	$\mathbf{Hg}$ (Note 1)	-	2,500	1.000
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	mercury	$\mathbf{Hg}$	7439-97-6	2,500	1.000
	HP 12			EUH031 [B]	1.0	mercury(II) sulphide [S]	HgS	1344-48-5	8,622	1.160
Mo 042	HP 7	Σ		Carc. 1B; H350	0.1	lead chromate molybdate sulfate C.I. Pigment Red 104	$\mathbf{Pb}CrO_4$, $\mathbf{Pb}MoO_4$, $\mathbf{Pb}SO_4$ (Note 1)	12656-85-8	see lead	
	HP 7	Σ		Carc. 2; H351	1.0	molybdenum trioxide	$\mathbf{Mo}O_3$	1313-27-5	6,666	1.500
Ni 028	HP 7	Σ		Carc. 1A; H350	0.1	nickel diiodide	$\mathbf{Ni}I_2$	13462-90-3	188	5.324
	HP 7	Σ		Carc. 1A; H350	0.1	nickel dichromate	$\mathbf{Ni}Cr_2O_7$	15586-38-6	214	4.680
	HP 7	Σ		Carc. 1A; H350	0.1	nickel dibromide	$\mathbf{Ni}Br_2$	13462-88-9	269	3.723
	HP 7	Σ		Carc. 1A; H350	0.1	nickel selenate	$\mathbf{Ni}SeO_4$	15060-62-5	see selenium	
	HP 7	Σ		Carc. 1A; H350	0.1	nickel(II) selenite	$\mathbf{Ni}SeO_3$	10101-96-9	see selenium	
	HP 7	Σ	HP 12	Carc. 1A; H350	0.1	nickel dithiocyanate	$\mathbf{Ni}(SCN)_2$	13689-92-4	336	2.979
	HP 7	Σ		Carc. 1A; H350	0.1	nickel chromate	$\mathbf{Ni}CrO_4$	14721-18-7	336	2.976
	HP 7	Σ		Carc. 1A; H350	0.1	nickel hexacyanoferrate	$\mathbf{Ni}_2Fe(CN)_6$	14874-78-3	357	2.806
	HP 7	Σ		Carc. 1A; H350	0.1	nickel sulfate	$\mathbf{Ni}SO_4$	7786-81-4	380	2.637
	HP 7	Σ		Carc. 1A; H350	0.1	nickel selenide	$\mathbf{Ni}Se$	1314-05-2	see selenium	
	HP 7	Σ		Carc. 1A; H350	0.1	nickel dichloride	$\mathbf{Ni}Cl_2$	7718-54-9	453	2.208
	HP 7	Σ		Carc. 1A; H350	0.1	nickel(II) carbonate	$\mathbf{Ni}CO_3$	3333-67-3	495	2.022
	HP 7	Σ	HP 12	Carc. 1A; H350	0.1	nickel dicyanide	$\mathbf{Ni}(CN)_2$	557-19-7	531	1.887
	HP 7	Σ		Carc. 1A; H350	0.1	nickel difluoride	$\mathbf{Ni}F_2$	10028-18-9	608	1.647
	HP 7	Σ		Carc. 1A; H350	0.1	nickel dihydroxide	$\mathbf{Ni}(OH)_2$	12054-48-7 11113-74-9	634	1.579
	HP 7	Σ		Carc. 1A; H350	0.1	nickel sulphide	$\mathbf{Ni}S$	16812-54-7	647	1.546
	HP 7	Σ		Carc. 1A; H350	0.1	nickel dioxide; nickel(IV) oxide;	$\mathbf{Ni}O_2$	12035-36-8	648	1.545
	HP 7	Σ		Carc. 1A; H350	0.1	dinickel trioxide	$\mathbf{Ni}_2O_3$	1314-06-3	710	1.409
	HP 7	Σ		Carc. 1A; H350	0.1	nickel monoxide; nickel(II) oxide	$\mathbf{Ni}O$	1313-99-1	786	1.273
	HP 7 HP 5	Σ		Carc. 2; H351 STOT RE 1; H372	1.0	nickel	$\mathbf{Ni}$	7440-02-0	10,000	1.000
K 019	HP 7	Σ	HP 2	Carc. 1B; H350	0.1	potassium bromate	$K\mathbf{Br}O_3$	7758-01-2	235	4.271
	HP 7 HP 11	Σ	HP 2	Carc. 1B; H350 Muta. 1B; H340	0.1	potassium dichromate	$K_2\mathbf{Cr}_2O_7$	7778-50-9	266	3.762
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	potassium chromate	$K_2\mathbf{Cr}O_4$	7789-00-6	403	2.483
	HP 14	Σ	HP 2	Aquatic Chronic 1; H410	0.25	potassium permanganate	$K\mathbf{Mn}O_4$	7722-64-7	see manganese	

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
	HP 12	Σ		EUH031 [B]	0.5	potassium sulphide	K_2S	1312-73-8	3,546	1.410
	HP 3	Σ		Water-react. 1; H260 [A]	0.4	potassium	K	7440-09-7	4,000	1.000
	HP 4	Σ		Skin Corr. 1A; H314	1.0	potassium hydroxide	KOH	1310-58-3	6,969	1.435
	HP 14	Σ	HP 2	Aquatic Chronic 2; H411	2.5	potassium chlorate	$KClO_3$	3811-04-9	7,977	3.134
	HP 8	Σ		Skin Corr. 1B; H314	5.0	potassium hydrogen sulphate	$KHSO_4$	7646-93-7	14,357	3.483
	HP 6	Σ	HP 2	Acute Tox. 3; H301	5.0	potassium nitrite	KNO_2	7758-09-0	22,971	2.177
	HP 6	Σ		Acute Tox. 3; H331	3.5	potassium fluoride	KF	7789-23-3	23,555	1.486
	HP 6 HP 8	Σ		Acute Tox. 3; H301 Skin Corr. 1B; H314	5.0	potassium bifluoride	KHF_2	7789-29-9	25,031	1.998
	HP 6	Σ	HP 2	Acute Tox. 4; H302	25.0	potassium perchlorate	$KClO_4$	7778-74-7	70,550	3.544
	HP 6	Σ		Acute Tox. 4; H302	25.0	potassium cyanate	$KCNO$	590-28-3	120,503	2.075
P 015	HP 12	Σ	HP 3	EUH029 [B]	0.1	phosphorus pentasulfide	P_2S_5	1314-80-3	279	3.588
	HP 6	Σ	HP 12	Acute Tox. 2; H300	0.25	phosphorous trichloride	PCl_3	7719-12-2	564	4.434
	HP 6	Σ	HP 12	Acute Tox. 2; H330	0.5	phosphorous pentachloride	PCl_5	10026-13-8	744	6.723
	HP 6	Σ	HP 12	Acute Tox. 2; H330	0.5	phosphoryl trichloride	$POCl_3$	10025-87-3	1,011	4.950
	HP 6	Σ	HP 3	Acute Tox. 2; H300	0.25	white phosphorous	P_4	12185-10-3	2,500	1.000
	HP 4	Σ		Skin Corr. 1A; H314	1.0	phosphonic acid; phosphorous acid	H_3PO_3	13598-36-2 10294-56-1	3,778	2.647
	HP 4	Σ		Skin Corr. 1A; H314	1.0	phosphorous pentoxide	P_4O_{10}	1314-56-3	4,365	2.291
	HP 6	Σ	HP 3	Acute Tox. 2; H330	0.5	phosphine	PH_3	7803-51-2	4,556	1.098
	HP 8	Σ		Skin Corr. 1B; H314	5.0	phosphorous tribromide	PBr_3	7789-60-8	5,722	8.739
	HP 8	Σ		Skin Corr. 1B; H314	5.0	phosphoric acid	H_3PO_4	7664-38-2	15,804	3.164
	HP 6 HP 14	Σ	HP 3	Acute Tox. 4; H302 Aquatic Acute 1; H400	25.0	tetraphosphorus trisulphide; phosphorus sesquisulphide	P_4S_3	1314-85-8	140,731	1.776
	HP 14	Σ	HP 3	Aquatic Chronic 3; H412	25.0	red phosphorous	P	7723-14-0	250,000	1.000
Se 034	HP 7	Σ		Carc. 1A; H350	0.1	nickel selenate	$NiSeO_4$	15060-62-5	392	2.554
	HP 7	Σ		Carc. 1A; H350	0.1	nickel(II) selenite	$NiSeO_3$	10101-96-9	425	2.351
	HP 7	Σ		Carc. 1A; H350	0.1	nickel selenide	$NiSe$	1314-05-2	574	1.743
	HP 6	Σ	HP 12	Acute Tox. 2; H300	0.25	sodium selenite	Na_2SeO_3	10102-18-8	1,142	2.190
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	selenium compounds with the exception of those …	Se as SeO_2	-	1,779	1.405
	HP 6	Σ		Acute Tox. 3; H331	3.5	selenium	Se	7782-49-2	35,000	1.000
Ag 047	HP 14	Σ	HP 2	Aquatic Chronic 1; H410	0.25	silver nitrate	$AgNO_3$	7761-88-8	1,588	1.575
Na 011	HP 7 HP 11	Σ	HP 2	Carc. 1B; H350 Muta. 1B; H340	0.1	sodium dichromate	$Na_2Cr_2O_7$	10588-01-9	176	5.698
	HP 7 HP 11	Σ		Carc. 1B; H350 Muta. 1B; H340	0.1	sodium chromate	Na_2CrO_4	7775-11-3	284	3.523
	HP 6	Σ		Acute Tox. 2; H300 Acute Tox. 1; H310	0.25	sodium fluoroacetate	$NaFCH_2CO_2$	62-74-8	575	4.351
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	sodium hypochlorite	$NaClO$	7681-52-9	773	3.238
	HP 3			Water-react. 1; H260 [A]	0.1	sodium hydride	NaH	7646-69-7	959	1.044
	HP 12	Σ		EUH032 [B]	0.2	sodium fluoride	NaF	7681-49-4	1,096	1.826
	HP 3	Σ		Water-react. 1; H260 [A]	0.2	sodium	Na	7440-23-5	2,000	1.000
	HP 12	Σ	HP 3	EUH031 [B]	0.9	sodium dithionite; sodium hydrosulphite	$Na_2S_2O_4$	7775-14-6	2,377	3.787
	HP 14	Σ	HP 2	Aquatic Chronic 2; H411	2.5	sodium chlorate	$NaClO_3$	7775-09-9	5,400	4.630
	HP 4	Σ		Skin Corr. 1A; H314	1.0	sodium hydroxide; caustic soda	$NaOH$	1310-73-2	5,748	1.740
	HP 4	Σ	HP 2	Skin Corr. 1A; H314	1.0	sodium peroxide	Na_2O_2	1313-60-6	5,897	1.696

Metal	First HP	Additive	HP not evaluated	Triggering hazard statement	Thresh-old %	Metal species / CLP entry	Molecular formula	CAS No. of CLP entry	Conc. limit of metal mg/kg	Conver. Factor (CF)
	HP 6	Σ	HP 2	Acute Tox. 3; H301	5.0	sodium nitrite	$\mathrm{Na}\mathbf{N}\mathrm{O}_2$	7632-00-0	16,661	3.001
	HP 4	Σ		Eye Dam. 1; H318	10.0	sodium hydrogensulphate	$\mathrm{NaH}\mathbf{S}\mathrm{O}_3$	7631-90-5	19,149	5.222
	HP 4	Σ	HP 12	Eye Dam. 1; H318	10.0	sodium metabisulphite	$\mathrm{Na}_2\mathbf{S}_2\mathrm{O}_5$	7681-57-4	24,186	4.135
	HP 6	Σ	HP 12	Acute Tox. 4; H302	25.0	sodium hydrogensulphite … %; sodium bisulphite … %	$\mathrm{NaH}\mathbf{S}\mathrm{O}_3$	7631-90-5	55,231	4.526
	HP 6	Σ	HP 2	Acute Tox. 4; H302	25.0	sodium perchlorate	$\mathrm{Na}\mathbf{Cl}\mathrm{O}_4$	7601-89-0	77,206	3.238
Sr 038	HP 7	Σ		Carc. 1B; H350	0.1	strontium chromate	$\mathrm{Sr}\mathbf{Cr}\mathrm{O}_4$	7789-06-2	431	2.324
S 016	HP 8	Σ		Skin Corr. 1B; H314	5.0	sulphur dichloride	$\mathbf{S}\mathrm{Cl}_2$	10545-99-0	15,570	3.211
	HP 6	Σ		Acute Tox. 3; H331	3.5	sulphur dioxide	$\mathbf{S}\mathrm{O}_2$	7446-09-5	17,519	1.998
	HP 4	Σ		Skin Irrit. 2; H315	20.0	sulfur	$\mathbf{S}$	7704-34-9	200,000	1.000
Tl 081	HP 7	Σ		Carc. 1A; H350	0.1	thallium compounds with the exception of those …	**Tl** as $\mathrm{Tl}_2\mathrm{CrO}_4$ as $\mathrm{Tl}_2\mathrm{O}_3$	-	779 895	1.284 1.117
	HP 6	Σ		Acute Tox. 2; H300	0.25	thallium thiocyanate	$\mathrm{Tl}\mathbf{SCN}$	3535-84-0	1,947	1.284
	HP 6	Σ		Acute Tox. 2; H300	0.25	dithallium sulphate; thallic sulphate	$\mathbf{Tl}_2\mathrm{SO}_4$	7446-18-6	2,025	1.235
	HP 6	Σ		Acute Tox. 2; H300	0.25	thallium	$\mathbf{Tl}$	7440-28-0	2,500	1.000
Ti 022	HP 7			Carc. 2; H351	1.0	titanium dioxide	$\mathbf{Ti}\mathrm{O}_2$	13463-67-7	5,994	1.668
	HP 8	Σ		Skin Corr. 1B; H314	5.0	titanium tetrachloride	$\mathbf{Ti}\mathrm{Cl}_4$	7550-45-0	12,618	3.963
Sn 050	HP 14	Σ		Aquatic Chronic 1; H410	0.25	tributyltin compounds with the exception of those …	$\mathbf{Sn}(\mathrm{C}_4\mathrm{H}_9)_3$ (Note 1)	-	2,500	1.000
	HP 14	Σ		Aquatic Chronic 2; H411	2.5	tin(II) methanesulphonate	$\mathbf{Sn}(\mathrm{CH}_3\mathrm{SO}_3)_2$	53408-94-9	9,608	2.602
	HP 8	Σ		Skin Corr. 1B; H314	5.0	tin tetrachloride; stannic chloride	$\mathbf{Sn}\mathrm{Cl}_4$	7646-78-8	22,784	2.195
U 092	HP 7			Carc. 1A; H350	0.1	nickel triuranium decaoxide	$\mathbf{Ni}\mathrm{U}_3\mathrm{O}_{10}$	15780-33-3	766	1.306
	HP 6	Σ		Acute Tox. 2; H300	0.25	uranium compounds with the exception of those …	**U** as UO_2	-	2,204	1.134
	HP 6	Σ		Acute Tox. 2; H300	0.25	uranium	$\mathbf{U}$	7440-61-1	2,500	1.000
V 023	HP 5 HP 11	Σ		STOT RE 1; H372 Muta. 2; H341	1.0	vanadium pentoxide	$\mathbf{V}_2\mathrm{O}_5$	1314-62-1	5,602	1.785
Zn 030	HP 7	Σ		Carc. 1A; H350	0.1	zinc chromate	$\mathrm{Zn}\mathbf{Cr}\mathrm{O}_4$	13530-65-9	361	2.774
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	zinc sulphate heptahydrate ^{T}	$\mathbf{Zn}\mathrm{SO}_4.7\mathrm{H}_2\mathrm{O}$	7446-20-0	568	4.398
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	zinc sulphate monohydrate ^{T}	$\mathbf{Zn}\mathrm{SO}_4.1\mathrm{H}_2\mathrm{O}$	7446-19-7	911	2.745
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	zinc sulphate (anhydrous) ^{T}	$\mathbf{Zn}\mathrm{SO}_4$	7733-02-0	1,013	2.469
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	zinc chloride	$\mathbf{Zn}\mathrm{Cl}_2$	7646-85-7	1,200	2.085
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	trizinc bis(orthophosphate)	$\mathbf{Zn}_3(\mathrm{PO}_4)_2$	7779-90-0	1,271	1.968
	HP 14 HP 6	Σ Σ		Aquatic Chronic 1; H410 Acute Tox. 2; H300	0.25	trizinc diphosphide; zinc phosphide	$\mathrm{Zn}_3\mathbf{P}_2$	1314-84-7	1,900	1.316
	HP 14	Σ		Aquatic Chronic 1; H410	0.25	zinc oxide	$\mathbf{Zn}\mathrm{O}$	1314-13-2	2,009	1.245
	HP 14	Σ	HP 3	Aquatic Chronic 1; H410	0.25	zinc powder	$\mathbf{Zn}$	7440-66-6	2,500	1.000

Key

🟩 Substance not in CLP - data source(s) in footnote: self-classification

🟥 Modified CLP substance – explanation in footnote

General Notes

1. Tables 2 and 3 were compiled in autumn 2020. Moving forwards, knowledge about substances changes and therefore both the ranking and the triggering hazard property published in these tables may change as updated information is published, either through ATPs or through self-classifications that find evidence for missing hazard classes.
2. The CLP hasn't been consistent in its naming conventions; so for example, sulfate and sulphate are both in common usage in the data set. The use of oxidation numbers is also inconsistent e.g. and copper sulphate and copper(II) oxide.
3. While sulfur (S) has been speciated, typically the laboratory concentration a classifier receives reflects the sulfur present in anions such as sulfates, sulfides and thiocyanates. For some waste streams, it could also be reflecting the sulfur present in natural organosulfur compounds such as amino acids or thiophene found in coal tars.

Table Footnotes

A. HP 3 - H260 and H261 were also assessed based on calculation methods: WM3 (2018) Table C3.2 and EU (2018) Table 11
B. HP 12 - EUH029, EUH031 and EUH032 were also assessed based on calculation methods: WM3 (2018) Table C12.2 and EU (2018) Table 21
C. IARC (2020) considers these compounds to be Group 1 Carcinogenic to humans; H350 Carc. 1A added
D. IARC (2020) considers these compounds to be Group 1 Carcinogenic to humans; H350 Carc. 1B added
E. Data sources: C&L (2020), worst case
F. Data sources: Sigma Aldrich, 2020: SDS barium chromate, version 6.2, dated 08.05.2020; C&L (2020)
G. Data sources: Sigma Aldrich, 2020: SDS barium oxide, version 6.0, dated 06.02.2020; C&L (2020)
H. Data sources: Sigma Aldrich, 2020: SDS barium sulfate, version 6.1, dated 15.04.2020; C&L (2020)
I. Data sources: Sigma Aldrich, 2019: SDS beryllium chloride, version 6.0, dated 24.10.2019; C&L (2020)
J. Data sources: Sigma Aldrich, 2020 SDS calcium hydroxide, version 6.0, dated 10.02.2020; C&L (2020) EU (2018)
K. Data sources: Sigma Aldrich, 2019 SDS calcium oxide, version 6.0, dated 24.10.2019; C&L (2020) EU (2018)
L. Data sources: Sigma Aldrich, 2019 SDS copper(II) chloride dihydrate, version 6.0, dated 24.10.2019; C&L (2020)
M. Data sources: Sigma Aldrich, 2019 SDS copper(II) chloride, version 6.0, dated 24.10.2019; C&L (2020)
N. The CLP entry for "lead compounds" does not have an entry for HP 7 carcinogenic. IARC (2020) considers all lead compounds to be "Group 2A - Probably carcinogenic to humans". For hazard classes not covered by Annex VI of the CLP, the manufacturer or importer is required to self-classify the substance in accordance with the CLP criteria. The Lead REACH Consortium (https://ila-reach.org/) compared the IARC approach to the CLP approach and concluded that most common lead compounds (oxides, chlorides sulphates etc.) should be Carc. 2; H351 (Lead REACH Consortium (2015a)), while only those lead compounds from smelting industries and flue dust should be worst case Carc. 1A; H350.
O. Self-classification; Lead Reach Consortium (2015b), Substance grade data sheet dated October 2017
P. Formula source: lithium nickel cobalt oxide, CAS 113066-89-0 www.sigmaaldrich.com SDS accessed 29 May 2020; no molecular formula or CAS listed in ECHA (C&L 2020)
Q. Data sources: Sigma Aldrich, 2019 SDS manganese(II) chloride, version 6.0, dated 05.10.2019; C&L (2020)
R. Acute Tox. 2* H300: Minimum entry confirmed by Sigma Aldrich 2019: SDS mercury(II) chloride, version 6.0, dated 24.10.2019; C&L (2020)
S. Data sources: Sigma Aldrich, 2019 SDS mercury(II) sulfide red, version 6.0, dated 17.09.2019; C&L (2020)
T. The actual CLP entry is: zinc sulphate (hydrous) (mono-, hexa- and hepta hydrate) [1]; zinc sulphate (anhydrous) [2]

Evidence can include information discovered by the desktop study, observations from investigations, SDS for chemicals used in industrial processes, use of existing laboratory test results and optimization of further laboratory testing, combined with an understanding of some basic chemistry to achieve a more reasonable case. If not already commissioned, further laboratory testing can include measuring the leachable concentrations of key cations and anions and information on the physico-chemical status of the waste including pH, acid/alkali reserve and redox potential.

In the example discussed below, all the metadata, including typical uses of the substances, chemical formulas and chemical properties, like solubility, can be found using Google, Wikipedia or the HazWasteOnline™ Wiki, with support from reference books such as CRC (2020). Note also that the example below is simplified to a single sample result and one metal and does not assess all the other determinands. It also does not attempt to further justify decisions based on the analysis of a suitable sample population or statistical analysis. Appendix D of WM3 (2018) discusses these aspects in more detail.

The scenario is a builder's yard that is going to be redeveloped, with contaminated soils removed for disposal to a waste management facility. Prior to the use by the builder, the site was a field used for agriculture. A site walkover found evidence for the burning of waste wood and also steel belts resulting from the combustion of car tyres. Empty aerosol cans containing lead oxide and zinc oxide primer were also observed. Finally, no evidence was found for the presence of zinc compounds that are not already listed in Table 3.

Laboratory testing included ten heavy metals, total petroleum hydrocarbons, the standard 16 PAHs and moisture, plus the anions: sulphate, phosphate and chloride. With respect to zinc, analysis of a one soil sample found a (dry weight) concentration of 3,000 mg/kg.

Focusing on the selection of a reasonable worst case species for zinc, the exercise will start from the worst case zinc species, zinc chromate and work down the listings in Table 3.

All chromates (i.e. the anion, CrO_4^{2-} and dichromates, $Cr_2O_7^{2-}$) are HP 7 Carcinogenic at compound concentrations of 0.1% or 1,000 mg/kg. The chromium in chromates in known as chromium(VI) or hexavalent chromium due to its oxidation state. If total chromium is measured by the laboratory, this includes both common oxidation states of chromium, namely chromium(III) and chromium(VI). Stoichiometrically, 3,000 mg/kg of total zinc equates to 8,322 mg/kg of zinc chromate (CF=2.774), of which 2,386 mg/kg would be chromium(VI). In this example, only total chromium was measured, the result being 30 mg/kg. Assuming the worst case and thus the measured chromium is all in the form of chromium(VI), it is clear that there is nowhere near enough chromium to make 8,322mg/kg of zinc chromate. (30 mg/kg of chromium(VI) limits the amount of zinc chromate to only 105 mg/kg, which is far below the hazardous threshold.)

A more thorough test to confirm that there are no chromates of, for example, zinc, nickel and lead, is to test for speciated chromium(VI) (EN 15192) and for total chromium, the difference being chromium(III).

Both of the above arguments can be used to justify discounting the worst case zinc compound and moving to the next worse case metal species in the list.

Zinc sulphate and zinc chloride (and their hydrous forms) will be discussed together as all are soluble compounds. The lines of evidence are:

- No evidence for the use of zinc chloride or zinc sulphate on the site.
- $ZnSO_4$ (and hydrous forms) and $ZnCl_2$ are both more soluble than table salt (577 g/l and 4,320 g/l (25°C) respectively (CRC 2020)).
- The soil has been exposed to the elements and the water table for some significant period, so these compounds are unlikely to be present, if they were ever there.

With respect to the last bullet, if there was evidence for the presence of either of these two compounds, the leaching away argument would not be enough to justify removing them from consideration. However, the argument can be strengthened by two further chemical test solutions.

The first is including laboratory tests for soluble sulphates and chlorides. If there are no soluble sulphates or chlorides or the concentrations that are measured limit the amounts of these species, then this can be used as evidence that these species can be discounted. However, these results can be inconclusive as sulphates and chlorides can be related to other inorganic compounds potentially present in a builder's yard or soils, for example, plaster is calcium sulphate dihydrate.

The best supporting evidence is to consider including an eluate test; i.e. a measure of any soluble metals at the pH of the material, as in EN 12457-2. If this test shows no soluble zinc for example, then that rules out both zinc sulphate and zinc chloride and their hydrated forms. Note that for zinc, this information can also be found in the WAC test, so the classifier may already have the extra evidence.

Zinc phosphate, ($Zn_3(PO_4)_2$) is the next in the list. Note that CLP Table 3 calls it trizinc bis(orthophosphate). It is used in corrosion resistant coatings, putties and fillers and is insoluble in water. If this compound were present in the builder's yard, we would expect 2,905 mg/kg of orthophosphate in the laboratory results. In this example, the laboratory only measured 30 mg/kg of orthophosphates so this compound can also be discounted.

The next suspect is zinc phosphide, Zn_3P_2. The substance is used in products like photovoltaic cells and rodenticides, neither of which has been used on the site. If you look at the metadata for this compound, either in HazWasteOnline™ or the entry in CLP Table 3, this substance has six hazard statements including EUH029 Contact with water liberates toxic gas. As the site is not arid and subject to rainfall/water table; if this material was ever present, it has long since reacted with water to generate zinc hydroxide and the flammable gas, phosphine.

So zinc phosphide can be ruled out.

The next worst case is zinc oxide, ZnO which is used in both car tyres and paints, both entities identified on site. Zinc oxide is virtually insoluble in water at pH 7 (CRC 2020), so won't be leached away.

With the evidence available, zinc oxide is the most reasonable worst case zinc species to use in the classification of these contaminated soils. It would trigger HP 14 Ecotoxic.

9. CONCLUSIONS

A complete set of more than two hundred worst case to less worst case metal species, for thirty two elements, is now available for use in the hazardous waste classification of mixtures. The list includes harmonised entries from Annex VI, Table 3 of the CLP (equivalent to the mandatory entries in the United Kingdom's GB CLP Regulation (UK 2018, 2019, 2020)), plus a further set of metal species that are not currently in the CLP but are needed by waste classifiers in order to better complete their hazardous waste classifications. The paper defines the methodology used, the limitations and exceptions so that other metal species that are not included in Table 3 can be appraised in the same way.

The paper also provides a worked example showing how a waste classifier can use the lists in Table 3 and guidance in this paper to help optimize both their laboratory testing and utilise other information to move from a precautionary, worst case metal species towards a more reasonable worst case species. The discussion provides examples of the various lines of evidence, such as physical properties like solubility, and extra laboratory tests that can be undertaken to achieve a more reasonable classification.

With the advent of sophisticated waste classification software, that manage both the compounds, their metadata and automates all the calculations and exceptions, the classifier is now able to move rapidly from worst case to more reasonable case metal species and document the lines of evidence for their decisions.

REFERENCES

AFNOR XP 30-489: 2013. Characterization of waste — Determination of the content of elements and substances in waste (in French). AFNOR, France

Bishop, I. and Gill, T., 2018. Why you shouldn't assume your non-hazardous feedstock is non-hazardous: The forensic analysis of a filter cake produced from the manufacture of firefighting foam from hoof and horn meal. 6th International Conference on Industrial and Hazardous Waste Management, CRETE 2018. Paper available from www.hazwasteonline.com

C&L 2020. European Chemicals Agency. Classification and Labeling Inventory Database: www.echa.europa.eu/information-on-chemicals/cl-inventory-database.

CL:AIRE 2011. The Definition of Waste: Development Industry Code of Practice, Version 2, published by Published by Contaminated Land: Applications in Real Environments (CL:AIRE), March 2011.

Concawe 2020. Literature Review: Effects-Based Analysis for Soils, Risk Management and Waste Disposal; Report no. 16/20, prepared by Marks, B., Leverett, D. and Bishop, I., August 2020.

CRC 2020. CRC Handbook of chemistry and physics, 101st edition, Editor: Rumble, J.R., CRC Press, July 2020.

EA 2018. Performance Standard for Laboratories undertaking chemical testing of soil. Environment Agency, November 2018, version 5.

ECHA 2017. European Chemicals Agency. Guidance on the application of the CLP criteria, version 5.0, July 2017. ISBN 978-92-9020-050-5. Available from https://echa.europa.eu/guidance-documents/guidance-on-clp.

EEC 1967. Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances

EN 12457-2:2002. Characterization of waste – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction). CEN, Belgium.

EN 15192:2007. Characterization of waste and soil - Determination of chromium (VI) in solid materials by alkaline digestion and ion chromatography with spectrophotometric detection. CEN, Belgium.

ESA 2018. A sampling and testing protocol to assess the status of incinerator bottom ash, Environmental Services Association, www.esauk.org, January 2018.

EU 1999. Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations.

EU 2003. Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.

EU 2004. Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC.

EU 2006. Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

EU 2008a. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

EU 2008b. Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008, on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

EU 2008c. Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

EU 2009. Regulation (EC) No 790/2009 of 11 August 2009 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures.

EU 2011. Regulation (EC) No 286/2011 of 10 March 2011 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures.

EU 2014a. Commission Decision 2014/955/EU of 18 December 2014, amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council.

EU 2014b. Commission Regulation (EU) No 1357/2014 of 18 December 2014, amending Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives.

EU 2014c. Commission Regulation (EU) No 1342/2014 of 17 December 2014 amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes IV and V.

EU 2016. Regulation (EU) 2016/1179 of 19 July 2016 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures.

EU 2017. Regulation (EU) No 2017/997 of 8 June 2017, amending Annex III to Directive 2008/98/EC of the European Parliament and of the Council as regards the hazardous property HP 14 'Ecotoxic'.

EU 2018. European Commission; Commission notice on technical guidance on the classification of waste, 2018/C 124/01.

EU 2020. Regulation (EU) 2020/1182 of 19 May 2020, amending, for the purposes of its adaptation to technical and scientific progress, Part 3 of Annex VI to Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures.

GHS 2019. Globally Harmonized System of Classification and Labelling of Chemicals, United Nations Economic Commission for Europe, Revision 8, May 2019.

Hennebert, P., 2019. Hazard classification of waste: Review of available practical methods and tools. Detritus, Volume 07, p 13-28 Sept 2019.

Hennebert, P., Humez, N., Conche, I., Bishop, I. and Rebishung, F., 2016. Assessment of four calculation methods proposed by the EC for waste hazardous property HP 14 'Ecotoxic'. Waste Management Vol. 48, p 24-33.

Hennebert P., Papin A., Padox J-M., Hasebrouck B., 2013. The evaluation of an analytical protocol for the determination of substances in waste for hazard classification. Waste Management Vol. 33, p 1577–1588.

IARC 2020. International Agency for Research on Cancer, World Health Organisation. IARC monographs on the identification of carcinogenic hazards to humans. Accessed 24 July 2020. https://monographs.iarc.fr/list-of-classifications

INERIS 2015. Study Report DRC-15-149793-04619A: Waste Hazardousness Assessment – Proposition of methods (version 2), 15 May 2015.

INERIS 2016. Study Report DRC-16-159393-04351A: Etude comparative des regles de classement des melanges au titre du reglement CLP et des dechets au titre des proprietes de danger HP, 12 November 2016.

Lead REACH Consortium 2015(a). Industry proposed self-classification for lead compounds. Substance grade data sheets accessed 24 July 2020: https://ila-reach.org/our-substances/lead-compounds/.

Lead REACH Consortium 2015(b). Industry proposed self-classification for lead metal. Substance grade data sheets accessed 24 July 2020: https://ila-reach.org/our-substances/lead-metal/.

MAIB 2017. Report on the investigation of the explosion of gas released from a cargo of un-processed incinerator bottom ash on Nortrader at anchorage in Plymouth Sound on 13 January 2017. Marine Accident Investigation Branch, Report No. 26/2017.

Norden 2016. Nordic Council of Ministers. Hazardous waste classification – Amendments to the European Waste Classification regulation – what do they mean and whet are the consequences. Margarete Wahlstron, Jutta Laine-Ylijoki, Ola Wik, Anke Oberender and Ole Hjelmar. ISBN978-92-893-4532-3.

UK 2018. European Union (Withdrawal) Act 2018.

UK 2019. The Chemicals (Health and Safety) and Genetically Modified Organisms (Contained Use) (Amendment etc.) (EU Exit) Regulations 2019.

UK 2020. The Chemicals (Health and Safety) and Genetically Modified Organisms (Contained Use) (Amendment etc.) (EU Exit) Regulations 2020.

WM3 2018. Waste Classification: Guidance on the classification and assessment of waste (1st Edition v1.1): Technical Guidance WM3. Environment Agency, NIEA, SEPA, Natural Resources Wales. Available from: http://www.gov.uk/government/publications/waste-classification-technical-guidance.

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[1] Cut-off – for a substance with one or more additive hazard statements (see next footnote), the measured concentration can be ignored in the calculations if the measured concentration is below the cut-off concentration.

[2] Additive (Σ) means that if two or more substances have the same additive hazard statement, then the concentrations of those substances need to be added together before the sum is compared to the threshold (e.g. H300 Acute Tox. 1 is Σ ≥ 0.1% or 1,000 mg/kg). HP 4, HP 5, HP 6 & HP 8 have one or more additive type hazard statements. HP 14 is also additive but the calculations are more complex. PCDD/PCDF substances require a different additive calculation based on Toxic Equivalency Factors (TEF).

[3] Individual (Ind.) indicates that if any single substance has a concentration that exceeds the threshold then it will trigger the hazardous property (e.g. H350 Carc 1A is Ind. ≥ 0.1% or 1,000 mg/kg).

[4] In 2017, a vessel carrying a cargo of un-processed IBA suffered a gas explosion following the accidental release of fresh water into the vessel's hold and subsequently, hydrogen gas leaking into an electrical switch box (MAIB 2017). IBA has the potential to release hydrogen where finely divided aluminium is present and water is added. Although the quantities of hydrogen produced are likely to be less than the threshold for classification of the IBA as hazardous, under HP 3 (fifth indent) (H260, H261), it is considered best practice for both IBA hazard and risk assessments to consider the potential for of the ash to generate hydrogen gas, test if necessary and take appropriate precautions to minimise the risk of fire or explosion. This includes the handling and storage arrangements for buildings, transport vessels or containers having adequate ventilation to ensure that any gas is dispersed safely.

[5] M factors or multiplication factors are scaling factors (M=1, 10, 100, up to 1,000,000 for some pesticides) that are applicable to products (but not to wastes). They can reduce the hazardous threshold for a given hazard statement e.g. H410 Aquatic chronic 2; M=100 would reduce the 0.25% (2,500 mg/kg) threshold to 0.0025% (25 mg/kg).

[6] Species – there may be more than one species of a particular metal in a waste; for example an incinerator ash may comprise zinc oxide and other zinc minerals such as zinc silicates. Unless more specialised testing and modelling is undertaken, most classifiers of mixtures assume that a given metal is only present as a single species or phase.

[7] In the England and Wales, larger construction projects can follow the

CL:AIRE Definition of Waste: Code of Practice (CL:AIRE 2011). A Materials Management Plan defines the different types of soils on the site (including contaminated soils) and which soils can be re-used and which have to leave site as a waste and hence require classification. The guidance is derived from Article 2 of the WFD.

[8] A lab tells us that we have **360.5** mg/kg of zinc in our waste which we assume is in the form of zinc chromate. How much zinc chromate do we have?
Molecular formula: $ZnCrO_4$
Atomic weights for each element (www.ptable.com): Zn=65.38; Cr=51.996; O=15.999
Molecular Weight (MW): (1 x 65.38) + (1 x 51.996) + (4 x 15.999) = 181.372 g/mole

Conversion Factor (CF): 181.372 / (1 x 65.38) = **2.774**
Therefore the concentration of zinc chromate is: **360.5** x **2.774** = **1,000** mg/kg

[9] Minimum entry – these are entries in CLP Table 3 that have a hazard statement's category code marked with a single *

[10] Note H – in the older European chemical legislation (Dangerous Substances Directive (EEC 1967)), the note H was published in CLP Table 3 to indicate a known, incomplete entry.

[11] ICP-OES – Inductively Coupled Plasma - Optical Emission Spectroscopy is a technique that uses a plasma as a source and uses the optical emission spectra to identify and quantify the elements present.

[12] For 1,000 mg/kg zinc chromate $ZnCrO_4$, how much chromium(VI) is present?
Atomic weights for each element (www.ptable.com): Zn=65.38; Cr=51.996; O=15.999
Molecular Weight (MW): 181.372 g/mole
Amount chromium(VI): 51.996/181.372 * 1,000 = 286.682 mg/kg

[13] "significantly less" - perhaps 10% to 20% less - because in most mixtures you can never expect a good stoichiometric match, a judgement has to be made when trying to undertake some element of a mass balance. This is due to a combination of a) the accuracy of lab testing (for soils under MCERTS (EA, 2018) measurement precision is 7.5%-15% and bias 10%-30%, depending on determinand), b) sampling density and c) the presence of other (un-investigated) metals (and/or metal species) and organic compounds in the waste.

[14] Note that: (#9 x #10) / 10,000 = #5 for each species in Table 3.

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HOW TO INCREASE CIRCULARITY IN THE SWISS ECONOMY?

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ABSTRACT

Environmental threats are triggered by the overconsumption of raw materials. It is therefore necessary to move towards a society that both reduces extraction and keeps the majority of the extracted raw materials in the socio-economic system. Circular economy is a key strategy to reach these goals. To implement it effectively, it is necessary to understand and monitor material flows and to define hotspots, i.e. materials that need to be tackled with the highest priority. This paper is aimed at determining how to increase circularity in the Swiss economy by means of a Material Flow Analysis coupled with a simplified Life Cycle Assessment. After having characterized material flows, we analyzed two types of hotspots: i) Raw materials consumed and/or disposed at high level, and ii) Raw materials whose extraction and production generates high environmental impacts. The Material Flow Analysis shows that each year 119 Mt of raw materials enter the Swiss economy. Therefrom, 15 Mt are derived from recycled waste inside the country; 67 Mt leave the system yearly; 27 Mt towards disposal. Out of the disposed materials, 56% are recycled and re-enter the socio-economic system as secondary materials. Looking at hotspots; concrete, asphalt, gravel and sand are among materials that are consumed and disposed at high level. Yet, looking at greenhouse gas emissions generated during extraction and production, metals - including the ones in electrical and electronic equipment - as well as textiles are among the categories that carry the biggest burden on the environment per unit of material.

1. INTRODUCTION

The publication of the Planetary Boundaries concept in 2009 (Rockström et al., 2009) and its update in 2015 (Steffen et al., 2015) showed that global-scale alteration of biogeochemical flows, biosphere integrity, land-system change and climate change are the major environmental threats that humanity is facing nowadays. These threats are a consequence of human overconsumption of natural resources (O'Neill et al. 2018). It is therefore essential to understand factors that drive raw material consumption and the flows of materials that this generates. This allows tackling hotspots and developing pathways to reach a 'safe operating space for humanity' (Heijungs et al., 2014; O'Neill et al. 2018), for example by reducing extraction and keeping the majority of the extracted raw materials in the socio-economic system.

Broken down the Swiss economy, we see a need for quantifying flows of materials and energy with their related environmental impacts. Studies exist assessing the material input and the environmental consequences (Jungbluth et al., 2011; Frischknecht et al., 2014; Frischknecht et al., 2018), or the environmental consequences of resource and energy recovery in waste management systems (Haupt, 2018). However, to our knowledge there are no studies focusing on the material inputs and outputs of the entire economic system, including considerations about the recycling efficiencies and losses (incineration, landfilling).

This paper aims at determining how to increase circularity of raw materials in the Swiss economy. It does so by: i) Characterizing mass flows, ii) Assessing the environmental impacts generated by these flows, and iii) Defining which raw materials are hotspots, i.e. are either consumed and/or disposed at high level or their extraction and production generates high environmental impacts. The result of this research is meant to support the Swiss government in taking decisions for moving towards more circularity in material management.

2. MATERIALS AND METHODS

2.1 Material flows of Swiss economy

To address the circularity of the Swiss economy and to answer the research question of this paper, we carried out a static Material Flow Analysis (MFA) covering the material metabolism within the Swiss economy and coupled it

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with a Life Cycle Assessment (LCA). Material Flow Analysis (Baccini & Brunner, 2012) helps to assess the material input into a national economy, its accumulation within the system and its output to other economies or to the environment (OECD, 2008). This research is based on the methodology developed in three sectoral studies. In each of them, a particular area of the Swiss economy was analyzed: construction (Gauch et al., 2016), mobility (Gauch et al., 2017), and production & consumption (Matasci et al., 2018). For construction and mobility, we used a stock-driven approach. For the remaining production and consumption area, we applied an inflow-driven approach due to the lack of information on the existing stock and the impossibility to perform a bottom-up estimate. The reference year is 2018. Calculations were done using Microsoft Excel 2016.

Official statistics on masses of imported, domestically extracted and exported goods served as a basis for the calculation. In this research, we considered about 750 classes of goods registered, covering the entire Swiss economy, as for example industrial buildings, private cars, airplanes, stoves, pullovers, computers, or medicaments. For each of them, we determined the raw material composition and service lifetime. Additionally, we grouped them into 28 consumption categories (Table 1).

We examined 195 types of raw materials (e.g., reinforced concrete, sawn softwood, low-alloyed steel, wrought alloy aluminum, crude oil, cotton fiber, or polyethylene). We grouped them into 18 categories, as presented in Table 2. Materials in electric and electronic equipment as well as in batteries were aggregated in a distinct category called 'Electronics, batteries' to be able to look at them specifically.

Water and gold were not included in the frame of this study. Water was excluded due to the enormous quantities consumed (630 Mt/a) generating nonetheless relatively small environmental impacts (0.1 Mt CO_2-eq./a, less than 1% of the total). Gold was disregarded for the opposite reason: the small quantities consumed (about 800 Mt in 2018) generating massive environmental impacts (12 Mt CO_2-eq., which is about 15% of the GHG emissions created

TABLE 1: Twenty-eight consumption categories covering the entire Swiss economy, classified by areas and sub-areas of the socio-economic system.

Areas of the socio-economic system	Sub-areas	Consumption categories	Number of classes of goods
Construction	Buildings	Single-family houses	1
		Apartment buildings	1
		Service buildings	1
		Industrial buildings	1
		Agricultural buildings	1
		Other buildings	1
	Civil engineering	Streets	1
		Rail	1
		Infrastructure for supply and disposal	1
Mobility	Mobility	Two wheels	6
		Passenger cars	6
		Transporters	10
		Lorries	6
		Buses	4
		Agricultural and industrial vehicles	20
		Trailers	3
		Trams	1
		Trains	7
		Boats	4
		Airplanes	7
		Cable cars	3
Production & consumption	Food	Food	36
	Living, working	Furniture	187
		Clothing, accessories	19
		Communication, education	24
		Leisure, entertainment	28
		Health	8
	Industry	Industry	361

TABLE 2: Eighteen categories of raw materials, classified by type. Electricity is expressed in tons of oil equivalents (toe) as described in Gauch et al. (2017).

Type	Categories of raw materials	Number of classes of materials
Energy carriers	Electricity (toe)	2
	Motor fuel	5
	Combustible	3
Food products	Food	38
	Fodder, animals	23
Solid materials	Gravel, sand	5
	Asphalt	2
	Concrete	4
	Brick	6
	Glass, ceramics	10
	Steel	3
	Aluminum	4
	Other metals	24
	Plastics	14
	Textiles	6
	Wood, paper	11
	Electronics, batteries	10
	Chemicals	25

by all other materials consumed annually in the country put together). An analysis of the material flows and the environmental impacts produced by the consumption of these two materials can be found in Matasci et al. (2018). Finally, for each category of raw materials, we defined a disposal pathway.

2.2 Environmental impacts generated by mass flows

Based on the determination of quantities and compositions of the flows we calculated a simplified Life Cycle Assessment (LCA). LCA is a method developed to assess environmental impacts associated with the different life stages of a product or a process, from cradle to grave. As functional unit, we considered a ton of used raw material. We employed the Life Cycle Inventory database ecoinvent v. 3.2-3.5 (ecoinvent 2016, 2018). This was combined with the results of the MFA to assess the environmental impacts in terms of greenhouse gas (GHG) emissions and total environmental impact of the different mass flows. The calculation of the total environmental impact is based on the Ecological Scarcity Method (Frischknecht & Büsser Knöpfel 2013), developed specifically for Switzerland. This method allows measuring the current distance to politically determined targets on the broadest possible basis.

System boundaries for raw material flows were set on the level of the political borders of Switzerland. Environmental impacts are however not limited by these borders and can take place inside and/or outside the country. Consequently, the GHG emissions and other environmental impacts hidden behind imported products are also taken into account.

We considered both primary and secondary materials. Primary raw materials are 'virgin materials, natural inorganic or organic substances, such as metallic ores, industrial minerals, construction materials or energy fuels, used for the first time' (EU 2017). Secondary raw materials are raw materials derived from recycling of waste that can be used in manufacturing a new product. Imported raw materials can be a combination of both.

3. RESULTS AND DISCUSSION

According to the results of the MFA, about 119 Mt of raw material flew into the Swiss economy in 2018. Of these, 104 Mt/a came from either domestic extractions or imports. The remaining 15 Mt (13%) re-entered the system annually as secondary raw materials either for the same purpose (recycling) or for a different one (downcycling, upcycling). From the 119 Mt/a, 52 Mt/a stayed in the stock, mainly concrete, sand and gravel in construction. The remaining 67 Mt/a exited the Swiss economy. Thereof; 22 Mt/a were dissipated into the environment, for example in form of burned fuel for mobility and combustible, consumed food or dispersed chemicals (e.g. pesticides). On top of that, 18 Mt/a were exported and 27 Mt/a were disposed (Figure 1). Of the disposed materials, 18 Mt/a (67%) were either recycled or composted (Figure 2). We consider composted materials to go into the environment (either into the ground or into air) and are therefore not part of the flow of secondary materials reentering the system (Figures 1, 2).

The disposal phase is composed of various intermediate stages. These include cross-exchanges of solid materials between disposal processes (Figure 2). Examples are residues from incineration plants (slag), which are returned to the recycling process, or residues from waste water treatment plants (sewage sludge), which are incinerated. Figure 2 shows some of the modelled flows in more details. To note that a share of the substances entering the disposal process 'disappears' from the mass balance, for example by being converted into gaseous substances in incineration or composting/biogas plants.

Figure 3 shows both masses and environmental impacts for the 18 categories of raw materials in more details. On the left-hand side of the figure, information on the mass entering the disposal path is depicted for each category of raw materials, split in the different fates these are facing (recycling, incineration, landfill, compost and biogas). Masses consumed are shown for comparison by a broken line. Statistical data corroborate these results where information is available (FOEN, 2019). In the center of Figure 3, the GHG generated by disposal and consumption are illustrated. The figure shows how emissions produced by disposal are much smaller than the ones created by extraction, production and consumption of these raw materials (broken line in the figure). It is however important to note that these results are connected with a certain level of uncertainty, as specific values for the end of life of many raw materials are lacking in the ecoinvent database. On the right-hand side of Figure 3, the GHG emissions generated by the production and transport to the consumer of a mass

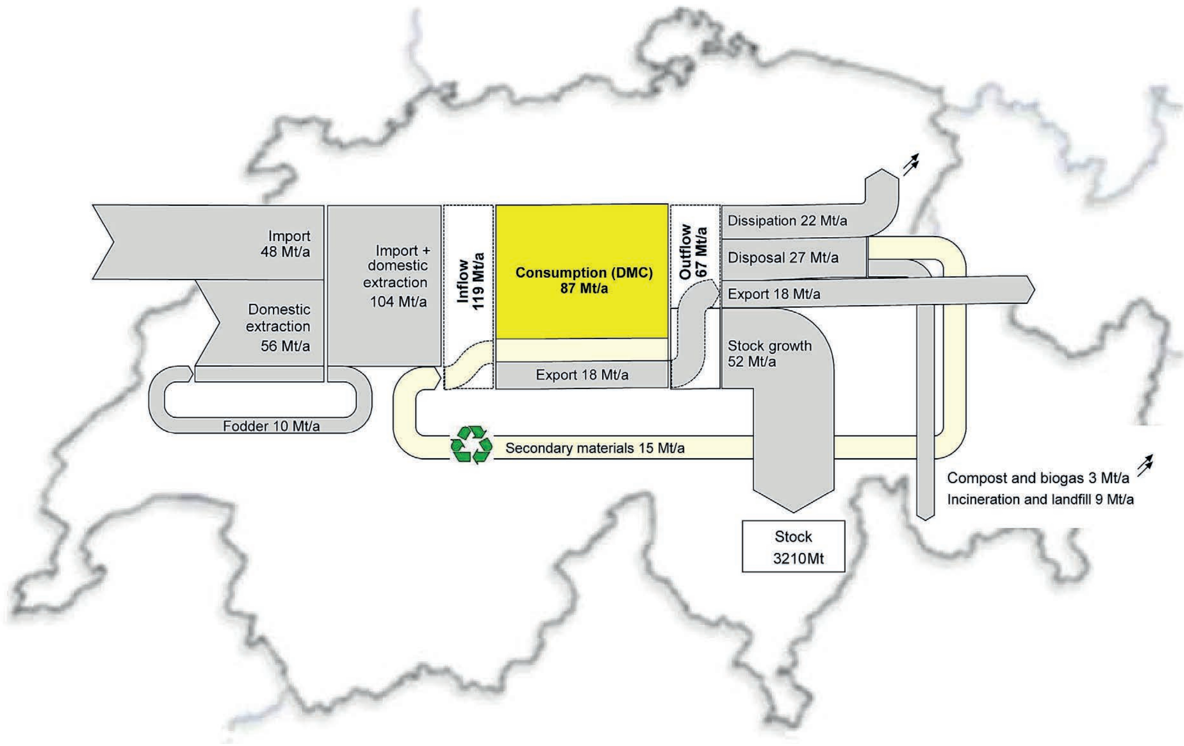

FIGURE 1: Aggregated mass flow for Switzerland in 2018. In yellow the Domestic Material Consumption (DMC), in light yellow the flow of secondary materials reentering the system (Matasci et al., in preparation). Composted materials are considered to go directly into the environment (in the ground / into air) and are not part of the flow of secondary materials reentering the system.

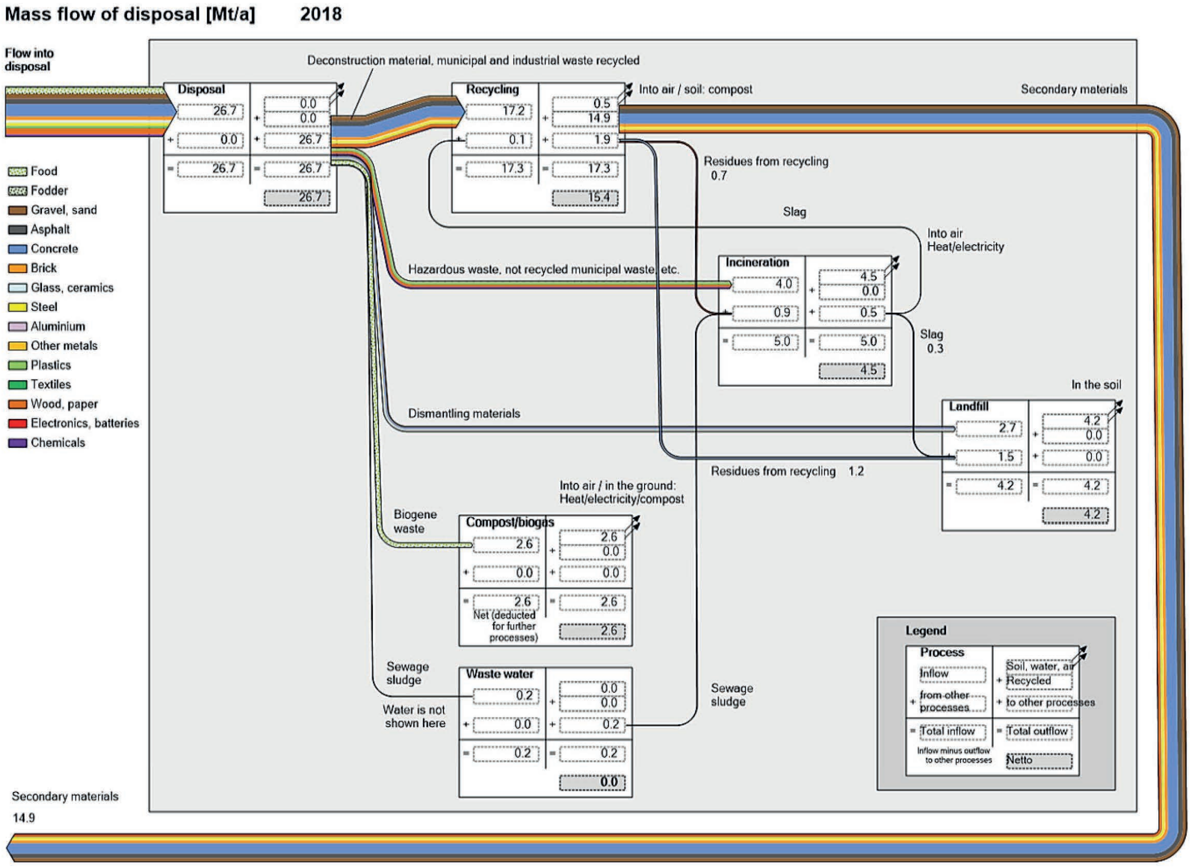

FIGURE 2: Disposal mass flows. The width of the arrows shows the relative mass of raw materials being disposed annually. Some of the raw materials are dissipated into the environment. These are marked with a double arrow.

unit of primary vs. a mass unit of secondary raw material are shown.

Figures 2 and 3 illustrate that the majority of the disposed raw materials are inert materials coming from the construction sector (concrete, sand and gravel, asphalt, brick). As Switzerland decided to stop landfilling of organic waste back in 2000 (FOEN, 1999), organic waste is nowadays either composted, incinerated or recycled.

Many raw materials re-enter the system as secondary raw materials. Among them, concrete is mainly downcycled in civil engineering structures. Recycled concrete in the building sector is only slowly gaining acceptance in Switzerland. Food is also eliminated in high quantities. The 2.9 Mt/a of disposed food (about 1/3 of the food entering the system) is food waste generated either by consumers or within the supply chain (Beretta & Hellweg, 2019). Fuel for mobility and combustible consumed are dissipated into the environment during combustion and therefore do not appear in the disposal path.

An additional result established by this study and depicted in Figure 3 is the recognition that big masses of disposed materials do not necessarily carry the highest environmental burden. The disposal of concrete for example generates a relatively small amount of GHG emissions in absolute terms, whereas the disposal of chemicals and plastics creates far higher emissions even if the discarded masses are smaller. This is also true for consumption: the raw materials depleted in higher amount are not the ones that generate the highest burden for the environment during their extraction, transport and consumption. The life phases of concrete up to consumption for example produce a far smaller amount of GHG per unit of material as the ones of electronics and batteries, metals, or textiles.

Another aspect shown on the right hand-side of Figure 3 is that the production of secondary raw materials develops much lower emissions than the one of primary raw materials. This highlights the importance of moving from the current linear economy towards a circular economy. This is particularly true for metals in waste electrical and electronic equipment, WEEE) which are often critical. Critical raw materials are raw materials of a high importance to the economy and whose supply is associated with a high risk (EU 2017). Examples are indium and neodymium contained respectively in flat screens and in magnets. The recycling of these metals is not yet established in Switzerland (Böni et al. 2015). If the totality of electronics and batteries category (WEEE) would be recycled and used for the same purpose, emissions generated by Swiss consumption could decrease of about 3 t CO_2-eq./a. On the other hand, some materials disposed contain pollutants that should not return into the system as for example brominated flame-retardants (BFR) in plastics (Haarman et al. 2018). Recycling is therefore not always possible or not the best option.

This study presents three main methodological limitations. The first one concerns the different approaches used for the various sectors of the economy, namely a stock-driven approach for the building and the mobility sectors and an inflow-driven method for the remaining sectors of the economy. In future research, a common methodology should be used instead. The second limitation

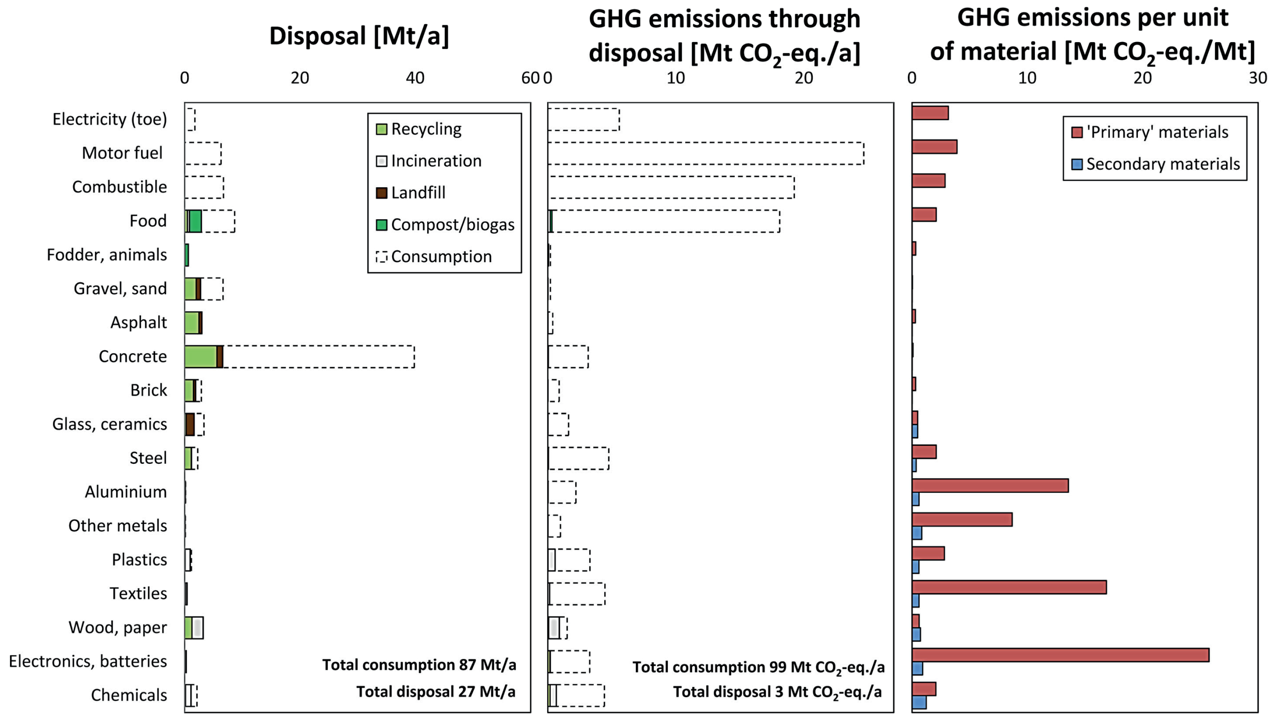

FIGURE 3: From left to right: i) Annual masses of disposed raw materials, differentiated by their disposal fate (recycling, incineration, landfill, compost/biogas). ii) GHG emissions created during the disposal of these raw materials. In i) and ii) the mass of annually consumed raw materials respectively the GHG emission developed are also shown for comparison (broken line). iii) GHG emissions generated by production and transport per unit of consumed material for both primary and secondary raw materials. What is illustrated here as 'primary' material can also contain secondary materials if imported, for example metal scraps.

concerns the limited information on the average material composition of the different categories of goods analyzed. Data came from different sources and do vary in quality. When data was not available, best guess assumptions of the authors were necessary. Finally, it was not possible to find an equivalent in the ecoinvent database for all raw materials embedded in the approx. 750 categories of goods. Sometimes proxies had to be selected instead, in particular for chemicals.

4. CONCLUSIONS

This study highlights the necessity to increase circularity for most categories of raw materials due to three reasons: i) the large masses being consumed and disposed, ii) the high environmental impacts generated either ii) during the lifespan and/or iii) by primary production in relation to the recovery of secondary materials.

The disposed amount and the environmental impact caused can vary largely depending on the type of raw material considered. Material hotspots identified due to the large mass eliminated yearly in Switzerland are concrete, asphalt, gravel and sand. For concrete, even if the environmental impacts generated by its disposal are relatively small, there are other aspects to be examined. These are for example the finite nature of its main component, gravel and the potential conflict with other land uses; the amount of energy required to produce its binder, cement; as well as conflicts in land use through the disposal of waste concrete and for the extraction of gravel (FSKB, 2017). Nowadays, concrete from demolition activities in Switzerland is mainly downcycled. The use of recycled concrete in the construction sector consequently needs to be further promoted.

Concerning environmental impacts created through the disposal of materials; hotspots identified are plastics, chemicals and food. The avoidance of food waste and the recycling of plastics could therefore be two pertinent measures to reduce the actual environmental burden of the Swiss waste management system. It is worth noting that the environmental impacts caused by the consumption of materials are generally much higher than the ones generated during the disposal phase. Hence, more effort should also be put into limiting consumption in the first place and into keeping raw materials in the system. This can be done for example by expanding the lifespan of goods or by reusing them.

In addition, for many raw materials the primary production has a higher environmental impact in comparison to their secondary production. This is particularly the case for metals, including those embedded in electrical and electronic equipment. For some metals as aluminum in beverage cans or tinplate in tin cans, the recycling rate is already rather high (Haupt, 2018). However, for some others, as for example critical metals like indium and neodymium in electronic waste, the actual recycling rate in Switzerland is close to zero (Böni et al., 2015) and therefore should be further improved.

An additional outcome of this study is the recognition that there is a need for a better monitoring of some flows. Our results show that not all flows related to disposal are covered by official statistics or that data collected for some of them are approximate. This is the case, for example, for waste flows generated by industry or for the composition of waste produced by households. The last one is only investigated in-depth every 10 years (FOEN, 2014).

Finally, this study shows that circularity cannot be applied to all raw materials entering a socio-economic system. In fact, some raw materials are dissipated into the environment when consumed, as for example motor fuel, combustible, food or some chemicals. Circularity alone can therefore not bring us to a more sustainable society. Other measures as the phasing-out of fossil fuels are also needed.

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REFERENCES

Baccini, P., Brunner, P., 2012. Metabolism of the Anthroposphere: Analysis, Evaluation, Design (2nd Edition).

Beretta, C., Hellweg, S., 2019. Lebensmittelverluste in der Schweiz: Umweltbelastung und Vermeidungspotenzial. ETH Zürich, commissioned by the Swiss Federal Office for the Environment FOEN.

Böni, H., Wäger, P., Thiébaud, E., Du, X., Figi, R., Nagel, O., Bunge, R., Stäubli, A., Spörry, A., Wolfensberger-Malo, M., et al., 2015. Rückgewinnung von kritischen Metallen aus Elektronikschrott am Beispiel von Indium und Neodym. Projekt e-Recmet. Schlussbericht; sine nomine.

Ecoinvent, 2018. ecoinvent database v.3.5 (Status August 2018).

Ecoinvent, 2016. ecoinvent database v.3.2 (Status January 2016).

EU, 2017. Study on the review of the list of Critical Raw Materials Criticality Assessments. Final report. European Union EU.

FOEN, 2019. Abfallmengen und Recycling 2018 im Überblick. Swiss Federal Office for the Environment FOEN.

FOEN, 2014. Erhebung der Kehrichtzusammensetzung 2012. Swiss Federal Office for the Environment FOEN.

FOEN, 1999. Keine brennbaren Abfälle mehr auf Deponien nach dem 1. Januar 2000. Swiss Federal Office for the Environment FOEN. https://www.admin.ch/gov/de/start/dokumentation/medienmitteilungen.msg-id-2855.html

Frischknecht, R., Nathan, C., Büsser Knöpfel, S., Itten, R., Wyss, F., Hellmüller, P., 2014. Entwicklung der weltweiten Umweltauswirkungen der Schweiz - Umweltbelastung von Konsum und Produktion von 1996 bis 2011.

Frischknecht, R., Nathani, C., Alig, M., Stolz, P., Tschümperlin, L., Hellmüller, P., 2018. Umwelt-Fussabdrücke des Schweizer Konsums - Zeitlicher Verlauf 1996 bis 2015.

Frischknecht, R., Büsser Knöpfel, S., 2013. Swiss Eco-Factors 2013 According to the Ecological Scarcity Method. Swiss Federal Office for the Environment FOEN.

FSKB, 2017. Info - Informationsmagazin des FSKB Fachverband der Schweizerischen Kies- und Betonindustrie. Fachverband der Schweizerischen Kies- und Betonindustrie FSKB.

Gauch, M., Matasci, C., Hincapié, I., Böni, H., 2017. Projekt MatCH - Mobilität: Material- und Energieressourcen sowie Umweltauswirkungen der Mobilität Schweiz. Empa, commissioned by the Swiss Federal Office for the Environment FOEN.

Gauch, M., Matasci, C., Hincapié, I., Hörler, R., Böni H., 2016. Projet MatCH - Bau: Material- und Energieressourcen sowie Umweltauswirkungen der baulichen Infrastruktur der Schweiz. Empa, commissioned by the Swiss Federal Office for the Environment FOEN.

Haarman, A., Gasser, M., Böni, H., Rösslein, M., Wäger, P., 2018. Brominated Flame Retardants in Large Household Appliances. Empa.

Haupt, M., 2018. Environmental Assessment of Resource and Energy Recovery in Waste Management Systems. ETH Zurich.

Heijungs, R., de Koning, A. & Guinée, J.B., 2014. Maximizing affluence within the planetary boundaries. Int J Life Cycle Assess 19, 1331–1335. https://doi.org/10.1007/s11367-014-0729-y.

Jungbluth, N., Stucki, M., Leuenberger, M., 2011. Environmental Impacts of Swiss Consumption and Production. Swiss Federal Office for the Environment FOEN.

Matasci, C., Gauch, M., Böni, H., in preparation. Projet MatCH - Synthese: Material- und Energieflüsse der schweizerischen Volkswirtschaft – Mit Bewertung der Umweltbelastungen. Empa, commissioned by the Swiss Federal Office for the Environment FOEN.

Matasci, C., Gauch, M., Böni, H., 2018. Projekt MatCH – Produktion&Konsum: Material- und Energieressourcen von Produktion und Konsum in der Schweiz. Empa, commissioned by the Swiss Federal Office for the Environment FOEN.

OECD, 2008. Measuring Material Flows and Resource Productivity – Synthesis Report. Organisation for Economic Co-operation and Development OECD.

O'Neill, D. W., Fanning, A.L., Lamb, W.F. et al., 2018. A good life for all within planetary boundaries. Nat Sustain 1, 88–95. https://doi.org/10.1038/s41893-018-0021-4

Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F. S., Lambin, E. F., Lenton, T. M., et al., 2009. A Safe Operating Space for Humanity. Nature 461 (7263): 472–75.

Steffen, W., Richardson, K., Rockström, J., Cornell, S. E., Fetzer, I., Bennett, E. M., Biggs, R., et al., 2015. Planetary Boundaries: Guiding Human Development on a Changing Planet. Science 347 (6223): 1259855.

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A MAGNETIC HUMUS CORE-SHELL COMPOSITE SYNTHESIZED BY ABIOTIC HUMIFICATION METHOD FOR CR(VI) REMOVAL

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ABSTRACT

Synthesized humus displays a high adsorption capacity for heavy metals in water due to an abundance of active functional groups and to a flexibility of modification resulting from the readily controllable synthesis process. Herein, a new method is proposed to prepare magnetic humus with high performance in the removal of Cr(VI) in water. The synthesized humus is produced through the abiotic humification technology with small molecular precursors including phenols, amino acids, and glucose. Nanoferroferric oxide (Fe_3O_4) plays an important role in the enhancement of the humus synthesis process. The high affinity of humus towards Fe_3O_4 nanoparticles, enables growing of humus on the surface of Fe_3O_4 nanoparticles. The surface morphology of the manufactured magnetic humus suggests that this material has a core-shell structure. The magnetite nanoparticles in magnetic humus show the largest amount of humus (~33.37 w/w%) at pH 8. The high loading ability of humus results in a high removal efficiency of 99.95% in a 7.30 mg/L Cr(VI) solution involving 4 mg/mL magnetic humus. Therefore, the present method is feasible to construct a core-shell magnetic humus composite to achieve high removal of Cr(VI) in water.

1. INTRODUCTION

Humus is a type of naturally transformed organic macromolecular material obtained from fresh organic residues, mainly animal and plant remnants. This compound is suitable for use as a sorbent material due to the presence of a variety of active functional groups, including carboxyl, phenolic hydroxy, carbonyl, methoxy, and amino groups, which feature a high capacity of adsorption for heavy metals in water resources (Liu et al., 2016; Singhal et al., 2017;Yang et al., 2012). However, the high solubility of humus limits its practical applications.

To compensate for the disadvantage of high solubility of humus, immobilization of this material on different solid materials such as biochar and TiO_2 particles is recommended. Magnetic nanoparticles (Fe_3O_4) resemble remarkable merits in separation of materials due to magnetic properties and efficient immobilization because of high surface area and rich hydroxyl groups on their surface (Peng et al., 2012; Singhal et al., 2019, 2020a, 2020b). As reported, the high affinity of humus to Fe_3O_4 nanoparticles strongly inproves stability of magnetic humus and promotes the nanodispension of Fe_3O_4 nanoparticles (Koesnarpadi et al., 2017; Rashid et al., 2018; Tang et al., 2016). But the weight of natural humus loaded on Fe_3O_4 is limited because of the district steric hindrances in the humus loading process. These limitations have a negative effect on the performance of magnetic humus in water treatment.

The artificial humus obtained from a polyphenol-maillard polymerization reaction has the advantages of controllable synthesis process and is considered as an acceptable alternative (Zhang et al., 2017, 2019). The humification process can easily attain synthesized humus with different molecular sizes via regulation of temperature, time and air supply. This kind of mouldability in molecular size is an effective approach to reduce steric hindrances in the humus loading process. The structure of humus highly relies on the variety of humus precursors and humification conditions (Zhang et al., 2017). According to Yang's study, the amount of acidic functions on the synthesized humus is much higher than that of the natural one, allowing the former to possess a better complexation ability towards heavy-metal contaminated soil remediation (Yang & Hodson, 2018). This means that the structure of synthesized humus could be designed as required. Therefore, these advantages enabled humus to be applied in the environmental remediation.

In this work, a new method is disclosed to prepare magnetic humus (Figure 1) with a high efficacy in the removal of heavy metals. Fe_3O_4 nanoparticles were used to enhance humification, integrating small molecular precursors including catechol, glycine, and glucose into humus. To improve loading of the synthesized humus on Fe_3O_4 nanopar-

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ticles, pH was regulated in the synthesis process. The surface morphology of magnetic humus was confirmed by TEM. Eventually, the performance of the generated humus was evaluated in the removal of Cr(VI) from a solution contaminated by 7.30 mg/L hexavalent chromium.

2. MATERIALS AND METHOD

2.1 Chemicals and apparatus

Catechol (> 99% purity) was purchased from Tokyo Chemical Industry. Glycine (> 99% purity) and glucose (> 99% purity) were obtained from Nacalai Tesque. Potassium dichromate was purchased from Beijing Chemical Works. Fe_3O_4 nanoparticles were obtained under oxygen-free conditions. Briefly, $FeCl_3 \cdot 6H_2O$ (24.35 g) was dissolved in 250 mL ultrapure water (70°C) and added to a 250 mL solution of $FeSO_4 \cdot 7H_2O$. Then, $NH_3 \cdot H_2O$ solution (90 mL) was added to the above mixture and incubated at 300 rpm for 90 min. After that, the mixture was set in an external magnetic field, the precipitate was separated and washed for five times using deionized water. Finally, the synthesized magnetic humus was resuspended in ultrapure water for further usage.

The transmission electron microscope (TEM) images were obtained using a Tecnai G2 F20 S-Twin electron microscope (FEI, USA). The TOC-V CSN type analyzer (Shimadzu, Japan) was used to analyze the DOC of humus. A PE-Optima 8000 Inductively Coupled Plasma Emission Spectrometer was used to analyze the total amount of Cr, while the amount of Cr(VI) was determined by UV-1601 (Shimadzu, Japan).

2.2 Experiments

Magnetic humus was synthesized in a conical flask (1000 mL) at 35°C with shaking at 200 rpm. Fe_3O_4 nanoparticles (2000 mg/L) were added into the solution involving the precursors of catechol (3500 mg C/L), glycine (1750 mg C/L) and glucose (1750 mg C/L). To investigate the effect of pH on the weight of loaded humus on the surface of Fe_3O_4 nanoparticles, the initial pH of Na_2HPO_4/NaH_2PO_4 solution (0.2 M, 500 mL) was set to 4, 6, 8, and 10.

1.0 mL samples were withdrawn from the flask at 0, 4, 9, 20, 32, 45, 80, 120, 160, 260, 360 and 500 h intervals and set in an external magnetic field for solid-liquid separation. A 0.1 mL aliquot withdrawn from the above supernatant was diluted to 10 mL and subjected to UV-Vis absorption spectroscopy at 400 nm. Another 0.5 mL sample was diluted to 20 mL and used to dissolve the organic carbon content before analysis, while, the magnetic humus was used to humus loading analysis. Briefly, the magnetic humus was separated from a 10 mL solution with an external magnet and extracted for three times by 3 × 10 mL NaOH solution (0.1M). After that, the obtained NaOH solutions were analyzed by a TOC analyzer with the extraction efficiency of 84.86%. The magnetic humus separated from the incubated samples for 500 h was applied for the TEM surface morphology study.

3. RESULTS AND DISCUSSION

3.1 Reinforcement effect in the darkening experiment

The formation of organic chromophoric groups due to the darkening effect of humification and generation of the browning substances, as a key process of humification, can be justified through studying absorbance at 400 nm. Fe_3O_4 nanoparticles were used to enhance the humification in four systems with the pH of 4, 6, 8 and 10. The absorbance of supernatant solutions at 400 nm was varied with incubation time, as shown in Figure 2A. When pH was set to 4, the slow increase of supernatant absorbance indicated slow humification reaction throughout the entire experimental process. While, absorbance of the extracted humus from the magnetic counterpart was sharply increased in the first 45 h and, then, remained constant (Figure 2B). This observation could be explained by the fact that humus has been formed fast in the first 45 h, followed by adsorption on Fe_3O_4 nanoparticles to form a core-shell composite through electrostatic forces. However, the shell-like humus directly covered the active sites of Fe_3O_4 nanoparticles and weakened its ability to enhance humification. This behavior can also be found in the humification process at pH 6, but

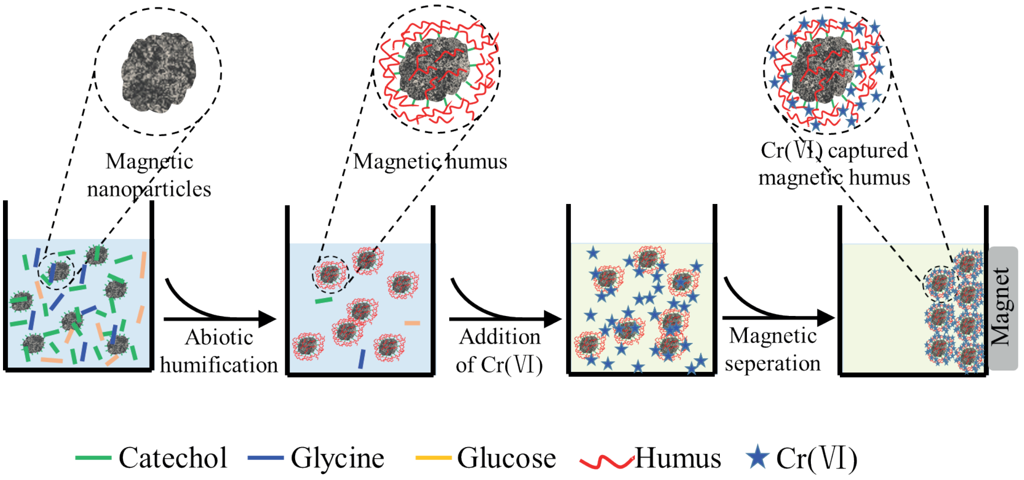

FIGURE 1: Representations of the procedures for magnetic humus preparation and Cr(VI) removal.

the supernatant samples were gradually darkened as the extension of incubation time and, finally, the absorbance reached to 0.60 after 500 h incubation. This finding suggested that the colored humus has been continuously generated. By contrast, the absorbance of supernatant solution at pHs of 8 and 10 was sharply increased over time within the first 45 h, and then set at a nearly constant value of 1.15, suggesting that the humus has been significantly generated and reached to a maximum weight after 45 h. On the other hand, absorbance of the extracted humus showed a similar trend with that of supernatant samples. The slight increase of absorbance after 45 h could be due to the connection of free small amount of humus to magnetic humus under the action of metal oxides. Therefore, the alkaline condition is suitable to enhance humification on Fe_3O_4 nanoparticles in the presence of catechol, glycine, and glucose as precursors.

3.2 Generation of magnetic humus

The TEM image of Fe_3O_4 nanoparticles confirmed that Fe_3O_4 nanoparticles have a regular spherical shape with the uniform size of about 11.59 ± 0.23 nm (n = 17), as shown in Figure 3A. The inset of this figure shows a lattice with the width of 0.26 nm for Fe_3O_4 nanoparticles. The magnetite nanoparticles were surrounded by a layer of an organic material after coating with humus (Figure 3B). This organic material can be extracted by 0.1 M NaOH for total organic carbon analysis.

The weight of humus loaded on Fe_3O_4 nanoparticles was analyzed, as depicted in Figure 4. The total organic carbon of humus on the surface of Fe_3O_4 nanoparticles was detectable, confirming the successful synthesis of magnetic humus. It is clearly demonstrated that humus can gradually grow on the surface of Fe_3O_4 nanoparticles, as the carbon content was varied with the incubation time throughout the entire experiments. Due to the faster generation of humus in an alkaline condition, the humus loading on Fe_3O_4 nanoparticles was higher under this condition compared to that in the acidic environment. The Fe_3O_4 nanoparticles separated at pH 8 and under the incubation time of 500 h revealed the largest amount of humus with the total carbon content of 243.13 mg per gram of

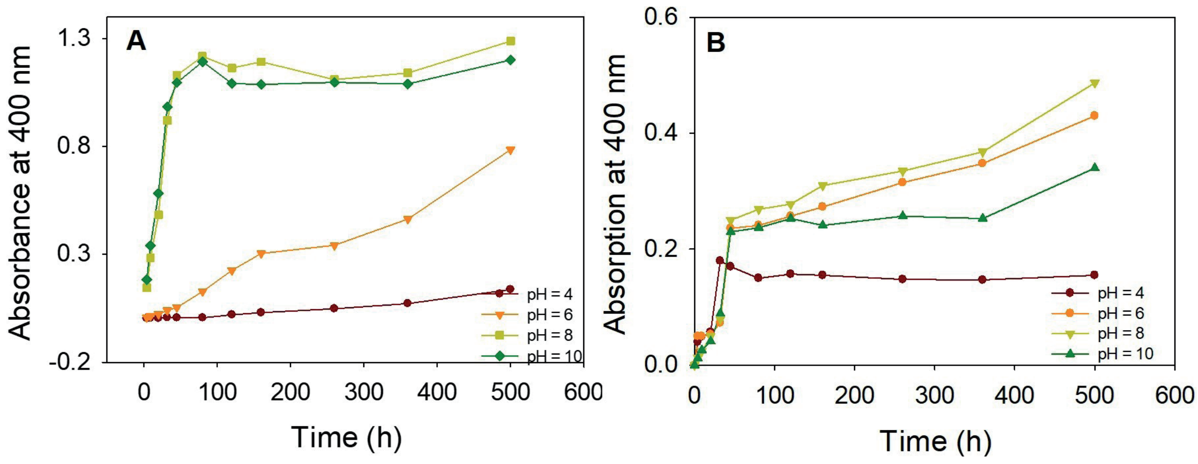

FIGURE 2: Absorbance at 400 nm of (A) the supernatant solutions after 100 times dilution (B) the extracted humus from the magnetic humus after 50 times dilution.

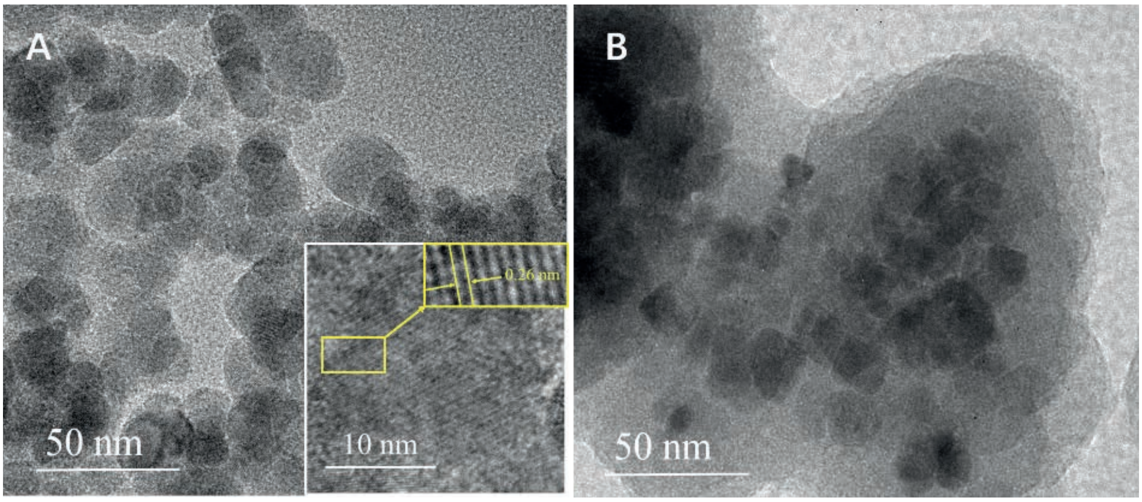

FIGURE 3: TEM images of (A) Fe3O4 and (B) magnetic humus.

nanoparticles, which was about 0.5 mg humus/mg Fe_3O_4 based on the humus carbon percentage of 48.54% (Zhang et al., 2015). Therefore, the magnetic humus should be contained 33.37% humus, which is much higher than 11% attained in the previous report (Liu, et al., 2008). This observation can be explained by consideration of the further exposure of Fe_3O_4 active sites involved in the humification process under alkaline condition. These active sites contribute to the formation of humus with a higher aromaticity, so more active sites mean a higher generation rate of humus (Zou et al., 2020). Instead of the spherical structure at a low pH, humus was existed in a rather linear or stretched structure at high pH values, as alkaline conditions contribute to the formation of further amounts of humus. This is because the dissolution process of humus avoids occupying further spaces and provides more free spaces for the humus formation near the metal oxide surface. However, too high pH is not conducive to the binding of humus with nanoparticles, therefore, the pH of 8 was adjusted for the generation of magnetic humus.

3.3 Availability of the synthesized magnetic humus

To investigate the ease of separation, performance of the magnetic humus was evaluated in an external magnetic field. As shown in Figure 5, the magnetic humus was scattered in the solution, even after 1 h incubation, in the absence of an external magnetic field. This finding proved good dispersion of the magnetic humus. However, the suspended magnetic humus can be quickly attracted towards a permanent magnet in 2 min, confirming the utility of magnetic humus separation in the presence of an external magnetic field.

The stability of magnetic humus was evaluated in distilled water. After shaking at 200 rpm for 12 h, the supernatant was collected and analyzed with a TOC analyzer to detect the leached humus. The concentration of free carbon was less than 15 mg/L (as TOC), indicating only 6.17% of humus has been leached. The main reason to explain this phenomenon is that the surface of Fe_3O_4 nanoparticles bear a negative charge (PZC = 7.9) at pH 8, which avoids the electrostatic attraction of Fe_3O_4 nanoparticles to the negatively charged humus and achieves growing of humus on the surface of Fe_3O_4 by covalent binding. Thus, the humus loading would be further enhanced apart from pH variation, upon addition of a non-magnetic metal oxide with enhanced humification function. Therefore, the outer humus molecules can be connected to form a bigger humus molecule through covalent bonding, which result in a big network, enclose the inner humus and avoid the inner humus molecular diffusion. In this way, the humus loading, as well as its stability would be enhanced.

In order to evaluate application of the synthesized humus in water treatment, the magnetic humus was added to a water sample solution containing 7.30 mg/L of Cr(VI). After 6 h, the synthesized magnetic humus (4 mg/mL) showed a high adsorption efficiency of 99.17% to Cr(VI) with the final concentration of 60 μg/L, which was lower than the maximum contaminant limits for the total chromium in drinking water (100 μg/L), as announced by the United States Environmental Protection Agency.

4. CONCLUSIONS

A new abiotic humification method is presented to synthesize magnetic humus with a high performance for Cr(VI) adsorption. The change of TEM image after humus loading indicated the successful synthesis of magnetic humus. pH greatly affects formation of humus and weight of the humus loaded on Fe_3O_4 nanoparticles. When pH is set to 8, the largest loading weight would be obtained, which accounts for 33.37% of the synthesized magnetic humus. The prepared magnetic humus exhibits good separation ability in aqueous solution and a high adsorption efficiency of 99.17% can be attained for Cr(VI). Therefore, the synthesized magnetic humus can be recommended as a potential candidate to remove Cr(VI) from water resources.

ACKNOWLEDGEMENTS

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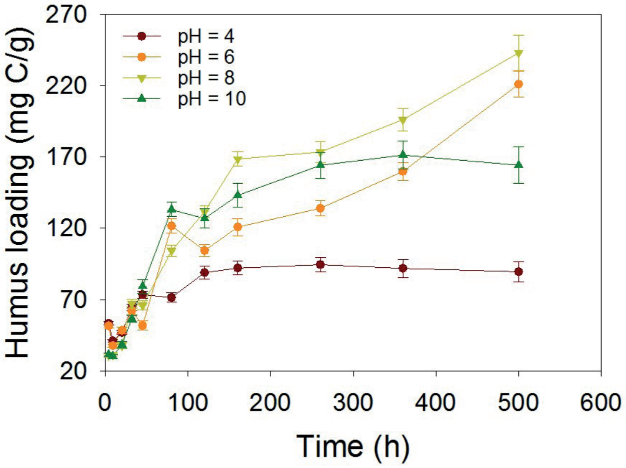

FIGURE 4: Effect of pH on humus loading in different incubation times.

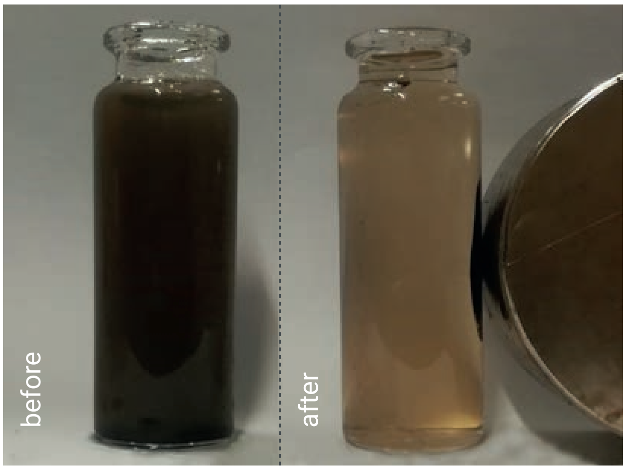

FIGURE 5: Digital images of magnetic humus without or with an external magnetic field added.

REFERENCES

Koesnarpadi, S., Santosa, S. J., Siswanta, D., & Rusdiarso, B. (2017). Humic Acid Coated Fe3O4 Nanoparticle for Phenol Sorption. Indonesian Journal of Chemistry, 17(2), 274-283. doi:10.22146/ijc.22545

Liu, J. F., Zhao, Z. S., & Jiang, G. B. (2008). Coating Fe3O4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environmental Science & Technology, 42(18), 6949-6954. doi:10.1021/es800924c

Liu, Y. G., Li, T. T., Zeng, G. M., Zheng, B. H., Xu, W. H., & Liu, S. B. (2016). Removal of Pb(I) from aqueous solution by magnetic humic acid/chitosan composites. Journal of Central South University, 23(11), 2809-2817. doi:10.1007/s11771-016-3344-1

Peng, L., Qin, P. F., Lei, M., Zeng, Q. R., Song, H. J., Yang, J., Shao J., Liao B.H., Gu, J. D. (2012). Modifying Fe3O4 nanoparticles with humic acid for removal of Rhodamine B in water. Journal of Hazardous Materials, 209, 193-198. doi:10.1016/j.jhazmat.2012.01.011

Rashid, M., Sterbinsky, G. E., Pinilla, M. A. G., Cai, Y., & O'Shea, K. E. (2018). Kinetic and Mechanistic Evaluation of Inorganic Arsenic Species Adsorption onto Humic Acid Grafted Magnetite Nanoparticles. Journal of Physical Chemistry C, 122(25), 13540-13547. doi:10.1021/acs.jpcc.7b12438

Singhal, P., Jha, S. K., Pandey, S. P., & Neogy, S. (2017). Rapid extraction of uranium from sea water using Fe3O4 and humic acid coated Fe3O4 nanoparticles. Journal of Hazardous Materials, 335, 152-161. doi:10.1016/j.jhazmat.2017.04.043

Singhal, P., Pulhani, V., Ali, S. M., & Ningthoujam, R. S. (2019). Sorption of different metal ions on magnetic nanoparticles and their effect on nanoparticles settlement. Environmental Nanotechnology, Monitoring & Management, 11, 100202. doi:https://doi.org/10.1016/j.enmm.2018.100202

Singhal, P., Vats, B. G., & Pulhani, V. (2020a). Magnetic nanoparticles for the recovery of uranium from sea water: Challenges involved from research to development. Journal of Industrial and Engineering Chemistry, 90, 17-35. doi:https://doi.org/10.1016/j.jiec.2020.07.035

Singhal, P., Vats, B. G., Yadav, A., & Pulhani, V. (2020b). Efficient extraction of uranium from environmental samples using phosphoramide functionalized magnetic nanoparticles: Understanding adsorption and binding mechanisms. Journal of Hazardous Materials, 384, 121353. doi:https://doi.org/10.1016/j.jhazmat.2019.121353

Tang, Z., Zhao, X. L., Zhao, T. H., Wang, H., Wang, P. F., Wu, F. C., & Giesy, J. P. (2016). Magnetic Nanoparticles Interaction with Humic Acid: In the Presence of Surfactants. Environmental Science & Technology, 50(16), 8640-8648. doi:10.1021/acs.est.6b01749

Yang, S. T., Zong, P. F., Ren, X. M., Wang, Q., & Wang, X. K. (2012). Rapid and Highly Efficient Preconcentration of Eu(III) by Core-Shell Structured Fe3O4@Humic Acid Magnetic Nanoparticles. Acs Applied Materials & Interfaces, 4(12), 6890-6899. doi:10.1021/am3020372

Yang, T., & Hodson, M. E. (2018). The copper complexation ability of a synthetic humic-like acid formed by an abiotic humification process and the effect of experimental factors on its copper complexation ability. Environmental Science and Pollution Research, 25(16), 15873-15884. doi:10.1007/s11356-018-1836-2

Zhang, Y. C., Yue, D. B., Lu, X. F., Zhao, K. Y., & Ma, H. (2017). Role of ferric oxide in abiotic humification enhancement of organic matter. Journal of Material Cycles and Waste Management, 19(1), 585-591. doi:10.1007/s10163-015-0435-2

Zhang, Y. C., Yue, D. B., & Ma, H. (2015). Darkening mechanism and kinetics of humification process in catechol-Maillard system. Chemosphere, 130, 40-45.

Zhang, Y. C., Yue, D. B., Wang, X., & Song, W. F. (2019). Mechanism of oxidation and catalysis of organic matter abiotic humification in the presence of MnO2. Journal of Environmental Sciences-China, 77, 167-173. doi:10.1016/j.jes.2018.07.002

Zou, J., Huang, J., Yue, D., & Zhang, H. (2020). Roles of oxygen and Mn (IV) oxide in abiotic formation of humic substances by oxidative polymerization of polyphenol and amino acid. Chemical Engineering Journal, 393, 124734. doi:https://doi.org/10.1016/j.cej.2020.124734

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CISA

COMMUNICATING SOURCE SEPARATION OF URINE

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ABSTRACT

One of the main issues regarding the implementation of source-separation-based sanitation systems is user acceptance, which is related directly to the state of knowledge of citizens. A communication platform for the exhibition and interactive information on the topic of resource-oriented sanitation (ROS) was developed as part of the P-BANK transdisciplinary project. The P-BANK platform is based on a toilet in the public space. The communication concept focusses on the actual use of the toilets and the surrounding nutrient cycle. The central object of the communication at the P-BANK, as its name suggests, is the macronutrient phosphorus. This simplification creates a symbolic effect which is supported by the ambiguity of the sound of the chemical symbol "P" for phosphorus in connection with urinating (to pee). Furthermore, this reduction aims at shortening the messages and simplifying the information transfer. In the first project phase, the transportable system was field-tested and evaluated in the context of the 100th anniversary of the Bauhaus in Weimar. After positive reviews and experiences concerning the performance of the technical facilities and the success of the communication concept, the P-BANK will be tested and evaluated in further awareness-raising campaigns.

1. INTRODUCTION

In addition to water supply and solar energy, macronutrients in the soil are of outstanding importance for flora. Along with nitrogen and potassium, phosphorus is one of the main nutritional elements that is essential for plant health and development. All three macronutrients represent a global challenge in many ways, both now and in the future. This is reflected in the extraction of the nutrients as resources as well as in its role as potential contaminants in urban water management (Schaum, 2018).

1.1 The role of nutrients

Modern agriculture is covering the lack of macronutrients (nitrogen, phosphorus, and potassium) and micronutrients by synthetic fertilisers. These fertilisers are produced on the basis of geological resources, e.g. the use of fossil fuels in the production of nitrogen in the Haber-Bosch process and the extraction of phosphate and potassium from mines. Potassium and phosphorus are mined in only a few countries in the world, which leads to geopolitical tensions and may be exacerbated in the future on the basis of the in part already insufficient nutrient supply of the soil (Ciceri et al., 2015; Cordell et al., 2009; Manning, 2015; Manning, 2018). Studies show that a high rate of soils both in developing regions like India as well as developed countries like the UK are deficient in at least one micronutrient (Jones et al., 2013). Alternative sources of phosphorus, nitrogen, and potassium same as micronutrients are essential to maintain food security but also to prevent the increase of considerable geopolitical stress (EcoSanRes, 2005; Razon, 2018; Steen, 1998).

The nutrients important for the soil (especially phosphorus and nitrogen) have a negative impact on the biodiversity of water bodies. The main cause is the massive human impact on the global P and N cycles (Rockström et al. 2009) because human excreta that are returned to the natural cycle in the wrong place and in a concentrated form can, for example, lead to eutrophication of waters (Schaum, 2018). Requirements for the elimination of these nutrients contained in human excreta and greywater are already manifested in legislation (Council Directive 91/271/EEC, 1991).

1.2 The fate of nutrients in human excreta

Properly treated faecal material flows are non-problematic substances but valuable resources. Agriculture and food production are connected inevitably to human excreta management (Harder et al., 2020). Of the phosphorus used in Europe, 30% is lost from human excreta into water bodies or sewage sludge (Schaum, 2018). This is where Resource-Oriented Sanitation Systems (ROS)

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can come into play. As an alternative to the conventional central water-borne sewage system, the core objective of these technical solutions is the recovery of valuable substances from urine, faeces, and greywater. The nutrients are contained primarily in urine and faeces. In conventional sanitation systems, approximately 30% of the daily drinking water amount per inhabitant (Shouler et al., 1998) is contaminated with nutrients and trace substances, such as pathogenic germs, hormones, heavy metals, and pharmaceuticals, transporting them over long distances to central sewage treatment plants. While the above-mentioned micropollutants pass through mechanical-biological wastewater treatment plants (Ebert, 2013), nutrients are removed from the wastewater without recovery. In principle, nutrient recovery in wastewater treatment plants is possible but related to a high additional procedural expenditure. Regarding this and the mentioned dilution and discharge of nutrient-rich excreta, the adequacy of the central approach is questionable. The approach of ROS is the separation of urine, faeces and greywater at source followed by a targeted treatment and focused reuse of the contained resources. In consequence nutrient cycles can be closed more easily. A separate collection requires modified technical installation facilities, with numerous daily user interactions (Kraus et al., 2019, Larsen et al., 2013; Lienert and Larsen, 2006).

1.3 Challenges in the implementation of Resource-Oriented Sanitation

New types of sanitation systems have been the subject of technical research and development in urban water management for several years. These technologies can be considered technologically mature on the basis of various fact sheets and worksheets. Nevertheless, these concepts so far have been implemented exclusively within the framework of pilot projects and research projects and are not of much concern to society at large (Larsen et al., 2013, Blanken et al., 2019, Schramm et al., 2018).

The reasons for this are diverse and are based largely on the status quo of the water management infrastructure and existing laws. For example, one of the main reasons for rejecting the implementation of ROS is the constructional expenditure for material flow separation in existing buildings, which is associated with extensive investments. Another issue is the limited approval of fertilisers produced from human excreta. Of particular relevance is the acceptance by society, some of which, according to various focus group studies (e.g. Lienert and Larsen, 2006, Pahl-Wostl et al., 2003), are in favour of the use of ROS in general but have concerns about the use of fertilisers recovered from human excreta. For example, a large part of society understands the term "alternative toilets" to mean primitive latrines, which leads to doubts about aesthetic standards and toilet comfort (Del Morales et al., 2014).

For the general restructuring of urban water management towards a sustainable and ecological approach, it is inherently important to consider different levels of perspective. The challenge of closing the loop for a material such as phosphorus, potassium and nitrogen must therefore be met not only at the political, economic, and technical level. In particular, society and the public are the foundation for the success of such far-reaching restructuring processes. Creation and expansion of the overall social awareness and thus acceptance is decisive for this. The reframing of human excreta management as part of food and farming systems has potential to support long-term global food, soil, and nutrient security while also reducing the risk of compromising other priorities related to health and environmental issues (Harder et al., 2020).

Accordingly, knowledge and user acceptance are essential for a broad implementation of ROS in municipal sanitation systems. Citizens are important decision-makers in their role as tenants, home owners, and buyers of recycled products from human excreta (Pahl-Wostl et al., 2003).

1.4 The perception of the role of excreta

The transformation of research results and elite knowledge into education and information for the general public is of great importance for the social acceptance of such approaches. In modern society, the issues of human excreta and excretion itself are viewed primarily negatively or avoided altogether. Individuals want to be disassociated from the act of producing urine and faeces and view the substances as disgusting and worthless. The very wording of the visit to the toilet implies a distancing from the activity itself, such as going to the bathroom or restroom. In addition, terms referring to excreta and the associated body parts are used often as swear words or jokes. These psychological effects can lead to health impairments. For example, it can lead to inhibition of micturition in the presence of other people in public toilets or, in the worst case, not using the toilet, and can even affect the hydration of the body (Haslam, 2012; Kira, 1976; Lundblad and Hellstrom, 2005; Michels et al., 2019; Middlemist et al., 1976; Weinberg and Williams, 2005).

With regards to the psychological and social aspects of excretion per se, a fundamental change in the associations of quickest possible disposal and the consideration of human excreta as worthless, disgusting substances to the actual usability and value of the nutrient-rich substrates is crucial.

1.5 Objectives and approach

Our approach to solving the problem is to create and expand public attention and awareness. The project "Phosphorus Bank" (P-Bank), funded by the German Federal Foundation for the Environment, combines the advantages of material flow separation with the treatment of urine for the production of fertilisers. The aim of the project was to create an information platform that enables an interactive approach to the aforementioned topics for a wide range of target groups. The focus was on the transport of straightforward information and the communication of contexts. For a wide audience reach and a seamless integration of the new approaches into the daily life of the users, the object chosen was the toilet in public space.

2. DEVELOPING THE P-BANK

For the design of the communication, we have considered and applied a variety of approaches from pedagogy and architecture. The key basis for all awareness-raising and information campaigns of new technologies and in particular of new sanitation systems is to ensure the functionality of the technical equipment. Most important for the communication of a topic that is regarded negatively or reluctantly addressed in society is architectural interior design. Transforming the toilet visit into a positively connotated activity and enabling pleasant associations, the design, and the resulting atmosphere are essential. In addition, a pleasant environment is crucial for the sense of well-being and thus conducive to learning processes. Based on studies like Fich et al. (2014), Krüger and Zannin (2004) and Vartanian et al. (2013), the top priority for the design of the communication platform was an aesthetic design of the rooms and pleasant acoustic, thermal, and lighting conditions.

The public space is not a defined place but is always formed by the individual values of those whom it comprises (Wildemeersch, 2012). For progress and a sustainable change of views, public space, social encounters, and civic pedagogy must be kept open and undecided (Ellsworth, 2005). The communication concept of the P-Bank is based on an open installation in the public space for a visitor selection that is as heterogeneous as possible.

The basic ideas for the information design are based on the combination of learning concepts such as experiential (Kolb, 1984), active (Krempl et al., 2016), and subject-oriented learning (Teichmann et al., 2019). To take into account the complexity of the learning styles, skills, and modes discussed in pedagogy (Biesta, 2006; Boyatzis and Kolb, 1991; Davidson, 1984; Kolb and Kolb, 2018; Ryan and Charman, 2014), different learning channels are used and all senses are addressed to make the transported information more memorable (Falk and Dierking, 1998). The focus is on very open non-verbal or short verbal information provided to make the most of the potentially very short time windows and to give the visitor control over the information and learning process.

The theory of reasoned action and planned behaviour includes several aspects that influence behaviour (Ajzen, 1991). In addition to social and moral values, factual knowledge plays a major role. However, many studies describe the connection between factual knowledge and behaviour with regards to environmental knowledge and ecological behaviour as low to non-existent. According to Kaiser et al. (1999), when the connections are stronger, knowledge about ecological behaviour (e.g. what and how it can be done) is of more interest than knowledge about the environment itself. According to Arshad et al. (2020), awareness and concern are also more important than the more difficult to change (Sayers, 2006) environmental attitude.

To initiate reflection and learning, normal flows of experience must be interrupted (Kolb and Kolb, 2018; Wildemeersch, 2012; Ellsworth, 2005). The goal of the P-BANK-concept is to create a transitional space, where the self-evident understanding of public toilets is interrupted and the user is invited or provoked to reconsider understandings and emotions. The P-BANK identifies alternatives without providing a ready-made opinion. The information on windows of opportunity in alternative system design is shown as an example in terms of urine recycling. Here the visitor receives a stimulus for independent information in discourse with others and, if desired, more in-depth research.

3. THE P-BANK

The P-BANK collaborative project combines the technical implementation of ROS with aesthetic design components. As an information platform combining a public toilet with nutrient recycling, the P-BANK creates opportunities for the identification with various individual interfaces concerning urine disposal and resource recovery. The main objective was to present and evaluate a newly designed toilet concept in public spaces to present ROS as an alternative to conventional sewage systems. Sensitising users to the shortage of the life-essential resource phosphorus (P = "phosphorus") as well as the simultaneous misallocation of nutrients (P = to "pee") and the resulting harmful impact on the environment is the stated purpose. Use in the public space enables the evaluation of the level of knowledge of the users as well as the supply of information to the users. The focus lies on the scarcity of resources and the solution approaches of ROS mentioned above. In addition, the user acceptance for alternative sanitation concepts amongst the population can be investigated.

3.1 Transforming an everyday need into an interactive learning space

The P-BANK is intended to create identification possibilities for the user with the help of an experiential space based on interfaces between urine disposal and potential resource recovery. The linked objective includes, on the one hand, the raising of awareness around the issues of phosphorus scarcity and sustainable use of vital resources such as plant nutrients (especially phosphorus, nitrogen and potassium) and water. The aim is not only to present the problems, but also to present solutions that work directly. The second sub-goal is therefore to demonstrate marketable sanitation product solutions that contribute to closing natural cycles. Communicating ways to recycle urine, faeces and grey water using existing products such as recycled fertiliser is also aimed at.

The technical equipment combined with a communication and service concept is the key element of the P-BANK. The transformation of the toilet as a "quiet little place" into a design object in the form of a donation bank for nutrients leads to an image change of public toilets.

The idea of conveying information with the communication concept of the P-BANK follows different principles. Essential is an aesthetically pleasing design that ensures a convenient learning atmosphere but does not interfere with the original purpose of the site visit. The toilet visit should be framed by a pleasant atmosphere to make the activity itself and the presented sanitary systems as attractive as possible. The interactive design of the concept is decisive for the possibility of identification with the presented problem as well as the solution approaches. With the direct link to the use of the public toilet, a specific cycle can be shown as an excerpt from the possibilities of novel sanitary systems. The resulting simplification of the context is an important point for the comprehensibility of the information and the sustainability of the information transfer.

By focusing on nutrient recycling from urine or yellow water, an excerpt from the transformation potential of wastewater disposal is conveyed in an exemplary manner (Figure 1).

3.2 Raising the awareness of ROS as an alternative to conventional sewers

Based on the communication and information concept of the P-BANK, the user interaction points with urine disposal and resource recovery are arranged logically by the order of the stations related to a visit to the toilet. The visitor is led through a guided tour, which starts with the arrival at the entrance to the stairs of the P-BANK. The signs on the stairs introduce visitors to the topic of P scarcity (Figure 2 and Figure 3).

3.2.1 Nutrient donation

Once aware of the singularity of the P-BANK public toilet and the topic, the user enters the waiting room, where the doors to the actual toilet rooms are located. The two rooms, containing a waterless urinal (WU) and a urine diversion toilet (UDT), are marked as donor rooms (Figure 4).

In short, the P-BANK is intended as a platform for presenting diverse sanitary installations and ROS concepts. In the current configuration "save!" (Gründl, 2018), a new type of flush separation toilet, is implemented, in which the separation is performed with a so-called urine trap based on the principle of surface tension at the bowl edge. This sanitary installation is characterised by differences to conventional flush toilets that are invisible to the user, which is a relevant aspect for the well-being and thus the impact of the P-BANK communication concept. The functionality of the separation of the urine either in the WU or in the UDT is explained with the help of labels and graphic illustrations. In the donor rooms, the user is invited to donate urine (pee) and in consequence the phosphorus (P) by signs on the wall or the floor (dependent on the type of sanitary installation). During the toilet visit, the phosphorus cycle is presented to the user graphically in a simplified form (Figure 5).

3.2.2 Nutrient recycling from urine

The guided tour continues at the next station - the washbasin. Here the user is introduced to the urine treatment units, which are located behind a transparent PET screen instead of a mirror above the basin (Figure 6). As with the sanitary facilities, the P-BANK will also serve as a modular presentation platform for the treatment processes.

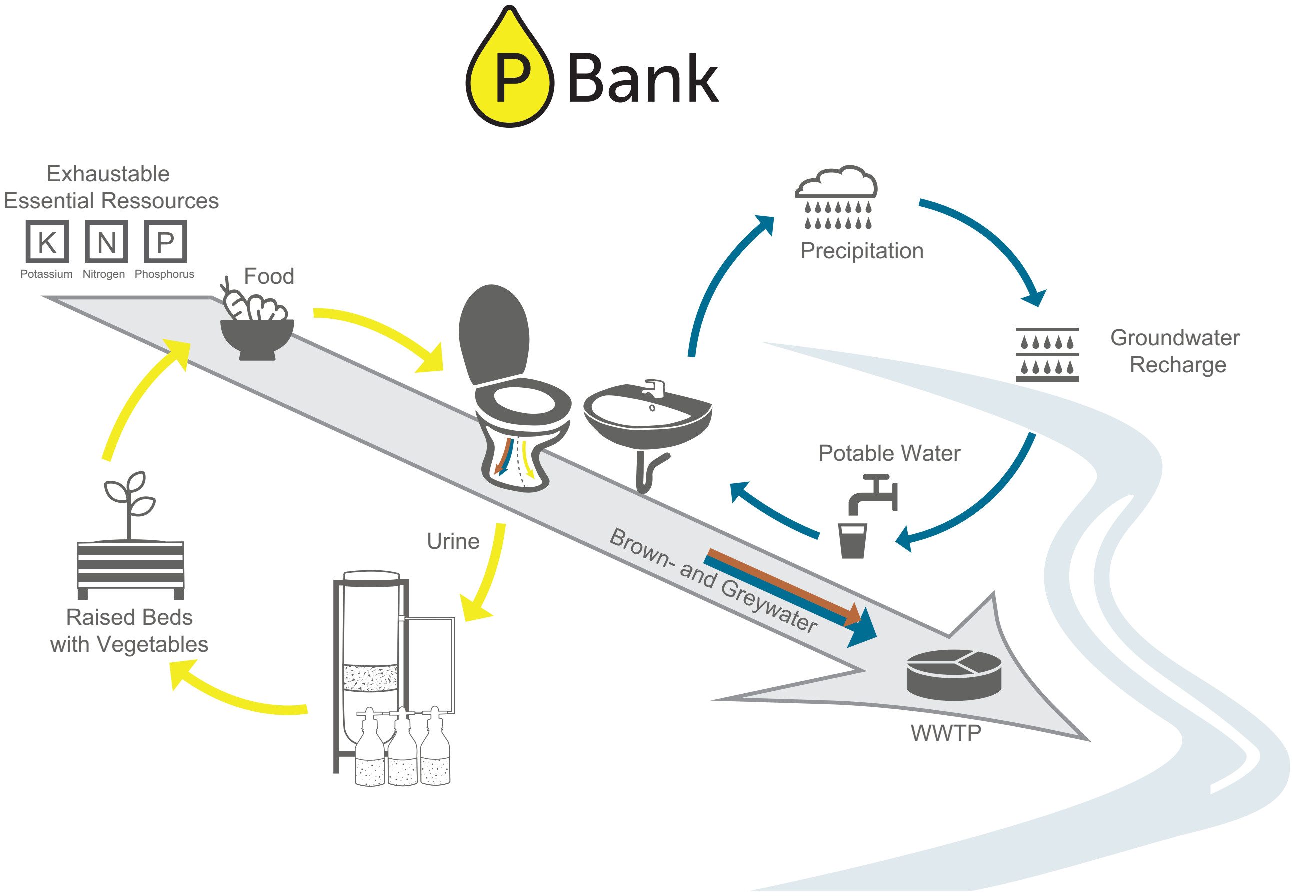


FIGURE 1: Decreased information content for a simplified knowledge transfer at the P-BANK.

FIGURE 2: Exterior view of the P-BANK on the premises of the Bauhaus-Universität Weimar in 2019.


We are almost 9 billion people and completely depend on modern agriculture for our food security.

Wir sind fast 9 Milliarden Menschen und für die Ernährungssicherung auf moderne Landwirtschaft angewiesen.

WE NEED FOOD TO GROW

WIR BRAUCHEN NAHRUNG ZUM WACHSEN

Phosphorus is an essential nutrient for plants to grow. Modern agriculture relies on it as fertilizer.

Phosphor ist ein essentieller Nährstoff für das Wachstum von Pflanzen. Die moderne Landwirtschaft setzt darauf als Düngemittel.

FOOD NEEDS P TO GROW

NAHRUNG BRAUCHT P ZUM WACHSEN

Phosphorus is currently still obtained from mines, but these are almost depleted.

Phosphor wird derzeit noch aus Minen gewonnen, diese sind jedoch fast erschöpft.

P-SOURCES ARE RUNNING LOW

UNSERE VORHANDENEN P-QUELLEN SIND BALD AUFGEBRAUCHT

Our future food security depends on Phosphorus. Without Phosphorus there will be not enough to eat.

Die Gewährleistung unserer Nahrungsversorgung hängt von Phosphor ab. Ohne Phosphor werden wir nicht genug zu essen haben.

WE NEED NEW P-SOURCES NOW!

WIR BRAUCHEN DRINGEND NEUE P-QUELLEN!

FIGURE 3: Stair signs of the P-BANK telling the causal chain from P use to P recycling.

The selection of the methods has to be made straightforward to explain and to generate substances that can be used as fertilisers to enable the nutrient cycle to be closed. While installing the treatment processes, particular attention was paid to ensuring the best possible clarity and transparency. The production of the nutrient-containing end products was also to be illustrated. The order of the individual process steps is indicated by a numbered sequence identification. In addition, for each sub-process, a simple short explanation, understandable for non-experts, is provided in close proximity to the processing.

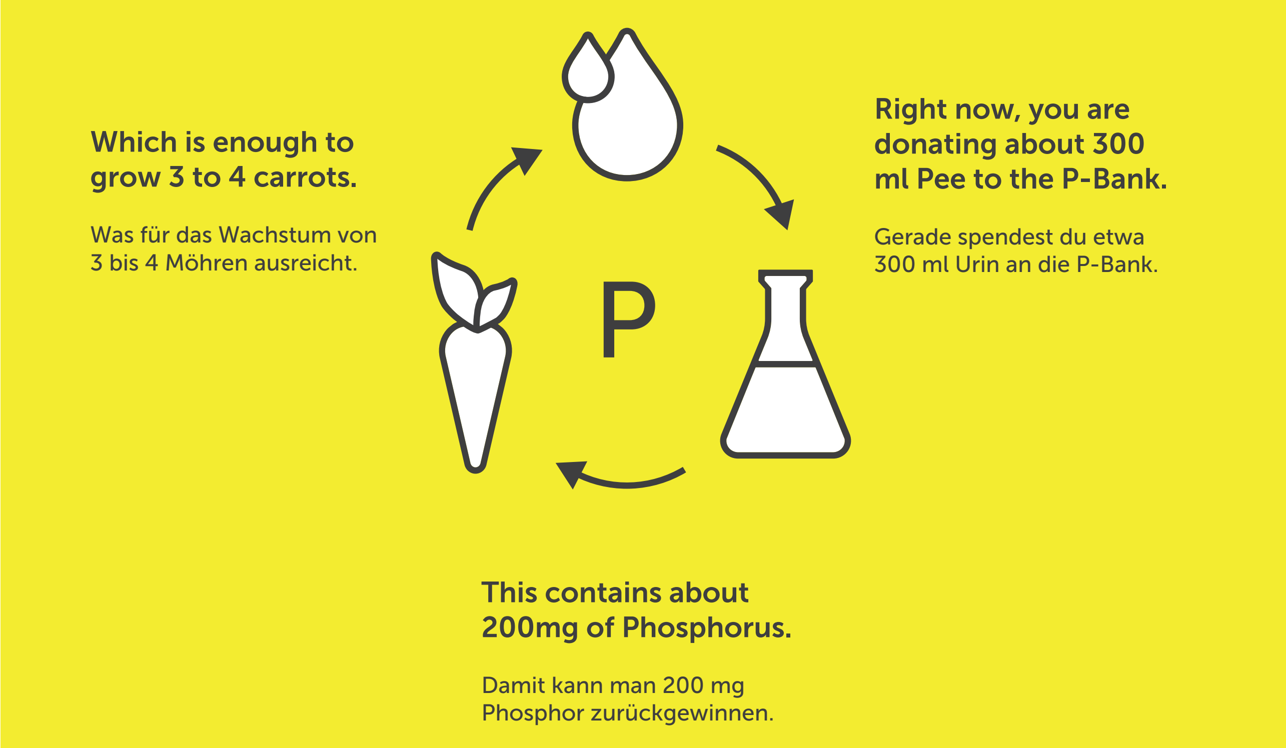
In the current setup, the urine treatment consists of two recycling lines, which are operated independently of each other for demonstration purposes to indicate the large variety of possible treatment processes of ROS.

Line 1 (Figure 6, left-hand side) includes treatment us-

FIGURE 4: Donor room with waterless urinal.

ing the biological and physical processes of urea hydrolysis followed by ammonia stripping with simultaneous precipitation on a carrier material and subsequent acidic gas scrubbing. The advantage of this combination of treatment steps is the simple structure and the visible introduction of air followed by the removal of ammonia from the urine and its washing in sulphuric acid. All components of the treatment process are transparent. For the gas stripping by air injection, a large bubble process was chosen to increase visibility. For the same reason, the indicator solution methyl orange was added to the gas scrubbing to indicate the consumption of the sulphuric acid and a change in the state and thus the composition of the solution. The resulting products are phosphorus salts on the carrier material and liquid ammonia sulphate.

Line 2 (Figure 6, right-hand side) based on the urine treatment unit in the blue diversion toilet of Eawag consists in the first step of the alkaline stabilisation using hydrated lime addition (Decrey and Kohn, 2017, Randall et al., 2016). This is followed by the drying of valuable substances by trickling the stabilised urine at a greatly reduced flow rate onto distribution plates with a low slope combined with simultaneous aeration of the plates (Antonini et al., 2012, Pahore et al., 2010, Udert et al., 2003, Udert et al., 2006). The exhaust air is cleaned by an activated carbon filter to avoid odour disturbance. Regarding the visibility of processes and products, the most important point of building this treatment line is the transparency of the evaporation reactor in the form of a display case with flow plates. This enables the presentation of the produced phosphorus salts on the plates.



Right now, you are donating about 300 ml Pee to the P-Bank.

Gerade spendest du etwa 300 ml Urin an die P-Bank.

This contains about 200mg of Phosphorus.

Damit kann man 200 mg Phosphor zurückgewinnen.

Which is enough to grow 3 to 4 carrots.

Was für das Wachstum von 3 bis 4 Möhren ausreicht.

FIGURE 5: The Phosphorus cycle explained in relation to the P-BANK stations.

FIGURE 6: Urine treatment units inside the P-BANK.

FIGURE 7: AURIN fertiliser as a thank you gift for the P donator.

3.2.3 Nutrient reuse

On leaving the P-BANK, the P-donor receives a thank-you gift in the form of a sample of AURIN, a urine-based liquid fertiliser from VUNA GmbH (Etter et al., 2015) designed for the P-BANK using the unique style (Figure 7). On the way out, the user's path is flanked by raised beds of herbs and vegetables that symbolise the final use of the generated fertiliser (see Figure 2). At this point, the phosphorus cycle is completed.

4. EVALUATING THE P-BANK

The first location of the P-BANK was the campus of the Bauhaus-Universität Weimar during the celebrations of the 100th anniversary of the Bauhaus. The facility was operated for four months close to the pop-up restaurant "Die Lücke", which was particularly suitable as a location because of the sustainability concept used and the raised beds for herb production. Based on sample counts on 7 unrelated days (Figure 8, left-hand side), the number of users of the whole P-Bank system during this first test period was approximately 4,700 (extrapolated on the basis of the median of the sample measurements). Of these, on average 70% used the UDT. The measured urine volume shows a slightly lower mean value for the UDT compared with the sum of both toilet types (Figure 8, right-hand side).

The evaluation of the P-Bank included in the first step

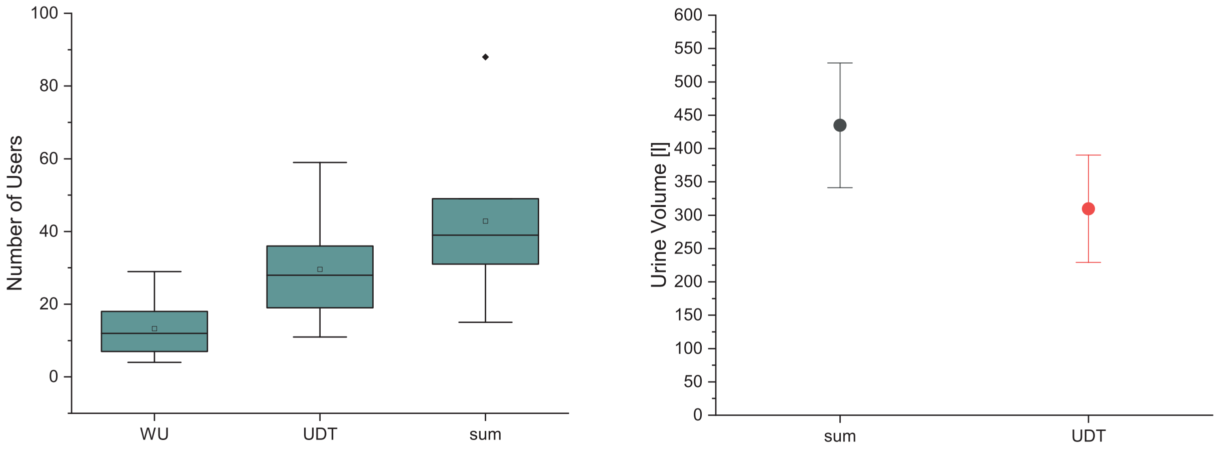


FIGURE 8: Number of visitors and urine volume per use during test period 1.

the examination of the functionality of the technologies used. In detail, the separation performance of the urine collection units was examined and compared with common volumes and substance concentrations in urine (Bauhaus-Institute for Infrastructure Solutions, 2016). To evaluate the functionality of the urine treatment units of the P-BANK, we analysed the characteristics of the solid products of both treatment lines.

The investigation of the effectiveness of the communication concept was based on a combination of quantitative and qualitative analyses. The advantages of combining both research methods lie in the extension and deepening of the results and conclusions by increasing openness and questioning the quantitative analysis (Harland and Holey, 2011; Mayring, 2001; Reja et al., 2003).

4.1 Technical Evaluation

4.1.1 Degree of separation of the collection system

During the first test phase, the urine was collected and analysed on a sample basis and compared with the guideline values according to Bauhaus-Institute for Infrastructure Solutions (2016). The results (Figure 9) show that the collected urine had lower concentrations for COD and total nitrogen (marked as outliers), while values for sulphate and potassium were within the expected range. The neighbouring pop-up restaurant was characterised by the fact that meals were not offered continuously during opening hours. It can therefore be assumed that beverages were consumed predominantly. As most toilet users were restaurant guests, it can be assumed that this may be a reason for the dilution.

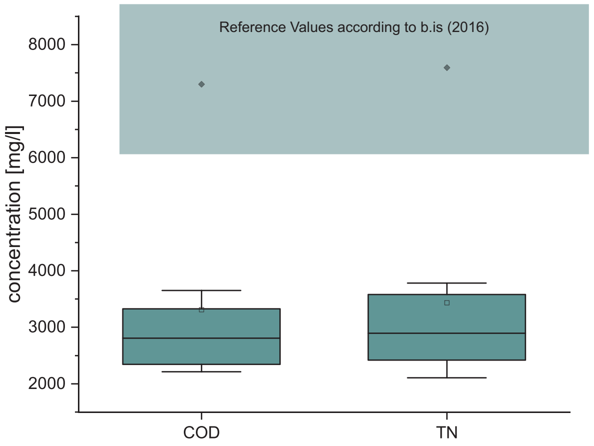


FIGURE 9: Boxplots of parameters of samples of the P-BANK users during test period 1.

4.1.2 Analysis of the produced materials

The analysis of all carrier materials showed little accumulation of phosphates, calcium, potassium, and magnesium, although the values are very low (Table 1). Additional crystalline substances were found inside the stripping unit that also consisted of the aforementioned elements. As the treatment units were built for demonstration issues without aiming for high efficiency, the low values are not surprising but still demonstrate the functionality.

4.2 Reception of the P-BANK

The interviewees were P-Bank users who were willing to participate in the survey by filling in the questionnaire themselves. The use of the P-Bank was voluntary and on their own initiative. This was ensured by its location in public space. The quantitative analysis (n = 55) consisted of a demographic survey of the respondents and the collection of five-point Likert-data on the effectiveness of the P-BANK. The investigation of the learning effects was evaluated using dichotomous questions in correlation with the personal previous knowledge as this knowledge is relevant particularly for the understanding of the communicated contents (Wilde, 2007). To extend the closed analysis, open questions were asked about subjective optimisation possibilities.

The individual environmental attitude varies depending on the topic. Furthermore, better predictions for specific environmental behaviour are based on the measurement of specific attitudes (Kaiser et al., 1999). For this reason, Likert-scaled questions such as the understanding of the function of resource-oriented sanitation systems, the environmental impact of such technologies, and the willingness to use them at home were used to investigate the

TABLE 1: Analysis of the solid substances.

Sampling point	K	Ca	P	Mg
	m-%			
Crystalline Substances (stripping unit)	3,15	0,43	4,98	0,02
Carrier Material (stripping unit)	3,01	0,37	2,16	0,021
Carrier Material (Evaporation unit)	1,39	0,65	0,76	0,042

specific attitude towards novel sanitation systems.

In order to estimate the reach in its entirety, we draw conclusions about the number of people reached on the basis of media-effective publications. This is based on publications on the Internet, social media posts as well as print media and television and radio reports.

4.2.1 Demographic data and user experience

The quantitative and qualitative data collection was performed during the time of operation in summer 2019 to obtain an overview of the perception of the P-BANK concept. Of the users who took part in the survey, 38% were male, 58% female and 4% gave no information. 9% of respondents were under 25, 42% were between 26 and 40 years old, 36% were between 41 and 65 years old, 13% were over 65. In terms of employment status, the largest share of participants (67%) were professionals. 2% of participants were school students, 15% retired and 7% said "other". Despite being located close to the university campus, only 9% were students.

The median and mode value of the Likert data on the convenience of the P-BANK was five. In detail, the visit to P-BANK was considered a very positive experience with very good hygiene and comfort. The clarity of the explained contents was evaluated with 4 out of 5 points in median and mode. The majority of respondents answered this question with 4 to 5 out of 5 points.

4.2.2 Knowledge enhancement

An interesting aspect of the survey is the symmetrical nature of the knowledge gained during the P-BANK visit in correlation with prior knowledge. Visitors with no previous knowledge of resource-oriented sanitation systems perceived the visit as a gain in knowledge; visitors with previous knowledge did not attest to this.

From the group of respondents who had heard about such sanitary systems in advance, the response to the question of whether such systems are environmentally friendly and the question of home use in the median and mode was 5 (I strongly agree). In the group of respondents with no prior knowledge, resource-oriented sanitation systems were also classified as environmentally friendly, and the question of private use was given a somewhat more cautious rating of 4 (I agree) in the median and mode. The qualitative part of the survey revealed in many cases a desire for more in-depth information on the systems propagated but also for basic knowledge of the existing conventional approach. Also, there were many questions about why this system is not yet implemented on a larger scale.

4.2.3 Response of press and public

The response of the press and public was reflected in radio and television reports, newspaper articles and social media contributions. The radio and television reports were shown in regional and national programmes of the public-law institutions. The total of all audience ratings of the relevant TV and radio programmes amounted to around 2,178,000 listeners and viewers. The primarily regional daily newspapers have a total daily circulation of 874,478 copies. Social media contributions were made by companies, public institutions and private individuals on the platforms Facebook, Instagram and Twitter. The total number of followers of all pages was 1,633,232, of which 5,798 interacted with the posts. In summary, in addition to the local P-Bank users, a potential audience of 4,685,710 can be assumed and the number of users who confirmed their knowledge of the content through active interaction can be determined at 5,798.

5. OUTLOOK

There are some limitations associated with the results. Therefore, the examination must be regarded as a pilot study. The investigation of the degree of separation of urine in the collection units was conducted on a random basis and therefore represents the investigation period as an example. During the first study, the location of the P-BANK on the university campus was near an alternative pop-up restaurant, thus providing a special setting. The age structure and distribution of the professional status of the respondents is acceptable at best. The voluntary use of the P-Bank and participation of the respondents in the evaluation could limit the picture of the impact of the P-Bank. The assessment of the press and public response makes no claim to completeness. Therefore, the assumed values should only be regarded as estimates. In addition, use was linked predominantly to a visit to a restaurant, which influences the status of the installation in public space and the characterisation of the collected urine.

The first testing campaign showed that the concept of the P-BANK interactive platform, in general, is appropriate for information campaigns and awareness-raising for the users on topics such as nutrient scarcity and possibilities of resource recovery from urine collected separately. The adaptation of the treatment plant for demonstration purposes resulted in losses in the efficiency of the recycling processes. Nevertheless, the functionality was still provided and the visible production of nutrient containing substances was guaranteed.

The portable unit will serve as an information and evaluation platform for alternative sanitation systems at other locations in the future and will be further investigated to optimise communication concepts regarding the functionality and advantages of ROS. The P-BANK can also be hired for information campaigns featuring other treatment methods for separately collected faeces or urine.

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REFERENCES

Ajzen, I. (1991). The Theory of Planned Behavior. Organizational Behavior and Human Decision Processes 50, 179–211.

Antonini, S., Nguyen, P.T., Arnold, U., Eichert. T., Clemens, J. (2012). "Solar thermal evaporation of human urine for nitrogen and phosphorus recovery in Vietnam." Sci Total Environ 414: 592-599.

Arshad, H; Saleem, K; Shafi, S; Ahmad, T. and Kanwal, S. (2020). Environmental Awareness, Concern, Attitude and Behavior of University Students: A Comparison Across Academic Disciplines. Polish Journal of Environmental Studies 30 (1), 561–570. https://doi.org/10.15244/pjoes/122617.

Bauhaus-Institute for Infrastructure Solutions (b.is) (Hrsg.) (2016). New Alternative Sanitation Systems - NASS. Weimar: Weiterbildendes Studium Wasser und Umwelt, Bauhaus-Universität Weimar. — ISBN: 978-3-95773-213-2

Biesta, G. (2006). Beyond learning. Democratic education for a human future. London/New York, Routledge/Taylor and Francis Group.

Blanken, M.; Verweij, C.; Mulder, K. (2019): „Why novel sanitary systems are hardly introduced?“. In: Journal of Sustainable Development of Energy, Water and Environment Systems. 7 (1), S. 13–27, DOI: 10.13044/j.sdewes.d6.0214.

Boyatzis, R.E. and Kolb, D.A. (1991). Assessing Individuality in Learning: the learning skills profile. Educational Psychology 11 (3-4), 279–295. https://doi.org/10.1080/0144341910110305.

Ciceri, D.; Manning, D.A.C. and Allanore, A. (2015). Historical and technical developments of potassium resources. The Science of the total environment 502, 590–601. https://doi.org/10.1016/j.scitotenv.2014.09.013.

Cordell, D.,Drangert, J.O. and White, S. (2009). The story of phosphorus: Global food security and food for thought. Global Environmental Change, 19(2), pp.292–305.

Council Directive 91/271/EEC on the approximation of the laws of the Member States concerning urban waste water treatment' (1991) Official Journal L135, p. 40.

Davidson, B. (1984). Styles in Teaching and Learning. Special Education: Forward Trends 11 (1), 19.

Decrey, L., and Kohn, T. (2017) Virus inactivation in stored human urine, sludge and animal manure under typical conditions of storage or mesophilic anaerobic digestion. Environmental Science: Water Research and Technology.

Del Morales, Margaret Carmen; Harris, Leila & Öberg, Gunilla (2014). Citizenshit: The Right to Flush and the Urban Sanitation Imaginary. Environment and Planning A: Economy and Space 46 (12), 2816–2833. https://doi.org/10.1068/a130331p.

Ebert, I. (2013). Pharmaceuticals in the Environment – A first Compilation of German Monitoring Data. Technical report, EPA.

EcoSanRes (2005). Closing the Loop on Phosphorus. , pp.1–2. Stockholm En-vironmental Institute (SEI). Schweden.

Ellsworth, E.A. (2005). Places of learning. Media, architecture, pedagogy. New York, RoutledgeFalmer.

Etter, B.; Gounden, T. and Udert, K. (2015). VUNA: Valorisation of Urine Nutrients – Final Project Report.

Falk, J.H.and Dierking, L.D. (1998). The museum experience. Washington, D.C, Whalesback Books.

Fich, L.B.; Jönsson, P.; Kirkegaard, P.H.; Wallergård, M.; Garde, A.H. and Hansen, Å. (2014). Can architectural design alter the physiological reaction to psychosocial stress? A virtual TSST experiment. Physiology and behavior 135, 91–97. https://doi.org/10.1016/j.physbeh.2014.05.034.

Fust, A.P.; Jenert, T. and Winkler, C. (2018). Experiential or Self-Regulated Learning: A Critical Reflection of Entrepreneurial Learning Processes. Entrepreneurship Research Journal 8 (2). https://doi.org/10.1515/erj-2017-0098.

Gründl, H. (2018). Urine trap by: EOOS, EOOS Design GmbH, Vienna, Austria. Online available at http://urinetrap.com/src/assets/img/UrineTrap.pdf

Harder, R.; Wielemaker, R.; Molander, S. and Öberg, G. (2020). Reframing human excreta management as part of food and farming systems. Water research 175, 115601. https://doi.org/10.1016/j.watres.2020.115601.

Harland, N. and Holey, E. (2011). Including open-ended questions in quantitative questionnaires—theory and practice. International Journal of Therapy and Rehabilitation 18 (9), 482–486. https://doi.org/10.12968/ijtr.2011.18.9.482.

Haslam, N. (2012). Psychology in the bathroom. Basingstoke, Palgrave Macmillan.

Jones, D.L.; Cross, P.; Withers, P.J.A; DeLuca, T.H; Robinson, D.A.; Quilliam, R.S; Harris, I.M; Chadwick, D.R. and Edwards-Jones, G. (2013). REVIEW: Nutrient stripping: the global disparity between food security and soil nutrient stocks. Journal of Applied Ecology 50 (4), 851–862. https://doi.org/10.1111/1365-2664.12089.

Kaiser, F.G.; Wölfing, S. and Fuhrer, U. (1999). Environmental Attitude and Ecological Behaviour. Journal of Environmental Psychology 19, 1–19.

Kira, A. (1976). The Bathroom. 2. Aufl. New York, N.Y., Viking Pr.

Kolb, A. and Kolb, D. A. (2018). Eight important things to know about the experiential learning cycle. Australian Educational Leader 40 (3).

Kolb, D. (1984). Experiential learning: experience as the source of learning and development. New Jersey, Prentice-Hall Inc.

Kraus, F.; Zamzow, M.; Conzelmann, L.; Remy, C.; Kleyböcker, A.; Seis, W.; Miehe, U.; Hermann, L.; Hermann, R. and Kabbe, C.. (2019): Life cycle assessment comparison of P-recovery from the waste water stream with fertilizer production from rock phosphates, including consequential environmental damage and its prevention. Dessau.

Krempl, G; Lemaire, V; Lughofer, E. and Kottke, D. (2016). Active Learning: Applications, Foundations and Emerging Trends (Tutorial). In: G. Krempl/V. Lemaire/E. Lughofer et al. (Hg.). CEUR Workshop Proceedings. Graz.

Krüger, E.L. and Zannin, P.H.T. (2004). Acoustic, thermal and luminous comfort in classrooms. Building and Environment 39 (9), 1055–1063. https://doi.org/10.1016/j.buildenv.2004.01.030.

Larsen, T.A.; Udert, K.M.; Lienert, J. (2013): Source Separation and Decentralization for Wastewater Management. In: Water Intelligence Online. 12, DOI: 10.2166/9781780401072. — ISBN: 9781843393481

Lienert, J., Larsen, T.A. (2006) Considering user attitude in early development of environmentally friendly technology: A case study of NoMix toilets. Environmental Science and Technology 40(16): 4838-4844.

Lundblad, B. and Hellstrom, A.-L. (2005). Perceptions of school toilets as a cause for irregular toilet habits among schoolchildren aged 6 to 16 years. Journal of School Health 75 (4), 125–128. https://doi.org/10.1111/j.1746-1561.2005.00009.x.

Manning, D.A.C. (2018). Innovation in Resourcing Geological Materials as Crop Nutrients. Natural Resources Research 27 (2), 217–227. https://doi.org/10.1007/s11053-017-9347-2.

Manning, D.A.C. (2015). How will minerals feed the world in 2050? Proceedings of the Geologists’ Association 126 (1), 14–17. https://doi.org/10.1016/j.pgeola.2014.12.005.

Mayring, P. (2001). Combination and Integration of Qualitative and Quantitative Analysis. Forum: Qualitative Social Research 2 (1).

Michels, N.; van den Bussche, K.; Vande Walle, J. and de Henauw, S. (2019). School Policy on Drinking and Toilets: Weaknesses and Relation With Children's Hydration Status. Journal of nutrition education and behavior 51 (1), 32–40. https://doi.org/10.1016/j.jneb.2018.07.001.

Middlemist, R.D.; Knowles, E.S. and Matter, C.F. (1976). Personal space invasions in the lavatory: Suggestive evidence for arousal. Journal of Personality and Social Psychology 33 (5), 541–546. https://doi.org/10.1037//0022-3514.33.5.541.

Pahl-Wostl, C., Schönborn, A., Willi, N., Muncke, J., Larsen, T.A. (2003). Investigating consumer attitudes towards the new technology of urine separation. Water Sci. Technol. 48, 57–65. https://doi.org/10.2166/wst.2003.0015

Pahore, M.M., Ryusei, I., Funamizu, N. (2010). Rational design of an onsite volume reduction system for source-separated urine. Environ Technol 31(4): 399-408.

Randall, D.G.; Krähenbühl, M.; Köpping, I.; Larsen, T.A.; Udert, K.M. (2016). A novel approach for stabilizing fresh urine by calcium hydroxide addition, Water Research, 95, 361-369,

Razon, Luis F. (2018). Reactive nitrogen: A perspective on its global impact and prospects for its sustainable production. Sustainable Production and Consumption 15, 35–48. https://doi.org/10.1016/j.spc.2018.04.003.

Reja, U; Manfreda, K.L; Hlebec, V. and Vehovar, V. (2003). Open-ended vs. close-ended questions in web questionnaires. Developments in applied statistics 19 (1), 159–177.

Rockström, J.,Steffen, W.,Noone, K.,Persson, Å.,Chapin, F.S.,Lambin, E.F.,Lenton, T.M.,Scheffer, M.,Folke, C.,Schellnhuber, H.J.,Nykvist, B.,Wit, C.A. De,Hughes, T.,Leeuw, S. Van Der,Rodhe, H.,Sörlin, S.,Snyder, P.K.,Costanza, R.,Svedin, U.,Falkenmark, M.,Karlberg, L.,Corell, R.W.,Fa-Bry, V.J.,Hansen, J.,Walker, B.,Liverman, D.,Richardson, K.,Crutzen, P. and Foley, J.A. (2009). A safe operating space for humanity. Nature, 461(September), pp.472–475.

Ryan, M. and Charman, K. (2014). Learning and teaching in public spaces (LTPS). Final report of the project titled Collaborative exchanges with museums to engage humanities and education students in experiential learning and citizenship. Department of Education. Sydney.

Sayers, R. (2006). Principles of awareness-raising for Information Literacy. A case study. Bangkok, Thailand, UNESCO.

Schaum, C. (2018). Phosphorus: Polluter and Resource of the Future: Motivations, Technologies and Assessment of the Elimination and Recovery of Phosphorus from Wastewater. Integrated Environmental Technology Series. London: IWA Publishing.

Schramm, E.; Kerber, H.; Trapp, J.H.; Zimmermann, M. and Winker, M. (2018): „Novel urban water systems in Germany: governance structures to encourage transformation“. In: Urban Water Journal. Taylor and Francis 15 (6), S. 534–543, DOI: 10.1080/1573062X.2017.1293694.

Shouler, M., Griggs, J. and Hall, J. (1998). Water conservation. British Research Establishment (BRE)

Steen, I. (1998). Phosphorus availability in the 21st Century: management of a non- renewable re-source. Phosphorus and Potassium, 217, pp.25–31.

Teichmann, M.; Ullrich, A. and Gronau, N. (2019). Subject-oriented learning - A new perspective for vocational training in learning factories. Procedia Manufacturing 31, 72–78. https://doi.org/10.1016/j.promfg.2019.03.012.

Udert, K.M.; Larsen, T.A.; Biebow, M.; Gujer, W. (2003) Urea hydrolysis and precipitation dynamics in a urine-collecting system, Water Research, 37(11), 2571-2582, doi:10.1016/S0043-1354(03)00065-4, Institutional Repository

Udert, K.M.; Larsen, T.A.; Gujer, W. (2006): Fate of major compounds in source-separated urine. In: Water, Science and Technology 54 (11-12), S. 413–420. DOI: 10.2166/wst.2006.921

Vartanian, O.; Navarrete, G.; Chatterjee, A.; Fich, L.B.; Leder, H.; Modroño, C.; Nadal, M.; Rostrup, N. and Skov, M. (2013). Impact of contour on aesthetic judgments and approach-avoidance decisions in architecture. Proceedings of the National Academy of Sciences of the United States of America 110 Suppl 2, 10446–10453. https://doi.org/10.1073/pnas.1301227110.

Weinberg, M. S. and Williams, C. J. (2005). Fecal Matters: Habitus, Embodiments, and Deviance. Social Problems 52 (3), 315–336. Online available at http://socpro.oxfordjournals.org.

Wilde, M. (2007). Das Contextual Model of Learning — ein Theorierahmen zur Erfassung von Lernprozessen in Museen. In: Dirk Krüger/Helmut Vogt (Hg.). Theorien in der biologiedidaktischen Forschung. Berlin, Heidelberg, Springer Berlin Heidelberg, 165–175.

Wildemeersch, D. (2012). Imagining pedagogy in public space: visions of cultural policies and practices in a city in transformation. International Journal of Lifelong Education 31 (1), 77–95. https://doi.org/10.1080/02601370.2011.63638.

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CISA

UTILIZATION OF DIGESTED SEWAGE SLUDGE IN LACTIC ACID FERMENTATION

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ABSTRACT

The management of sewage sludge is mostly limited to anaerobic digestion, incineration of digestate and recovery of phosphorous. In terms of resource efficiency, it is recommended to make use of the potential of all organic compounds. Nitrogen compounds, for instance, can find application as nutrients in biotechnological processes. To follow this approach, sewage sludge collected after anaerobic digestion, which had carbon and nitrogen contents of 35.9% (w/w) and 5.6% (w/w), respectively, was first hydrolyzed using 0-1% (w/w) sulphuric acid for 15 minutes at 121°C and the hydrolysate used as nitrogen source in lactic acid fermentation. Even though the focus was on a recovery of nitrogen compounds, the hydrolytic treatment with 1% (v/v) sulphuric acid resulted in a release of 28 mg g^{-1} glucose. Because of the complex composition of the obtained hydrolysate it was not possible to quantify the released organic nitrogen compounds. Lactic acid fermentations, however, revealed that the concentration of organic nitrogen compounds was sufficient to efficiently convert 10 g L^{-1} of added glucose into 9 g L^{-1} lactic acid, and thus it is expected that digested sewage sludge may be an alternative nitrogen source in lactic acid fermentation, possibly combined with the utilization of a carbon-rich feedstock. Such a utilization approach goes beyond the conventional management strategies of digestated sewage sludge and allows a material utilization even after anaerobic digestion.

1. INTRODUCTION

Germany produced around 3 million tons of sewage sludge in 2016. Most of it was anaerobically digested followed by incineration or other thermal treatment (Schnell et al., 2020). Despite the development regarding a materially use of sewage sludge during the last years it is state-of-the-art in wastewater treatment plants to anaerobically digest it for biogas and eventually energy generation (Agabo-García et al., 2019). Alternative possibilities are the use of carbon compounds in sewage sludge in the co-fermentation with grass residues (Yang & Wang, 2019), fallen leaves (Hu & Wang, 2019) or ryegrass (Yang & Wang, 2017) for hydrogen production. Furthermore, activated sludge from secondary clarifier of a sewage treatment plant (Li et al., 2018) or from a sewage disposal plant (Ma et al., 2014) has been used in microbial lactic acid formation and for the formation of short-chain fatty acids via acidogenic fermentation (Liu et al., 2020).

Anaerobically digested sewage sludge is rich in phosphorous (15-40 mg g^{-1} P_2O_5) and nitrogen (16-60 mg g^{-1}) (Metcalf, 1991). While phosphorous recovery is mandatory for sewage sludge with a content above 20 mg g^{-1} and can be achieved by struvite formation after anaerobic digestion (Raheem et al., 2018) or from ash after incineration (Günther et al., 2018), recovery or use of nitrogen compounds has not been considered. In 2020, the new German fertilizer ordinance came into force with the aim to reduce the emission of nitrogen and phosphorus from arable land to water bodies. The new ordinance challenges the application of (digested) sewage sludge as it is usually not incorporated into soil within 4 hours, a prerequisite for fertilizer application. In a value chain where carbon and phosphorus compounds in sewage sludge are used or recovered for energy and fertilizer generation, respectively, nitrogen compounds remain unused which may be used as nitrogen source in biotechnological processes, such as lactic acid fermentation.

Lactic acid has a moderate value. Its applicability, however, illustrates the relevance for food and chemical industries, where it is often used as a preservative or for the synthesis of the biopolymer poly(lactic acid), respectively (Juturu & Wu, 2016; Klotz et al., 2016). The applicability of lactic acid thereby originates from its properties as

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an α-hydroxy acid. It can be polymerized by forming ester bonds between lactic acid molecules to form poly(lactic acid) (Masutani and Kimura, 2015). Lactic acid is efficiently formed by microorganism. Under homofermentative conditions 1 mole glucose results in 2 moles lactic acid (Pleissner, 2019) and serves due to its acidic characteristics as natural conserving agent. When obtained from fossil-oil, lactic acid forms a racemate, while its homofermentative production allows the production of either the D- or L-enantiomeric form (van Velthuijsen, 1996).

Due to the increasing interest of industry in lactic acid, fermentations fed with cost-efficient organic residues or waste streams have been investigated. It was shown that carbon compounds from agricultural residues (Alves de Oliveira et al., 2019; Glaser & Venus, 2018), organic municipal solid waste (López-Gómez et al., 2020), food waste (Peinemann et al., 2020) or activated sewage sludge (Li et al., 2018; Ma et al., 2014) can be utilized by microbes to produce lactic acid. The activity of microbes also requires the presence of utilizable nitrogen compounds, and thus alternative nitrogen sources, such as green biomass (Dietz et al., 2016) and protein hydrolysate from municipal solid waste (Izaguirre et al., 2020), were investigated as well. To combine waste management and waste utilization, aim of this short communication was to make nitrogen compounds available from DSS to open new utilization paths for this underutilized material.

2. MATERIAL AND METHODS

2.1 Digested sewage sludge

DSS was collected from the wastewater treatment plant in Lüneburg (Germany) in April 2018 and used for experiments between May and July 2018. The composition of DSS is shown in results and discussion.

2.2 Inoculum

Inoculum consisted of an indigenous consortium isolated from food waste. The food waste was collected from Leuphana University canteen in April 2018. It consisted of uneaten food, such as vegetables, meat and noodles. After blending, food waste was fermented at pH 6 and 35°C in a bioreactor (ELOFERM, Germany) for 48 hours. Samples were taken regularly, centrifuged for 5 minutes at 4,000g and applied as inoculum for lactic acid fermentations.

2.3 Hydrolysis of digested sewage sludge

For screening of appropriate sulphuric acid concentration for acid-catalyzed hydrolysis of DSS to make nitrogen sources available for lactic acid fermentation, 150 g DSS was resuspended in 100 mL demineralized water. Concentrated sulphuric acid (98%, v/v, 0, 0.1, 0.2, 0.5 or 1 mL) was added to the different approaches (A-E), resulting in a final sulphuric acid concentration of 0, 0.1, 0.2, 0.5 or 1% (v/v), respectively (Martín et al., 2019). Afterwards, suspensions were heated for 15 minutes at 121°C to enhance acid-catalyzed hydrolysis followed by a centrifugation at 4,000g for 5 minutes after cooling to 20°C. Supernatants were removed and the pH set to 6 using 2 M NaOH.

For fermentation purpose, 467.2 g DSS was resuspended in 300 mL demineralized water and the volume of concentrated sulphuric acid added which was found appropriate for nutrient release. The suspension was treated as described above.

2.4 Fermentation

Fermentation 1 was conducted twice in 100 mL flasks containing 30 mL hydrolysate at a temperature of 35°C and shaken at 160 rpm on an orbital shaker for 48 hours. Initial pH was 6.8 and kept uncontrolled during fermentation. As carbon source 10 g L^{-1} glucose was added. A 5% (v/v) inoculum was used. Beside the actual fermentation, a control fermentation without hydrolysate was conducted once where 30 mL water was used instead of hydrolysate. Flasks, hydrolysate and water were autoclaved at 121°C for 15 minutes prior to experiments. Samples were taken regularly, centrifuged at 4,000g for 5 minutes and stored at -20°C until analysis.

To assess the impact of pH on performance, fermentation 2 was conducted twice using 500 mL DSS hydrolysate at a set pH of 6 and a temperature of 35°C in a bioreactor (ELOFERM, Germany) for 28 hours. Stirring was conducted using a magnetic bar at 200 rpm. As carbon source 10 g L^{-1} glucose was added. Hydrolysate and reactor were autoclaved at 121°C for 15 minutes prior to experiment. pH was kept constant by automatically adding 2 M HCl or 2 M NaOH. A 5% (v/v) inoculum was used. Samples were taken regularly, centrifuged at 4,000g for 5 minutes and stored at -20°C until analysis.

2.5 Analytics

To determine the dry matter of DSS an aliquot was weighed and dried at 105°C until constant weight (Dupré et al., 2020).

Organic matter was quantified by heating 1 g dry DSS for 4 hours at 575°C in a muffle furnace and weighing the remainder (Dupré et al., 2020).

Protein, cellulose and hemicellulose contents were quantified in dried DSS by near infrared spectroscopy (NIR) using a NIR-spectrometer (Unity Scientific GmbH, Weiler bei Bingen, Germany).

Total carbon (C) and nitrogen (N) contents of dried DSS were measured with an elemental CN analyzer at 1150°C (Elementaranalysator vario Max CN).

Ammonium quantification was based on the phenol hypochlorite assay (Berthelot reaction) described in Vega-Mas et al. (2015).

Phosphate concentration was determined photometrically via generation of molybdenum blue. At first, four separate solutions were prepared: (I) Sulfuric acid (2.5 M), (II) potassium antimonyl tartrate solution (1.3715 g $K(SbO)C_4H_4O_6 \times 1/2\ H_2O$ in 500 mL demineralized water), (III) ammonium molybdate solution (20 g $(NH_4)_6Mo_7O_{24} \times 4\ H_2O$ in 500 mL demineralized water) and (IV) ascorbic acid solution (1.76 g ascorbic acid in 100 mL demineralized water). Molybdenum reagent (V) was prepared by combining 2.5 mL (I), 0.25 mL (II), 0.75 mL (III) and 1.5 mL (IV). Sample (100 µL), 900 µL demineralized water, 10 µL (III) and 160 µL (V) were mixed. After incubating at 60°C for 15 minutes, absorption was measured at 880 nm.

Glucose, lactic acid and acetic acid concentrations were determined using HPLC (Shimadzu: LC-10AD pump, SIL-10AD auto-sampler, CTO-10AD oven, refractive index detector RID-20A, CBM-20A communication module): 10 µL of sample was injected on an Aminex HPX-87H column (300 mm × 7.8 mm) and eluted isocratically with 0.4 mL minute^{-1} 5 mM H_2SO_4 at 27°C. For each analyte, calibration curves were generated with pure solutions of known concentration.

3. RESULTS AND DISCUSSION

3.1 Hydrolysis

DSS had a dry matter of 20.9 ± 0.1% (w/w) and based on dry weight an organic matter content of 72.5 ± 0.1% (w/w), a C-content of 35.9% (w/w), a N-content of 5.6% (w/w) and a C-to-N-ratio of 6.4. Protein, cellulose and hemicellulose contents (w/w) were 29.5, 14.7 and 18.5%, respectively. Hydrolytic treatment with different concentrations of sulphuric acid was carried out to make nitrogen compounds, but also other nutrients available from DSS.

In Table 1 yields in mg of glucose, acetic acid, ammonium and phosphate per g DSS are shown. Glucose and acetic acid were released at yields of 0.28 and 0.33 mg, respectively, per g DSS when 1% (v/v) sulphuric acid was used. Results revealed that the respective yields slightly decreased with decreasing sulphuric acid concentration (Table 1). The low yield of carbon compounds was expected beforehand and is explainable by the metabolization of easily accessible carbon sources during anaerobic digestion. The cellulose content in DSS can range between 88 and 150 mg g^{-1} (Metcalf, 1991) and is in agreement with the 147 mg g^{-1} found in this study. By the hydrolytic treatment, 28 mg g^{-1} glucose was released, and thus only a small fraction of hemicellulose and cellulose was degraded after the treatment 1% (v/v) sulphuric acid. A harsher treatment in form of increased acid concentration, higher temperature and/or longer reaction time, however, was skipped to avoid a degradation of amino acids.

While it was possible to quantify carbon compounds which have been released from DSS, the quantification of free amino nitrogen compounds was hindered by the complex composition of hydrolysates. For sewage sludge a nitrogen content of 15-40 mg g^{-1} and for DSS 16-60 mg g^{-1} was found (Metcalf, 1991). The material used in this study contained 56 mg g^{-1} (5.6%, w/w) nitrogen, which agrees with the reported values and represents a protein content of 295 mg g^{-1} (29.5%, w/w). The release of ammonium ranged from minimum 1.16 mg g^{-1} using 0.1% (v/v) to maximum 1.61 mg g^{-1} using 0.5% (v/v) sulphuric acid. It should however be admitted that already 1.39 mg g^{-1} ammonium was obtained when DSS was soaked in water and thermally treated (Table 1).

TABLE 1: Yield of compounds obtained after hydrolysis of DSS in 0% (A), 0,1% (B), 0.2% (C), 0.5% (D) or 1% (E) (v/v) sulphuric acid.

mg g^{-1}	A	B	C	D	E
Glucose	0.14	0.16	0.16	0.21	0.28
Lactic acid	0	0.22	0.05	0	0
Acetic acid	0.13	0.17	0.12	0.23	0.33
Ammonium	1.39	1.16	1.34	1.61	1.56
Phosphate	8.63	9.65	8.79	10.72	9.42

In parallel to carbon and nitrogen compounds also phosphate was released. Phosphate in digested sewage sludge was already solubilized when DSS was soaked in water and thermally treated (Table 1). Irrespective the treatment, 7.10 mg g^{-1} was released which indicates the unnecessity of acid treatment for phosphate release. DSS contains around 15-40 mg g^{-1} P_2O_5 (Metcalf, 1991). Even though the phosphorous content is dependent on the material used it can be assumed that a considerable fraction has been released in this study. To obtain 80-90% (w/w) of phosphorous, Falayi recommends a treatment for 120 minutes using 8 M KOH, 95°C and a solid-to-liquid-ratio of 4 (Falayi, 2019).

3.2 Fermentations

In Figure 1A and B is shown the production of lactic acid in two fermentations carried out under pH-uncontrolled conditions using DSS hydrolysate and one fermentation without hydrolysate as control (Figure 1C). When DSS hydrolysate was mixed with 10 g L^{-1} glucose lactic acid concentration increased from 1 to around 4 g L^{-1} and glucose was completely consumed after 48 hours, while the optical density increased slightly and the pH decreased from 6.9 to around 3.7 (Figure 1A and B). The concentration of acetic acid did only marginally change by the activity of acetogenic bacteria present in the inoculum and remained below 0.25 g L^{-1} (Figure 1A) or was not formed at all in the repeated fermentation (Figure 1B). Contrarily, the absence of DSS hydrolysate resulted in a reduced formation of lactic acid (increase from 1 to 2 g L^{-1}) and consumption of glucose (from 10 to 5 g L^{-1}) after 48 hours. The pH decreased from 6.9 to 4.2. Acetic acid was not present and the optical density (Figure 1C) was below the optical densities found in fermentations carried out with hydrolysate (Figure 1A and B).

Figure 2 illustrates the repeated fermentative production of lactic acid using DSS hydrolysate under pH-controlled conditions. Glucose concentration decreased from 10 to 0 g L^{-1}, while lactic acid concentration increased from 1 to 10 g L^{-1} within 24 hours in both fermentations. No changes in optical density was noted, and thus around 90% of carbon from glucose was most likely converted into lactic acid. Acetic acid concentration differed between both fermentations shown in Figure 2. In one fermentation (Figure 2A) the concentration was constant at around 1.6 g L^{-1}, while in the other fermentation (Figure 2B) the acetic acid concentration was 0.1 g L^{-1}. The differences result from the application of different DSS hydrolysate batches.

As a general remark, ammonium concentration was in all fermentations between 1.4 and 1.8 g L^{-1} and did not change over time (data not shown). It should be noted that an inhibition of bacteria by a high concentration of ammonium nitrogen, as observed in anaerobic digestion, can be excluded (Liu et al., 2018). The tolerance of lactic acid bacteria regarding high ammonium nitrogen concentration is an asset for the application of DSS as nitrogen source.

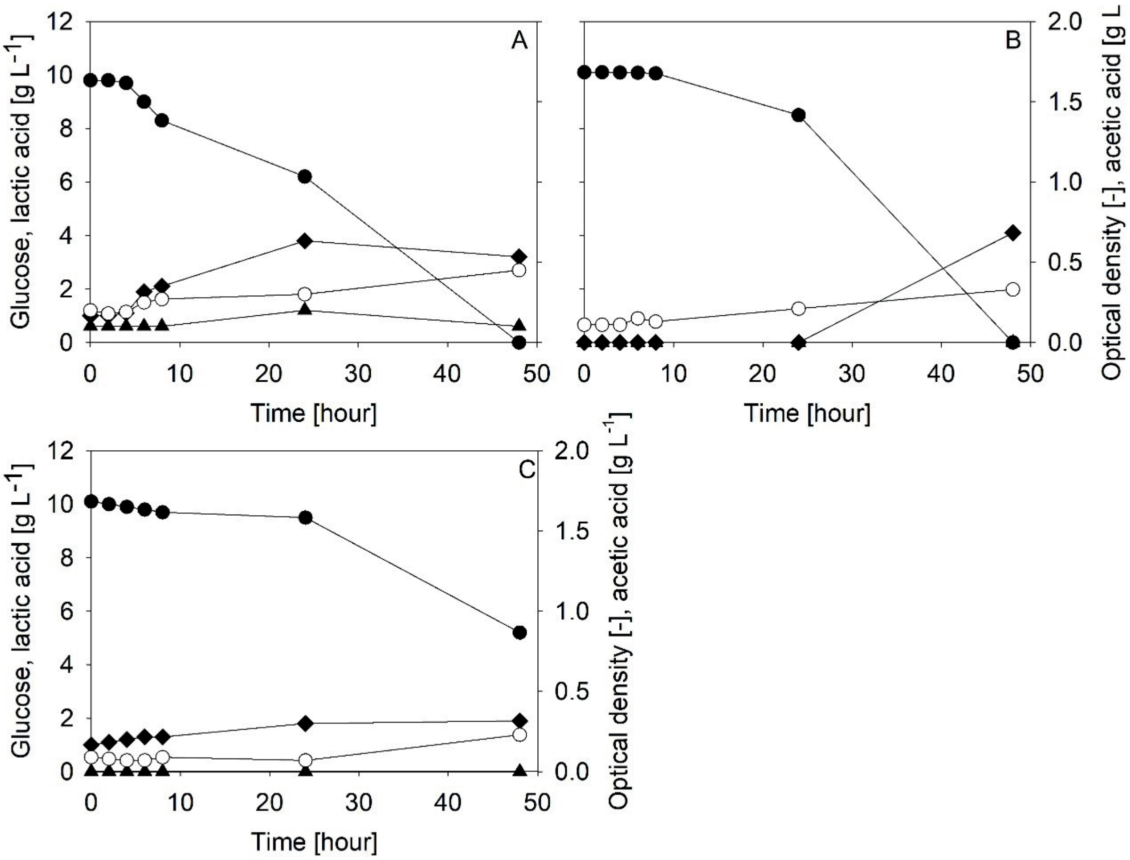

FIGURE 1: Time profiles in glucose (closed circle), acetic acid (closed triangle) and lactic acid (closed diamond) concentrations as well as optical density (open circle) in fermentations carried out under pH-uncontrolled conditions using DSS hydrolysate and inoculum (A and B) and without hydrolysate (C) as control.

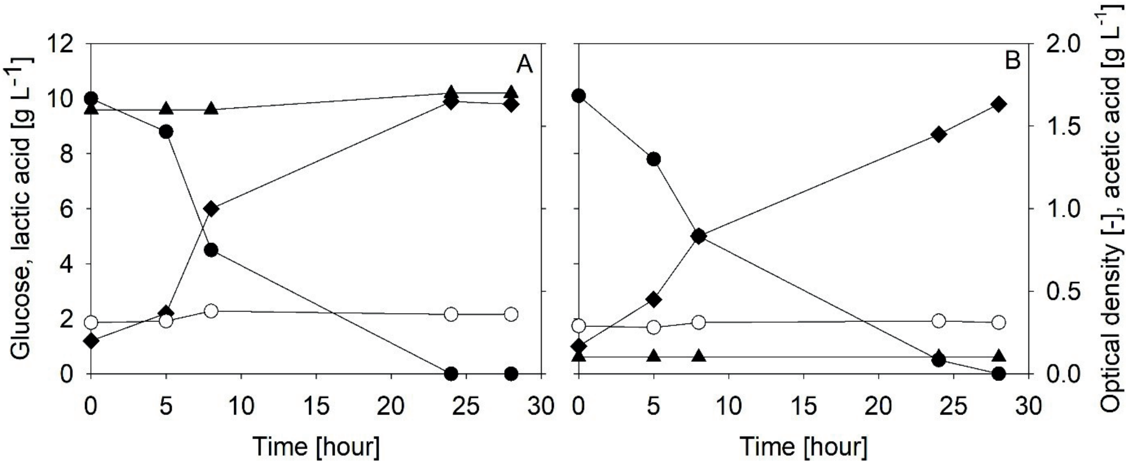

FIGURE 2: Time profiles in glucose (closed circle), acetic acid (closed triangle) and lactic acid (closed diamond) concentrations as well as optical density (open circle) in two fermentations (A and B) carried out under pH-controlled conditions using DSS hydrolysate and inoculum.

The formation of lactic acid is predominantly associated to the growth of lactic acid bacteria. Berry et al. (1999) reported from defined cultures of Lactobacillus rhamnosus lactic acid constants of 0.389 moles per gram growing cells, while only 0.0025 moles per gram were formed by non-growing cells. The supply of a nitrogen source which is cost-efficient and useable by lactic acid bacteria is therefore essential to achieve high productivities. Dietz et al. (2016) applied alfalfa green juice as nitrogen source and obtained a yield of 0.69 g lactic acid g^{-1} glucose in batch fermentation. It is of interest for further process development that the juice was not further pre-treated or supplemented with other nutrients, and thus could be directly applied. However, Dietz et al. (2016) admitted that differences in alfalfa culture conditions (e.g., environmental and soil conditions) may have an impact on the nitrogen content of juice and this aspect needs further investigation. To illuminate this aspect, Papendiek and Venus (2014) used the juice of legumes grown at different locations and harvested at different times of the year as nitrogen source in lactic acid fermentation. They found not only considerable differences in protein content in legumes but also differences up to 40% and 60% in lactic acid yield between study sites and sampling dates, respectively. Ma et al. made use of the high protein and carbohydrate contents of waste activated sludge to substitute yeast extract in lactic acid fermentation (Ma et al., 2014). In their experiments the yield of lactic acid per g glucose was 0.97 and the final titer 96.7 g L^{-1} after 48 hours when 7 g L^{-1} hydrolyzed sewage sludge and 100 g L^{-1} glucose were applied. An application of DSS, however, has not been investigated. Generally, the applicability of DSS as nitrogen source in lactic acid fermentation is given. The control fermentation carried out without DSS resulted only in the formation of around 1 g L^{-1} lactic acid. In the control, microorganisms may have consumed remaining nitrogen originating from the food waste inoculum. However, it should be admitted that also wastewater exhibits seasonal variations in concentration of nitrogen compounds. Tuncal et al. (2009) detected a difference in mean concentrations of total nitrogen between summer and winter of 8.9 mg L^{-1}. Therefore, further investigations using DSS obtained at different seasons are needed to assess whether DSS is a suitable nitrogen source with constant quality throughout the year.

Results further revealed that lactic acid fermentation should not be carried out pH-uncontrolled when DSS-hydrolysate is used. As seen in this study at a pH of 5 and below lactic acid bacteria seem inhibited (Figure 1). Similar observation was made by Darwin et al. (2018) and Peinemann et al. (2020) when pH dropped below 5. However, fermentation was effective at a controlled pH of 6.8 (Figure 2) and the yield of 0.9 g g^{-1} was comparable to the one found by Ma et al. using sewage sludge (0.97 g g^{-1}, Ma et al., 2014) and higher compared to the yields obtained in presence of green biomass juice (0.6-0.7 g g^{-1}, Dietz et al., 2016; Papendiek and Venus, 2014). It should, however, be noted that a variation in pH can be used to steer the product portfolio. In a co-cultivation of yeast and lactic acid bacteria, for instance, the product can be steered towards ethanol at a pH below 5, while lactic acid is formed at higher pH-values (Darwin et al., 2018; Peinemann et al., 2020).

Sewage sludge can be, contrarily to DSS, rich in carbohydrates and contents from 10 to 15% (w/w, Hu & Wang, 2019; Maeda et al., 2009) have been reported. However, since it seems necessary to add an additional carbon source even though activated sewage sludge is used (Ma et al., 2014) it seems irrespective whether lactic acid formation is performed prior to or after anaerobic digestion.

4. CONCLUSIONS

DSS can be applied as nutrient source in pH-controlled lactic acid fermentation. The potential as carbon source is due to low yields obtained rather limited. However, the hydrolysis of proteins in DSS provides organic nitrogen compounds usable by lactic acid bacteria and resulting in a decent conversion of glucose into lactic acid at a yield of around 0.9 g g^{-1}. The combination with other organic feedstocks, such as food waste as carbon source, could result in cost-efficient fermentations. Further work is recommended on the investigation of the hydrolytic treatment to improve the recovery of nitrogen compounds available and to substitute sulphuric acid.

REFERENCES

Agabo-García, C., Pérez, M., Rodríguez-Morgado, B., Parrado, J., Solera, R. 2019. Biomethane production improvement by enzymatic pre-treatments and enhancers of sewage sludge anaerobic digestion. Fuel, 255, 115713.

Alves de Oliveira, R., Schneider, R., Vaz Rossell, C.E., Maciel Filho, R., Venus, J. 2019. Polymer grade l-lactic acid production from sugarcane bagasse hemicellulosic hydrolysate using Bacillus coagulans. Bioresource Technology Reports, 6, 26-31.

Berry, A.R., Franco, C.M.M., Zhang, W., Middelberg, A.P.J. 1999. Growth and lactic acid productionin batch culture of Lactobacillus rhamnosus in a defined medium. Biotechnology Letters, 21, 163-167.

Darwin, Cord-Ruwisch, R., Charles, W. 2018. Ethanol and lactic acod production from sugars and starch wastes by anaerobic acidification. Engineering in Life Sciences, 18, 635-642.

Dietz, D., Schneider, R., Papendiek, F., Venus, J. 2016. Leguminose green juice as an efficient nutrient for l(+)-lactic acid production. Journal of Biotechnology, 236, 26-34.

Dupré, C., Burrows, H.D., Campos, M.G., Delattre, C., Encarnação, T., Fauchon, M., Gaignard, C., Hellio, C., Ito, J., Laroche, C., Legrand, J., Michaud, P., Pais, A.A.C.C., Pierre, G., Serive, B., Watanabe, M.M. 2020. Microalgal biomass of industrial interest: Methods of characterization. In: Handbook on Characterization of Biomass, Biowaste and Related By-products, 537-639.

Falayi, T. 2019. Alkaline recovery of phosphorous from sewage sludge and stabilisation of sewage sludge residue. Waste Management, 85, 166-172.

Glaser, R., Venus, J. 2018. Co-fermentation of the main sugar types from a beechwood organosolv hydrolysate by several strains of Bacillus coagulans results in effective lactic acid production. Biotechnology Reports, 18, e00245.

Günther, S., Grunert, M., Müller, S. 2018. Overview of recent advances in phosphorus recovery for fertilizer production. Engineering in Life Sciences, 18, 434-439.

Hu, Y., Wang, J. 2019. Biohydrogen production from co-fermentation of fallen leaves and sewage sludge. Bioresource Technology, 285, 121342.

Izaguirre, J.K., Dietrich, T., Villarán, M.C., Castañón, S. 2020. Protein hydrolysate from organic fraction of municipal solid waste compost as nitrogen source to produce lactic acid by Lactobacillus fermentum ATCC 9338 and Lactobacillus plantarum NCIMB 8826. Process Biochemistry, 88, 15-21.

Juturu, V., Wu, J.C. 2016. Microbial production of lactic acid: The latest development. Critical Reviews in Biotechnology, 36(6), 967-977.

Klotz, S., Kaufmann, N., Kuenz, A., Prüße, U. 2016. Biotechnological production of enantiomerically pure d-lactic acid. Applied Microbiology and Biotechnology, 100(22), 9423-9437.

Li, J., Zhang, W., Li, X., Ye, T., Gan, Y., Zhang, A., Chen, H., Xue, G., Liu, Y. 2018. Production of lactic acid from thermal pretreated food waste through the fermentation of waste activated sludge: Effects of substrate and thermal pretreatment temperature. Bioresource Technology, 247, 890-896.

Liu, S., Yang, X., Yao, X. 2018. Impacts of ammonia nitrogen on autothermal thermophilic microaerobic digestion for sewage sludge treatment. Chemosphere, 213, 268-275.

Liu, W., Yang, H., Ye, J., Luo, J., Li, Y.-Y., Liu, J. 2020. Short-chain fatty acids recovery from sewage sludge via acidogenic fermentation as a carbon source for denitrification: A review. Bioresource Technology, 311, 123446.

López-Gómez, J.P., Alexandri, M., Schneider, R., Latorre-Sánchez, M., Coll Lozano, C., Venus, J. 2020. Organic fraction of municipal solid waste for the production of L-lactic acid with high optical purity. Journal of Cleaner Production, 247, 119165.

Ma, K., Maeda, T., You, H., Shirai, Y. 2014. Open fermentative production of l-lactic acid with high optical purity by thermophilic Bacillus coagulans using excess sludge as nutrient. Bioresource Technology, 151, 28-35.

Maeda, T., Yoshimura, T., Shimazu, T., Shirai, Y., Ogawa, H. 2009. Enhanced production of lactic acid with reducing excess sludge by lactate fermentation. Journal of Hazardous Matter, 168, 656-663.

Martín, C., Peinemann, J.C., Wei, M., Stagge, S., Xiong, S., Jönsson, L.J. 2019. Dilute-sulfuric acid pretreatment of de-starched cassava stems for enhancing the enzymatic convertibility and total glucan recovery. Industrial Crops and Products, 132, 301-310.

Masutani, K., Kimura, Y. 2015. PLA synthesis. From the monomer to the polymer. RSC Polymer Chemistry Series, 3-36.

Metcalf. 1991. Wastewater engineering: Treatment, disposal and reuse. Metcalf Eddy Inc.

Papendiek F., Venus J. 2014. Cultivation and fractionation of leguminoses biomass for lactic acid production. Chemical and Biochemical Engineering Quarterly, 28, 375-382.

Peinemann, J.C., Rhee, C., Shin, S.G., Pleissner, D. 2020. Non-sterile fermentation of food waste with indigenous consortium and yeast – Effects on microbial community and product spectrum. Bioresource Technology, 306, 123175.

Pleissner, D. 2019. Assessment of upstr.,eam bioprocessing, 3 Biotech, 9, 260.

Raheem, A., Sikarwar, V.S., He, J., Dastyar, W., Dionysiou, D.D., Wang, W., Zhao, M. 2018. Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: A review. Chemical Engineering Journal, 337, 616-641.

Schnell, M., Horst, T., Quicker, P. 2020. Thermal treatment of sewage sludge in Germany: A review. Journal of Environmental Management, 263, 110367.

Tuncal, T., Pala, A., Uslu, O. 2009. Determination of microbial responses to seasonla variations of wastewater compostion in the Izmir wastewater treatment plant. Fresenius Environment Bulletin, 18, 2114-2122.

van Velthuijsen, J.A. 1996. Lactic acid production and utilization. In: Carbohydrates as Organic Raw Materials III, 129-140.

Vega-Mas, I., Sarasketa, A., Marino, D. 2015. High-throughput quantification of ammonium content in Arabidopsis. Bio-Protocol, 5.

Yang, G., Wang, J. 2019. Biohydrogen production by co-fermentation of sewage sludge and grass residue: Effect of various substrate concentrations. Fuel, 237, 1203-1208.

Yang, G., Wang, J. 2017. Co-fermentation of sewage sludge with ryegrass for enhancing hydrogen production: Performance evaluation and kinetic analysis. Bioresource Technology, 243, 1027-1036.

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EXTENDING THE THEORY OF PLANNED BEHAVIOUR USING BEHAVIOURAL ECONOMICS TO REDUCE AND ACCESS SMALL WEEE ANTHROPOGENIC STOCKS

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ABSTRACT

From an urban mining perspective stockpiles of Waste of Electronic and Electrical Equipment (WEEE) by individuals represent anthropogenic stocks that could be exploited for precious and critical resources. The current challenge resides in minimising these stocks generation, as well as accessing the resources they represent. Behavioural models such as the Theory of Planned Behaviour (TPB) have been used in waste and resources management studies to understand WEEE end-of-use intentions and behaviours. But the results have been uneven and the very presence of these anthropogenic stocks is the acknowledgement that these models need to be adapted. Based on a review from the waste and resources management literature we found that TPB models incorporating emotions tended to have higher variance explained for intention, but the intention-behaviour gap remained strong. To explain this gap for small WEEE we propose using variables associating emotions with decision-making biases and tendencies that affect individual behaviours. This study is a theoretical elaboration supporting future empirical testing. A TPB extended with behavioural economics could better model small WEEE end-of-use decisions. Improved understanding of small WEEE urban mines generation could, in turn, inform policy and incentives design to transform these anthropogenic stocks into flows of resources within a circular economy.

1. INTRODUCTION AND BACKGROUND

Household stockpiles of unwanted or disused electronics constitute urban mines that could be exploited. The difficulty resides in accessing these stocks, in effect convincing consumers to part from their unused electronic items. To enhance access to these stocks, we should better understand why these stocks were constituted in the first place. We chose to use small electronics such as mobile and smart phones as a case study since they are ubiquitous and their small size invites for convenient storage, even if not broken. Some waste and resource management studies use behavioural models to measure variance explained for intention and behaviour, with uneven successes. Even fewer studies focus on small electronics stockpiling behaviour. Behavioural models trying to evaluate mobile and smart phones stockpiling behaviour could use variables that are specifically associated with small electronics. How consumers have used their device could influence why they are stockpiling it, especially if the device is still in working order.

1.1 WEEE situation and issues

In 2019 alone, close to 54 million tonnes of e-waste across all categories were generated globally (ISWA, 2020). Close to two billion mobile and smart phones were shipped globally in 2019, of which smart 'phone shipments comprised the majority (>75%; Gartner, 2020). Electronic handsets are now globally ubiquitous and individuals' ownership is high. In 2010, an estimated 3.7 million mobile handsets were stockpiled by students in the UK alone (Ongondo & Williams 2011). Silveira and Chang (2010) evaluated that between 50 and 90 million devices were stockpiled worldwide. The Ellen MacArthur Foundation (2013) estimated that only 10-15% of mobile and smart phones are recycled. Accurate figures are difficult to obtain, but the most optimistic estimate is that 20% are recycled in the UK (Green Alliance, 2015). These low recycling figures could be due to the device working status. Why destroying an item, albeit safely, its utility is higher if untransformed. Waste Electrical and Electronic Equipment (WEEE) regulation addresses waste but in most cases when EEE is replaced

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it is unwanted and still working, especially for small items. Hence most people do not likely recognise it as “waste” per se (Ongondo and Williams, 2011), despite being formally recognised as waste (EU Directive 851, 2018). In this paper, we will refer to (W)EEE instead of WEEE to underline the uncertainty regarding the status of some electrical and electronic equipment. An unwanted device in working order might not trigger the same end-of-use decision compared to a broken device.

Four key global issues make (W)EEE a priority waste stream: global quantities of (W)EEE; environmental and health impacts; potential and ethical concerns; resource impacts (Ongondo and Williams, 2011). Legislative drivers have provided the impetus for EU Member States to progress from approximately 2.5 kg of (W)EEE collected per year per capita in 2005 to more than 7.6 kg in 2016 (Figure 1). A “glass-ceiling” seems to have been reached as the amount of WEEE collected yearly tends to stagnate (Figure 1), despite the growth of EEE placed on the market (UNEP, 2019).

1.2 (W)EEE anthropogenic stocks, urban mining, the circular economy and sustainability

To break this “glass-ceiling” new approaches could be explored, notably how improving access to these stocks would enhance urban mining initiatives, therefore increase (W)EEE collection rates.

(W)EEE Distinct Urban Mines (DUM) (Ongondo et al., 2015) represent stocks of critical and precious materials. These anthropogenic sources can be characterised according to their availability, approachability and accessibility (Mueller et al., 2017). Urban mining is the process of reclaiming compounds and elements from any kind of anthropogenic stocks (Cossu and Williams, 2015). It can be associated with closed-loop supply chain management, specifically for (W)EEE management and material classification (Vence and Pereira, 2019). It is a useful construct that facilitates an assessment of secondary materials stocks within an urban environment since it delimits an area in which the type/amount of materials accessible at a fixed point in time can be recorded. Cities represent urban mines for secondary materials and efforts should be made to transform these stocks into flows for a circular economy (Kuong et al., 2019).

Recent studies have shown that urban areas are extremely plausible as DUMs. Wilkinson and Williams (2019) reported the ownership, use and hoarding levels of home entertainment EEE in a typical city DUM, highlighting that hoarding is common, especially for smaller or older equipment, due to the perceived residual value. For a specific UK university DUM rich in EEE category 3 (IT and telecommunication equipment), as much as 107 tonnes of secondary materials could be exploitable within a 4-year cycle (Ongondo et al., 2015). Given the 3 to 4 years typically taken to complete a degree, the annual replenishment rate is likely 25% to 33% (Ongondo and Williams, 2011). Pierron et al. (2017) estimated that 189 tonnes of ferrous and non-ferrous materials from (W)EEE Category 2 could be exploitable within a university campus DUM.

There is clear economic potential for developing urban mines from household stockpiled small (W)EEE (Pierron et al., 2017). To be exploitable, a mine (urban or otherwise) needs to be economically viable, located within reach of an existing logistics network and with materials concentration at an optimal level (Zhang and Kleit, 2016). Therefore, a DUM is a viable concept to evaluate the: i) potential to secure secondary resources from within the anthroposphere and ii) possible cost-effective methods that could be imple-

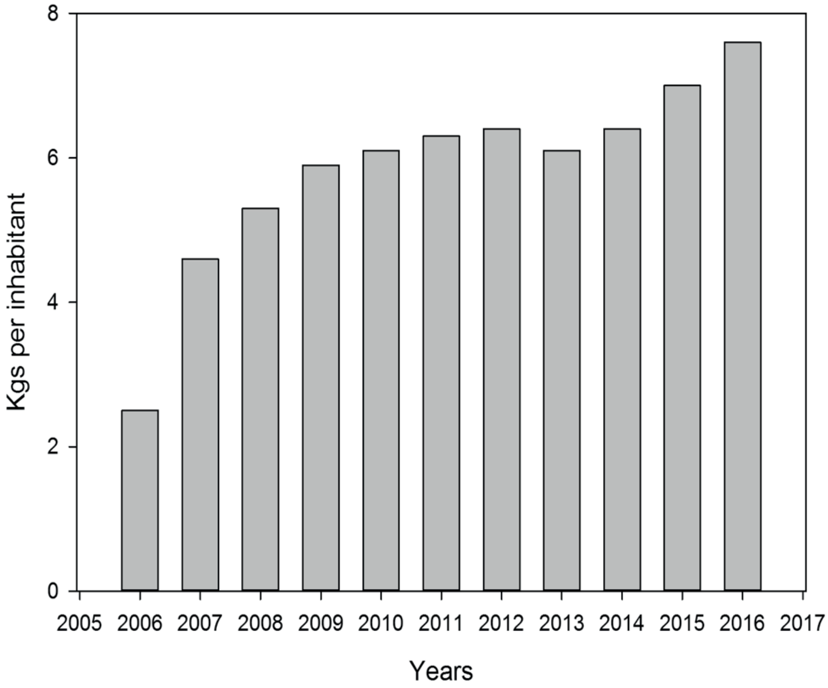

FIGURE 1: EU average (W)EEE collection per inhabitant per year over the period 2006 to 2016 (data sourced from Eurostat, 2019).

mented to access them. Exploiting anthropogenic stocks within urban mines could participate to gradually shift from a linear to a circular economy.

The circular economy is serving the sustainability agenda with end-of-life management and responsible sourcing. On the other hand, more efforts should be devoted to increasing circular products design and circular business models (Stewart and Niero, 2018). To achieve sustainability, a regenerative system such as advocated by the circular economy principles is required as an initial step. Sustainability is a balanced integration of economic performance, social inclusion, environmental resilience (Geissdoerfer et al., 2017). The circular economy represents environmental, economic and social wins at input and output levels (Korhonen et al., 2018). Accessing anthropogenic stocks is one element of urban mining, therefore creating a loop of materials back into the economy.

To enable urban mining by transforming material stocks into flows, concepts linking anthropogenic stocks to stockpiling behaviour could be investigated further. The legislative framework represents a top-down approach that has resulted in the creation of formal collection systems. However, most of the stock is in "hibernation" (i.e. storage) within households (Wilson et al., 2017). Bottom-up efforts to alter individuals' behaviour are necessary to feed (W)EEE into existing collection systems and reinject products and materials into the economy.

This review of TPB models associated with waste and resources management studies is the basis of a theoretical adaptation offered for future empirical testing. Factors included in WEEE end-use-decisions modelling usually stem from household recycling behaviour and might not be fully adapted, notably for small WEEE such as mobile and smart phones. TPB studies on small WEEE could be extended with factors that are more closely associated with small WEEE characteristics and their influence on users' end-of-use decisions.

2. LITERATURE REVIEW AND THEORETICAL STANCE

2.1 Introduction

Modelling the variables influencing small electronics stockpiling behaviour could enable access to precious and critical materials, as well as reducing environmental harm when WEEE is not safely disposed of. Initiatives to change behaviour are routinely informed by and relate to explanatory models. The Theory of Planned Behaviour (TPB) is a widely-used model for predicting human social behaviour in health-care, psychology, decision analysis and consumer behaviour (Ajzen, 2011) as well as waste and resources management (Chan and Bishop, 2013; Davies et al., 2002; de Leeuw et al., 2015; Joseph R. Hopper and Joyce McCarl Nielsen, 1991; Ojedokun, 2011; Pakpour et al., 2014; Richetin et al., 2010; Wan et al., 2014).

2.2 Waste and resources management behaviour theory and intrinsic motivators

Behavioural models have gradually built on the successes and limits set by previous models. Fishbein and Ajzen (1975) and Ajzen (1985) developed models based on psychological principles: Theory of Reasoned Action (TRA) and Theory of Planned Behaviour respectively, were both based on intrinsic motivators such as beliefs, attitudes, intentions, social norms and awareness of consequences. Recent developments have indicated that models associated with emotions, feelings and desires reached higher levels of statistically explained variance than models using TPB and environmental factors. An overview of different models used in waste management and environmental behaviour is provided (Table 1). Most studies use TPB factors as the core and explore other variables of interest (Table 1). Psychological understanding is associated with consumer behaviour and has been used to predict recycling behaviour. Fishbein and Ajzen (1975) proposed the Theory of Reasoned Action (TRA) using beliefs, attitudes and intentions to predict human behaviour (Figure 2). This framework associates attitudes towards the act with subjective norms to determine behavioural intentions, which subsequently influence behaviour.

Although the TRA has proved a reliable model to assess intentions, there was a significant gap between variance explained for intention and behaviour (Carrus et al., 2008; Ajzen,1985). To reduce this gap, Ajzen (1985) extended the TRA by adding perceived behavioural control (PBC) to attitude and subjective norms, resulting in the Theory of Planned Behaviour (Figure 3). PBC is the perception of the ease or difficulty of the specific behaviour, which mitigates or enhances the perception towards an intended behaviour and the social pressure to execute (or not) an identified behaviour (Ajzen, 2011). Individuals assess potential actions against their consequences and perceived value; the decision-making process is influenced by the "acquisition, evaluation, execution and interruption of abstract actions"

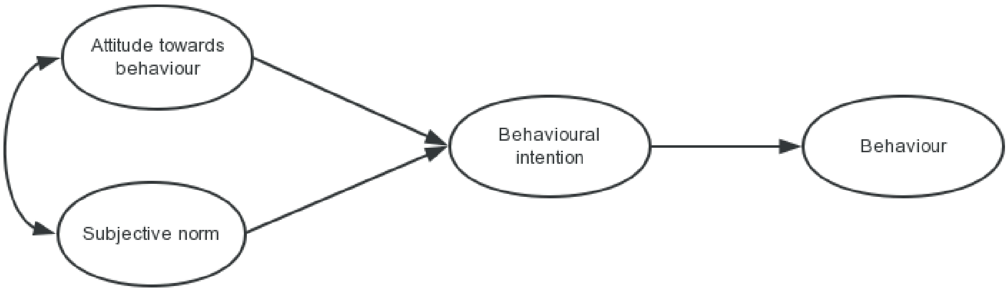

FIGURE 2: Theory of Reasoned Action and factors influencing intentions (Redrawn after Fishbein and Ajzen, 1975).

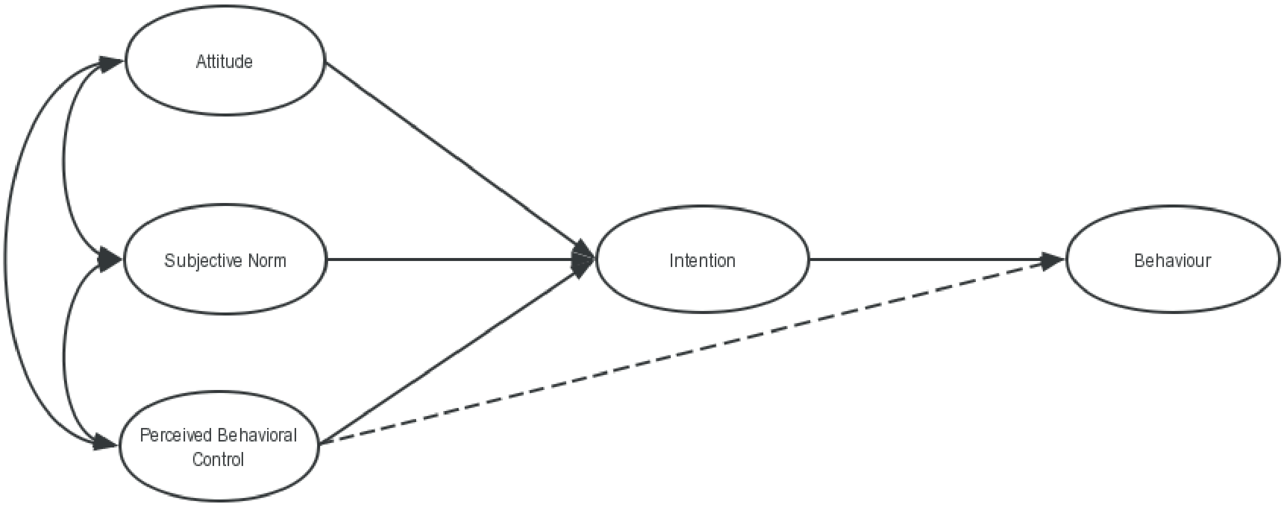

FIGURE 3: The Theory of Planned Behaviour and factors that influence intentions and behaviour (Redrawn after Ajzen, 1985). Solid lines represent a more consistent influence than dotted lines.

(Balleine et al., 2015:2). However, behaviour is difficult to predict accurately and is an unsteady process (Bouton, 2014). Individuals tend to follow behavioural patterns but they can change their behaviours for multiple reasons. Anticipating accurately individuals' actions is thus science and art, ascription of responsibility, personal norms, past behaviour and values.

Despite the widespread use of the TPB, the variance explained for intention and behaviour generally remains low, at 39% and 27% respectively (Armitage and Conner, 2001). Therefore, researchers tend to add variables to the TPB framework in an attempt to increase the variance explained. Perugini and Bagozzi (2001) derived a new model based on TPB and emotions, the model of goal-directed behaviour (MGB). This model was subsequently adapted by (Carrus et al., 2008), with minor alterations, in a study of household recycling behaviour. The MGB used the TPB as the base model and includes anticipated negative as well as positive emotions, before engaging in a specific activity (Figure 4). Carrus et al. (2008) found that perceived behavioural control, negative anticipated emotions, desires and frequent recycling behaviour were significant predictors of intentions. Their study explained 85% of intentions but variance for behaviour was not reported (Table 1). Both Perrugini and Baggozi (2001), and Carrus et al. (2008) used self-reported data. Aside from the TPB factors used as a basis among most of the studies, there is not a set of common factors consistently used to increase variance explained or bridge the intention-behaviour gap (Barr and Gilg, 2005).

Barr et al. (2001) examined predictors of behaviour towards recycling and critiqued the TPB model. The complexity of associations between household attitude and environmental behaviour was acknowledged and aggregated into four categories rather than one: environmental values, situational variables (personal situation in a behavioural context such as access to static recycling centres), socio-demographics, and individual knowledge (Barr et al., 2001). Davies et al. (2002) conducted one of the few studies to measure behaviour directly rather than self-reported behaviour; 48% of the variance was explained using a combination of factors from TPB (Ajzen, 1985) and Altruism (Schwartz, 1968), highlighting the need to investigate how emotions could be further incorporated in to improve predictive power. Davies et al. (2002:10) found the Norm Activation Model from Schwartz (1968) "a more satisfying point for understanding recycling behaviour in affluent industrial societies" than the TRA and TPB.

The model developed by Davies et al. (2002) is linked to social norms but reinforces the link between intentions and behaviours, and in combination with an awareness of consequences and ascription of responsibility. One limitation, however, is that their sample was drawn from an affluent area in the UK, the Cotswolds, that is not broadly representative of the British population. In evaluating the predictive power of TRA, TPB and the altruistic model, Davies et al. (2002) found the altruistic model more reliable (15%) compared with TPB (9%) or TRA (3%). However, 15% is still insufficient to provide robust predictive factors.

These models are useful to take a "snapshot" of a current behaviour for specific intrinsic motivators. The TPB forms a robust basis and models including factors associated with emotions tend to have higher variance explained for intention (Table 1), although the explained variance for behaviour is inconsistent. Additionally, studies focus more on intention than actual behaviour. The TPB has been useful to a certain point (Armittage and Conner, 2001). Studies tend to extend the TPB with various factors with mixed results; and there is no set of consistent factors, especially for e-waste. Now the next step is to use behavioural economics and identify which elements could be used to extend the TPB for e-waste.

2.3 Emotions and decision-making biases

Behavioural scientists have long investigated the effects of emotions and perceptions on judgment. Tversky and Kahneman (1991) associated the concept of "utility" with ownership, and demonstrated that owning a product

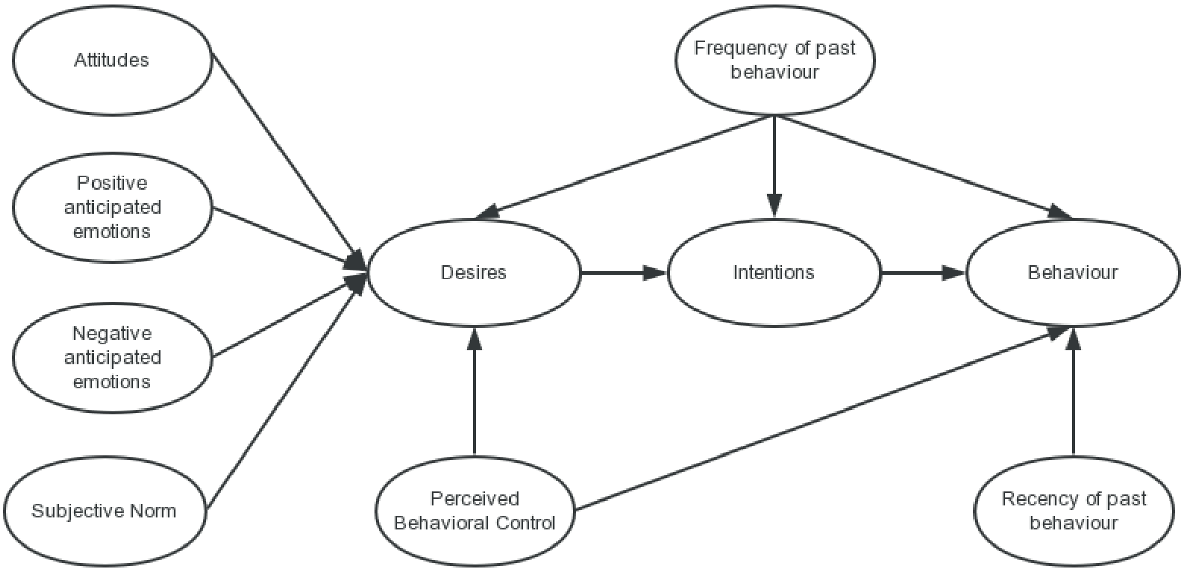

FIGURE 4: The Model of Goal-directed Behaviour (Redrawn after: Perugini and Bagozzi, 2001).

distorts market valuations: if one possesses a product, one will tend to overvalue its price, compared with its actual market value.

Therefore, whilst behavioural models derived from psychology can be applied to understand householders' recycling behaviour, techniques from behavioural economics could be adapted to change behaviour regarding urban mining. Behavioural economics has integrated at the heart of its theoretical approach decision-making biases and how to nudge individuals towards desired outcomes. In other words, how emotions and beliefs, such as risk aversion, influence decisions. And how in turn behaviours can be influenced. Adding behavioural economics to TPB models is a logical step taken in the direction set by studies that have included emotions in their modelling.

For example for small electronic devices, given that there are millions of units sitting in people's households (Davies, 2002; Ongondo and Williams, 2011; Wilkinson and Williams, 2019), mobile and smart phone end-of-use barriers could be better understood, reduced and prevented by using the concepts associated with behavioural economics. The works of Kahneman et al. (1991) - on users' endowment effect - and Thaler et al. (2008) - on choice architecture - could also be integrated to the TPB and applied to model altered behaviour.

2.4 Behavioural economics: The endowment effect

The endowment effect is the overvaluation of owned objects compared with an object's actual market valuation (Thaler, 1980). "People typically demand more to relinquish the goods they own than they would be willing to pay to acquire these goods" (Morewedge et al., 2009:947). The effect is influenced by factors such as "status quo bias" (Samuelson and Zeckhauser, 1988) and "loss aversion" (Kahneman and Tversky, 1983) experienced by owners when they foresee parting from a possession. Status quo bias is illustrated when an owner takes a decision leading to non-action i.e. an individual tends to remain in a known situation rather than deciding with an uncertain outcome as "the disadvantages of leaving it loom larger than advantages" (Tversky and Kahneman, 1991:198). Loss aversion is the anticipation of a potential future loss. When one foresees parting with an owned object, one projects the situation without the object and associates emotions. If these emotions are negative due to missing the object, one is averse to these negative emotions and is consequently unfavourable to the loss of the object. Losses equivalent to gains are perceived as more painful than the potential positive emotion associated with a symmetrical gain (Kahneman and Tversky, 1983). For example, a loss of $100 represents more negative emotion than the positive sensation for a $100 gain. The endowment effect is associated with the pain felt when an owner contemplates parting from an owned object (Tversky and Kahneman, 1991). To alleviate the potential pain, individuals tend to overvalue an object they own when entering a transaction. According to the endowment effect, someone who has just acquired a brand-new smartphone, if asked to part from it immediately, would ask for more than the device market value. This price increase would be justified to overcome the loss of ownership of an object that has been hitherto desired and the time spent to acquire it.

In addition to loss aversion and status quo bias, other factors have an influence on the endowment effect, such as time and emotional affect. The endowment effect has been demonstrated as immediate by Kahneman et al. (1990). Individuals may experience loss aversion a few moments after acquiring a new object and hence tend to prefer the status quo rather than trading their item. Strahilevitz and Loewenstein (1998) demonstrated that, the longer the duration of ownership of an object, the stronger the endowment effect. These phenomena have been termed the "duration-of-current-ownership effect" and the "duration-of-prior-ownership" effect (Strahilevitz and Loewenstein, 1998:285). The first effect refers to the association of time and ownership. The second effect refers to lost property; the longer it was owned, the more emotionally painful the loss. The influence of time may be explained by the sentimental attachment one might have for an object (Kahneman et al., 1990). On the other hand, strong negative emotions have opposite influences on the endowment effect; Lerner et al. (2004) have shown that disgust actually cancels the effect and that sadness can reverse it.

Other research on the endowment effect has demonstrated some limitations to the concept. Morewedge et al. (2009) disagree with the proposition that loss aversion creates the endowment effect and argue that ownership is a better predictor. Professionals who were employed in trading goods (such as brokers) did not express the endowment effect, as opposed to owners who acquire an object for personal purposes (Morewedge et al. 2009). Dommer and Swaminathan (2013) suggested that the positive feelings associated with possessing an object are more relevant than the negative emotion associated with parting from it. Nevertheless, all studies within this realm acknowledge factors influencing individuals' perception of monetary valuations.

2.5 Behavioural economics: Choice architecture

Thaler et al. (2008) developed the concept of "choice architecture" that connects with the notion of routines to complete sets of tasks, such as eating habits, work habits, or end-of-use habits. They argue that if individuals were perfectly rational, they would set their default routines to achieve anticipated outcomes, such as engaging in a healthy lifestyle or saving regularly for the future. Thaler et al. (2008) also demonstrate that habits and routines overcome these rational outcomes. To help individuals making the "right" decisions, they suggest the design of specific alternatives set as default options. Users would then use these default options and start creating new routines. Adapting choice architecture theory to end-of-use decisions for small EEE could improve end-of-use decision-making by creating default options that would prevent stockpiling and disposing of.

Lyengar and Lepper (2000) have postulated that too many choices for common decisions are not helpful to everyday decision-makers; too many alternatives may be confusing and require too much cognitive effort for simple recurring decisions. Tversky and Kahneman (1974) argued that humans use heuristics to approximate complex situations and make rapid decisions. Decision-makers tend to evaluate alternatives based on their past experiences, emotions, state-of-mind and other affective biases. Thaler (1980) claimed that choices should be designed as per expected outcomes for the benefit of the decision-maker. Thaler et al. (2014:429) described a choice architect as the person "who has the responsibility to organise the context in which people make decisions." Thaler et al. (2008) agree with Tversky and Kahneman (1974) in that humans tend to make decisions based on emotions and previous experiences rather than acting as purely rational decision-makers with abilities to rationalise all decisions made constantly. Choice architects can be compared with designers, who reflect on the purpose of objects and design them as per their intended use. A good design should intuitively lead a layperson to make good use of an object without having to be inducted. For example, products made by the company Apple are known for the quality of their hardware and software designs and the relationship the company can create with its users through its products (The Economist, 2016). Choice architects act similarly by focusing on intangible decisions by associating default options (Thaler et al., 2014). Among several alternatives, choices are influenced by creating default options for the most desired outcome.

Thaler et al. (2014) recommended using choice architecture to help consumers to make better decisions for themselves without necessarily noticing that this decision was framed externally. Choice architecture aims to set defaults as per the intended aims. Consumers can opt-out but Thaler et al. (2008) showed that consumers rarely move away from the default option. They give examples such as in health-care or retirement saving plans where the default option is set to select the best value for health-care coverage or optimise the amount saved regularly for future retirement. To go further than defaults and to engage consumers on a decision path, Thaler et al. (2008) suggest "nudging" consumers. Nudging can be associated with orienting consumers to their decision-making process towards a favoured outcome, as suggested in the health-care example above. To create defaults options and nudge consumers, Thaler and Sunstein (2008) have used the NUDGES acronym to structure the approach one should have when designing choice architecture: iNcentives, Understand mappings, use Defaults, Give feedback, Expert error and Structure complex choices into manageable sub-choices (NUDGES).

Johnson et al. (2012:489) draw upon the work of Thaler et al. (2008) to propose 11 tools for choice architecture: reduce the number of alternatives, use technology for decision aids, use defaults, focus on satisfying, create limited time windows, set the decision process in stages, partition options, limit the number of attributes, translate information for better "evaluability", customise information as per the decision-maker profile, and focus on experience.

These recommendations, outlined by Thaler et al. (2008) and Johnson et al. (2012:489), are not inflexible and can be adapted to different situations. Gigerenzer (2002) expressed the idea of a modular toolbox, wherein the choice architect can take any technique that might be suitable to achieve a desired outcome.

Choice architecture is also referred to as libertarian paternalism by Thaler and Sunstein (2003). This apparent contradiction is justified by the decisions set by policy (paternalism) but decision-makers remain free to opt-out (libertarian). This has been described as: "an approach that preserves freedom of choice but that authorises both private and public institutions to steer people in directions that will promote their welfare" (Thaler and Sustein, 2003:179). Mitchell (2005) recognises the power of defaults but argues that this approach is benevolent; this study notes that there is a concern that central planners could have too much power influencing individuals, and defaults would not be set in favour of individuals but rather in the interests of policy-makers. Smith et al. (2013:159) question the ethical implications of "choice without awareness". Instead of placing the decision-maker in a passive decision-making framework, they recommend the use of "smart defaults" to make "active choices". Smart defaults comprise the proposition of options in real-time according to consumer preferences. These live updates are suitable for online settings. For example, when consumers are shopping online, they select a set of criteria and a series of products / options are presented. Smith et al. (2013) show evidence that smart defaults are now a staple of online shopping experiences, suggesting that they should become the norm when consumers make more important decisions for their future, for example in terms of health care and pensions, especially as these decisions can now be made online with access to large amounts of information.

In 2010 in the UK, choice architecture gained public attention when the British government set the Behavioural Insights Team (BIT, 2010). The BIT aimed to reduce policy production by offering nudges through partnerships with various public bodies such as the Department of Health (to increase organ donation by testing message framing) or HM Treasury (to reduce poverty by setting a decision-making framework aimed at enhancing household economic decisions). As behavioural economics and choice architecture become more widely accepted by public bodies and organisations, examples have also been found in the field of waste/resource management. Baxter and Gram-Hanssen (2016:100) have applied NUDGES to environmental messaging. They argue that messages aimed at promoting mobile 'phone recycling should move away from promoting benefits, as this has limited impact on consumer decisions, but rather focus on focus on the detrimental effects of "do nothing" and the negative environmental consequences. This approach connects with the creation of guilt and negative emotions, which is supposed to trigger an intended behaviour. This may be an over-simplification and may only explore a subset of the "adaptive toolbox" formulated by Gigerenzer (2002). Meder et al. (2018) argue that NUDGES are even more effective when the wider environment is taken into account, rather than solely in the decision-maker's immediate sphere.

The choice architecture approach not yet been applied to urban mining (Pierron et al., 2017). Current end-of-use decisions about small EEE have not yet been framed within a choice architecture intention. (W)EEE collection solutions offered to users are presently unsatisfactory and users would rather stockpile or discard unwanted EEE (Ongondo and Williams, 2011). Individuals choose to hold on to their electronic devices if there is no valid alternative available, despite the legislation in place and the take-back schemes offered by retailers. If the device has some monetary value remaining and the market valuation of the device meets households' expectations, then the device is likely to be sold (Ongondo and Williams, 2011). If this is not the case, it will probably be stockpiled. It seems thus clear that stockpiling behaviour is not a rational economic decision as a household's utility for the devices will continue to decrease over time, and the longer the (W)EEE is stockpiled the more likely it is destined for general refuse (Gutiérrez et al., 2010).

A choice architecture toolbox for small high-end electronics could be implemented to change end-of-use behaviour and support urban mining development (Gigerenzer, 2002). For example, it may be possible to counter the trend of stockpiling mobile electronic devices by offering better end-of-use alternatives to consumers when reaching this decision point. Barr et al. (2013:68) outline that NUDGES and social marketing are effective methods to promote recycling. However, these methods need to be combined with efforts to promote reuse and repair, as end-of-use decision formulations are made in a complex decision-making environment involving many possible alternatives. Consequently, NUDGES and other choice architecture techniques should be adapted simultaneously to the entire palette of end-of-use decisions: reusing, reselling, recycling and discarding.

2.6 Research Gap and Study Aim

The literature has showed that the TPB is a useful construct to model end-of-use behaviour in waste and resources management studies. TPB studies integrating emotions in the decision-making process, tend to have a higher variance explained for intention but more rarely for behaviour. But there is no set of factors for small (W)EEE that consistently support a higher variance explained for intention, let alone behaviour when reported.

This study aims at extending the TPB specifically for small (W)EEE end-of-use behaviour, using behavioural economics factors.

To achieve this aim, we have:

- Reviewed TPB models frequently used in waste and resources management studies to establish which core concepts could be used for small (W)EEE stockpiling behaviour evaluation;
- Suggested variables that could explain and reduce the intention-behaviour gap for small (W)EEE.

A dedicated TPB model for small (W)EEE integrating behavioural economics variables could improve modelling end-of-use decisions. Better understanding how anthropogenic stocks are generated could help preventing them as well as accessing these resources within an urban mining environment.

3. METHODS

The TPB is one of the most prevalent models in waste management literature to evaluate household recycling behaviour and environmental attitudes. The TRA is rarely used to model waste separation; to our knowledge, only Barata and Castro (2013) have deployed the TRA to investigate waste separation, and among teenagers. The TPB has seldom been used for (W)EEE behavioural modelling with significant results; only Thi Thu Nguyen et al. (2018) have applied the TPB in comparing (W)EEE recycling with household recycling behaviour in general. Therefore, a decision was made to select from a larger pool of research in waste and resource management for this study.

The Science Direct repository was selected for searching as most environmental science journals are referenced herein: Resources, Conservation and Recycling, Waste Management, Journal of Cleaner Production, Journal of Environmental Psychology, Journal of Environmental Management, Sustainable Cities and Society. The search terms used were "TPB "or "TRA" and "Waste" or "e-waste" or "(W) EEE". There was no country restriction, the intention being to have as large a pool of publications as possible. Some studies not directly linked to the TPB or TRA were identified as they used a different set of factors but were associated with end-of-use behaviour and yielded high variance explained. They were incorporated in order not to leave out factors that could be associated with end-of-use behaviour (Barr, 2007; Liu et al., 2019; Nduneseokwu et al., 2017).

For each study selected, the factors were listed and the overall variance explained using the Coefficient of Determination (R^2) for intention, and when available for behaviour (Table 2). R^2 is a statistical measure representing the percentage of variation from one independent variable (y) to variation in a dependent variable (x). For example, if the R^2 of a model is 0.40 it signifies that 40% of the observed variation can be explained by the model's input. If $R^2 = 1$, the model and associated factors explain all the variance. There is no consensus on the cut-off value used to determine if a model explains observed variation. However, a cut-off value set at $R^2 = 0.75$ implies that approximately three-quarters of the variance observed can be explained by the model, which is significant and the associated factors are influential. The investigated studies often used Likert scales to assess self-reported intention and behaviour. To compute R^2 some studies used Confirmatory Factor Analysis (CFA) or Structural Equation Modelling (SEM), depending if they were confirming an existing set of factors or exploring new variables and their relationships.

4. BASIS FOR THEORETICAL ELABORATION ON THE TPB EXTENSION

This theoretical elaboration rests on studies that have used the TPB in the waste and resources management field. It identified specific studies that have achieved higher variance explained for intention and behaviour. Using their advances in the field, we suggest taking another step in this direction using behavioural economics to improve our understanding of mobile and smart phones end-of-use decisions.

4.1 Literature Review TPB Data

Based on the criteria outlined above, 23 suitable previous studies were identified (Table 1). All variables studied are presented, as well as the R^2 results for intention, and

TABLE 1: Published studies relating to applications explanatory models of behaviour in the context of waste and resources management. N/A: data not available.

Authors	Topic	R^2	
		Intention	Behaviour
1 - Swami et al. (2011)	Household recycling in the UK	0.22	0.22
2 - Huffman et al. (2014)	Students' recycling attitudes	0.23	0.08
3 – Vassanadumrongdee et al. (2018)	Behavioural factors for waste management in Bangkok	0.25	N/A
4 – Le et al. (2013)	E-waste recycling in Vietnam	0.27	N/A
5 - Knussen et al. (2004)	Household recycling in the UK	0.29	N/A
6 - Wan Ab et al. (2012)	Household food waste separation in Malaysia	0.33	0.09
7 - Tonglet et al. (2004)	Recycling behaviour in the UK	0.33	0.33
8 - Seacat et al. (2010)	Household recycling	0.36	0.36
9 – Liu et al. (2019)	Mobile phone recycling behaviour in China	0.39	N/A
10 - Manetti et al. (2004)	Recycling behaviour in Italy	0.39	N/A
11 - Chan (1998)	Household recycling in Hong Kong	0.44	N/A
12 - Pakpour et al. (2014)	Household waste behaviour in Iran	0.47	N/A
13 - Kals et al. (1999)	Emotional affinity towards nature	0.47	N/A
14 - Davies et al. (2002)	Recycling behaviour in the UK	0.48	0.48
15 - Bortoleto et al. (2012)	Household waste prevention in the UK	0.59	0.59
16 – Nduneseokwu et al., (2017)	Formal e-waste collection in Nigeria	0.62	N/A
17 - de Leeuw et al. (2015)	High-school students' pro-environmental behaviour	0.68	0.27
18 - Barr and Gilg (2005)	Household recycling in the UK	0.68	0.46
19 - Barr (2007)	Household waste management in the UK	0.7	0.83
20 - Perugini & Bagozzi, (2001)	Bodyweight regulation in Italy	0.76	0.3
21 - Carrus et al. (2008)	Household recycling in Italy	0.82	N/A
22 - Wan et al. (2014)	Household recycling in Hong Kong	0.84	0.88
23 - Bamberg et al. (2007)	Public transportation in Germany (Dortmund and Frankfurt)	0.9	0.8

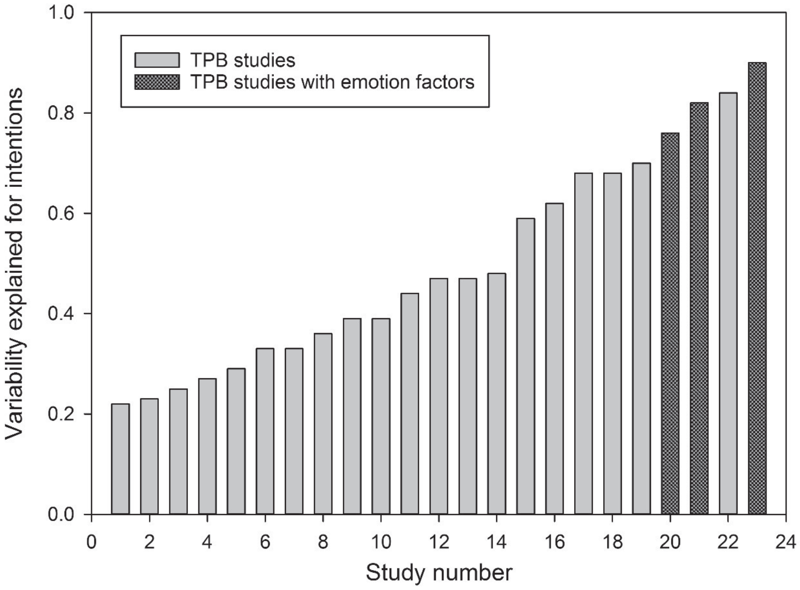

FIGURE 5: Studies ranked in increasing order of variance explained for intention (see Table 1). Studies integrating emotion factors are highlighted.

behaviour when reported. Studies are ranked in increasing order based on R^2 for intention.

Usually, variance explained for behaviour is lower than for intentions (Table 2). This observation is partially explained by the difference between declaring a future act and realising this act, i.e. the difference between self-reported behaviour and actual behaviour (e.g. Corral-Verdugo, 1997); and the difference caused by the so-called “value-action gap” (Barr, 2006; Williams and Gunton, 2007).

The study with the lowest variance explained for intention is from Swami et al. (2011) with 22% (Figure 5); the lowest variance explained for behaviour (8%) was observed by (Huffman et al., 2014). These studies obtained data from both self-reported questionnaires and observations on students’ recycling attitudes in the USA. Three studies focusing on the TPB and (W)EEE were carried out in Vietnam (Le et al., 2013) with 27% of variance for intention explained, China with 39% of variance explained (Liu et al. 2019) and Nigeria (Nduneseokwu et al., 2017) with 62% of intention explained. None of these studies reported variance explained for behaviour, only intention.

In contrast, there are four studies with marked variance explained for intention ($R^2 > 0.75$): 0.76 for Perugini and Bagozzi (2001), 0.82 for Carrus et al. (2008), 0.84 for (Wan et al. (2014) and 0.9 for Bamberg et al. (2007), i.e. two studies relate to household recycling, one to body weight regulation and one to public transportation. In three studies out of four, variables specifically associated with emotions (Perugini and Bagozzi, 2001), feelings (Bamberg et al. (2007), and desires (Carrus et al., 2008) were retained in the models due to their influence on R^2 for intentions.

It appears that studies integrating emotions, feelings and desires tend to yield the highest variance explained (Table 1 and Figure 5). These observations suggest that an approach using behavioural economics, which integrates individuals’ decision-making biases due to emotions, could be added to the TPB to improve model variance explained for intention and behaviour.

4.2 Extending the TPB with Behavioural Economics

Behavioural economics could help explaining the intention-behaviour gap for small (W)EEE. For example, with a smart phone that is still in working order but unused because it has been replaced by a newer version, the owner might still have some utility for the spare device. He might have a higher utility for a backup device than for the monetary incentive reselling the device would generate. There might be a disconnect between what the owner thinks the device is worth and what the device is worth on the secondary market. The Endowment Effect could be used to measure this gap between subjective and objective valuations. Therefore, the strength of the endowment effect could explain stockpiling decisions, thus the generation of anthropogenic stocks when taken on a larger scale. On the other hand, if choice architecture could be adapted to reduce the endowment effect strength, this could prevent the generation of small (W)EEE anthropogenic stocks and facilitating access to existing stocks by enticing individuals’ to part from their unused mobile and smart phones.

4.2.1 Extending with variables associated with emotions to explain the intention-behaviour gap

As Perugini and Bagoozi (2001) carried out with the MGB (Figure 4), a model based on the TPB with behavioural economics variables could better model small (W)EEE end-of-use behaviour. The TPB has proven to be a robust base (Armitage and Conner, 2001; Ajzen, 2015) to expand from and enhance variance explained for intention and behaviour (Table 1). Behavioural economics variables such as the endowment effect, loss aversion or status quo bias could have certain impacts on stockpiling decisions, therefore on small (W)EEE anthropogenic stock levels. Users might find the resale value of their device lower than their expectations. Thus preferring not to engage in this resale activity they might find not worthwhile and keep the device as a spare or backup (endowment effect). Owners might have used their phone for a significant amount of time. Or they might be extremely attached to it as it might have helped them capturing many fond memories. They might feel an emotion such as regret if they parted from their valued and cherished smart phone by reselling it (loss aversion and status quo bias). Hence they might prefer simply keeping it and store it away.

Once these intrinsic factors associated with behavioural economics, such as the endowment effect or loss aversion or status quo bias, are identified for mobile and smart phones end-of-use decisions and behaviour, they could be added to the TPB. This extended TPB would better model and measure small (W)EEE end-of-use behaviour, therefore contributing to close the intention-behaviour gap and informing on the factors influencing the generation of anthropogenic stocks.

4.2.2 Extending with variables associated with choice architecture to reduce the intention-behaviour gap

If these end-of-use decisions (or rather the non-behaviour to engage in positive actions to support urban mining) are influenced by the endowment effect, choice architecture could reduce this effect. The endowment effect represents a hindrance that could explain the intention-behaviour gap for small (W)EEE and choice architecture represents a force to counter this effect by using a combination of monetary and non-monetary incentives. The concept of choice architecture to exploit a DUM (Ongondo et al., 2015) already been explored (Pierron et al. 2017) and could be adapted to mobile and smart phones as a case study. As an "adaptive toolbox" (Gigerenzer, 2002), NUDGES can be shaped as per any small (W)EEE specifics (Table 2).

To change behaviour and access anthropogenic stocks, and to render an urban mine exploitable, non-monetary incentives targeted at the endowment effect could be designed using choice architecture (Table 2). Since objective valuations are based on market principles, non-monetary incentives based on users' preferences should be designed to bridge the gap between subjective and objective assessments of value. Enhanced take-back schemes that take into account the endowment effect and users' subjective valuation could offer to give the cash equivalent to a charity, instead of giving back to the user. Strahilevitz and Loewenstein (1998) estimated that charity incentives provide more utility to decision-makers than a cash equivalent. Take-back schemes could provide information on the environmental benefits of reusing a 'phone, instead of manufacturing it e.g. an estimate of the quantity of water saved or the positive impact this action has on carbon reductions. Providing immaterial benefits in addition to monetary rewards could rebalance the misalignment between small (W)EEE second-hand market values and users' perceived values. They would be convenient to implement for take-back schemes and aligned with users' expectations. These incentives should be designed to reduce the barriers set by the EE. NUDGES could represent the framework used to change behaviour for urban mining (Table 2). This framework can and should be adapted (Johnson, 2012:489).

To date, the TPB has been used in few studies dedicated to small (W)EEE end-of-use decision-making (Table 1). However, methods using extrinsic motivators may be applied to alter (W)EEE end-of-use behaviour also need consideration. To be exploitable efficiently, DUMs need end-users to behave in such a fashion that it becomes possible to access stockpiles and transform discarding habits into recycling opportunities and stockpiling into reuse decisions. Behaviour change is a complex process that requires the use of various incentives, intrinsic and/or extrinsic (Schultz et al., 1995).

4.2.3 TPB extended for small electronics end-of-use decisions

This extended TPB could help explaining the weakness between intention and behaviour for small (W)EEE. Many

TABLE 2: Choice architecture principles applied to nudging mobile and smart phone users to trade-in their hoarded device (Thaler et al., 2008).

Nudges	Description
iNcentives	Incentive mix (monetary and non-monetary) based on device characteristics and owners' categorical variables (loss aversion, status quo bias, endowment effect)
Understanding mappings [1]	Small electronics collectors explain stockpiled mobile devices' value declines over time to nudge decision to use hoarded devices as an additional discount toward the acquisition of a new device
Defaults	Default decision for mobile and smart phones tends to be stockpiling. Small electronics collectors to counter this default and nudge owners to trade-in their stockpiled device within a time period
Giving feedback	Giving information to each owner: small electronics collectors deliver information on hoarded device second-hand value, incentive mix based on device characteristics and owner's categorical variables, information on sustainable practice (what happens to the phone when collected by small electronics producers with a positive impact on carbon footprint and reduced resources depletion)
Expecting errors	Incentive mix not adapted to user preferences. Small electronics collectors to use data gathered over time and experience to improve incentive mix
Structuring complex choices	Structure decision into logical steps: Owner to understand that stockpiling has marginal utility as usually devices are not used for their intended purpose Stockpiled devices' value declines over time so will the incentive mix. Immediate decision has the highest utility for owner User is contributing to positive outcome for the environment and the circular economy

[1] *How information presentation influences decisions*

studies (Table 1) have reported only intention and not behaviour. When reported, behaviour is significantly lower than intentions in terms of explained variance (Perugini and Bagozzi, 2001). The willingness to extend the TPB with variables that are not directly associated with attitudes towards the environment is supported by Echegaray and Hansstein (2017). They found that despite respondents having a positive attitude towards the environment, they failed to engage in a (W)EEE recycling behaviour. The most successful TPB studies in waste and resources management had integrated emotions in their set of factors (Table 1). Using variables that take into account emotions and their influence on the decision-making process, such as in behavioural economics, could be worth investigating. Especially for stockpiled small (W)EEE still in working order. Individuals who have kept a spare mobile or smart phone as a back up might not perceive this device as waste. Hence the environmental factors usually associated with TPB studies in waste and resources management might not be relevant. Integrating behavioural economics variables for small (W)EEE could reduce the intention-behaviour gap (Figure 6).

We propose to take the TPB as a proven and robust basis but we acknowledge the intention-behaviour gap remains problematic in most studies. We suggest that the endowment effect is at work between the intention and the actual behaviour to safely dispose of an unwanted device still in working order. Individuals prefer keeping the unwanted device as a spare because they have higher utility for this status quo and might regret their decision at a later stage. This endowment effect could have an influence on small (W)EEE stockpiling decisions. Undersanting the nature of the intention-behaviour gap for mobile and smart phones end-of-use decisions could inform the design of solutions directly targeted at the endowment effect (Table 2). Choice architecture is an adaptable and flexible approach aiming at altering behaviour towards a desired outcome (Thaler et al., 2008). An extended TPB with behavioural economics could be further investigated to limit the generation of small (W)EEE anthropogenic stocks as well as accessing these resources to support the development of urban mining using existing formal collection systems.

5. CONCLUSIONS AND RECOMMENDATIONS

Historically, most behavioural models for waste and resources management have been based on variations of the TPB. These models have evolved and improved, but they still need refinement. From this review, we can conclude that behavioural models derived from psychology – such as the TPB - have been applied to understand individuals' recycling behaviour but the variance explained for intention and behaviour-related factors generally remains low. Models that incorporate emotional variables tend to have a higher explained variance for intention. The endowment effect is likely to be a significant barrier to the release of (W)EEE back into the circular economy. To overcome the endowment effect, non-monetary incentives based on users' preferences could be designed to bridge the gap between subjective and objective assessments of the value of (W)EEE. Techniques integrating emotional variables such as behavioural economics and choice architecture could be incorporated into behavioural models such as the TPB to better evaluate small (W)EEE anthropogenic stocks generation and facilitating access to these resources.

This paper uses secondary data as the basis for the analyses and interpretation presented. Future research could test and apply behavioural economics concepts to

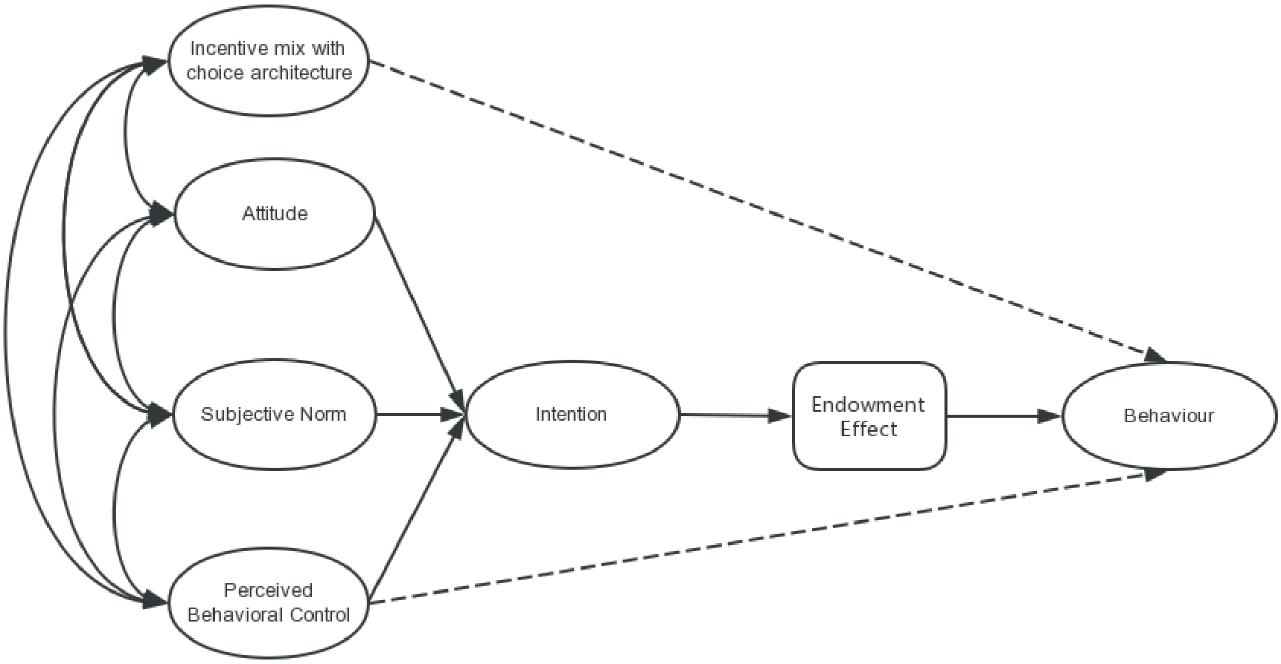

FIGURE 6: TBP extended illustrating the potential influence of the endowment effect on behaviour and choice architecture to counter the endowment effect and alter end-of-use behaviour, based on Tables 1 and 2.

small (W)EEE using primary qualitative and quantitative data. Most TPB studies report explained intention but fewer explained behaviour. Future research accessing small (W)EEE anthropogenic stocks for urban mining could focus therefore on end-of-use behaviour rather than intention. Furthermore, the behavioural economics theories discussed in this paper could be tested using loss aversion, status quo bias and the endowment effect affecting small (W)EEE end-of-use decisions and behaviour. Based on these findings, incentives could be designed using choice architecture to access small (W)EEE anthropogenic stocks and improve urban mining efforts to reinsert devices and resources into the economy.

REFERENCES

Ajzen, I. (2011). The theory of planned behaviour: reactions and reflections. Psychology & health 26, 1113–27. https://doi.org/10.1080/08870446.2011.613995

Ajzen, I. (1985). ‘From Intentions to Actions: A Theory of Planned Behavior’, in: Kuhl, P.D.J., Beckmann, D.J. (Eds.), Action Control, SSSP Springer Series in Social Psychology (pp. 11–39). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-69746-3_2

Ajzen, I., (2015) The theory of planned behaviour is alive and well, and not ready to retire: a commentary on Sniehotta, Presseau, and Araújo-Soares, Health Psychology Review, 9:2, 131-137, DOI: 10.1080/17437199.2014.883474

Armitage, C.J., Conner, M. (2001). Efficacy of the Theory of Planned Behaviour: a meta-analytic review. The British journal of social psychology / the British Psychological Society 40, 471–99.

Baldé, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P. (2017). Quantities, Flows, and Resources (No. 3), The Global E-waste Monitor. United Nations University, Bonn/Geneva/Vienna.

Balleine, B.W., Dezfouli, A., Ito, M., Doya, K. (2015). Hierarchical control of goal-directed action in the cortical–basal ganglia network. Current Opinion in Behavioral Sciences, Neuroeconomics 5, 1–7. https://doi.org/10.1016/j.cobeha.2015.06.001

Bamberg, S., Hunecke, M., Blöbaum, A. (2007). Social context, personal norms and the use of public transportation: Two field studies. Journal of Environmental Psychology 27, 190–203. https://doi.org/10.1016/j.jenvp.2007.04.001

Barata, R., Castro, P. (2013). “I feel recycling matters… sometimes”: The negative influence of ambivalence on waste separation among teenagers. The Social Science Journal 50, 313–320. http://dx.doi.org/10.1016/j.soscij.2013.05.007

Barba-Gutiérrez, Y., Adenso-Díaz, B., Hopp, M. (2008). An analysis of some environmental consequences of European electrical and electronic waste regulation. Resources, Conservation and Recycling 52, 481–495. https://doi.org/10.1016/j.resconrec.2007.06.002

Barr, S. (2007). Factors Influencing Environmental Attitudes and Behaviors A U.K. Case Study of Household Waste Management. Environment and Behavior 39, 435–473. https://doi.org/10.1177/0013916505283421

Barr, S. (2006). Environmental Action in the Home: Investigating the “Value-Action” Gap. Geography 91, 43–54.

Barr, S., Gilg, A.W. (2005). Conceptualising and analysing household attitudes and actions to a growing environmental problem: Development and application of a framework to guide local waste policy. Applied Geography 25, 226–247. https://doi.org/10.1016/j.apgeog.2005.03.007

Barr, S., Gilg, A.W., Ford, N.J. (2001). A conceptual framework for understanding and analysing attitudes towards household-waste management. Environment and Planning A 33, 2025–2048. https://doi.org/10.1068/a33225

Barr, S., Guilbert, S., Metcalfe, A., Riley, M., Robinson, G.M., Tudor, T.L. (2013). Beyond recycling: An integrated approach for understanding municipal waste management. Applied Geography 39, 67–77. https://doi.org/10.1016/j.apgeog.2012.11.006

Baxter, J., Gram-Hanssen, I. (2016). Environmental message framing: Enhancing consumer recycling of mobile phones. Resources, Conservation and Recycling 109, 96–101. https://doi.org/10.1016/j.resconrec.2016.02.012

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., Buchert, M. (2013). Recycling of rare earths: a critical review. Journal of Cleaner Production 51, 1–22. https://doi.org/10.1016/j.jclepro.2012.12.037

BIT (2010). About us [WWW Document]. URL https://www.bi.team/ (accessed 10.31.19).

Bouton, M.E. (2014). Why behavior change is difficult to sustain. Preventive Medicine, Behavior Change, Health, and Health Disparities 68, 29–36. https://doi.org/10.1016/j.ypmed.2014.06.010

Carrus, G., Passafaro, P., Bonnes, M. (2008). Emotions, habits and rational choices in ecological behaviours: The case of recycling and use of public transportation. Journal of Environmental Psychology 28, 51–62. https://doi.org/10.1016/j.jenvp.2007.09.003

Chan, L., Bishop, B. (2013). A moral basis for recycling: Extending the theory of planned behaviour. Journal of Environmental Psychology 36, 96–102. https://doi.org/10.1016/j.jenvp.2013.07.010

COM614. (2015). Closing the loop - An EU action plan for the Circular Economy.

Comply Direct (2019). Demanding 2019 WEEE Collection Targets Confirmed [WWW Document]. URL https://www.complydirect.com/news/demanding-2019-weee-collection-targets-confirmed/ (accessed 10.28.19).

Corral-Verdugo, V. (1997). Dual ‘Realities’ of Conservation Behavior: Self-Reports vs Obervations of Reuse and Recycling Behavior. Journal of Environmental Psychology 17, 135–145. https://doi.org/10.1006/jevp.1997.0048

Cossu, R., Williams, I.D. (2015). Urban mining: Concepts, terminology, challenges. Waste Management, Urban Mining 45, 1–3. https://doi.org/10.1016/j.wasman.2015.09.040

Craig Smith, N., G. Goldstein, D., J. Johnson, E. (2013). Choice Without Awareness: Ethical and Policy Implications of Defaults. American Marketing Association 32, 159–172.

Daum, K., Stoler, J., Grant, R., Daum, K., Stoler, J., Grant, R.J. (2017). Toward a More Sustainable Trajectory for E-Waste Policy: A Review of a Decade of E-Waste Research in Accra, Ghana. International Journal of Environmental Research and Public Health 14, 135. https://doi.org/10.3390/ijerph14020135

Davies, J., Foxall, G., Pallister, J. (2002). Beyond the Intention–Behaviour Mythology An Integrated Model of Recycling. Marketing Theory 2, 29–113. https://doi.org/10.1177/1470593102002001645

de Leeuw, A., Valois, P., Ajzen, I., Schmidt, P. (2015). Using the theory of planned behavior to identify key beliefs underlying pro-environmental behavior in high-school students: Implications for educational interventions. Journal of Environmental Psychology 42, 128–138. https://doi.org/10.1016/j.jenvp.2015.03.005

Department for Business Innovation and Skills (2013). Implementation of the WEEE Recast Directive 2012/19/EU and Changes to the UK WEEE System (Business Regulation No. BIS/11/1179), BIS. Department for Business Innovation and Skills, London.

Di Maria, F., Micale, C., Sordi, A., Cirulli, G., Marionni, M. (2013). Urban Mining: Quality and quantity of recyclable and recoverable material mechanically and physically extractable from residual waste. Waste Management 33, 2594–2599. https://doi.org/10.1016/j.wasman.2013.08.008

Directive 125/EC. (2009). Directive 2009/125/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products. Text with EEA relevance.

Directive 2002/96/EC (2002). Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE). Joint declaration of the European Parliament, the Council and the Commission relating to Article 9, 037.

Directive 2012/19/EU. (2012). Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Text with EEA relevance, 197.

Dommer, S.L., Swaminathan, V. (2013). Explaining the Endowment Effect through Ownership: The Role of Identity, Gender, and Self-Threat. Journal of Consumer Research 39, 1034–1050.

Echegaray, F., & Hansstein, F. V. (2017). Assessing the intention-behavior gap in electronic waste recycling: the case of Brazil. Journal of Cleaner Production, 142, 180–190. https://doi.org/10.1016/j.jclepro.2016.05.064

Eliseeva, S.V., Bünzli, J.-C.G. (2011). Rare earths: jewels for functional materials of the future. New Journal of Chemistry 35, 1165.

Ellen MacArthur Foundation (2013). Economic and business rationale for an accelerated transition (Online No. 1), Towards the Circular Economy. Ellen MacArthur Foundation, Cowes, Isle of Wight.

EU Directive 851, 2018. Directive (EU) 2018 of the European Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC on waste.

European Commission, 2017a. Critical Raw Materials List for the EU. European Commission.

European Commission, 2017b. Report on the implementation of the Circular Economy Action Plan (Text No. 1). Brussels.

European Commission, 2014. Report on Critical Raw Materials for the EU (No. 2), Report of the Ad hoc Working Group on defining critical raw materials. European Commission, Brussels.

European Commission, 2010. Critical Raw Materials (No. 1). European Commission.

European Parliament, 2019. Establishment of a framework to facilitate sustainable investment.

Eurostat, 2016. Waste Electrical and Electronic Equipment (WEEE) - Eurostat [WWW Document]. URL http://ec.europa.eu/eurostat/web/waste/key-waste-streams/weee (accessed 9.3.16).

Fishbein, M., Ajzen, I. (1975). Belief, attitude, intention, and behavior: an introduction to theory and research. Addison-Wesley Pub. Co.

Gartner. (2020). Gartner Says Global Smartphone Sales Declined 2.7% in First Quarter of 2019 [WWW Document]. Gartner. URL https://www.gartner.com/en/newsroom/press-releases/2020-06-01-gartner-says-global-smartphone-sales-declined-20--in- (accessed 11.24.20).

Geissdoerfer, M., Savaget, P., Bocken, N. M. P., & Hultink, E. J. (2017). The Circular Economy – A new sustainability paradigm? Journal of Cleaner Production, 143, 757–768. https://doi.org/10.1016/j.jclepro.2016.12.048

Gigerenzer, G. (2002). Bounded Rationality: The Adaptive Toolbox, New Ed edition. ed. MIT Press, Cambridge, Mass.

Green Alliance (2015). A circular economy for smart devices / Opportunities in the US, UK and India, Green Alliance. Green Alliance, London.

Gutiérrez, E., Adenso-Díaz, B., Lozano, S., González-Torre, P. (2010). A competing risks approach for time estimation of household WEEE disposal. Waste Management 30, 1643–1652. https://doi.org/10.1016/j.wasman.2010.02.032

Huffman, A.H., Van Der Werff, B.R., Henning, J.B., Watrous-Rodriguez, K. (2014). When do recycling attitudes predict recycling? An investigation of self-reported versus observed behavior. Journal of Environmental Psychology 38, 262–270. https://doi.org/10.1016/j.jenvp.2014.03.006

Huisman, J. (2013). WEEE recast : from 4kg to 65 %: the compliance consequences. United Nations University.

Iswa.org. 2020. ISWA: The Global E-Waste Monitor 2020. [online] Available at: <https://www.iswa.org/home/news/news-detail/article/-21c8325490/109/> [Accessed 25 November 2020].

Iyengar, S.S., Lepper, M.R. (2000). When Choice is Demotivating: Can One Desire Too Much of a Good Thing? Journal of Personality and Social Psychology 79, 995–1006.

Jonhson, E.J., G. C. Dellaert, B., Fox, C., G. Goldstein, D., Haubl, G., P. Larrick, R., W. Payne, J., Peters, E., Schkade, D., Wansick, D., U. Weber, E. (2012). Beyond nudges: Tools of a choice architecture. Mark Lett 23, 487–504.

Hopper, J.R., Nielsen, J.M. (1991). Recycling as Altruistic Behavior: Normative and Behavioral Strategies to Expand Participation in a Community Recycling Program. Environment and Behavior 23, 195–220. https://doi.org/10.1177/0013916591232004

Kahneman, D., Knetsch, J.L., Thaler, R.H. (1991). Anomalies: The Endowment Effect, Loss Aversion, and Status Quo Bias. The Journal of Economic Perspectives 5, 193–206.

Kahneman, D., Knetsch, J.L., Thaler, R.H. (1990). Experimental Tests of the Endowment Effect and the Coase Theorem. Journal of Political Economy 98, 1325–1348.

Kahneman, D., Tversky, A. (1983). Choices, Values, and Frames. American Psychological Association 39, 341–350.

Korhonen, J., Honkasalo, A., & Seppälä, J. (2018). Circular Economy: The Concept and its Limitations. Ecological Economics, 143, 37–46. https://doi.org/10.1016/j.ecolecon.2017.06.041

Krook, J., Baas, L. (2013). Getting serious about mining the technosphere: a review of recent landfill mining and urban mining research. Journal of Cleaner Production, Special Volume: Urban and Landfill Mining 55, 1–9. https://doi.org/10.1016/j.jclepro.2013.04.043

Krook, J., Carlsson, A., Eklund, M., Frändegård, P., Svensson, N., (2011). Urban mining: hibernating copper stocks in local power grids. Journal of Cleaner Production 19, 1052–1056.

Kuong, I. H., Li, J., Zhang, J., & Zeng, X. (2019). Estimating the Evolution of Urban Mining Resources in Hong Kong, Up to the Year 2050. Environmental Science and Technology, 53(3), 1394–1403. https://doi.org/10.1021/acs.est.8b04063

Lambeth, Veolia UK. (2017). Waste Electrical and Electronic Equipment (WEEE) recycling event | Lambeth Council [WWW Document]. URL https://www.lambeth.gov.uk/events/waste-electrical-and-electronic-equipment-weee-recycling-event (accessed 10.28.19).

Le Bozec, A. (2008). The implementation of PAYT system under the condition of financial balance in France. Waste Management, Pay as you throw: a tool for urban waste management 28, 2786–2792. https://doi.org/10.1016/j.wasman.2008.03.028

Le, H.-L., Yamasue, E., Okumura, H., Ishihara, K.N. (2013). 'Analysis of Intentions to Recycle Electronic Waste (E-Waste) Using the Theory of Planned Behavior: A Case Study in Urban Areas of Vietnam', Green Energy and Technology (pp. 73–79) Springer Japan

Lerner, J., Small, D., Loewenstein, G. (2004). Heart Strings and Purse Strings. American Psychological Society, Psychological Science 15, 337–342.

Let's Recycle. (2019). DEFRA proposes WEEE target hike [WWW Document]. letsrecycle.com. URL https://www.letsrecycle.com/news/latest-news/defra-proposes-weee-target-hike/ (accessed 10.28.19).

Liu, J., Bai, H., Zhang, Q., Jing, Q., Xu, H. (2019). Why are obsolete mobile phones difficult to recycle in China? Resources, Conservation and Recycling 141, 200–210. https://doi.org/10.1016/j.resconrec.2018.10.030

Meder, B., Fleischhut, N., Osman, M. (2018). Beyond the confines of choice architecture: A critical analysis. Journal of Economic Psychology 68, 36–44. https://doi.org/10.1016/j.joep.2018.08.004

Milovantseva, N., Saphores, J.-D. (2013). Time bomb or hidden treasure? Characteristics of junk TVs and of the US households who store them. Waste Management, Special Thematic Issue: Urban Mining Urban Mining 33, 519–529. https://doi.org/10.1016/j.wasman.2012.07.020

Mitchell, G., 2005. Libertarian Paternalism Is an Oxymoron. Nortwestern University Law Review 99, 1–42.

Morewedge, C.K., Shu, L.L., Gilbert, D.T., Wilson, T.D. (2009). Bad riddance or good rubbish? Ownership and not loss aversion causes the endowment effect. Journal of Experimental Social Psychology 45, 947–951. https://doi.org/10.1016/j.jesp.2009.05.014

Mueller, S.R., Wäger, P.A., Turner, D.A., Shaw, P.J., Williams, I.D. (2017). A framework for evaluating the accessibility of raw materials from end-of-life products and the Earth's crust. Waste Management 68, 534–546. https://doi.org/10.1016/j.wasman.2017.05.043

Nduneseokwu, C., Qu, Y., Appolloni, A., Nduneseokwu, C.K., Qu, Y., Appolloni, A., 2017. Factors Influencing Consumers' Intentions to Participate in a Formal E-Waste Collection System: A Case Study of Onitsha, Nigeria. Sustainability 9, 881. https://doi.org/10.3390/su9060881

Oguchi, M., Kameya, T., Yagi, S., Urano, K. (2008). Product flow analysis of various consumer durables in Japan. Resources, Conservation and Recycling 52, 463–480. https://doi.org/10.1016/j.resconrec.2007.06.001

Ojedokun, O. (2011). Attitude towards littering as a mediator of the relationship between personality attributes and responsible environmental behavior. Waste Management 31, 2601–2611. https://doi.org/10.1016/j.wasman.2011.08.014

Ongondo, F.O., Williams, I.D. (2011). Greening academia: Use and disposal of mobile phones among university students. Waste Management 31, 1617–1634. https://doi.org/10.1016/j.wasman.2011.01.031

Ongondo, F.O., Williams, I.D., Whitlock, G. (2015). Distinct Urban Mines: Exploiting secondary resources in unique anthropogenic spaces. Waste Management, Urban Mining 45, 4–9. https://doi.org/10.1016/j.wasman.2015.05.026

Oswald, I., Reller, A. (2011). E-Waste : A Story of Trashing , Trading , and Valuable Resources.

Pakpour, A.H., Zeidi, I.M., Emamjomeh, M.M., Asefzadeh, S., Pearson, H. (2014). Household waste behaviours among a community sample in Iran: An application of the theory of planned behaviour. Waste Management, Waste Management on Asia 34, 980–986. https://doi.org/10.1016/j.wasman.2013.10.028

Perugini, M., Bagozzi, R.P. (2001). The role of desires and anticipated emotions in goal-directed behaviours: Broadening and deepening the theory of planned behaviour. British Journal of Social Psychology 40, 79–98. https://doi.org/10.1348/014466601164704

Pierron, X., Williams, I.D., Shaw, P.J., Cleaver, V. (2017). Using choice architecture to exploit a university Distinct Urban Mine. Waste Management 68, 547–556. https://doi.org/10.1016/j.wasman.2017.06.034

Recycling Today (2018). Rare opportunity to recycle rare earths [WWW Document]. Recycling Today. URL http://www.recyclingtoday.com/article/rare-earth-metals-recycling/ (accessed 9.6.18).

Richetin, J., Sengupta, A., Perugini, M., Adjali, I., Hurling, R., Greetham, D., Spence, M. (2010). A micro-level simulation for the prediction of intention and behavior. Cognitive Systems Research 11, 181–193. https://doi.org/10.1016/j.cogsys.2009.08.001

Robinson, B.H. (2009). E-waste: an assessment of global production and environmental impacts. The Science of the total environment 408, 183–91. https://doi.org/10.1016/j.scitotenv.2009.09.044

Samuelson, W., Richard, Z. (1988). Status Quo Bias in Decision Making. Journal of Risk and Uncertainty 1, 7–59.

Schultz, P.W., Oskamp, S., Mainieri, T. (1995). Who recycles and when? A review of personal and situational factors. Journal of Environmental Psychology 15, 105–121. https://doi.org/10.1016/0272-4944(95)90019-5

Schwartz, S.H. (1968). Awareness of Consequences and the Influence of Moral Norms on Interpersonal Behavior. Sociometry 31, 355–369. https://doi.org/10.2307/2786399

Silveira, G.T.R., Chang, S.-Y. (2010). Cell phone recycling experiences in the United States and potential recycling options in Brazil. Waste Management, Special Thematic Section: Sanitary Landfilling 30, 2278–2291. https://doi.org/10.1016/j.wasman.2010.05.011

Simoni, M., Kuhn, E.P., Morf, L.S., Kuendig, R., Adam, F. (2015). Urban mining as a contribution to the resource strategy of the Canton of Zurich. Waste Management, Urban Mining 45, 10–21. https://doi.org/10.1016/j.wasman.2015.06.045

Singh, J., Ordoñez, I. (2015). Resource recovery from post-consumer waste: important lessons for the upcoming circular economy. Journal of Cleaner Production. https://doi.org/10.1016/j.jclepro.2015.12.020

Song, Q., Li, J. (2015). A review on human health consequences of metals exposure to e-waste in China. Environmental Pollution 196, 450–461. https://doi.org/10.1016/j.envpol.2014.11.004

Song, Q., Wang, Z., Li, J. (2012). Residents' behaviors, attitudes, and willingness to pay for recycling e-waste in Macau. Journal of Environmental Management 106, 8–16. https://doi.org/10.1016/j.jenvman.2012.03.036

Stahel, W. (1977). The potential for substituting manpower for energy: Final report 30 July 1977 for the Commission of the European Communities. Battelle, Geneva Research Centre.

Step Initiative (2014). Solving the E-Waste Problem (Step).

Stewart, R., & Niero, M. (2018). Circular economy in corporate sustainability strategies: A review of corporate sustainability reports in the fast-moving consumer goods sector. Business Strategy and the Environment. https://doi.org/10.1002/bse.2048

Strahilevitz, M., Loewenstein, G. (1998). The Effect of Ownership History on the Valuation of Objects. Journal of Consumer Research 25, 276–289.

Su, B., Heshmati, A., Geng, Y., Yu, X. (2013). A review of the circular economy in China: moving from rhetoric to implementation. Journal of Cleaner Production 42, 215–227. https://doi.org/10.1016/j.jclepro.2012.11.020

Swami, V., Chamorro-Premuzic, T., Snelgar, R., Furnham, A. (2011). Personality, individual differences, and demographic antecedents of self-reported household waste management behaviours. Journal of Environmental Psychology 31, 21–26. https://doi.org/10.1016/j.jenvp.2010.08.001

Thaler, R. (1980). Toward a Positive Theory of Consumer Choice. Journal of Economic Behavior and Organization 1, 39–60.

Thaler, R.H., Sunstein, C.R., Balz, J.P. (2008). Choice Architecture, in: The Behavioral Foundations of Public Policy. Eldar Shafir, pp. 428–439.

Thaler, R.H., Sustein, C.R. (2003). Libertarian Paternalism. The American Economic Review 93, 175–179.

The Economist (2016). The scientists who make apps addictive [WWW Document]. 1843. URL https://www.1843magazine.com/features/the-scientists-who-make-apps-addictive (accessed 3.29.17).

Thi Thu Nguyen, Hong, Hung, R.-J., Lee, C.-H., Thi Thu Nguyen, Hang. (2018). Determinants of Residents' E-Waste Recycling Behavioral Intention: A Case Study from Vietnam. Sustainability 11, 164. https://doi.org/10.3390/su11010164

Tonglet, M., Phillips, P.S., Bates, M.P. (2004). Determining the drivers for householder pro-environmental behaviour: Waste minimisation compared to recycling. Resources, Conservation and Recycling 42, 27–48. https://doi.org/10.1016/j.resconrec.2004.02.001

Tversky, A., Kahneman, D. (1991). Loss Aversion in Riskless Choice: A Reference-Dependent Model. The Quarterly Journal of Economics 106, 1039–1061. https://doi.org/10.2307/2937956

Tversky, A., Kahneman, D. (1982). Judgment under Uncertainty: Heuristics and Biases. Science 185, 1124–1131.

Vence, X., & Pereira, Á. (2019). Eco-innovation and Circular Business Models as drivers for a circular economy. Contaduria y Administracion. https://doi.org/10.22201/fca.24488410e.2019.1806

Wallsten, B., Magnusson, D., Andersson, S., Krook, J. (2015). The economic conditions for urban infrastructure mining: Using GIS to prospect hibernating copper stocks. Resources, Conservation and Recycling 103, 85–97. https://doi.org/10.1016/j.resconrec.2015.07.025

Wan, C., Shen, G.Q., Yu, A. (2014). The role of perceived effectiveness of policy measures in predicting recycling behaviour in Hong Kong. Resources, Conservation and Recycling 83, 141–151. https://doi.org/10.1016/j.resconrec.2013.12.009

Wilkinson, A., Williams, I.D. (2019, October). Why do (W)EEE hoard? The effect of consumer behaviour on the release of (W)EEE from home entertainment products into the circular economy [Paper presentation], in: Proceedings of the Seventeenth International Waste Management and Landfill Symposium. The 17th International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Sardinia, Italy (pp. 196-201).CISA.

Williams, I.D. (2016). 'Global Metal Reuse, and Formal and Informal Recycling from Electronic and Other High-Tech Wastes', Metal Sustainability (pp. 23–51). John Wiley & Sons, Ltd. https://doi.org/10.1002/9781119009115.ch2

Williams, I.D., Gunton, H. (2007, April). Waste minimisation using behaviour change techniques: a case study for students. in: Waste Matters: Integrating Issues. Proceedings of 2nd BOKU Waste Conference, Vienna, Austria (pp. 303–314). Waste Conference Ltd.,

Wilson, G.T., Smalley, G., Suckling, J.R., Lilley, D., Lee, J., Mawle, R. (2017). The hibernating mobile phone: Dead storage as a barrier to efficient electronic waste recovery. Waste Management, Special Thematic Issue: Urban Mining and Circular Economy 60, 521–533. https://doi.org/10.1016/j.wasman.2016.12.023

WRAP. (2013). Increase your small WEEE collection rates | WRAP UK [WWW Document]. URL http://www.wrap.org.uk/content/increase-your-small-weee-collection-rates (accessed 9.3.16).

Wright, M. (2015). How the circular economy is taking off in the US. The Guardian.

WTO. (2014). China — Measures Related to the Exportation of Rare Earths, Tungsten and Molybdenum (Dispute Settlement No. DS431). World Trade Organisation, Switzerland.

Zhang, K., Kleit, A.N. (2016). Mining rate optimization considering the stockpiling: A theoretical economics and real option model. Resources Policy 47, 87–94. https://doi.org/10.1016/j.resourpol.2016.01.005

Zhang, L., Qu, J., Sheng, H., Yang, J., Wu, H., Yuan, Z. (2019). Urban mining potentials of university: In-use and hibernating stocks of personal electronics and students' disposal behaviors. Resources, Conservation and Recycling 143, 210–217. https://doi.org/10.1016/j.resconrec.2019.01.007

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RECOVERY OF METALS FROM ELECTROACTIVE COMPONENTS OF SPENT Ni-MH BATTERIES AFTER LEACHING WITH FORMIC ACID

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ABSTRACT

This work describes a route for recovering nickel, cobalt, iron, zinc, and lanthanides from spent nickel-metal hydride batteries. Formic acid was used as leachant. Experiments were run at 25-50°C for 1-4 h. Under the best conditions leaching yields surpassed 99 wt.%, except for iron. The insoluble matter contains almost solely iron as iron(III) basic formate. The leachate went through six separation procedures, combining solvent extraction with D2EHPA as extractant, and precipitation reactions. Fe^{2+} and Zn^{2+} were extracted together (> 99 wt.%) from the original leachate (pH ~1.5). Yttrium and lanthanides were precipitated as oxalates directly from the raffinate (> 99.9 wt.%) upon addition of sodium oxalate. In the next steps, Mn^{2+} and Co^{2+} were extracted with D2EHPA at buffered pH (3 and ~4.8, respectively), after adding $NaOH_{aq}$. About 10 wt.% of leached Ni^{2+} was coextracted with Co^{2+}. The remaining Ni^{2+} was precipitated from the raffinate after addition of aqueous sodium oxalate at pH 6. After precipitation of Al^{3+} upon addition of $NaOH_{aq}$. until pH ~8, sodium formate was recovered after slow evaporation of the final aqueous solution at 60°C. It contains ~90 wt.% of the formate present in the leachant.

1. INTRODUCTION

Rechargeable nickel–metal hydride (Ni–MH) batteries are widely used as a power source for small devices such as mobile phones, digital cameras, toys (Fila et al., 2019) and are also found in hybrid electric vehicles (HEV) (Meshram et al., 2017; Korkmaz et al., 2018). Ni-MH batteries have replaced common AA and AAA sizes Zn-C (alkaline and Leclanché) batteries in Brazil (Fernandes et al., 2012, 2013) and nickel-cadmium (Ni–Cd) cells.

The cathode is a porous polymer impregnated with a "paste" containing active nickel compounds and Ni(II) hydroxide. The anode is also composed of a porous polymer impregnated with a mixture of metals including rare earth elements (REEs) and others such as Fe, Co, Ni, Cu, Zn, Al, capable of hydride formation. The active anode is hydrogen ions which during charging and discharging of the battery are absorbed and desorbed by the above mentioned metals. The electrodes are separated by a synthetic porous membrane which enables the contact of electrolyte (KOH solution) contained in electrode space with both electrodes (Fila et al., 2019). The electrode charging and discharging processes are described in the literature (Lucas et al., 2015).

Ni-MH batteries contain base and valuable metals such as REEs, nickel and cobalt in considerable amounts (Oliveira et al., 2017; Meshram et al., 2016). Consumption of REEs, a group of 17 elements including the lanthanides (La-Lu), Sc and Y, has increased significantly in recent years due to their application in high technology areas, including magnets (computers, wind turbines etc.), phosphor powders (fluorescent lamps/tubes), Ni–MH batteries, catalysts, special glasses and metal alloys. Resources of REEs are neither abundant nor evenly distributed across the world (Meshram et al., 2016). REEs have been declared as high supply risk materials by the European Commission (Korkmaz et al., 2018).

The cost and environmental problems associated with the disposal of wastes and scraps in landfills have emerged as the major concern for most nations (Musariri et al., 2019), and also means a waste of non-renewable resources (Gao et al., 2018; Shih et al., 2019; Fu et al., 2019). Recycling of such wastes and scraps may significantly reduce the dependence on primary resources of many elements. Spent Ni–MH batteries are one of such wastes which may be turned to a potential secondary resource (Meshram et al., 2019).

Several hydrometallurgical processes have been

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worked out on different scales to recover metals from spent Ni–MH batteries. Sulfuric and hydrochloric acids have been widely used as leachants (Fernandes et al., 2013; Santos et al., 2014; Turek, 2018; Korkmaz et al., 2018; Oliveira et al., 2017), in the concentration range from 1 to 12 mol L^{-1}, at a temperature range from 25 to 95°C, over a long period of time (> 80 min) (Turek, 2018). The addition of a reductant like hydrogen peroxide improves leaching of many metals as it converts sparingly soluble forms in higher oxidation states (e.g., Co^{3+}, Ni^{3+}, Mn^{4+}) to lower valence ions (e.g., Co^{2+}, Ni^{2+}, Mn^{2+}) which are leachable and stable in acidic solution (Vieceli et al., 2018; Santos et al., 2014).

Disposal of acidic leachates is one of the main problems leading to economic and energy losses (Wang et al., 2020; Chen et al., 2018). An opportunity to reduce the environmental impact of hydrometallurgical processes lies in the use of organic acids as leachants. They are biodegradable, delay corrosion of equipments, are safer to handle and emit less toxic gases than strong acids (Gao et al., 2018; Meshram et al., 2020). Studies involving organic acids (citric, oxalic, acetic) only focused the leaching step (Alonso et al., 2017; Colmenares et al., 2018). Separation and purification steps are required for recovery of metal ions from their leachates. It may be difficult to extract many elements due to the strong chelation of some metal ions with carboxylic anions (Fu et al., 2019).

Leached elements are usually separated one from each other by a combination of separation techniques. REEs may either be recovered by solvent extraction (Xie et al., 2014; Paulino et al, 2018) or precipitated as oxalates (Fernandes et al., 2013; Josso et al., 2018; Yang et al., 2014; Oliveira et al., 2017). The use of aqueous two-phase systems (ATPSs) and ion-exchange resins have been also tested for REE recovery (Valadares et al., 2018; Fila et al., 2019). Multiple stages are generally required to separate Co(II) from Ni(II), which have similar chemical properties (Gaines, 2018; Dhiman and Gupta, 2019).

Like oxalic acid, formic acid, the simplest aliphatic monocarboxylic acid, is a strong reductant, but does not precipitate metal ions as does oxalate (Lurie, 1978; Feigl, 1958). It is a versatile renewable reagent for green and sustainable chemical synthesis and processes. It is safer to handle than concentrated inorganic acids (Vieceli et al., 2018; Liu et al., 2015). It is a promising candidate as a leachant for spent batteries (Fu et al., 2019, Ibiapina et al., 2018, Silva et al., 2018), particularly Li-ion ones. Apparently, less attention has been paid to processing of spent Ni-MH batteries in the presence of organic acids. Therefore, the objective of the present investigation is to develop a hydrometallurgical process to recover base metals and REEs from the electroactive components of spent Ni–MH batteries in the presence of formic acid as leachant, while optimizing various parameters such as acid concentration, leaching time and temperature. The novelty elicited in this research is to determine the effectiveness of this acid as a leachant for spent Ni-MH batteries in the place of strong inorganic acids and the feasibility of leachate processing by current separation techniques.

2. MATERIALS AND METHODS

2.1 Samples

120 spent AA Ni-MH batteries (the most common rechargeable size in Brazil) were collected from the local market. To prevent short-circuiting and self-ignition during dismantling, samples were completely discharged first. After manual dismantling, the electroactive components (cathode, anode, electrolyte) were separated. This mass was dried at 105°C for 3 h before being ground using a ball mill and sieved through a 100 µm sieve. In previous work by this research group, elemental analysis was performed by X-ray fluorescence (Fernandes et al., 2013) using the same equipment and procedure described in Section 2.7. Data are presented in Table 1. Water is basically the volatile component lost during drying.

2.2 Reagents

Di-2-ethylhexylphosphoric acid (D2EHPA, 98 wt.%) was supplied by Sigma-Aldrich. n-Hexane (Sigma-Aldrich) was used as diluent. Formic acid (Sigma-Aldrich, 88 wt.%, ~20 mol L^{-1}), sulfuric acid (Merck, 98 wt.%, ~18 mol L^{-1}), sodium hydroxide (6 mol L^{-1}) and sodium oxalate (Merck) were of analytical grade. The solutions were prepared with distilled water.

2.3 Leaching

Baaed on leching studies involving electroative components of spent batteries (Meshram et al., 2019, 2020; Fernandes et al., 2013; Chen et al., 2018; Yang et al., 2014), the following variables were studied: temperature (25–50 °C), formic acid concentration (5–15 mol L^{-1}) and time (1-4 h). The sample mass to acidic leachant volume ratio was fixed at 100 g L^{-1}.

Experiments were performed in 150 mL glass beakers equipped with a magnetic stirrer. The leaching temperature

TABLE 1: Chemical analyses data of the electroactive components of spent Ni-MH batteries after drying at 105°C for 3 h (Fernandes et al., 2013).

Element	Amount (wt.%)	Relative standard deviation (%)
La	8.9 ± 0.3	3.4
Ce	2.3 ± 0.4	17.4
Pr-Sm	0.7 ± 0.1	14.3
Y	0.3 ± 0.1	33.3
Mn	1.3 ± 0.1	7.7
Fe	2.7 ± 0.1	3.7
Co	3.2 ± 0.6	18.8
Ni	27.2 ± 1.1	4.0
Zn	0.7 ± 0.1	14.3
Na	3.7 ± 0.6	16.2
K	10.4 ± 0.2	1.9
Ca	0.6 ± 0.2	28.6
Al	0.3 ± 0.1	33.3
Loss of volatiles	37.6 ± 1.4	3.7

was controlled by water bath. The aqueous formic acid was added to the beaker and heated to the required temperature at 200 rotations per minute. The instance when the solid was added to the acidic solution was considered as the start of the experiment.

At the end of the experiment the leachate was filtered (under vacuum) through a quantitative filter paper, yielding a green filtrate and a brown residue. This residue was washed with water (3 mL g^{-1} processed solid), dried at 110°C for 3 h and weighed. It was then placed in a ceramic crucible and calcined in a furnace (1000°C, 3 h). The roasted mass was cooled down in the furnace and weighed.

All experiments were performed to verify the reproducibility of them. It was found that the error percentage was on the order of ± 3%.

The separation procedure employed was based on precipitation and solvent extraction techniques conducted under increasing pH and evaporation of the final solution to recover the formate ion. Figure 1 presents the general scheme for elements separation from the leachates.

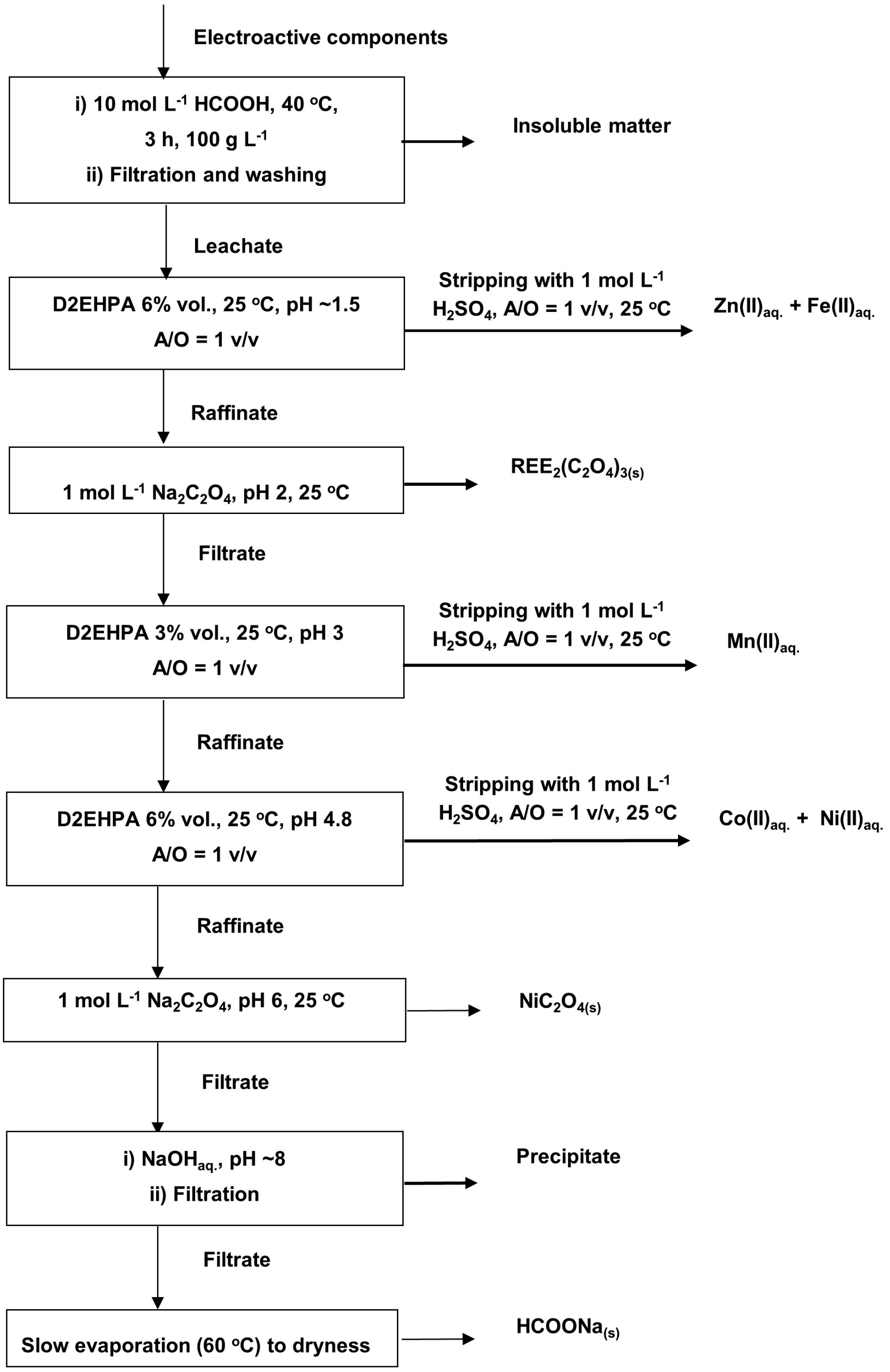

FIGURE 1: General scheme for elements separation from leachates from electroactive components of spent Ni-MH batteries after leaching with HCOOH.

2.4 Solvent extraction of Zn(II), Fe(II), Mn(II) and Co(II) and stripping procedures

Precipitation using hydroxide, sulphide and carbonate does not perform well in a system containing Co(II) and Mn(II) due to their similar chemical properties (Barik et al., 2017). D2EHPA, a cation exchanger, is frequently used as extractant in both research and industrial applications (Virolainen et al., 2011). Extraction experiments were performed in glass separatory funnels at 25°C. Extractant concentration varied from 1 to 10 vol.%. The aqueous/organic (A/O) phase ratio was fixed at 1 vol./vol. pH of the leachate was adjusted by adding the appropriate amount of 6 mol L^{-1} NaOH. The system was shaken for 5 min. Phase separation was achieved in ~10 min. The experiments were carried out in triplicate and the experimental error including the analytical error was 4% at a confidence level of 95%. The amount of element extracted was calculated by the difference between the concentration in the raffinate and the concentration in the original leachate.

Stripping was carried out at 25°C using aqueous sulfuric acid in glass separatory funnels. Its concentration varied from 0.05 to 5.0 mol L^{-1}. The aqueous/organic (A/O) phase ratio was fixed at 1 vol/vol. The system was shaken for 10 min. Phase separation was achieved in ~5 min. The experiments were carried out in triplicate and the experimental error including the analytical error was 3% at a confidence level of 95%.

2.5 Precipitation of REEs and Ni(II)

Given the high amounts of REEs in the material under study, the method chosen to recover them was the precipitation of their oxalates (Josso et al., 2018; Chiu et al., 2019) at low pH (< 2).

The experiments were accomplished in glass beakers. After solvent extraction of Zn(II) and Fe(II), the raffinate was stirred (200 rotations per minute) at 25°C. 6 mol L^{-1} NaOH was added dropwise (about 1 mL min^{-1}) in order to adjust pH at ~2. 1 mol L^{-1} $Na_2C_2O_4$ was added dropwise until ceased precipitation of a white solid ($X_2(C_2O_4)_3$, X = Y, La, Ce, Pr, Nd, Sm). It was filtered through a quantitative paper, washed with 0.01 mol L^{-1} $Na_2C_2O_4$ and water, dried at 110°C for 3 h and weighed.

After solvent extraction of Co(II), pH of the raffinate was adjusted at ~6 by adding 6 mol L^{-1} NaOH. 1 mol L^{-1} $Na_2C_2O_4$ was added dropwise at 25ºC and 200 rpm. A green precipitate (NiC_2O_4) was formed. It was filtered through a quantitative paper and washed with 0.01 mol L^{-1} $Na_2C_2O_4$ and water. The filtrate was colorless.

2.6 Crystallization of sodium formate

pH of the raffinate was adjusted to ~8 by adding 6 mol L^{-1} NaOH at 25°C and 200 rpm. A gelatinous precipitate was formed at pH ~6 (Hayrapetyan et al., 2006) and separated by filtration under vacuum.

The filtrate was slowly evaporated at 60°C (without stirring) in a glass vessel. A white crystalline solid was obtained. It was dried at 110°C for 2 h, ground with an agate mortar and pestle, weighed and kept in a tightly closed container.

2.7 Analytical methods

Metal ion concentrations in the aqueous solutions were determined by atomic absorption spectrometry (AAS) on a Varian/Agilent SpectrAA 50b spectrometer. pH measurements were performed using a combination of a glass electrode and an Ag/AgCl reference electrode (Orion 2AI^{3-}JG). The solids obtained during processing of the leachates were weighed in an analytical balance (Scientech SA 120) and analyzed by X-ray fluorescence (Shimadzu XRF 800 HS). Crystalline phases in the solid samples were identified by X-ray diffraction (Shimadzu XRD 6000) by continuous scanning method at 20 mA and 40 kV, using Cu Kα (1.5418 Å) as the radiation source. Data were collected in the two-theta range of 10°-70° (5° min^{-1}).

Classical qualitative tests for Fe(III), Fe(II), Mn(II), Co(II), Zn(II) and Ni(II) were also applied to monitor the presence of such species in the leachates or solids (Vogel, 1981; Feigl, 1958; Lurie, 1978). Detection limits are in the order of 0.1 -1.0 mg L^{-1}.

3. RESULTS AND DISCUSSION

3.1 Leaching

3.1.1 Effects of temperature and time

The effects of reaction temperature and time on leaching were investigated using 10 mol L^{-1} formic acid. The results are shown in Figure 2 and 3 for nickel, lanthanium and iron, the most abundant metals in the electroactive components (Table 1). An increase in the temperature greatly improved leaching of nickel and lanthanium, attaining ~100 wt.% at 40°C after 3 h. A similar effect was observed in some studies involving leaching of Zn-C and Li-ion batteries in the presence of organic acids (Ibiapina et al., 2018; Silva et al., 2018; Musariri et al., 2019). The other REEs behaved as lanthanium. Iron leaching was much less relevant, not surpassing 20 wt.%. Formic acid served the dual role of leachant and reductant for nickel, thus making addition of a reductant like hydrogen peroxide unnecessary.

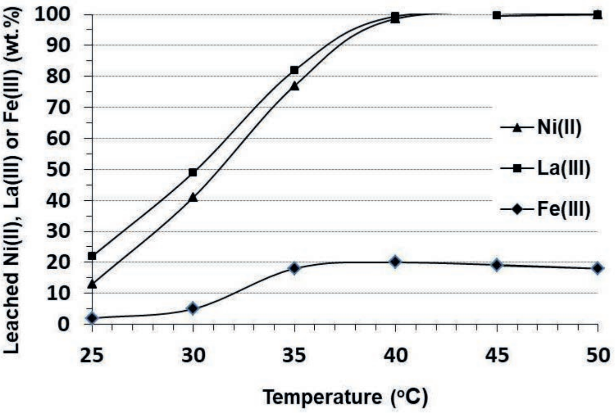

FIGURE 2: Effect of temperature on leaching (10 mol L^{-1} HCOOH, 3 h, S/L = 100 g L^{-1}).

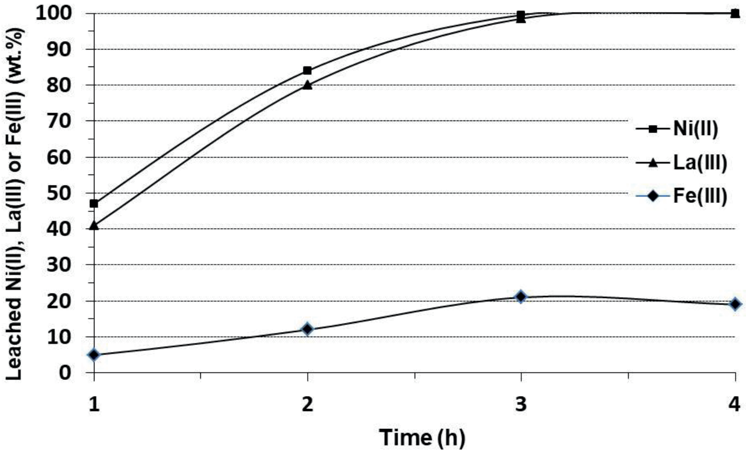

FIGURE 3: Effect of time on leaching (10 mol L-1 HCOOH, 40 °C, S/L = 100 g L-1).

3.1.2 Effect of acid concentration

Figure 4 shows the effect of formic acid concentration on metals leaching under the following conditions: S/L ratio, 100 g L^{-1}; leaching time, 3 h; temperature, 40°C. When the acid concentration increased from 5 to 10 mol L^{-1}, leaching increased from below 40% to almost 100 wt.%. Thereafter, acid concentrations did not significantly affect the leaching performance. Once again, iron leaching was low in all experiments.

The optimum experimental conditions found for formic acid in the present study are comparable to those normally reported for inorganic acids (Turek, 2018) and for leaching of Li-ion batteries in the presence of organic acids (Fu et al., 2019), except the S/L ratio. In general, literature reports a S/L ratio in the range 2-50 g L^{-1} (Alonso et al., 2017; Colmenares et al., 2018; Fu et al., 2019; Fernandes et al., 2013; Santos et al., 2014; Korkmaz et al., 2018; Oliveira et al., 2017), but the concentration of the organic acid is much lower (< 5 mol L^{-1}) than in the present study.

3.2 Leachates composition

Table 2 presents the average concentration of elements after leaching under the best experimental conditions (10 mol L^{-1} HCOOH, 40°C, 3 h). Based on the chemical analysis presented in Table 1, more than 99 wt.% of all metals present in the electroactive materials were leached under mild conditions with respect to temperature, except iron, where only ~20 wt.% were leached.

3.3 Analysis of the insoluble matter

Under the best conditions (10 mol L^{-1} HCOOH, 40°C, 3 h) the brown insoluble matter after leaching corresponds only to 2.2 wt.% of the initial mass. XRF data (Table 3) show that iron is by far the most abundant element, together with minute quantities of nickel and lanthanium. This result agrees with the low iron leaching by formic acid (Table 2). The diffractogram of the insoluble matter is presented in Figure 5. No crystalline phases were identified.

Based on the amount of insoluble matter recovered (2.2 g 100 g^{-1} electroactive materials), the amounts of iron

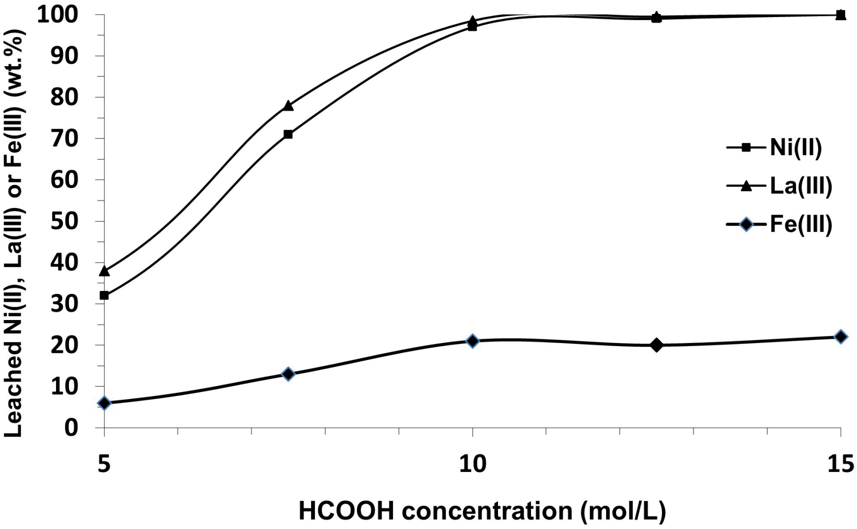

FIGURE 4: Effect of formic acid concentration on leaching (40 °C, 3 h, S/L = 100 g L-1).

TABLE 2: Element concentrations in the leachates.

Element	Concentration (g L^{-1})	Relative standard deviation (RSD, %)
Ni	27.7 ± 0.5	1.8
La	8.9 ± 0.4	4.5
Co	3.1 ± 0.3	9.7
Ce	2.3 ± 0.2	8.7
Mn	1.3 ± 0.1	7.7
Pr-Sm	0.7 ± 0.1	14.3
Zn	0.7 ± 0.1	14.3
Ca	0.5 ± 0.1	20.0
Fe	0.5 ± 0.1	20.0
Al	0.3 ± 0.0	0.0
Y	0.2 ± 0.0	0.0
Ca	0.6 ± 0.2	28.6
Al	0.3 ± 0.1	33.3
Loss of volatiles	37.6 ± 1.4	3.7

in both solids (Tables 1 and 3) and the leached iron (Table 2), one may conclude that 80 wt.% of iron is present in the insoluble matter. This solid was easily dissolved in 1 mol L^{-1} H_2SO_4 at 25°C. Only Fe(III) was found in the brown-orange solution formed (Vogel, 1981; Feigl, 1958), the test with thiocyanate in HCl medium was positive.

The ash recovered after calcination of the insoluble matter corresponds to 43 wt.% of the initial mass. It is very likely that the brown solid is iron(III) basic formate (Vogel, 1981):

$$6\ HCOO^- + 3\ Fe^{3+} \rightleftharpoons [Fe_3(HCOO)_6]^{3+} \qquad (1)$$

$$[Fe_3(HCOO)_6]^{3+} + 9H_2O \rightleftharpoons 3Fe(OH)_2HCOO\downarrow + 3\ HCOOH + + 3\ H_3O^+ \qquad (2)$$

Fe content in this solid is 41 wt.%, close to the experimental value found.

Soluble iron corresponds to Fe(II), since only the test with αα-dipyridyl was positive (Feigl, 1958; Vogel, 1981). This means that formic acid partially reduced Fe(III) (BRATSCH, 1989):

$$2Fe^{3+} + HCOO^- + OH^- \rightleftharpoons H_2O + CO_2 + 2Fe^{2+}$$
$$\Delta E^{o} = + 0{,}885\ V \qquad (3)$$

3.4 Solvent extraction of Zn(II), Fe(II), Mn(II) and Co(II)

Zn(II) and Fe(II) were directly extracted from the original leachate (pH ~1.5) using 6 vol.% D2EHPA with high yields (> 99.5 wt.%) in one stage (Figures 6 and 7a). These elements were not detected in the raffinate (Table 4). The tests with dithizone (Zn(II)) and αα-dipyridyl (Fe(II)) were negative in the raffinate (Vogel, 1981; Feigl, 1958). The organic phase is pale olive-green (Fe(II)) whereas the raffinate was green (Ni(II)). These results agree with data of Balesini et al. (2011). Stripping of both ions from the loaded organic phase in a single stage was feasible using 1 mol L^{-1} H_2SO_4 (Figure 8a).

Mn(II) was extracted from pH 2 and was removed from the aqueous phase at pH 3.5 (Figure 6) using 3 vol.% D2EHPA in one stage. The raffinate contains less than 0.5 wt.% of the element (Table 4). Stripping of Mn(II) from the loaded organic phase in a single stage was feasible using 1 mol L^{-1} H_2SO_4 (Ibiapina et al., 2018). Since the aqueous phase is colorless, the presence of Mn(II) was monitored using $NaBiO_3$ + 16 mol L^{-1} HNO_3 (Vogel, 1981; Feigl, 1958).

TABLE 3: Chemical analyses data of the insoluble matter after leaching with 10 mol L^{-1} HCOOH (40°C, 3 h).

Element	Amount (wt.%)
Fe	99.83
Ni	0.15
La	0.02

Co(II) began to be extracted at pH around 3.8 and was fully extracted at pH ~4.8 (Figure 6). The organic phase was blue due to Co(II). The raffinate was green due to Ni(II). The minimum D2EHPA concentration to ensure Co(II) extraction (> 99.5 wt.%) from the leachate at pH 4.8 in one stage was 6 vol.% (Figure 7b). Under these circumstances, the raffinate contains less than 0.5 wt.% of the element (Table 4). Stripping of Co(II) from the loaded organic phase in a single stage was accomplished using 1 mol L^{-1} H_2SO_4 (Figure 8b). About 10 wt.% of leached Ni(II) passed to the organic phase. Its concentration in the raffinate (Table 4) is ~10 wt.% lower than in the leachate (Table 2).

The amount of Ni(II) is 8 times higher than Co(II) (Tables 1 and 2). The traditional solvent extraction method

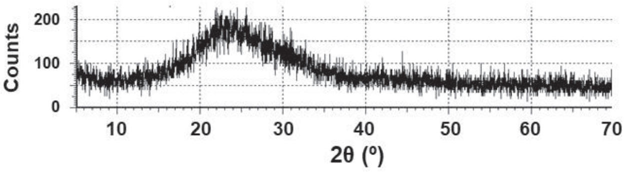

FIGURE 5: XDR patterns of the insoluble matter after leaching with 10 mol L^{-1} HCOOH (40°C, 3 h).

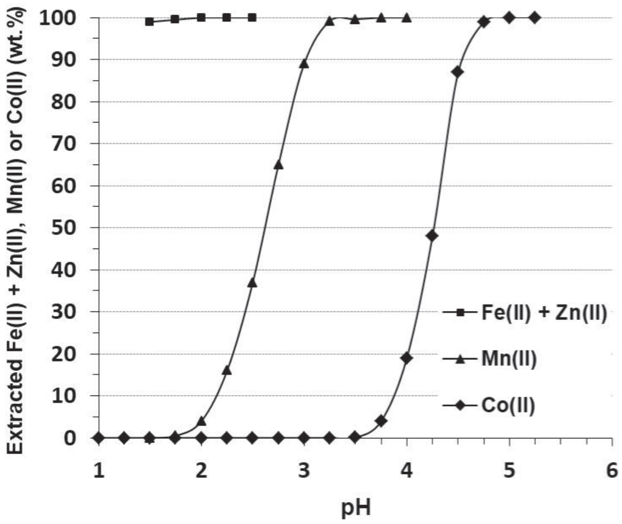

FIGURE 6: Extraction of Zn(II) + Fe(II), Mn(II) and Co(II) with D2EHPA diluted in kerosene as a function of pH of the leachate. A/O = 1 vol./vol., 25°C, [D2EHPA] = 6 vol%. Leachant: 10 mol L^{-1} HCOOH.

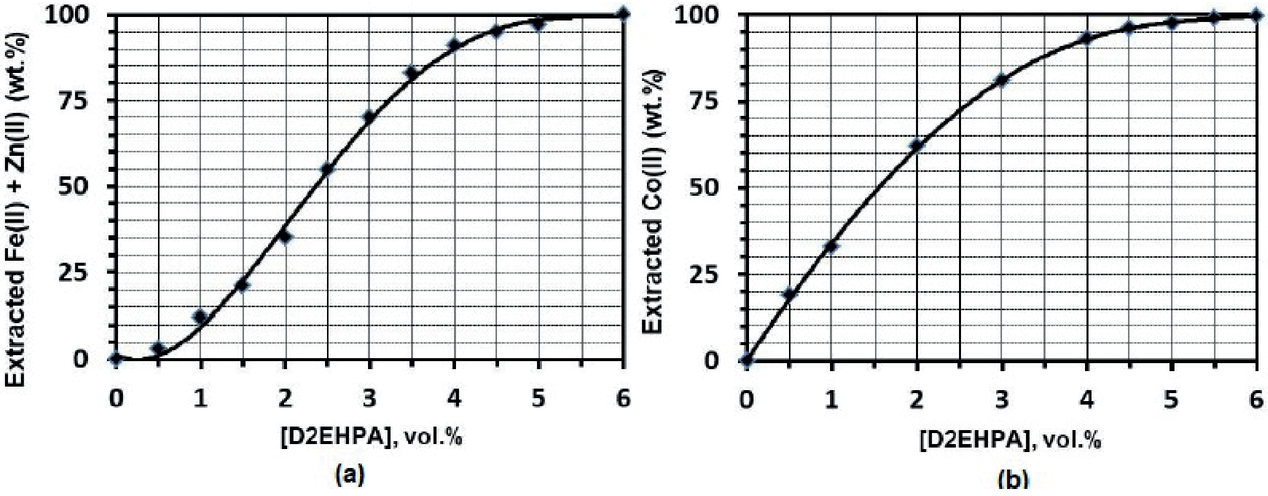

FIGURE 7: Influence of D2EHPA concentration on some elements extraction. A/O = 1 vol./vol., 25°C, pH = 1.5 (Zn(II) + Fe(II)) or 4.5 (Co(II)). Leachant: 10 mol L^{-1} HCOOH.

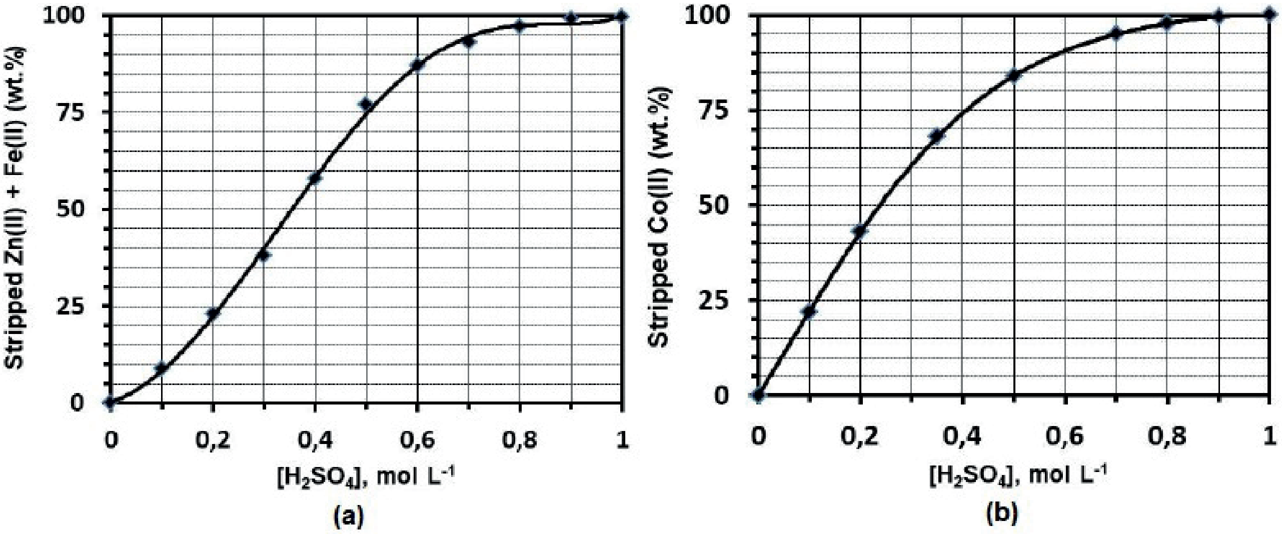

FIGURE 8: Influence of H_2SO_4 concentration on stripping of Zn(II) + Fe(II) and Co(II) from loaded organic phase (A/O = 1 vol./vol., 25°C).

for separating Ni and Co from a leach liquor rich in nickel is prone to cause nickel loss (van der Voorde et al., 2019; Yang et al., 2020). Extraction of Co(II) is more selective at pH below 4, but requires more stages, thus increasing consumption of the extractant and diluent (van der Voorde et al., 2019). Processing of Ni-rich spent materials is feasible by changing the extractant, for example, Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) (Janiszewska et al., 2019). It is very selective for cobalt over nickel in sulfate and chloride media (Ayanda et al., 2013).

pH was not practically changed after Mn(II) and Co(II) extractions. Formic acid is a weak acid and its ionization process in aqueous phase can be expressed as follows (Lurie, 1978):

$$HCOOH + H_2O \rightleftharpoons H_3O+ + HCOO^{-}\ pKa = 3.77 \tag{4}$$

Thus, the leachate was buffered during solvent extraction of Mn(II) and Co(II) by a formic acid/formate buffer (2.77 < pH < 4.77).

The extraction order Zn(II) + Fe(II) – Mn(II) – Co(II) under increasing pH found in this work is the same reported in the literature in sulfate (Ritcey and Ashbrook, 1984) and fluoride media (Silva et al., 2018). This result is in line with the weak ligand character of the formate anion (Lurie, 1978).

Stripping produces a dilute aqueous acidic solution (H_2SO_4) of a metal ion sulfate ($ZnSO_4$, $FeSO_4$, $MnSO_4$, $CoSO_4$ and $NiSO_4$) because the metal ion concentrations in the leachate are relatively low (Table 2) and the A/O phase ratio was fixed at 1 v/v. The concentrations in these acidic solutions are very close to the original leachate (Table 2) as both solvent extraction and stripping were prformed with high yields (> 99.5 wt.%). Zn(II) can be easily separated from Fe(II) by adding $NaOH_{aq}$. (pH ~11): $Fe(OH)_2$ precipitates in the presence of soluble $[Zn(OH)_4]^{2-}$. Zn(II) can be recovered as $Zn(OH)_2$ after neutralizing the alkaline solution with H_2SO_{4aq}. (Fernandes et al., 2012). Mn(II) can be precipitated as MnO_2 (or $MnO(OH)_2$) after adding $NaOH_{aq}$.

TABLE 4: Element concentrations in the raffinates after solvent extraction and in the aqueous acidic solutions after stripping the loaded organic phase with 1 mol L^{-1} H_2SO_4

Element	Solvent extraction procedure*	Concentration (g L^{-1})	
		Raffinate	Acidic solution
Fe	D2EHPA 6% vol., pH ~1.5	n.d	4.9×10^{-1}
Zn	D2EHPA 6% vol., pH ~1.5	n.d	7.2×10^{-1}
Mn	D2EHPA 3% vol., pH ~3	6.0×10^{-2}	1.3
Co	D2EHPA 6% vol., pH ~4.8	1.5×10^{-2}	3.0
Ni	D2EHPA 6% vol., pH ~4.8	2.5×10^{1}	2.6

** 25°C, A/O = 1 v/v; n.d. – not detected*

(pH ~11) + H_2O_2 (Ibiapina et al., 2018). Co(II) and Ni(II) can also be recovered as hydroxides ($Co(OH)_2$ and $Ni(OH)_2$) upon addition of $NaOH_{aq}$. (pH ~10) (Silva et al., 2018). In all cases an aqueous sodium sulfate is the final product, which can be recovered by slow evaporation of the final solution (Paulino et al., 2018).

3.5 Precipitation of REEs

According to data in Table 5, only small amounts of nickel (~0.1 wt.%) were found. Ni(II) oxalate precipitates at higher pH, usually above 3 (Lurie, 1978; Vogel, 1981; Feigl, 1958).

Based on data in Table 2, 23.4 g of REE oxalates ($REE_2(C2O_4)_3$) can be recovered from 1 L of lecahate. The experimental value found was 23.3 g L^{-1}. This means that over 99.5 wt.% of lanthanides and yttrium were recovered in this solid. Threfore, precipitation of REE oxalates was a very selective and effective technique under our experimental conditions, as the oxalates were recovered with high yield and purity.

TABLE 5: Chemical analyses data of the oxalates ($REE_2(C_2O_4)_3$ and NiC_2O_4) recovered after processing the leachates (Figure 1) (10 mol L^{-1} HCOOH, 40 °C, 3 h)

Element	Amount (wt.%)	
	$REE_2(C_2O_4)_3$	NiC_2O_4
Ni	0.1	98.0
La	73.4	n.d.
Ce	19.2	n.d.
Pr-Sm	5.6	n.d.
Y	1.7	n.d
Ca	n.d.	2.0

n.d. – not detected

An advantage of oxalate salts is their easy conversion to other REE compounds as they are easily thermally decomposed (Yang et al., 2014) and oxidized (Josso et al., 2018).

3.6 Precipitation of Ni(II)

XRF analysis (Table 5) of the green solid found calcium (1.9 wt.%). Based on data in Table 2, 69.2 g of nickel oxalate can be recovered from 1 L of lecahate. 63.9 g were recovered, 62.6 g of which correspond to NiC_2O_4 (~90.5 wt.% of the theoretical value). This difference is due to partial solvent extraction of Ni(II) by D2EHPA at pH 4.8 (Section 3.4). 1.3 g of CaC_2O_4 contains ~80 wt.% of leached calcium.

3.7 Crystallization of sodium formate

The solid precipitated at pH ~8 (~0.1 g L^{-1} processed leachate) contains aluminum and the remaining calcium. According to XRF data (Table 6), the solid also contains minute amounts of nickel (~0.1 wt.%). This step is essential to recover sodium formate with high purity.

The diffractogram (Figure 9) of the white crystalline solid obtained after evaporation of the final aqueous solution corresponds to anhydrous HCOONa. The peaks agree with the standard pattern of monoclinic HCOONa (ICDD PDF Card No. 00-014-0812).

XRF data (Table 6) did not show significant amounts of other metals. However, addition of sodium oxalate to precipitate NiC_2O_4 must be carefully controlled in order to avoid an undesirable excess of oxalate ions, otherwise sodium formate would be contaminated with sodium oxalate.

Sodium formate is a very versatile reactant in laboratory syntheses, in pharmaceutical, textile, paper and leather industries for buffering and regulating of pH (Hietala et al., 2016). This salt is used to produce formic acid. It is a raw material for manufacturing sodium dithionite. Oxalic acid production employs sodium formate as an intermediate. Sodium formate is used in chrome tanning and as a mordant in the dyeing and printing of fabrics by the textile industry. The reducing power of sodium formate is utilized in electroplating baths and photographic fixing baths. (Reutmann and Kieczka, 2012). It is also a food additive (E237) and a deicing agent (Kulyakthin and Paste, 2021).

3.8 Mass balance for formate ion

Based on the composition of the leachant (10 mol L^{-1} HCOOH), and the mass of the recovered salt, sodium for-

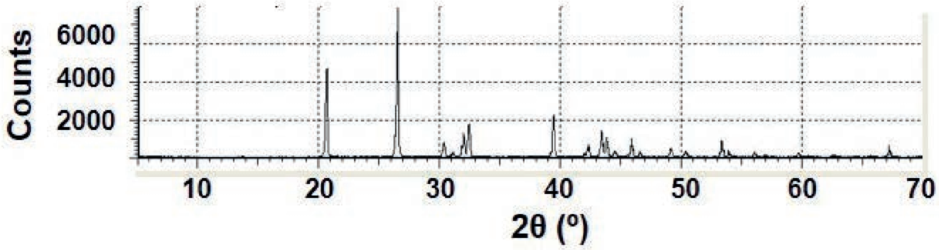

FIGURE 9: XRD patterns of the solid recovered after evaporation of the final solution. The peaks represent HCOONa.

TABLE 6: Chemical analyses data of the solid precipitated at pH ~8 and of sodium formate after evaporation of the final aqueous solution.

Element	Amount (wt.%)	
	Solid	HCOONa
Ni	0.1	n.d.
Ca	25.0	n.d.
Al	74.6	n.d.
Na	0.3	100
REEs	n.d.	n.d.

n.d. – not detected

TABLE 7: Mass balance for formate ion (base: 1 L leachate).

Product/ Leachant	Mass (g)	Mass of HCOO- (g)	Relative amount (wt.%)
10 mol L^{-1} HCOOH	-	450.0	100
HCOONa	603.7	399.5	89
Losses	-	50.5	11

mate contains around 90 wt.% of the total formate (Table 7). Two potential sources of loss of formate ions were identified: (i) during leaching, when it acts a reductant; (ii) as iron(III) basic formate. The huge amount of the salt recovered is due to the concentration of formic acid in the leachant (10 mol L^{-1}).

On an average basis, the price of sodium formate (99 wt.%) is about 1.5 times the cost of formic acid (95-98 wt.%) (Hietala et al., 2016; Reutmann & Kieczka, 2012).

4. CONCLUSIONS

Under the best experimental conditions (10 mol L^{-1} HCOOH, 40°C, 3 h), nickel, manganese, cobalt, zinc and REEs were leached from the electroactive components of spent Ni-MH batteries with very high yields as found for common inorganic acids. The insoluble matter contains ~80 wt.% of the iron present in the original mass as Fe(III) basic formate. The remaining iron was in the leachate as Fe(II).

Recovery of leached elements by solvent extraction using D2EHPA and precipitation of REE and Ni(II) oxalates at suitable pH was possible. The original leachate allowed direct extraction of Zn(II) + Fe(II) and REE oxalates were direcly recovered from the raffinate. However, the recovery of Co(II) in the presence of large amounts of Ni(II) by solvent extraction requires further studies. About 90 wt.% of formate present in the leachant was recovered as sodium formate after evaporation of the final solution.

Formic acid has proven a promising leachant for spent Ni-MH batteries: i) it played the dual role of leachant and reductant for nickel, thus avoiding addition of a reductant like hydrogen peroxide; ii) the elements were leached with very high yields (except iron); iii) its leahates were easily processed; iv) a high-value added byproduct was recovered (sodium formate), thus reducing generation of final wastes.

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REFERENCES

Almeida, J. R., Moura, M. N., Barrada, R. V., Barbieri, E. M. S., Carneiro, M. T. W. D., Ferreira, S. A. D., Lelis, M. F. F., Freitas, M. B. J. G. & Brandão, G. P., 2019. Composition analysis of the cathode active material of spent Li-ion batteries leached in citric acid solution: A study to monitor and assist recycling processes. Sci. Total Environ., 685, 589–595. https://doi.org/10.1016/j.scitotenv.2019.05.243

Alonso, A.R., Pérez, E.A., Lapidus, G.T. & Luna-Sánchez, R.M., 2017. Hydrometallurgical process for rare earth elements recovery from spent Ni-MH batteries. Can. Metall. Q., 54, 310–317. https://doi.org/10.1179/1879139515Y.0000000013

Ayanda, O. S., Adekola, F. A., Baba, A. A., Ximba, B. J. & Fatoki, O. S., 2013. Application of Cyanex® extractant in Cobalt/Nickel separation process by solvent extraction. Int. J. Phys. Sci., 8, 89-97. https://doi.org/10.5897/ijps12.135

Balesini, A. A., Razavizadeh, H. & Zakeri, A., 2011. Solvent Extraction of Zinc from Acidic Solution Obtained from Cold Purification Filter Cake of Angouran Mine Concentrate Using D2EHPA. Iran. J. Chem. Chem. Eng., 8, 43-47. http://www.ijche.com/article_10282_813d0dccf4d682c66c2d73e654476a86.pdf

Barik, S. P., Prabaharan, G. & Kumar, L., 2017. Leaching and separation of Co and Mn from electrode materials of spent lithium-ion batteries using hydrochloric acid: Laboratory and pilot scale study. J. Cleaner Prod., 147, 37-43. https://doi.org/10.1016/j.jclepro.2017.01.095

Bratsch, S. G., 1989. Standard Electrode Potentials and Temperature Coefficients in Water at 298.5 K. J. Phys. Chem. Ref. Data, 18, n. 01. https://doi.org/10.1063/1.555839

Chen, X., Guo, C., Ma, H., Li, J., Zhou, T., Cao, L. & Kang, D., 2018. Organic reductants based leaching: A sustainable process for the recovery of valuable metals from spent lithium ion batteries. Waste Manage., 75, 459–468. https://doi.org/10.1016/j.wasman.2018.01.021

Chiu, K. L., Shen, Y. H., Chen, Y. H. & Shih, K. Y., 2019. Recovery of Valuable Metals from Spent Lithium Ion Batteries (LIBs) Using Physical Pretreatment and a Hydrometallurgy Process. Adv. Mater., 8, 12-20. https://doi.org/10.11648/j.am.20190801.12

Colmenares, A. Z., Salaverría, J. D. & Delvasto, P., 2018. Characterization of the chemical compounds obtained after using acetic acid as leaching agent in the hydrometallurgical treatment of spent Ni-MH batteries. Revista Producción + Limpia, 13, 19-29. http://dx.doi.org/10.22507/pml.v13n1a2

Dhiman, S. & Gupta, B., 2019. Partition studies on cobalt and recycling of valuable metals from waste Li-ion batteries via solvent extraction and chemical precipitation. J. Cleaner Prod., 225, 820-832. https://doi.org/10.1016/j.jclepro.2019.04.004

Feigl, F., 1958. Spot Tests in Inorganic Analysis. Amsterdam: Elsevier.

Fernandes, A., Afonso, J. C. & Dutra, A. J. B., 2013. Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation. Hydrometallurgy, 133, 37-43. http://dx.doi.org/10.1016/j.hydromet.2012.11.017

Fernandes, A., Afonso, J. C. & Dutra, A. J. B., 2012. Hydrometallurgical route to recover nickel, cobalt and cadmium from spent Ni-Cd batteries. J. Power Sources 220, 286-291. https://doi.org/10.1016/j.jpowsour.2012.08.011

Fila, D., Hubicki, Z. & Kołodyńska, D., 2019. Recovery of metals from waste nickel-metal hydride batteries using multifunctional Diphonix resin. Adsorption, 25, 367–382. https://doi.org/10.1007/s10450-019-00013-9

Fu, Y., He, Y., Chen, H., Ye, C., Lu, Q., Li, Xie, W. & Wang, J., 2019. Effective leaching and extraction of valuable metals from electrode material of spent lithium-ion batteries using mixed organic acids leachant. J. Ind. Eng. Chem., 79, 154–162. https://doi.org/10.1016/j.jiec.2019.06.023

Gaines, L., 2018. Lithium-ion battery recycling processes: Research towards a sustainable course. Sust. Mater. Technol., 17, e00068. https://doi.org/10.1016/j.susmat.2018.e00068

Gao, W., Liu, C., Cao, H., Zheng, X., Lin, X., Wang, H., Zhang, Y. & Sun, Z., 2018. Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries. Waste Manage., 75, 477–485. https://doi.org/10.1016/j.wasman.2018.02.023

Hayrapetyan, S. S.; Mangasaryan, L. G. Tovmasyan, M. R. & Khachatryan, H. G., 2006. Precipitation of aluminum hydroxide from sodium aluminate, by treatment with formalin, and preparation of aluminum oxide. Acta Chromatographica 16, 192-203. http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.baztech-article-BAT3-0037-0020

Hietala, J., Vuori, A., Johnsson, P., Pollari, I., Reutemann, W. & Kieczka, H., 2016. Formic acid. In Ullmann's Encyclopaedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, https://doi.org/10.1002/14356007.a12_013.pub3

Ibiapina, V. F., Florentino, U. S., Afonso, J. C., Gante, V., Vianna, C. A. & Mantovano, J. L., 2018. Processing of spent zinc-MnO_2 dry cells in various acidic media. Quim. Nova 41, 176-183. https://doi.org/10.21577/0100-4042.20170162

Janiszewska, M., Markiewicz, A. & Regel-Ros, M., 2019. Hydrometallurgical separation of Co(II) from Ni(II) from model and real waste solutions. J. Cleaner Prod., 228, 746-754. https://doi.org/10.1016/j.jclepro.2019.04.285

Josso, P., Roberts, S., Teagle, D. A. H., Pourret, O., Herrington, R. & Albarran, C. P. L., 2018. Extraction and separation of rare earth elements from hydrothermal metalliferous sediments. Miner. Eng., 118, 106-121. https://doi.org/10.1016/j.mineng.2017.12.014

Korkmaz, K., Alemrajabi, M., Rasmuson, Å. C. & Forsberg, K. M., 2018. Sustainable hydrometallurgical recovery of valuable elements from spent nickel–metal hydride HEV batteries. Metals, 8, 1062. https://doi.org/10.3390/met8121062

Kulyakthin, S. & Pastye, A. K., 2021. Can calorimetry be used to measure the melting rate of deicers? Cold Reg. Sci. Technol., 181, article 103170. https://doi.org/10.1016/j.coldregions.2020.103170

Liu, X., Li, S., Liu, Y. & Cao, Y., 2015. Formic acid: A versatile renewable reagent for green and sustainable chemical synthesis. Chinese J. Catal., 36, 1461–1475. https://doi.org/10.1016/S1872-2067(15)60861-0

Lucas, J., Lucas, P., Le Mercier, T., Rollat, A. & Davenport, W., 2015. Rare earths in rechargeable batteries. Rare Earths, 167-180 (Chapter 10). https://doi.org/10.1016/B978-0-444-62735-3.00010-3

Lurie, J., 1978. Handbook of Analytical Chemistry, 3rd ed. Mir, Moscow.

Meshram, P., Pandey, B. D. & Mankhand, T. R., 2016. Process optimization and kinetics for leaching of rare earth metals from the spent Ni–metal hydride batteries. Waste Manage., 51, 196-203. https://doi.org/10.1016/j.wasman.2015.12.018

Meshram, P., Somani, H., Pandey, B. D., Mankhand, T. R., Deveci, H. & Abhilash, 2017. Two stage leaching process for selective metal extraction from spent nickel metal hydride batteries. J. Cleaner Prod., 157, 322-332. https://doi.org/10.1016/j.jclepro.2017.04.144

Meshram, P., Pandey, B. D. & Abhilash, 2019. Perspective of availability and sustainable recycling prospects of metals in rechargeable batteries – A resource overview. Resour. Policy, 60, 9-22. https://doi.org/10.1016/j.resourpol.2018.11.015

Meshram, P., Mishra, & Sahu, R., 2020. Environmental impact of spent lithium ion batteries and green recycling perspectives by organic acids: a review. Chemosphere, 242, 125291. https://doi.org/10.1016/j.chemosphere.2019.125291

Musariri, B., Akdogan, G., Dorfling, C. & Bradshaw, S., 2019. Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries. Miner. Eng., 137, 108-117. https://doi.org/10.1016/j.mineng.2019.03.027

Oliveira, U. C. M., Rodrigues, G. D., Mageste, A. B. & Lemos, L. R., 2017. Green selective recovery of lanthanum from Ni-MH battery leachate using aqueous two-phase systems. Chem. Eng. J., 322, 346–352. https://doi.org/10.1016/j.cej.2017.04.044

Paulino, J. F., Neumann, R., Afonso, J. C., 2018. Production of sodium and aluminum chemicals and recovery of rare earth elements after leaching cryolite from Pitinga mine (Amazonas - Brazil) with sulfuric acid. Hydrometallurgy, 180, 254-261. https://doi.org/10.1016/j.hydromet.2018.08.004

Reutmann, W., Kieczka, H., 2012. Formic Acid. Ullmann's Encyclopedia of Industrial Chemistry. Weinhein: Wiley-VCH Verlag, vol. 16, p. 13-33. https://onlinelibrary.wiley.com/doi/epdf/10.1002/14356007.a12_013.pub2

Ritcey, G. M. & Ashbrook, A. W., 1984. Principles and Applications to Process Metallurgy (Part I). New York, Elsevier Science Publishers.

Shih, Y. J., Chien, S. K., Jhang, S. R. & Lin, Y. C., 2019. Chemical leaching, precipitation and solvent extraction for sequential separation of valuable metals in cathode material of spent lithium ion batteries. J. Taiwan Inst. Chem. E., 100, 151–159. https://doi.org/10.1016/j.jtice.2019.04.017

Santos, V. E. O., Celante, V. G., Lelisa, M. F. F. & Freitas, M. B. J. G., 2014. Método hidrometalúrgico para reciclagem de metais terras raras, cobalto, níquel, ferro e manganês de eletrodos negativos de baterias exauridas de Ni-MH de telefone celular. Quim. Nova, 37, 22-26. http://dx.doi.org/10.1590/S0100-40422014000100005

Silva, R. G., Afonso, J. C. & Mahler, C. F., 2018. Acidic leaching of Li-ion batteries. Quim. Nova, 41, 581-586. http://dx.doi.org/10.21577/0100-4042.20170207

Turek, A. S., 2018. Hydrometallurgical recovery of metals: Ce, La, Co, Fe, Mn, Ni and Zn from the stream of used Ni-MH cells. Waste Manage., 77, 213-219. https://doi.org/10.1016/j.wasman.2018.03.046

Valadares, A., Valadares, C. F., Lemos, L. R., Mageste, A. B. & Rodrigues, G. D., 2018. Separation of cobalt and nickel in leach solutions of spent nickel-metal hydride batteries using aqueous two-phase systems (ATPS). Hydrometallurgy, 181, 180-188. https://doi.org/10.1016/j.hydromet.2018.09.006

van der Voorde, I., Pinoy, L., Courtijn, E., Verpoort, F., 2006. Equilibrium Studies of Nickel(II), Copper(II), and Cobalt(II) Extraction with Aloxime 800, D2EHPA, and Cyanex Reagents. Solvent Extr. Ion Exc., 24, 893-914. https://doi.org/10.1080/07366290600952717

Virolainen, S., Ibana, D. & Paatero, E., 2011. Recovery of indium from indium-tin-oxide by solvent extraction. Hydrometallurgy, 107, 56-61. https://doi.org/10.1016/j.hydromet.2011.01.005

Vogel, A. I., 1981. Química Analítica Qualitativa, 5ª ed. São Paulo: Mestre Jou.

Wang, S., Wang, C., Lai, F., Yan, F. & Zhang, Z., 2020. Reduction-ammoniacal leaching to recycle lithium, cobalt, and nickel from spent lithium-ion batteries with a hydrothermal method: Effect of reductants and ammonium salts. Waste Manage., 102, 122–130. https://doi.org/10.1016/j.wasman.2019.10.017

Xie, F., Zhang, T.A., Dreisinger, D., Doyle, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. Miner. Eng., 56, 10-28. https://doi.org/10.1016/j.mineng.2013.10.021

Yang, X., Zhang, J. & Fang, X., 2014. Rare earth element recycling from waste nickel metal hydride batteries. J. Hazard. Mat., 279, 384–388. https://doi.org/10.1016/j.jhazmat.2014.07.027

Yang, L., Yang, L., Xu, G., Feng, Q., Li, Y., Zhao, E., Ma, J., Fan, S. & Li, X., 2019. Separation and recovery of carbon powder in anodes from spent lithium-ion batteries to synthesize graphene. Sci. Rep., 9, 9823. https://doi.org/10.1038/s41598-019-46393-4

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EVALUATION OF ELEMENTS DISTRIBUTION IN PRINTED CIRCUIT BOARDS FROM MOBILE PHONES BY MICRO X-RAY FLUORESCENCE

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ABSTRACT

A micro X-ray fluorescence-based approach for the chemical characterization of spent printed circuit boards (PCBSPCBSS) from mobile phones was applied. More in detail, twelve spent mobile phones were grouped into three clusters according to brands, models and year of release, and a study to evaluate the technological evolution of PCBSs over time was carried out. Precious metals and hazardous elements were investigated, revealing a few differences between samples from the different groups. For instance, the distribution of gold on PCBS layers was more widespread for the older analyzed samples, and smaller quantities of bromine and lead were detected in the more recent models in accordance with the *Restriction of Hazardous Substances Directive 2002/95/EC*. Analysis of PCBS composition should contribute towards correctly managing such a complex waste, maximizing the recovery of base, critical and precious metals and considering the possible presence of harmful elements requiring careful management. The experimental results showed how, using the proposed approach, distribution maps for chemical elements present in PCBSs could be obtained, thus allowing the definition of optimal strategies for further handling (i.e. classification) and processing (i.e. critical/precious metal recovery).

1. INTRODUCTION

Mobile phones are one of the main items present in WEEE (Waste from Electrical and Electronic Equipment). In recent decades, a dramatic increase has been witnessed in the use of this kind of product in line with the progress of technology (Kasper et al., 2011a; Hira et al., 2018; Singh et al., 2019). Although the technical lifespan of mobile phones is approx. 10 years, consumers frequently upgrade their devices, limiting use to 1-2 years (Tan et al., 2017). Moreover, the increasingly low cost of electronic equipment, together with the adoption of ever more aggressive marketing strategies for items such as mobile phones, has resulted in a continuous renewal of these devices by consumers (Paianoa et al., 2013). Therefore, the amount of spent mobile phones is constantly rising, thus implying a need to develop efficient strategies for the recycling of such a complex waste.

PCBSs from mobile phones are viewed as "rich boards" comprising a large quantity of components (i.e. processors and capacitors made up of precious and critical metals, such as rare earth elements) "concentrated" over a small surface with a characteristically reduced thickness. This aspect affects the future recovery of valuable elements. It is therefore evident that the recycling of materials from spent mobile phones represents a compelling challenge both from an economical and an environmental point of view.

Mobile phones represent a rich reserve of precious metals, i.e. gold (Au), silver (Ag), palladium, (Pd), etc. and critical raw materials, including tantalum (Ta), indium (In), rare earth elements such as yttrium (Y), lanthanum (La), neodymium (Nd) and praseodymium (Pr); indeed, specific recycling treatments should be implemented to recover the highest possible quantities of these metals.

On the other hand, the disposal of discarded mobile phones is fast becoming a serious problem, particularly due to the presence of hazardous elements such as arsenic (As), bromine (Br), cadmium (Cd), lead (Pb), mercury (Hg), dioxins and furans which, when released, are harmful to both the environment and human health (Kasper et al., 2011b). In this perspective, the preliminary detection of these substances using non-destructive methods could provide useful information for subsequent recycling treatments.

In Italy, the estimated rates of WMP (Waste Mobile Phones) alone are not effectively recorded, being included in an extensive heterogeneous group of electronic wastes known as "R4", which includes a large range of devices

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such as: mobile phones, personal computers, printers, tablets and notebooks and other small electronic units (Legislative Decrees 151/2005, 152/2006 implementing the EU Directives 2002/96/EC, 2003/108/EC and "ROHS" Directive 2002/95/EC). These wastes represent approx. 21 % of total household WEEE (Annual Report of WEEE - www.cdcraee.it). In addition, the structural and compositional complexity of WMPs largely depends on the period of manufacture.

Although WEEE composition strongly influences the performance of recycling operations, the implementation of a "recycling oriented characterization" of wastes fed to the process (Chancerel and Rotter, 2009) will enhance effectiveness. Accordingly, the aim of this study was to define a systematic method of characterization to be applied as a preliminary phase in the recycling of End Of Life (EOL) PCBSs, starting from information obtained in previous studies (Palmieri et al., 2014; Bonifazi et al. 2018). Namely, the possibility of using a micro X-ray fluorescence (micro-XRF) based approach to perform chemical element detection and mapping of discarded electronic boards from mobile phones of different brands and different years of release, was investigated.

2. MATERIALS AND METHODS

2.1 Investigated samples

Twelve spent mobile phones of different brands, models and/or year of release (Table 1) were collected and divided into 3 groups based on the technological evolution linked to year of release. A short description of the main "technological" characteristics of these groups is provided below:

- Group A: "*mobile phones*" (release period: 1999-2009), enabling phone calls, text messaging and little else. The majority of these devices were GSM phones, using digital rather than analog networks and the first ARM processors. They adopted a similar but smaller brick-style form factor. Parts and components on the PCBS structure were "easy" to access. Antenna and antenna switch were normally located at the top of mobile phone PCBS and the power frequency oscillator (PFO) was present beside the antenna switch, Network IC was located below or beside the antenna switch and PFO, the power IC was at the bottom of the PCBS and identified by several brown-colored capacitors. The Central Processing Unit is easily recognizable, being the largest integrated circuit (IC). Finally, to complete the mobile phone PCBS: RAM, charging, audio, flash and logic IC were present.
- Group B: "*Feature phones*" (release period: 2011-2012), with a wide range of features (i.e. built-in cameras), more advanced than mobile phones but not as advanced as smartphones. Feature phones represent a midway point between smartphones and basic phones. Indeed, compared to smartphones, these phones are typically easier to use and cheaper to boot. Feature phones usually have a limited proprietary operating system and do not all support third-party software. Should they do so, they usually run on Java or BREW environment and are often standalone items that do not integrate with other phone features. The majority of these phones were equipped with 3G technology. Accordingly, feature phone PCBSs were similar to mobile phones, with numerous miniaturized elements and a higher performance CPU capable of managing the presence of a series of multimedia apps and the first camera-phone.
- Group C: "*Smartphones*" (release period: 2013-2015), i.e. forefront phones. Smartphone devices combine computing functions of feature phones and mobile computing functions in a single device. They are distinguished from feature phones by their higher hardware capacities and extensive mobile operating systems, which facilitate extended software, internet and advanced multimedia functionality, alongside core phone functions such as voice calls and text messaging. PCBSIn addition to components of feature phones, Smartphone PCBSs contain a number of metal–oxide–semiconductor (MOS) integrated circuit (IC) chips, including various sensors that can be leveraged by their software (such as a magnetometer, proximity sensors, barometer, gyroscope, or accelerometer), and support wireless communications protocols (such as Bluetooth, Wi-Fi, or satellite navigation).

Mobile phones were manually dismantled in order to select PCBSs for analysis. PCBSs were investigated by means of micro-XRF to detect the presence and distribution of the different chemical elements on the sample surface.

2.2 Micro-XRF equipment

Micro-XRF tests were carried out at the Raw Materials Laboratory (RawMaLab) of the Department of Chemical Engineering, Materials & Environment (Sapienza - University of Rome, Italy). Micro-XRF was utilized to map the chemical composition of entire PCBSs.

A μ-XRF benchtop spectrometer (M4 Tornado, Bruker®), equipped with an Rh X-ray tube with polycapillary optics and XFlash® detector, providing an energy resolution of more than 145 eV, was used for analysis. Polycapillary optics enable tube radiation to focus on a very small spot size (approx. 30 μm) by multiple reflections, thus providing a spot intensity increase of up to 104x compared to use of a collimator, promoting the obtaining of faster results and more detailed (i.e. spatial resolution) analysis. Spectrum energy calibration was performed on a daily basis prior to analysis of each batch using zirconium (Zr) metal (Bruker® calibration standard). The sample chamber can be evacuated to 25 mbar and, therefore, light elements such as sodium measured. At constant excitation energies of 50 kV and 500 μA, measurement conditions were adapted for the different investigated samples. The estimated thickness of the material that fluoresces was complex to determinate in multilayer matrix as SPCB. As element maps show, PBCs are composed by different layers of materials and electronic components, as a results is X-ray absorption is strongly affected by the investigated area (i.e. lead solder cover the presence of other elements and silica wafer, mainly composed by plastic material, allows the detection of copper

TABLE 1: Mobile phone samples utilized to perform micro-XRF analyses on PCBSs.

Sample image	Brand	Model	Release year
	Nokia	3210	1999
	Sony Ericsson	T300	2002
	LG	KU 385	2007
	Nokia	5230	2009
	Samsung	GT S 5250	2010
	Samsung	GT N 7000	2011
	LG	E 610	2012
	Samsung	GT i8160	2012
	Samsung	GT S 6310	2013
	Samsung	GT i9505	2013
	Samsung	GT i9195	2013
	Wiko	Ridge 4S	2015

TABLE 2: Analytical set up adopted to perform micro-XRF analyses.

Tube parameter		Acquisition parameter		
High voltage	Anode current	Vacuum	Pixel time	Frame count
50 kV	499 μA	20 mbar	6 ms/pixel	3

layer under its surface). The thickness of the sample was found to be critical and had to be carefully determined for each group of elements (Al-Merey et al., 2005). In metal alloys, for example, the coating thickness determination, using X-ray, can be calculated through point analysis (Giurliani et al., 2019). In complex matrices, such as SPCBs it is possible to determine as thickness of the material that fluoresces changes from 0 to a few microns according to the detected elements (Ming-qing, 2016). Measurement conditions used for the operated mapping are reported in Table 2.

3. RESULTS AND DISCUSSION

An example of the results obtained by micro-XRF chemical analysis, in terms of false color maps, for one of the analyzed PCBSs (i.e. NOKIA 3210, released in 1999) is illustrated in Figure 1. Following identification of the chemical elements detected for each PCBS, a correlation with the different electrical and electronic components was defined (Figure 2). A comparison of the differences and similarities between PCBSs belonging to the three investigated mobile phone sets, revealed how topological assessment of the elements detected on PCBSs reflected, in all cases, the component characteristics. Copper (Cu) and silicon (Si) were the most extensively detected elements in all three Groups studied (A, B and C), comprising respectively PCBS layers (Cu) and electronic component housings (Si).

Copper concentration and distribution were mainly related to the multiple thin layers constituting the PBC structure. A non-conducting layer, largely made up of insulating support (i.e. resin) providing mechanical resistance to the PCBS was located between the copper layers.

The main components of the insulating layers included fiberglass, identifiable by silicon, and resins. This structure is well evidenced by XRF mapping allowing identification of the majority of CU present under PCBS surface.

Si was present over the entire surface, although at varying concentrations, identified on the board in the fiberglass in the PCBS structure; moreover, a higher concentration of silicon was detected in chip protection covers.

The elements found most extensively in the antenna were Cr and Fe.

Ca was detected in numerous small components, and was particularly abundant in the buzzer.

Pb and Sn were distributed throughout the same area, confirming the presence of an alloy for solder based on these elements.

Au was present in two different forms. A relevant concentration of Au was identified in the CPU, while a lower concentration was present as an alloy with Ni. In general, Ni-Au alloy is used in mobile phones as a conductor to connect analog devices such as the keyboard, the vibration motor, the jack connection or the connection for battery charging. The Ni-Au alloy is also present on the surface of the PCBS while the Au of the CPU is enclosed in the silicon cover of the CPU rendering extraction more complex.

Another interesting technological aspect concerns bromine (Br). The XRF map highlights how Br distribution is not uniform, but is located only in the areas characterized by a greater danger of overheating (i.e. CPU and power supply). This information is crucial, as Br concentration might differ based on the particle size selected in the comminution process.

Figure 3 illustrates examples of chemical map distribution obtained for three PCBSs deriving from the three groups analyzed. The variations detected in terms of distribution and concentration of elements were caused mainly by technological needs and reduction in the use of several elements deemed potentially harmful to humans and the environment.

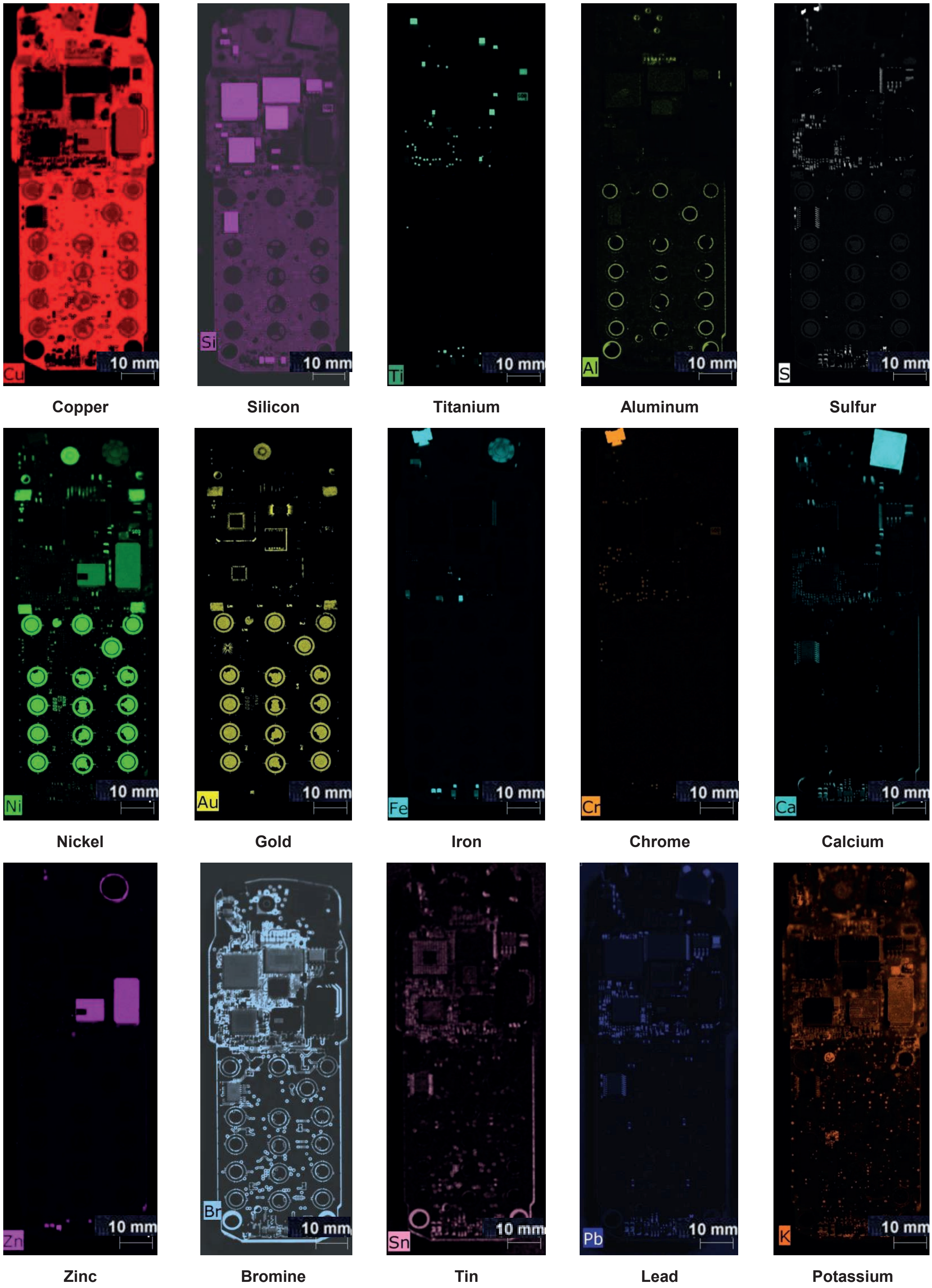
It was however consistently observed that: titanium (Ti) is present both in capacitors due to its heat resistance properties and in PCBS pins, chrome (Cr) is used as protective coating for iron (Fe) components and nickel (Ni) is present as an alloy with Au in printed circuits, but also as an alloy with zinc (Zn) for circuit protection. Several hazardous elements, such as Br, used as flame retardant, and Pb, used in connection solders, displayed a decrease in values over time (Figure 4). This could be a consequence of the Restriction of Hazardous Substances Directive 2002/95/EC emanation limiting the use of some substances in the production chain.

On the contrary, with regard to precious metals, Au was detected in all groups investigated, with a fairly constant percentage over time (Figure 5). It is however interesting to note how the older models of mobile phones analyzed (i.e. 1999) featured a widespread distribution of Au on the PCBS layer: on contacts, under the buttons and in the microprocessors. Au is concentrated in some specific areas as Ni alloy for all other samples. Feature phones and, particularly, smartphones were characterized by a low presence of Au on the surface, being concentrated in CPU chips. As previously mentioned, Au present in these technological components is more complex to extract compared to the Ni-Au alloy present on the surface of mobile phones.

4. CONCLUSIONS

Micro-XRF was applied to perform a preliminary characterization of PCBSs from spent mobile phones. More in detail, 12 mobile phones grouped into 3 sets according to their year of release and characteristics were analyzed. The results highlighted how analysis of the single element map facilitated both identification of the main elements of each PCBS component and evaluation of the issues to be addressed in maximizing the recovery of precious metals.

The procedure adopted enabled mapping of chemical element distribution throughout the entire PCBS surface,



Copper **Silicon** **Titanium** **Aluminum** **Sulfur**

Nickel **Gold** **Iron** **Chrome** **Calcium**

Zinc **Bromine** **Tin** **Lead** **Potassium**

FIGURE 1: Distribution of chemical elements (i.e. maps) detected by micro-XRF on the PCBS front of NOKIA 3210 mobile phone.

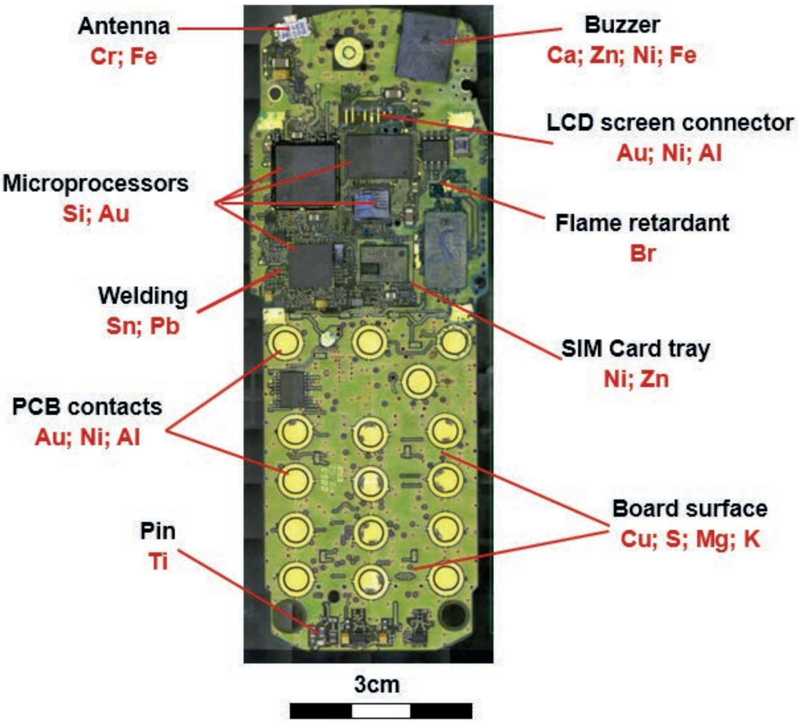


FIGURE 2: Summary of the outcomes, in terms of chemical elements, resulting from micro-XRF analysis carried out on NOKIA 3210 entire PCBS.

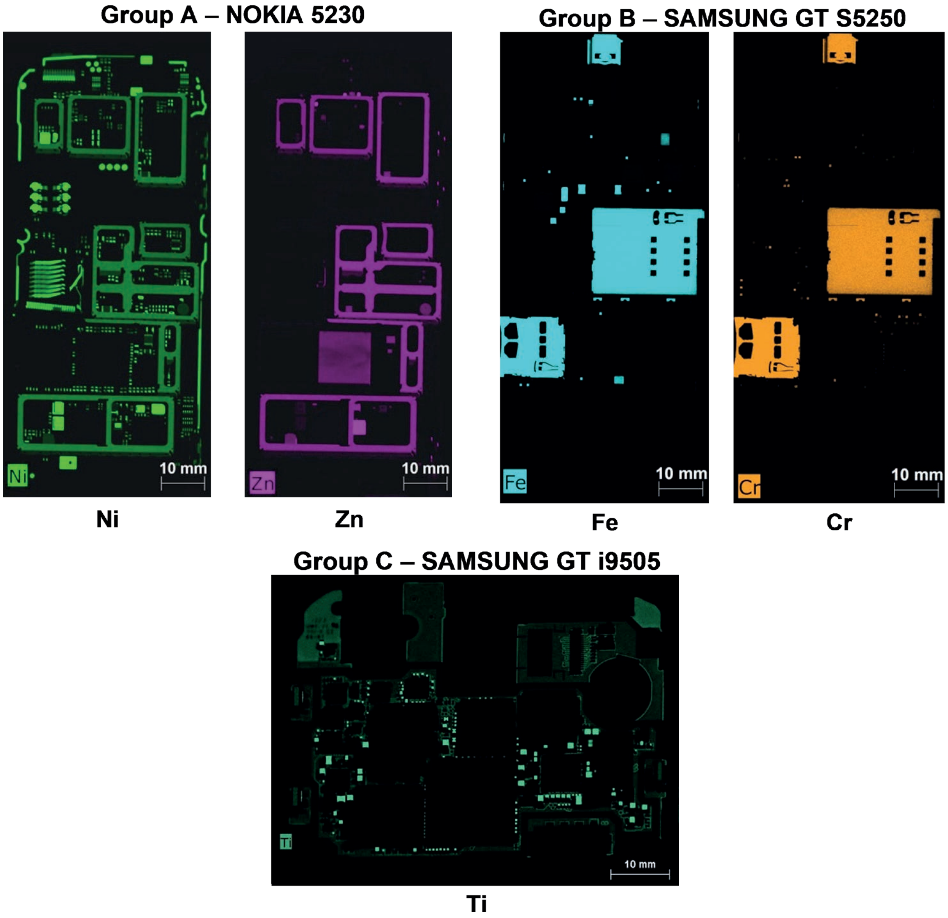


FIGURE 3: Examples of chemical element distribution (i.e. maps) on three PCBSs, belonging to the three different analyzed groups, detected by micro-XRF: Ni-Zn alloy for Nokia 5230 (a), Fe-Cr alloy for Samsung GT S5250 (b) and Ti pins for GTi9505 (c).

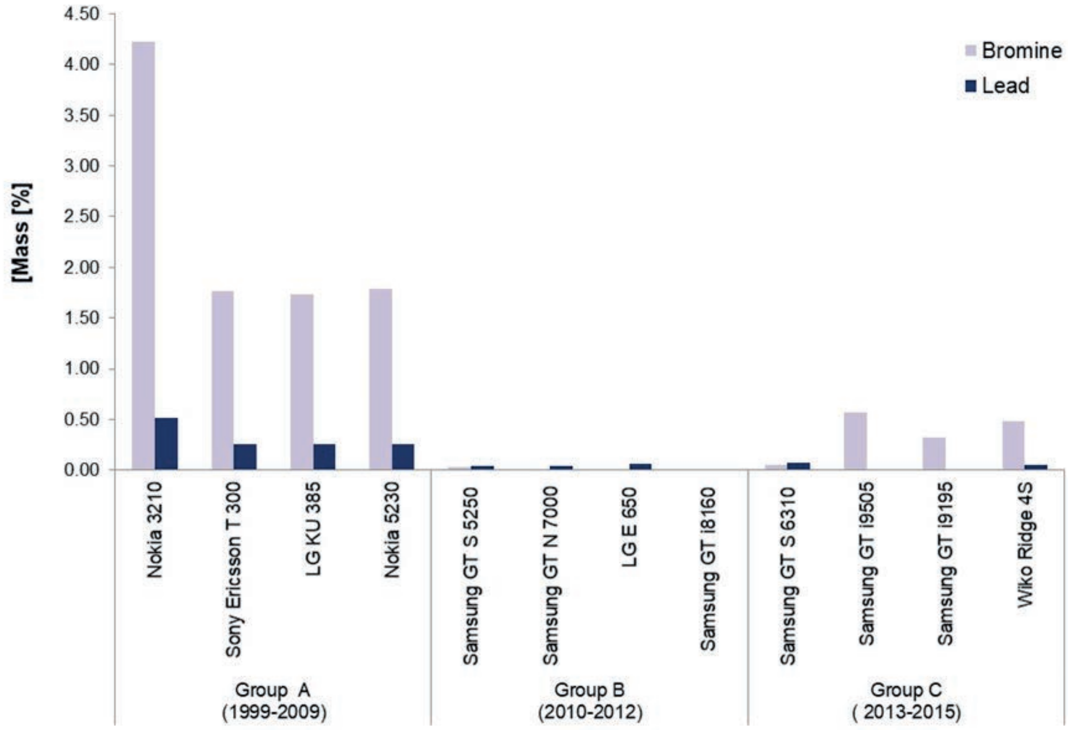


FIGURE 4: Evolution over time of hazardous Br and Pb elements inside PCBSs of mobile phones.

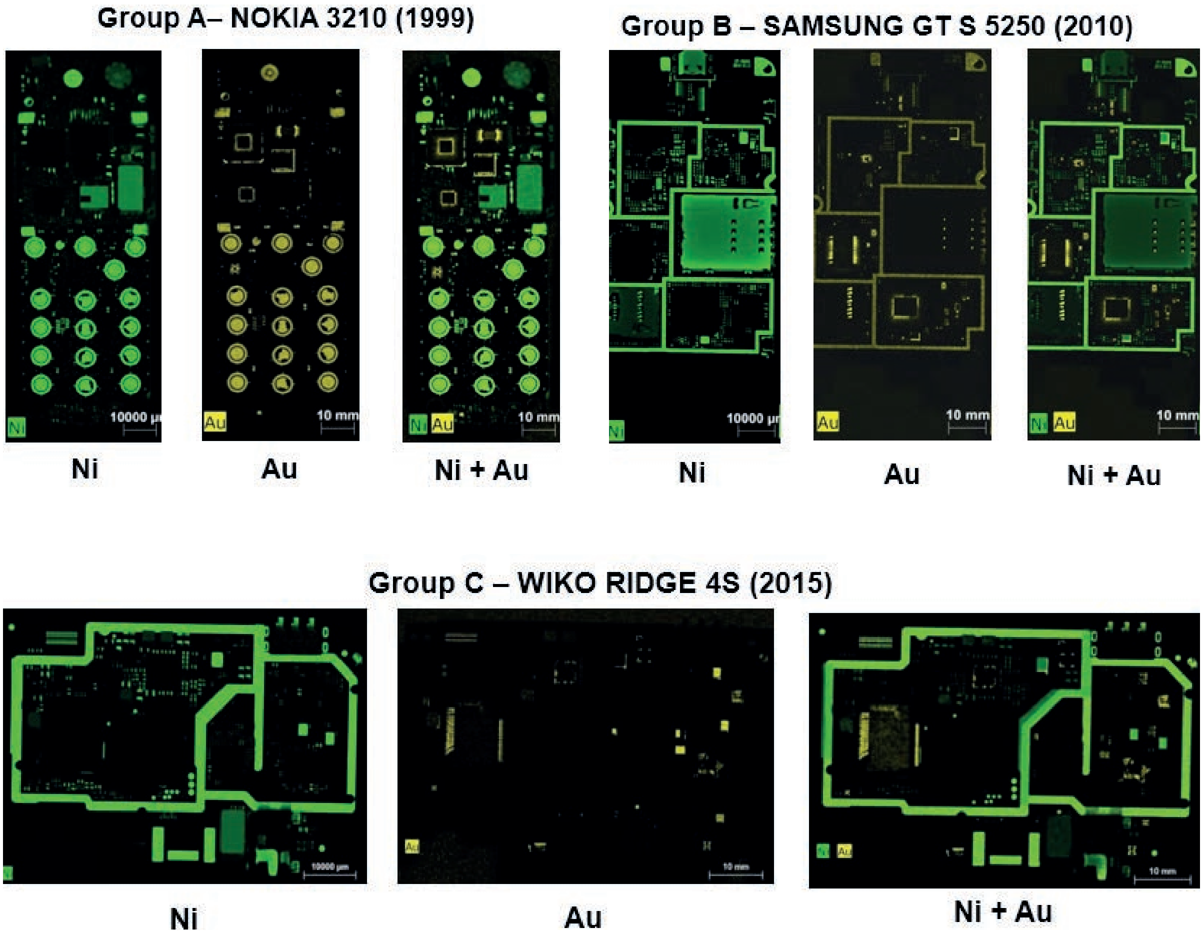


FIGURE 5: Examples of Au and Ni distribution (i.e. maps) on three PCBSs belonging to the three different analyzed groups, detected by micro-XRF: Nokia 3210 belonging to Group A (a), Samsung GT S 5250 belonging to group B (b) and WIKO RIDGE 4S belonging to group C (c).

thus promoting study of their evolution over time. The study confirmed that technological evolution influences the concentration and distribution of precious elements. This information suggests the advisability of adopting a different approach based on the utilized production technologies or the age of PCBS with an aim to optimizing the extraction process.

Further studies should be carried out to extend systematic application of the proposed approach to a larger quantity of PCBSs. Moreover, milled samples will be analyzed to explore the possibility of pre-concentrating useful chemical elements into defined particle size classes. A similar strategy could contribute towards developing “good practices” addressed at improving efficiency of the recycling chain, reducing and optimizing the number of processing stages by characterizing handling of the entire WMP, leading to a consequent reduction in costs and environmental impact.

REFERENCES

Bonifazi, G., Capobianco, G., Palmieri, R., Serranti, S., 2018. A methodological approach for the characterization of printed circuit boards from smartphones by micro x-ray fluorescence. Proceedings SUM2018, Fourth Symposium on Urban Mining, 21-23 May 2018 (Bergamo, Italia)

Chancerel, P., Rotter, S., 2009. Recycling-oriented characterization of small electrical and electronic equipment. Waste Manage., 29, 2336-235.

Hira, M., Yadev, S., Morthekai, P., Linda, A., Kumar, S., Sharma, A., 2018. Mobile Phones – An asset or a liability: A study based on characterization and assessment of metals in waste mobile phone components using leaching tests. J. Hazard. Mater., 342, 29-40.

Kasper, A.C., Bernardes, A.M., Veit, H.M., 2011a. Characterization and recovery of polymers from mobile phone scrap. Waste Manage. Res., 29(7), 714-726.

Kasper, A.C., Berselli, G.B.T., Freitas, B.D., Tenório, J.A.S., Bernardes, A.M., 2011b. Printed wiring boards for mobile phones: Characterization and recycling of copper. Waste Mange, 31, 2536-2545.

Paianoa, A., Lagioia, G., Cataldo, A., 2013. A critical analysis of the sustainability of mobile phones use. Resour. Conerv. Recycl. 73, 162-171.

Palmieri, R., Bonifazi, G., Serranti, S., 2014. Recycling-oriented characterization of plastic frames and printed circuit boards from mobile phones by electronic and chemical imaging. Waste Manage.,34, 2120-2130.

Singh, N., Duan, H., Ogunseitan, O.A., Li., J., Tang, Y., 2019. Toxicity trends in E-Waste: A comparative analysis of metals in discarded mobile phones. J. Hazard. Mater., 380, 1-9.

Tan, Q., Dong, Q., Liu, L., Song, Q., Liang, Y., Li, J., 2017. Potential recycling availability and capacity assessment on typical metals in waste mobile phones: A current research study in China. J. Clean. Prod., 148, 509-517.

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RECOVERY OF COPPER AND SILVER OF PRINTED CIRCUIT BOARDS FROM OBSOLETE COMPUTERS BY ONE-STEP ACID LEACHING

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ABSTRACT

Over the years, the generation of Waste Electric and Electronic Equipment has been significantly increased, which leads to environmental and economic concerns. Thus, it is fundamental to develop treatment methods for these residues. Printed Circuit Boards are essential components of electronic equipments. In this sense, printed circuit boards are composed of remarkable metals, in particular, copper and silver at high and low concentrations, respectively. These metals can be recovered by the hydrometallurgical process followed by a chemical purification step. Therefore, the aim of this study was to leach silver and copper from two different printed circuit boards (memory board and motherboard) from obsolete computers by hydrometallurgical route based on only one-stage leaching in oxidant media. When compared to the motherboard, a higher recovery rate of Ag was obtained from memory boards 83% and 33%, respectively. Whereas, similar recovery rates of copper were observed for memory board and motherboard, 48% and 46%, respectively.

1. INTRODUCTION

Over the past 20 years, there has been a massive increase in the production of electric and electronic equipments (EEEs). Simultaneously, the EEE have shorter and shorter life cycles. Consequently, there is a substantial and alarming generation of the waste electric and electronic equipments (WEEEs) (GHOSH et al., 2015).

Regarding WEEEs, its heterogeneous composition (ceramic, polymeric materials, and also a considerable amount of metals), hinders the control and development of efficient treatment methods. Thus, it is essential to do research on alternatives for the treatment and correct disposal of WEEE (Kumar et al., 2017; Shokri et al., 2017). In this sense, the European Parliament has published some instructions on the management of WEEEs (Official Journal of the European Union, 2003a, Official Journal Of European Union, 2003b).

Printed Circuit Boards (PCBs) are essential components of WEEEs, that is, PCBs represent a significant volume of WEEEs. PCBs are quite heterogenic materials, composed of different metals, for instance, Al, Cu, Fe, Ni, Sn, and Zn, and also high added-value metals as Au, Ag, and Pt. It is worth noting that toxic metals as Cd, Hg, and Pb can also be found in PCBs (Cui and Anderson, 2006).

Thus, taking into account the volume of WEEEs and their composition, in particular high added-value metals, it is a quite interesting strategy to recovery some metals - urban mining concept (Diaz et al., 2015).

Due to its remarkable properties such as high mechanical and corrosion resistance, good conductor of electricity and heat copper is widely used in industrial processes, including PCBs, in which can reach reach 20 wt%. In September of 2020, the market value of copper was US$ 6,788.5 per ton (Xu et al., 2016; LME, 2020a). In addition, according to the European Union - Restriction of Hazardous Substances Directive (RoHS), which is related to the restriction in the use of certain hazardous substances in electrical and electronic equipment, the production of traditional eletronic boards should be changed by lead free eletronic boards, in which Pb is replaced by Ag without any performance damage due to the great properties of the precious metal. Nevertheless, Ag is a high added-value metal. In September of 2020, the market value of silver reached US$ 911,311.59 per ton. It means that even in lower concentrations in comparison to another metal, the Ag market value, 134 times higher than Cu, turns it into a really important metal in terms of the intrinsic value of the board (Cayumil et al., 2016; KITCO, 2018; LME, 2020b).

The metal recovery from PCBs can be carried out by hy-

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drometallurgically (Cui and Anderson, 2016), pyrometallurgically (Bidini et al., 2015) or biohydrometallurgically (Ilyas et al., 2010). The hydrometallurgical process is based on the metal leaching using acid or alkali molecules, followed by chemical process that recover the metals of interest (Xu et al., 2016; Neto et al., 2016; Kumar et al., 2015; Choubey et al., 2015). In this sense, a new two-stage hydrometallurgical route was described by Silvas et al. (2015), the first stage is acidic medium composed of sulfuric acid, whereas the second stage is an oxidant solution composed of sulfuric acid and hydrogen peroxide. The authors extracted 100% of copper from PCBs from printers.

Therefore, the aim of this study was to leach silver and copper from two different PCBs (memory board and motherboard) from obsolete computers by hydrometallurgical route based on only one-stage leaching in oxidant media.

2. MATERIAL AND METHODS

2.1 Physical-chemical characterization of memory board and motherboard

Two different lead-free boards from obsolete computers were used (motherboard and memory board). The boards were obtained from Centro de Descarte e Reúso de Resíduos de Informática da Universidade de São Paulo (CEDIR-USP). The physical processing included: manual disassembling, comminution, and quartering. Approximately 1 kg of each board was comminuted, which corresponds to 5 motherboards and 20 memory boards. Then, the motherboards and memory boards without external and removable polymeric components were physical-chemical characterized (as below).

2.1.1 Physical processing

The comminution was performed using two mills in sequence: a knife mill (RONE FA2305) with a 9 mm grid, and a hammer mill (ASTECMA MDM 18/18) with a 2 mm grid. The resulting material was quartered in a Johnes quarter to separate homogeneously the samples into small fractions, of 20 ± 5 g.

2.1.2 Aqua regia digestion and chemical analysis

5 g of the sample was submitted of aqua regia digestion, with a solid-liquid ratio of 1:20 – a volume of 100 mL of aqua regia was used for the solubilization of the metals. The digestion occurred at room temperature and atmospheric pressure for 24 hours. After the reaction, the liquor was filtered using a quantitative filter paper (porosity of 0.75 μm). Then, 10 mL of permeate was used to quantify silver and copper by ICP-OES.

2.1.3 Loss on ignition test

The residue after aqua regia digestion was filtered using a quantitative filter paper (porosity of 0.75 μm). Then, the solid fraction was washed using deionized water and oven-dried at 60 ± 5°C for 24 hours. The material was transferred to a porcelain crucible and lead to a muffle with a heating rate of 10°C/min until it reaches 800°C and then maintained for 1 hour. After turned off, the muffle cooled to room temperature and then weighed again. The sample was maintained in a desiccator for 24 hours and after weighed again to verify the sample weight constant.

2.2 Hydrometallurgical Processing

The one-stage acid leaching in oxidant media were conducted for both boards. The leaching agent was sulfuric acid (H_2SO_4) 2M. 100 g of boards were solubilized in 2,000 mL of acid under the following conditions:

- Solid-liquid ratio: 1:20;
- Temperature: 95°C;
- Pressure:1 atm;
- Time: 12 hours.

Additionally, 15 mL of hydrogen peroxide (H_2O_2) 35% (oxidant agent) was added every 15 minutes for 12 hours. 10 mL sampling was carried out every hour. Then, the liquor was colled at room temperature and filtered using a quantitative filter paper (porosity of 0.75 μm). The permeate was used to quantify silver and copper by ICP-OES.

3. RESULTS AND DISCUSSION

3.1 Physical-chemical characterization of memory board and motherboard

3.1.1 Aqua regia digestion and chemical analysis

After the physical processing and aqua regia digestion, the analysis of ICP-OES data showed that both memory board and motherboard have several metals such as, Al, Au, Cu, Fe, Ni, Sn, and Zn (Table 1).

When compared to memory board, motherboard showed higher metal mass fraction 35.510% and 18.910%, respectively (Table 1). These results are aligned to Gosh et al. (2015) and Kaya (2016).

Regarding copper in terms of mass fraction, it was observed similar concentrations for both motherboard and the memory board. However, in terms of metal mass fraction, copper represents 55.3% for motherboard and 73.1% for memory board. In other words, the highest metallic concentration is related to copper (>50%). Thus, copper is the most promising metal that can be recovered from motherboard and memory board, whereas for silver, lower mass fraction was observed (≈ 340 x than copper). Nevertheless, a similar mass fraction was observed for both

TABLE 1: Metal mass fraction of motherboard and memory board.

Metal	Mass fraction	
	Motherboard	Memory board
Ag	0.045%	0.053%
Al	2.660%	1.403%
Au	0.002%	0.069%
Cu	19.650%	13.830%
Fe	8.340%	1.470%
Ni	0.270%	0.320%
Sn	1.990%	1.700%
Zn	2.550%	0.043%
Total	35.510%	18.910%

motherboard and the memory board. In addition, in terms of metal mass fraction, silver corresponds to 0.1% for the motherboard and 0.2% for the memory board. Thus, on the one hand, copper is the most abundant metals in both the motherboard and the memory board, on the other hand, even at low mass fraction (≈ 0.05%), silver can be recovered from PCBs due to its high added-value.

3.1.2 Loss on ignition test

Based on the stoichiometry, H+ in excess (around 10 times) dissolve all metals present in the PCBs and strongly acid pH conditions are suitable to maintain the formed salts in solution.

Thus, the remaining material (after aqua regia digestion) is composed of only ceramic and polymeric compounds. In this sense, polymers are thermal degradable. Thus, the loss on ignition test indicates the mass of polymeric fraction (volatile) by gravimetry method, in which the non-volatile mass fraction corresponds to the ceramic compounds of the boards (Ilyas et al., 2007).

Based on loss on ignition test and aqua regia digestion data, the material compositions of motherboard and memory board are shown in Figure 1.

For both memory board and motherboard, ceramic compounds were majority 48.4% and 38.7%, respectively. Very likely, due to the fiberglass that is widely applied for other PCB components. These results are aligned to Zhou and Qiu (2010) that described the composition of PCB wastes ≈ 28% of metals and 72% of non-metals such as plastic, ceramic, etc.

3.2 Hydrometallurgical processing

The chemical analysis by ICP-OES of the liquor obtained at the end of the acid leaching in the oxidant media process allowed to calculate the percentage of extraction of each metal on the boards, based on characterization results showed in Table 1. This analysis resulted in Table 2.

A previous study (Silvas et al., 2015) showed that the leaching of both Cu and Ag from PCB from printers can be carried out in acid solutions and oxidant medium.

3.2.1 Motherboard

The leaching curves of Ag and Cu for motherboard and memory board are shown in Figures 2 and 3.

TABLE 2: Percentage of extraction of metals for the motherboard and the memory board.

Metal	Extraction	
	Motherboard	Memory board
Ag	33%	83%
Al	99%	100%
Au	0%	0%
Cu	48%	46%
Fe	100%	81%
Ni	89%	83%
Sn	31%	15%
Zn	88%	100%

Considering the initial mass (100 g) and the concentration of each metal obtained by chemical characterization for the motherboard, the maximum mass that could be extracted was 0.045 g and 19.65 g for silver and copper, respectively. However, the one-step acid leaching reached 33% and 48%, respectively for silver (Figure 2) and copper (Figure 3), which corresponds to 0.015 g of Ag and 9.432 g of copper. Thus, the other metals in the liquor such as Ni, Sn, and Zn that form stable alloys in solution, can negatively affect the total leaching of Ag and Cu (SILVAS et al., 2015).

The high added-value metals need a quite high ORP for high yields of hydrometallurgical recovery. In addition, partial purification, mainly non-added value metals, can significantly enhance the yields of high added-value metals (Žiūkaitė et al., 2017). It was observed that the leaching of Ag only started began after 7 hours (Figure 2), very likely due to the acid reaction with other metals, such as copper. As far as the copper is being leached, the remained acid can start to leach the precious metals increasing the concentration through the process since the Ag leaching is generally performed after removal of Cu (GURUNG et al., 2013).

Thus, the partial purification of other metals, high ORP, favorable pH and at least 10 hours of leaching process could enhance the copper and silver yields of leaching from motherboard and memory board.

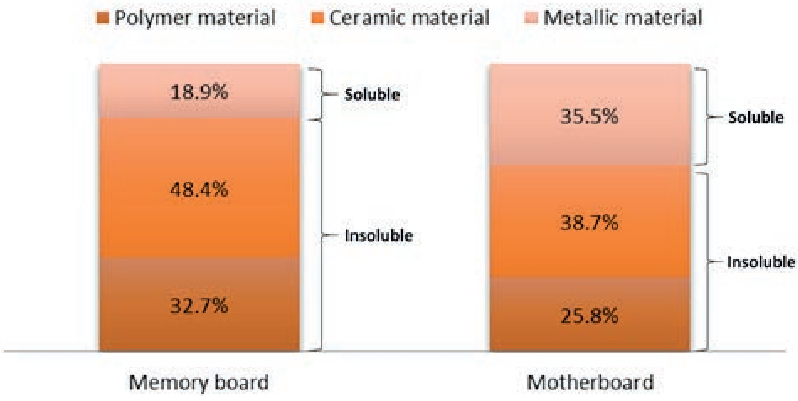

FIGURE 1: Material compositions of motherboard and memory board.

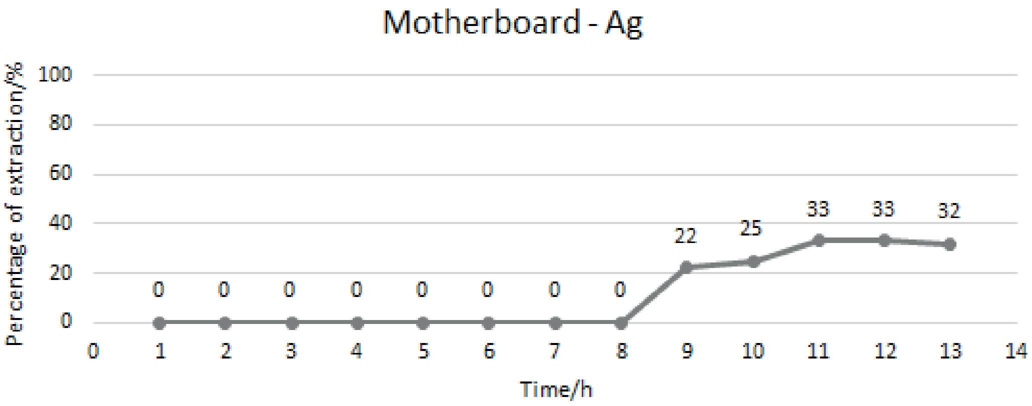

FIGURE 2: Leaching curve of Ag for the motherboard with the percentage of extraction over time.

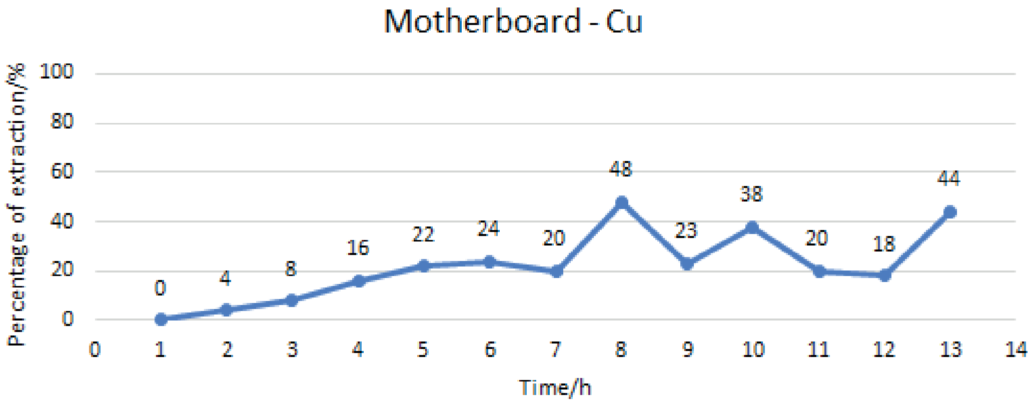

FIGURE 3: Leaching curve of Cu for the motherboard with the percentage of extraction over time.

3.2.2 Memory Board

The leaching curves of Ag and Cu for the memory board are shown in Figures 4 and 5, respectively. Taking into account the initial mass of the PCBs (100 g) and the concentration of each metal obtained by chemical characterization, the maximum mass that could be extracted from the memory board was 0.053g fo Ag and 13.83 g for Cu (Table 1). The one-step acid leaching of Ag and Cu reached, respectively, 83% and 46%, which corresponds to a mass of 0.044 g of Ag and 6.362 g of Cu, respectively.

The increased percentage of extraction over time for both metals, Ag and Cu, was also observed for the memory board. However, similarly to the observed for motherboard leaching, the remotion of impurities, longer leaching reaction time (at least 7 hours) combined with the ORP and pH optimum conditions could further improve the process maximizing the simultaneous extraction for Cu and Ag.

Additionally, the high yield of Ag extraction can be related to the metal mass fraction for both motherboard and memory board, and the solid-liquid ratio used for the acid leaching process. Whereas on the motherboard the metallic fraction is 35.5% and the Ag represents 0.1% of this amount, on the memory board Ag represents 0.2% of a smaller metallic fraction, 18.9%. It means that, on the memory board, a higher amount of acid was available to interact with the metals and promote the leaching, therefore improving the efficiency of the hydrometallurgical process.

4. CONCLUSIONS

The hydrometallurgical process of one-stage acid leaching in oxidant media allowed to recover Ag and Cu, the two most expressive metals in terms of intrinsic value and amount respectively, from PCBs from obsolete computers (motherboard and memory board). Both metals Ag and Cu were recovered by one-stage acid leaching in oxidant medium. When compared to motherboard, the memory board reached higher recovery of Ag, 83% after 12 hours. However, the partial purification of other metals, high ORP, favorable pH and at least 10 hours of leaching process could enhance the copper and silver yields of leaching from motherboard and memory board. Regarding Cu recovery, it was quite similar to both memory board and motherboard, since it reached 48% and 46%, respectively. Therefore, the one-stage leaching is a promising strategy to recover metals from PCBs from obsolete computers.

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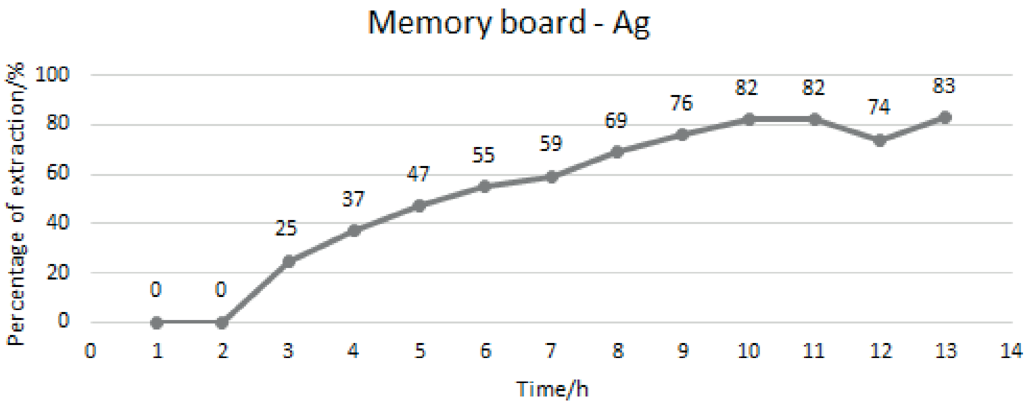

FIGURE 4: Leaching curve of Ag for the memory board with the percentage of extraction over time.

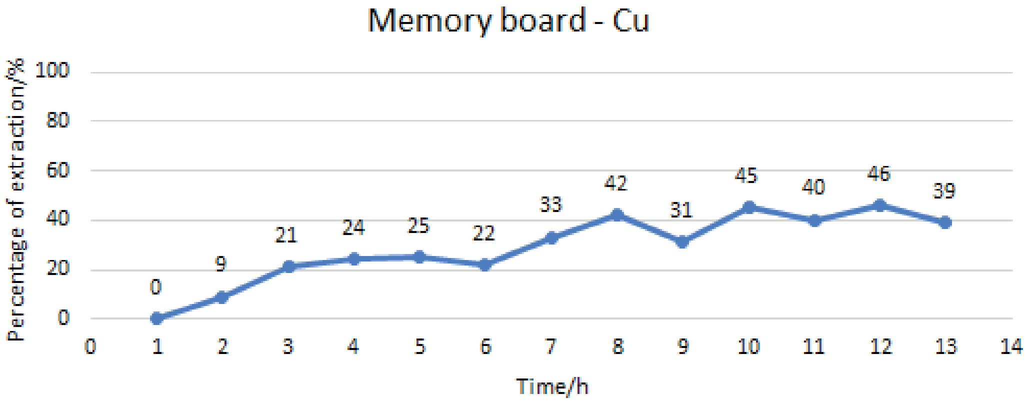

FIGURE 5: Leaching curve of Cu for the memory board with the percentage of extraction over time.

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REFERENCES

Bidini G., Fantozzi F., Bartocci P., D'Alessandro B., D'Amico M., Laranci P., Scozza E., Zagaroli M. (2015). Recovery of precious metals from scrap printed circuit boards through pyrolysis. J Anal Appl Pyrolysis., vol 111, 140-147.

Cayumil R., Khanna R., Rajarao R., Mukherjee P. S., Sahajwalla V. (2016). Concentration of precious metals during their recovery from electronic waste. Waste Mannag., vol. 57, 121-130.

Choubey, P. K., Panda, R., Jha, M. K., Lee, J., Pathak, D. D. (2015). Recovery of copper and recycling of acid from the leach liquor of discarded Printed Circuit Boards (PCBs). Sep. Purif. Technol. Vol 156, 269-275.

Cui H., Anderson C. G. (2016). Literature review of hydrometallurgical recycling of printed circuit boards (PCBs). J Adv Chem Eng., vol 6, n. 1.

Diaz L. A., Lister T. E., Parkman J. A., Clark G. G. (2015) Comprehensive process for the recovery of value and critical material from electronic waste. J Clean Prod., vol. 125, 236-244.

Ghosh B., Ghosh M. K., Parhi P., Mukherjee P. S., Mishra B. K. (2015). Wasted Printed Circuit Boards recycling: An extensive assessment of current status. J Clean Prod., vol 94, 5-19.

Gurung, M., Adhikari, B. B., Kawakita, H., Ohto, K., Inoue, K., Alam, S. (2013). Recovery of gold and silver from spent mobile phones by means of acidothiourea leaching followed by adsorption using biosorbent prepared from persimmon tannin. Hydrometallurgy, vol 133, 84–93.

Ilyas S., Ruan C., Bhatti H. N., Ghauri M. A., Anwar M. A. (2010). Column bioleaching of metals from electronic Scrap. Hydrometallurgy., vol. 101, n. 3-4, 135-140.

Ilyas, S., Anwar, M. A., Niazi, S. B. (2007). Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. Hydrometallurgy. vol. 88, 180-188.

Kaya M. (2016). Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manag., vol 57, 64-90.

KITCO. (2018). Live Silver Price. Available on: http://www.kitco.com/charts/livesilver.html.

Kumar A., Holuszko M., Espinosa D. C. R. (2017). E-waste: An overview on generation, collection, legislation and recycling practices. Resour Conserv Recy., vol. 122, 32-42.

Kumar, V., Lee, J., Jeong, J., Jha, M. K., Kim, B., Singh, R. (2015). Recycling of printed circuit boards (PCBs) to generate enriched rare metal concentrate. J. Ind. Eng. Chem., vol 21, 805-813.

LME (London Metal Exchange). 2020a. LME Copper official prices. Available on: https://www.lme.com/Metals/Non-ferrous/Copper#tabIndex=0.

LME (London Metal Exchange). 2020b. LME Silver. Available on: https://www.lme.com/Metals/Precious-metals/LME-Silver#tabIndex=2

Neto, I. F. F., SOUSA, C. A., Brito, M. S. C. A., Futuro, A. M, Soares, H. V. M. (2016). A simple and nearly-closed cycle process for recycling copper with high purity from end life printed circuit boards. Sep. Purif. Technol., vol 164, 19-27.

Official Journal of the European Union (2003a). Directive 2002/96/EC of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE). Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0019.

Official Journal of the European Union (2003b). Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS). Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32002L0095.

Shokri A., Pahlevani F., Levick K., Cole I., Sahajwalla V. (2017). Synthesis of cooper-tin nanoparticles from old computer printed circuit boards. J Clean Prod., vol. 142, 2586-2592.

Silvas F. P. C., Correa M. M. J., Caldas M. P. K., Moraes V. T., Espinosa D. C. R., Tenorio J. A. S. (2015). Printed circuit board recycling: physical processing and copper extraction by selective leaching. Waste Manag., vol. 46, 503-510.

Xu Y., Li J., LiliLiu. (2016). Current status and future perspective of recycling copper by hydrometallurgy from waste printed circuit boards. Procedia Environ Sci., vol. 31, 162-170

Zhou Y., Qiu K. (2010). A new technology for recycling materials from waste printed circuit boards. J Hazard Mater., vol. 175, 823-828.

Žiūkaitė S., Ivanauskas R., Tatariants M., Denafas G. (2017). Feasibilities for hydrometallurgical recovery of precious metals from waste printed circuit boards in Lithuania. Chemija, vol. 28, 109-116.

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CHARACTERIZATION AND PYROLYSIS OF POST-CONSUMER LEATHER SHOE WASTE FOR THE RECOVERY OF VALUABLE CHEMICALS

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ABSTRACT

Majority of post-consumer leather footwear currently ends up in landfill sites with adverse environmental impacts. Current waste recovery options have proven largely unsuccessful in minimizing this waste stream. This study investigates whether leather from post-consumer footwear can be pyrolyzed using gram-scale (fixed-bed) and microgram-scale (TGA) pyrolysis reactors. The investigation was conducted using final pyrolysis process temperatures between 450 and 650 °C and solid residence times of 5 to 15 minutes. The purpose of the experiments was to assess the waste recovery potential of leather pyrolysis products for valuable chemicals. The pyrolysis product fractions (solid, liquid, and gas) distribution were investigated, optimal pyrolysis conditions presented, and the product fractions characterized for their elemental and chemical composition using ultimate and GC-MS analysis. The distribution of the product fractions proved leather footwear pyrolysis was viable under the given conditions. The completion of leather footwear pyrolysis was evident at 650°C since the solid yield reached a constant value of approximately 25 wt.%. The liquid fraction was maximized within the temperature range of 550-650°C (Max= 54 wt.%), suggesting optimal pyrolysis conditions within this range. The higher heating values (HHVs) of the pyrolysis leather oil (33.6 MJ/kg) and char (25.6 MJ/kg) suggested their potential application for energy or fuel. The liquid fraction comprised predominantly of nitrogen derivatives and potential applications areas include use in the production of fertilizers, chemical feedstocks, or the pharmaceutical industry. This study proved that leather from post-consumer footwear can be pyrolyzed and provided valuable insight into its characterization and potential applications areas.

1. INTRODUCTION

Post-consumer shoe waste is a fundamental problem facing the footwear industry and waste management sectors. The footwear industry is rapidly growing, and it was estimated that in 2017 the production of shoes reached 23.5 billion pairs (Portuguese Shoes, 2018). The rapid production and consumption of footwear correspond to a substantial amount of post-consumer waste, the majority of which are currently disposed of in landfill sites (Kolomaznik et al., 2008, and Chowdhury, 2018). According to Mia et al. (2017), the most significant environmental challenge facing the footwear industry is the large amount of post-consumer waste generated in the End-of-Life (EoL) phase.

Leather waste constitutes a significant portion of waste emanating from the footwear industry because it is a prominent material used, with the average shoe constituting approximately 25% leather by weight (Staikos et al., 2006). Leather waste from post-consumer shoes is detrimental in its EoL phase because of the adverse environmental impacts associated with its disposal. Studies detailing the negative environmental impacts of leather shoe disposal highlight issues related to freshwater contamination, eutrophication, degradation of ecosystem quality, harmful emissions, and Global Warming Potential (GWP) (Albers et al., 2008, Joseph and Nithya, 2009, and Gottfridson and Zhang, 2015). Additionally, the footwear industry accounts for 1.4% of global climate impacts (Chrobot et al., 2018:18), and it is estimated that a single pair of leather shoes takes approximately 25-40 years to decompose in landfill sites (Fyvie, 2018). This study examines the poten-

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tial of pyrolysis as a waste recovery avenue to reduce the amount of post-consumer leather shoe waste disposed of in landfill sites.

According to Czajczyńska et al. (2017), pyrolysis is the thermochemical devolatilization of organic or inorganic materials at elevated temperatures in an inert atmosphere. The heating of materials through pyrolysis leads to the formation of solid, liquid, and gas fractions (Arabiourrutia et al., 2020). Pyrolysis is advantageous over other waste treatment processes such as incineration because the oxygen-free atmosphere in which pyrolysis takes place causes fewer CO_2 emissions, thus lowering the greenhouse effect (Jo et al., 2017). Moreover, incineration and open combustion are inefficient waste recovery methods as the technology merely recovers energy while reducing the remainder of the materials to ash (Aylón et al., 2010). Murugan et al. (2008) state that pyrolysis technology can process the materials into three main fractions (solid, liquid, and gas) to recover valuable chemicals that would otherwise be lost during incineration or open combustion. These chemicals can be further processed into valuable products and hence improve waste recovery efficiency from materials. Food waste (Joe et al., 2017), plastic (Sorum et al., 2001, Olazar et al., 2009, and Sharuddin et al., 2016), and waste tyres (Islam et al., 2013, Perondi et al., 2016, and Lopez et al., 2017) are among some of the most widely studied materials using pyrolysis experiments. There are, however, limited studies that examine the potential of pyrolysis for recovering leather shoe waste.

Previous studies on leather pyrolysis focus mainly on waste from tanneries. A study on the production of useful materials from different types of leather tannery wastes was conducted by Yilmaz et al. (2007). The study investigated the experimental characteristics of leather waste pyrolysis at 450 and 600°C. The pyrolysis experiments indicated that leather waste heated using a fixed bed reactor at 450 and 600°C yielded liquid, gas, and char products. Increasing the final temperature from 450 to 600°C caused the liquid yield to decrease from 32 to 28% and the gas yield to increase from 17 to 23%. The authors emphasized the desirability of activated carbon, a refined version of the pyrolysis solid fraction (char), from pyrolyzed leather waste. Similarly, a study by Sethuraman et al. (2013) subjected hazardous chrome tanned leather waste (CTLW) from tanneries to pyrolysis to obtain valuable products. The main useful products generated through this process included carbonaceous residual ash containing chromium, condensate oil, and fuel gas (Sethuramen et al., 2013).

Marcilla et al. (2012) investigated the effect of flash (450-550°C) and slow (up to 750°C) pyrolysis on bovine leather from tanneries. Flash pyrolysis generally involves a faster heating rate and a shorter solid residence time compared to slow pyrolysis (Al Arni, 2018). Authors indicated that the maximum liquid yield (42-45%) was achieved through flash pyrolysis between temperatures of 500-550°C, while slow pyrolysis presented significantly lower levels of liquid yield (29%). This finding is supported by literature indicating that flash pyrolysis generally optimizes the production of liquid yields while slow pyrolysis favors char as the main byproduct (Ronsse et al., 2012, and Al Arni, 2018). Kluska et al. (2019) focused on presenting the influence of temperature on the physicochemical properties of products obtained through the pyrolysis of leather tannery waste at lower temperature ranges. The leather waste was pyrolyzed at temperatures ranging from 300 to 500°C. The authors concluded that a maximum liquid yield of 42% was obtained at 400°C, followed by 40% at 500°C. A summary of the main leather waste pyrolysis studies and their corresponding yields is presented in Table 1.

Previous studies contribute to knowledge generation about the recovery of leather tannery waste, but they do not address the issue of post-consumer leather waste specifically for footwear products. It can thus be inferred that a gap in the literature exists to investigate whether leather shoe waste can be pyrolyzed similarly to tannery waste

TABLE 1: Summary of previous leather pyrolysis studies.

Reference	Pyrolysis type	Temperature (°C)	Solid yield (wt.%)	Liquid yield (wt.%)	Gas yield (wt.%)	Sample mass (g)	Reactor	Solid residence time (min)
Sethuraman et al. (2013)	Slow	800	34.7	33.3	32.0	2000	Fixed bed	n.a
Yilmaz et al. (2007)	Slow	450	50.2	32.0	17.8	50-60	Fixed bed	120
		600	47.4	28.9	23.6			
Marcilla et al. (2012)	Fast	450	38.5	41.0	20.5	2	Fixed bed	n.a
		500	30.4	44.5	25.1			
		550	31.0	42.3	26.6			
	Slow	700	28.6	29.6	41.8	4		
Kluska et al. (2019)	Slow	300	33.0	21.0	46.0	100	Fixed bed	30
		350	33.0	35.0	32.0			
		400	33.0	42.0	25.0			
		450	33.0	35.0	32.0			
		500	29.0	40.0	31.0			

to recover materials. This research is premised primarily as a concept proving and desirability study. The concept proving aspect is justified through the study's focus on investigating whether chrome tanned leather from post-consumer footwear has the potential to be pyrolyzed through experimental runs. The optimization of pyrolysis yields was also investigated through experimental runs, and this constituted the desirability aspect of the study. The novelty of the study reveals itself in the fact that leather from post-consumer footwear has yet to be pyrolyzed and hence motivates the need for this study as footwear presents challenges in the EoL phase.

The present study therefore examined waste recovery by thermochemical treatment by conducting pyrolysis experiments using samples of solid leather waste from post-consumer shoes. The main aim of this study was to assess the waste recovery potential of leather pyrolysis products for valuable chemicals. The aim was achieved through the following investigations (i) leather footwear pyrolysis experiments using fixed bed and TGA pyrolysis reactors; (ii) an analysis of the pyrolysis product distribution and optimal operating conditions; (iii) characterization of the elemental and chemical composition of the pyrolysis product yields using ultimate and GC-MS analysis, including an analysis of the higher heating value (HHV).

2. MATERIALS AND METHODS

2.1 Leather feedstock

Samples of leather shoes were obtained from various local shoe producers for pyrolysis. The samples consisted of reject shoes which are considered waste as they can no longer be used or sold. The shoe samples consisted of chrome tanned leather which was separated from the shoe soles to obtain leather in isolation from the other materials. The leather was cut into smaller pieces with particle sizes of approximately 0.5 cm. The shredded leather from various shoes was mixed before use in the experimental pyrolysis runs to ensure feedstock homogeneity. The weight of each sample was 40g.

Preliminary experimental preparations included characterizing the sample material. To characterize and understand the constituents of the sample material, a proximate and ultimate analysis was conducted. The proximate analysis was performed to determine the major constituents of the feed material used in pyrolysis, while the ultimate analysis provided an elemental composition of the material (Basu, 2018). The results of the proximate and ultimate analyses of leather shoe waste are depicted in Table 2. The results are shown in comparison to previous studies which have been conducted on leather waste. These characteristics are essential to understand as they provide a broad understanding of the combustion characteristics of solid leather shoe waste.

2.2 Experimental setup

2.2.1 Fixed bed reactor

The pyrolysis unit chosen for this study was a fixed bed reactor. The fixed bed pyrolysis system comprised of a fixed bed of feedstock which was pyrolyzed as a batch reaction (Guda et al., 2015). The main features of the fixed bed reactor used in this study included a sample capacity of approximately ±45g (depending on the density and type of material) and a reactor temperature range between 0-1200°C. The dimensions of the fixed bed reactor can be found in Figure 1. The fixed bed reactor provided technology that was reliable and simple for the research purposes in this study (Aziz et al., 2018). A fixed bed reactor feedstock system was thus suitable for this research study as it was conducted on a small-scale for research purposes and allowed for a proof of the concept.

2.2.2 Pyrolysis system

The pyrolysis system used in this study is illustrated in Figure 1. This system involved the input of the leather waste feedstock into the sample holder placed inside of

TABLE 2: Ultimate and proximate analysis of leather waste in previous studies.

Reference	Sethuraman et al. (2013)	Yilmaz et al. (2007)	Marcilla et al. (2012)	Kluska et al. (2019)	Rodrigues et al. (2010)	Godinho et al. (2011)	Present study
Proximate analysis (wt. %)							
Moisture content	5.50	7.10	11.20	35.30	12.40	14.10	12.56
Volatile matter	60.30	67.00	76.70	67.90	67.70	66.40	61.23
Fixed carbon	26.62	n.d	6.12	21.20	14.80	14.52	18.77
Ash	7.58	9.60	6.03	10.90	5.10	4.95	7.44
Ultimate analysis (wt. %) [a]							
Carbon	55.31	44.30	41.50	41.71	50.61	42.36	38.93
Hydrogen	7.86	3.10	6.85	7.12	8.79	7.32	5.62
Oxygen [b]	8.54	36.60	37.90	28.46	25.46	19.00	32.36
Nitrogen	12.56	14.20	12.90	11.01	12.80	10.67	8.88
Sulfur	4.68	1.80	0.83	3.43	1.89	1.57	1.65

[a] *Dry basis*
[b] *By difference*

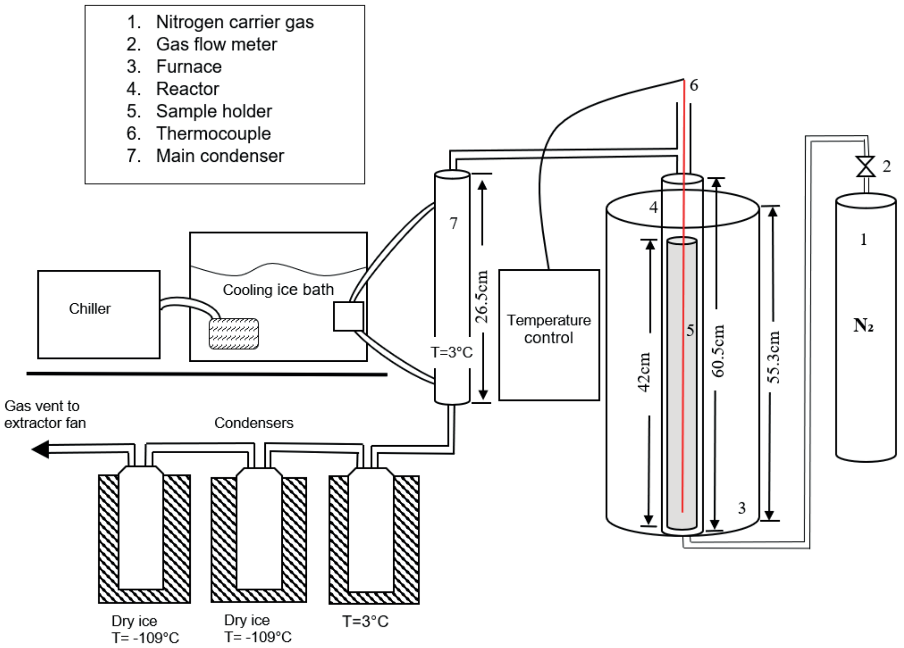

FIGURE 1: Pyrolysis system used in this study.

the fixed bed reactor. The feedstock was exposed to high temperatures within the fixed bed reactor in the absence of oxygen. The flow of the nitrogen (N_2) carrier gas created an inert atmosphere within the system. As the feedstock was heated, it experienced physical and chemical separation into different molecules. The thermal devolatilization led to the formation of products in the form of solids (char) and volatiles (condensable and non-condensable or permanent gases) (Hirvonen, 2017). The liquid only formed from the condensable volatiles when it cooled in the condenser to allow separation into pyrolysis oil and permanent gas. The cooling system used as a part of the pyrolysis unit was a chiller and an ice bath which was connected to the condenser to enable a cold temperature ranging between 1-3°C. Three collectors ensued after the condenser, and these were placed in dry ice to ensure sufficient time to allow further condensation of the high volatile condensables to liquid products from the leather feedstock. The inclusion of the last two condensers was motivated by the additional liquid fractions observed in these condensers. These condensers allowed for further condensation and therefore accounted for all liquid fractions. The non-condensable gases flowed through a vent into an extractor fan.

2.3 Experimental design

The processing factors considered in the experimental design of this study were temperature, solid residence time, and N_2 flow rate. The temperature range, solid residence time, and center points were chosen based on the typical ranges cited in the literature and the operability range of the existing pyrolysis setup.

Operating temperature is the most critical parameter in Thermochemical Conversions (TCCs) because the temperature of the reactor is directly correlated to the product yields obtained (He et al., 2000). For this study, the operating temperatures chosen were 450, 550, and 650°C, including lower and higher axial points of 409 and 691°C, respectively (Table 3). Previous studies were considered when selecting the temperature range used in the present study (Yilmaz et al., 2007, Marcilla et al., 2012, and Kluska et al., 2019). The center point temperature chosen for pyrolysis (550°C) was motivated by the fact that pyrolysis appears to be complete by this temperature as the majority of the sample devolatilization has taken place in this range. Choosing the temperature range of 450 and 650°C with a center point of 550°C enables the researcher to draw parallels with previous studies to verify whether pyrolysis of leather shoe waste is achievable in a comparable manner to leather tannery waste (Yilmaz et al., 2007, Marcilla et al., 2012, and Kluska et al., 2019). The use of different temperature ranges in the pyrolysis reactor enabled the researcher to determine the differences in product yields and the optimal conditions for leather footwear pyrolysis.

Solid residence time refers to the amount of time that the feedstock remains inside the reactor (Gao et al., 2017). The solid residence time used in pyrolysis studies is an important parameter that can influence product yields (Dhyani and Bhaskar, 2018). For this study, the solid residence time reflects the amount of time the sample was held inside the reactor once the processing temperature was met. The hold times used in this study had a center point of 10 minutes and lower and upper levels of 5 and 15 minutes, respectively (Table 3). The lower and higher axial points are 3 and 17 minutes, respectively. The continuous flow of N2 gas flow created an oxygen-free atmosphere within the reactor (Aziz et al., 2018). An inert atmosphere is imperative as it creates conditions which are chemically inactive to ensure pyrolysis takes place without the risk of contamination from oxidizing gases such as oxygen (Jo et

TABLE 3: Central composite design (CCD) factors.

Factor	Unit	Factor type	Lower level (-1)	Center point (0)	Upper level (+1)	Lower axial (-1.414)	Higher axial (+1.414)
Temperature	°C	Variable	450	550	650	409	691
Solid residence time	min	Variable	5	10	15	3	17
Nitrogen flow rate	L/min	Constant	±6.5	±6.5	±6.5	±6.5	±6.5
Particle size	cm	Constant	0.5	0.5	0.5	0.5	0.5
Sample amount	g	Constant	40	40	40	40	40
Solid yield	wt.%	Response					
Liquid yield	wt.%	Response					
Gas yield	wt.%	Response					

al., 2017). The nitrogen flow rate (99.5% purity, Afrox, South Africa) remained constant at 6.5L/min for the pyrolysis experiments in this study. It was essential to ensure the nitrogen flow rate remained constant to provide a controlled inert atmosphere and to prevent counter airflow that may have compromised the experimental runs.

This study used a two-level full factorial design with a replication of experiments to verify the results. A central composite design (CCD) was employed with three center points, and an overview of the design and response factors are provided in Table 3. This experimental design enabled the researcher to investigate the optimization of operating conditions for pyrolysis yields. A statistical analysis of the variance was also employed using Minitab® 19 Statistical Software. A response surface model was fitted to determine the effects of temperature and solid residence time on each of the pyrolysis yields. Moreover, this also aided the researcher in identifying conditions that optimized the pyrolysis yields within the study.

2.4 Mass balance

The mass balance was a central component used to calculate the yields for each experimental pyrolysis run. The reactor and condensers were weighed before and after each pyrolysis experiment to calculate the percentage of solid, liquid, and gas yields. The difference in weight within the reactor was attributed to the remaining char whilst the difference in the condenser weight was attributed to the liquid yield. The gas yield was calculated using the difference in weight, and hence the remaining fraction was allocated to the gas yield.

2.5 Analytical techniques

2.5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was one of the analytical methods employed in this study. Through TGA, it was possible to assess the weight loss function of temperature under the nitrogen atmosphere (Sethuraman et al., 2013). According to Januszewicz et al. (2016), TGA enables users to determine the characteristics of the temperature dependence of weight loss at a constant heating rate. TGA assumes that several products can form from a single substrate (Januszewicz et al., 2016). It can, therefore, be inferred that the number and types of products formed from the leather waste were proportional to changes in mass decomposition.

In this study, TGA experiments were performed on chrome-tanned leather waste using a sample mass of 10±0.5mg and particle size ranges of 0.5 to 0.8mm. The samples were inserted into 70 µL alumina sample holders and experiments were performed using the DTG-60AH detector (Shimadzu, Kyoto, Japan). The temperature range was between 25 and 800°C, and the heating rate was 25°C/min. An inert atmosphere was created using nitrogen (99.5% purity, Afrox, South Africa) with a flow rate of 80ml/min. TGA experiments were carried out three times to ensure reproducibility of the observed results.

2.5.2 Elemental analysis

The second analytical technique used in this study was an elemental analysis, which is also known as an ultimate analysis. This is the process through which the sample of leather material was analyzed for its elemental composition (Basu, 2018). The elemental composition in terms of Carbon, Hydrogen, Nitrogen, and Sulfur (CHNS) was determined for the raw leather shoe waste, the residual char, and the liquid oil fractions. This analysis was used to determine the ratio of elements from within the leather samples and the composition of the solid and liquid pyrolytic yields. The instrument used for this analysis was the Thermo Fisher Scientific Flash 2000 CHNS-O Organic Elemental Analyzer. The results of the ultimate analysis (C, H, N and O content) were also used to estimate the higher heating values (HHVs) of the pyrolysis product fractions using the correlation equation (1) (Mkhize et al., 2015, and Demirbas, 2016). The HHV is significant as it provides an indication of the amount of heat released and hence the energy density of the solid and liquid fractions.

$$HHV = 33.5[C] + 142.3[H] - 15.4[O] - 14.5[N] \times 10^{-2} \qquad (1)$$

2.5.3 Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) (Shimadzu GC-MS QP2010SE series model) was used to detect compounds from the liquid yield. The compounds were detected using the gas chromatographic retention times and identified in the mass spectrometer. The sample was swept through a capillary column (Zebron ZB-5MSplus 30m x 0,25mm, 0,25um id). using helium (99.9% purity, Air products, South Africa) as the carrier gas and components were separated based on the volatility and affinity of the mixture. The method used for the analysis was as follows: the initial temperature was set at 40°C; the final temperature was set at 270°C; the heating rate was 10°C per minute, and the total time for the run was 48 minutes. A qualitative analysis of the chromatogram was conducted using the NIST mass spectral library (version 4.0) to identify the compounds present in the liquid yield. Since the qualitative analysis was used the researcher emphasized determining what constituted the liquid yields rather than determining exactly how much of each compound was present. The qualitative nature of the study is elaborated on in the following section.

2.6 Concept proving and desirability study

This research was premised primarily as a concept proving and desirability study. The focus was placed on establishing whether chrome tanned leather from post-consumer footwear has the potential to be pyrolyzed. Pyrolysis experimental runs were used to determine optimal conditions for pyrolysis product yields, and this constituted the desirability aspect of the study. The quantities of the pyrolysis yields were considered concerning the processing temperature and solid residence time. In addition, the emphasis was placed on the replication of pyrolysis experimental runs to ensure the validity of the research findings. The GC-MS had a qualitative focus in its methodology for the analysis of the liquid yields. The constituents of the liquid yields were analyzed in this study with a greater focus on the composition of the yield rather than the quantities.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

The thermogravimetric analysis (TGA) of chrome-tanned leather samples for a heating rate of 25°C/min revealed that the first mass loss of the sample is apparent between 0 and 150°C (Figure 2). The mass loss observed in this temperature range is attributed to the release of inherent moisture contained within the sample. Yilmaz et al. (2007) describe this component of the liquid yield as the aqueous phase. An explanation for this peak is that the pyrolysis temperature reached close to 100°C, which is the temperature at which water evaporates (Kluska et al., 2019). According to Pham et al. (2018) water absorbs heat and uses it to evaporate and can also play a role in delaying devolatilization. The majority of the mass loss is observed between 250 and 550°C, with the most significant mass release peak occurring at 350°C (Figure 2). A 50% reduction in mass was experienced between 250 and 550°C resulting in the large weight loss peak in the DTG curve. This mass release is caused by the thermal devolitilisation of volatile organic compounds present in the leather sample. The maximum temperature peak demonstrates the significant impact that heat transport has on forming the mass loss curves. The TGA curve begins to flatten after 550°C indicating the near completion of pyrolysis. Additionally, it is observed that after pyrolysis is complete, the remaining mass accounts for approximately 25 wt.% of the sample (Figure 2).

3.2 Pyrolysis yields from leather shoe waste

This section outlines the product yields as a result of pyrolyzing leather shoe waste. Available data from the literature indicates that the mass balance of different types of pyrolysis products is dependent on the final temperature in the pyrolysis process (Yilmaz et al., 2007, and Xiao and Yang, 2013). The effect of temperature and solid residence time on the pyrolysis yields (solid, liquid, and gas) were investigated through CCD experiments according to the parameters outlined in Table 3. The results obtained from the CCD experiments are summarized in Table 4. The averages of the solid, liquid, and gas yields are presented in conjunction with the standard deviation (SD) in Table 4.

3.2.1 Solid yield

The solid yield consisted of char, a carbonaceous material generated through the thermal devolatilization of leather in the pyrolysis reactor. The solid yields ranged between

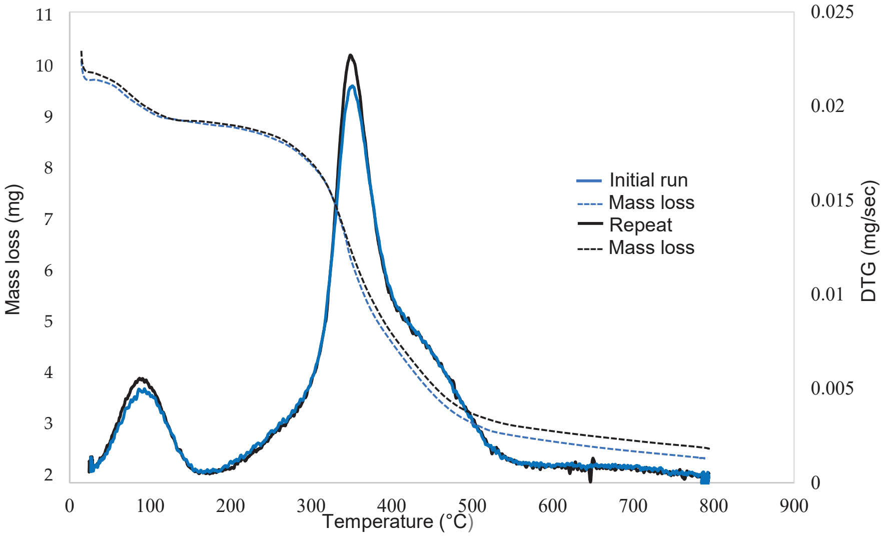

FIGURE 2: TGA and mass loss curve for leather waste in a nitrogen atmosphere with a heating rate of 25°C/min.

TABLE 4: Central Composite Design (CCD) of experiments.

Run no.	Pyrolysis parameters		Leather pyrolysis products		
	Temperature (°C)	Time (min)	Solid yield (wt.%)	Liquid yield (wt.%)	Gas yield[a] (wt.%)
			Average ±SD	Average ±SD	Average ±SD
1.	409	10	42.63±0.88	38.43±3.01	19.00±2.12
2.	450	5	38.38±2.30	45.50±1.06	16.13±3.36
3.	450	15	33.50±0.71	46.88±2.30	21.30±5.13
4.	550	3	29.63±1.59	49.63±3.36	20.75±4.95
5.	550	10	27.75±2.47	52.63±1.94	19.63±4.42
6.	550	17	27.75±2.30	40.38±1.94	32.25±4.24
7.	650	5	24.75±1.06	51.75±2.47	23.50±3.54
8.	650	15	24.63±0.88	46.25±2.12	29.13±3.01
9.	691	10	24.50±0.00	46.63±2.30	28.88±2.30

[a] *By difference*

42.63 to 35.94 wt.% at temperatures of 409 and 450°C, respectively (Table 4). This change in mass indicates that at lower temperatures, pyrolysis was incomplete. Molecular components were unable to devolatilise at lower temperatures fully and only the weak chemical bonds were broken (He et al., 2018). These yields are congruent with previous studies that revealed solid fractions from leather tannery waste between a similar range of 33 and 38.5 wt.% at 450°C (Marcilla et al., 2015, Kluska et al., 2018, and Fang et al., 2018). Moreover, at 550°C, the present study indicated a mass of 28.25 wt.% that is consistent with the yields obtained by Marcilla et al. (2012). The similar solid yields between studies reveal that leather waste from shoes can be pyrolyzed to yield similar results to leather tannery waste.

The response surface model in Figure 3 provides a visual representation of the interactions between temperature and hold time on the solid yield. It is observed that there is a negative correlation between temperature and solid yield because an increase in temperature corresponds to a decrease in the solid yield. As the temperature increases past 600°C, the response surface begins to flatten with lower yields indicating the near completion of pyrolysis. The relationship between solid residence time and solid yield appears to be less significant compared to temperature. This is because only minor differences in the solid fraction distribution were observed as a function of the hold time.

The solid yield reached a constant value of approximately 25 wt.% at 650°C, indicating the completion of leather pyrolysis under CCD conditions. The completion of pyrolysis can be verified since the solid yield remaining corresponds to the fixed carbon and ash proportions of the leather sample in Table 2. This is further verified through an examination of the remaining mass in TGA experiments which accounts for approximately 25 wt.% of the sample (Figure 2). The char yields obtained through pyrolysis operating at two different scales are illustrated in Table 5. The fixed bed pyrolyzer operated using a gram-scale whilst the TGA operated using a microgram-scale. The yields are comparable since the solid fractions are similar for both setups. The slight variations in the wt. % may be attributed

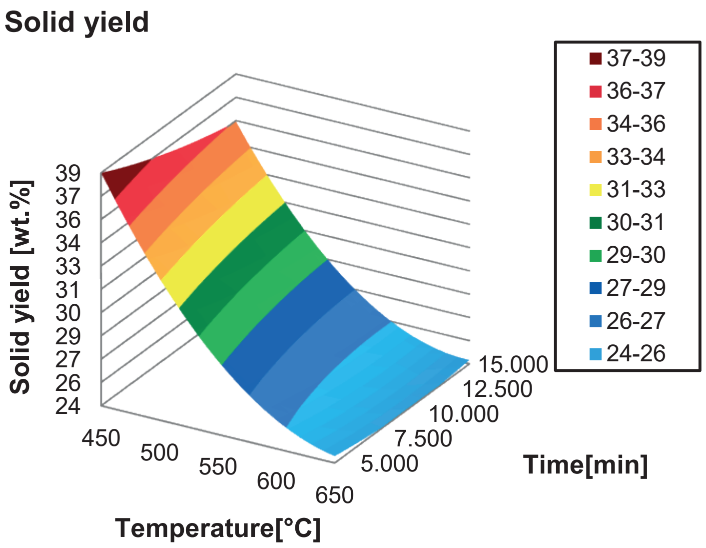

FIGURE 3: . Response surface model illustrating the effect of temperature and hold time on solid yield.

TABLE 5: Solid yields for CCD pyrolysis and TGA experiments.

Temperature (°C)	Fixed bed pyrolyzer (wt. %)	TGA (wt. %)
409	42.63	46.85
450	36.94	39.17
550	28.25	30.45
650	24.69	28.45
690	24.5	27.56

TABLE 6: Elemental composition of char obtained from leather shoe waste.

Components	Char (wt. %) [a]	TGA (wt. %)
Nitrogen	8.69	46.85
Carbon	62.67	39.17
Hydrogen	2.36	30.45
Sulfur	0.74	28.45
Oxygen [b]	12.98	27.56

[a] Dry basis [b] By difference.

to differences in the heating rates across the two setups. TGA had a controlled heating rate whilst the fixed bed pyrolyzer had a heating rate that was more variable and hence less constant in comparison. The comparability of the findings at different scales, as well as the consistency of the char yields with the fixed carbon and ash content, verifies the completion of pyrolysis under CCD conditions and further suggests the suitability of leather shoes for pyrolysis technology.

The elemental composition of char generated from leather shoe waste pyrolysis is shown in Table 6, with carbon taking the largest share of the composition. The higher heating value of the solid fraction was determined to be 25.55 MJ/kg. The char generated through pyrolysis could be used in the metallurgical sector. According to Filho et al. (2016), carbonized leather residues have the potential to partially replace coal in the metallurgical process, especially if they have a high heating value of 20.8MJ/kg. Since the HHV was 25.55 MJ/kg in this study this reinforces its potential use in this sector. Moreover, Bañón et al. (2016) pointed out that char may be used as cheap fuel, either pure or blended with other fuels. Yilmaz et al. (2007) also reported that char products from pyrolyzed leather could be used in the production of activated carbon and as an adsorbent of dyes from aqueous solutions.

3.2.2 Liquid yield and analysis

The liquid yield ranged between 36.25 and 54 wt.% at temperatures of 409 and 550°C, respectively. An increase in the process temperature corresponded to a rise in the liquid yield up to 550°C. It has been well documented that tar formation rate should increase with an increase in the pyrolysis temperature (Xiao and Yang, 2013, Bañón et al., 2016, and Baniasadi et al., 2016). The liquid fraction was maximized within the temperature range of 550-650°C. This finding is affirmed in Figure 4 since the liquid yield peaks between 550 and 650°C. The convex profile of the response surface reveals a well-defined optimum condition for the liquid yield. The highest liquid yield was achieved at 550°C with a hold time of 10 minutes (54 wt.%), and a close second was observed at 650°C with a hold time of 5 minutes (53.5 wt.%) (Table 4). The current findings are supported by Marcilla et al. (2012) and Kluska et al. (2019), who observed the maximum liquid yields within a similar temperature range of 500-550°C. The general findings from the CCD experiments and the convex shape of the response surface suggest that leather waste from shoes can be pyrolyzed between an optimal temperature range of 550-650°C.

Lower liquid yields were evident at lower temperatures corresponding with high solid yields. For instance, a liquid yield of 36.25 (wt.%) was reached at 409°C whilst solid yields remained high, accounting for 42.63 (wt.%) of the yield at 409°C. Since polymeric components could not fully

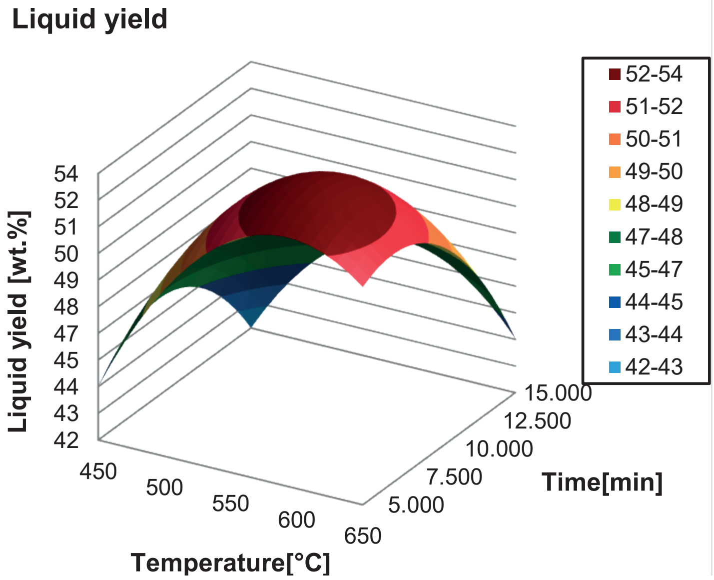

FIGURE 4: Response surface model illustrating the effect of temperature and hold time on liquid yield.

devolatilise at lower temperatures, this explains the high char yields at lower temperatures and corresponding low liquid yields.

The liquid fraction comprised of the aqueous phase (water content) and the organic phase (oil) (Yilmaz et al., 2007). The approximate weight basis ratio of the liquid content is 1-part oil to 3-parts water (1:3). The water-soluble fraction consists of lower molecular weight substances whilst the oil consists predominantly of brown tar that contains higher molecular weight compounds. The elemental composition of the oils obtained from leather shoe waste is shown in Table 7. It should be noted that the elemental weighting is comparable to those reported from chrome-tanned leather shavings in the study by Yilmaz et al. (2007). In both studies, carbon had the highest share of the elemental composition.

The high presence of carbon from the ultimate analysis indicates a high energy density within the leather pyrolysis oil. The higher heating value (HHVs) of the liquid fraction was determined to be 33.62MJ/kg at 550°C. This value is significantly higher than HHVs for many other waste pyrolysis oils. For instance, Table 8 shows a comparison of the HHVs between leather oil, biomass derived pyrolysis oils and conventional oils. The HHV of the leather pyrolysis oils are higher than biomass pyrolysis oils such as softwood lignin (30.04 MJ/kg) (Ben and Ragauskas, 2011), softwood barks (25.3-26.7 MJ/kg)(Ben et al., 2019), wood and agricultural residues (16.0-19.0 MJ/kg)(Zhang et al., 2007, and Meier et al., 2013) and pine/spruce wood (16.4-17.6 MJ/kg) (Chiaramonti et al., 2007). In addition, the leather oil HHVs are higher than low-grade coal (18 MJ/kg) (Dinçer and Zamfirescu, 2014) but lower than conventional oils such as diesel (45.7 MJ/kg) and gasoline (47.3 MJ/kg) (Channiwala and Parikh, 2002). The HHV of the leather oil therefore indicates it has potential as an energy source or fuel.

3.2.3 Gas yield

In general, the gas fraction comprised a smaller share of the product yield in comparison to the solid and liquid fractions. The results indicate that, within the evaluated temperature range, the highest gas yield occurred at 550°C and 650°C during experimental runs that had a longer hold time. The lowest gas yield was observed at 450°C with a short hold time of 5 minutes. The low gas yield is likely attributed to the incomplete pyrolysis at this temperature, which accounts for the corresponding high solid yield. Higher process temperatures led to an increase in the gas yields at 550°C and 650°C whilst the lower process temperature of 450°C with a hold time of 5 minutes caused the lowest gas yield. This finding was consistent with the work of Yilmaz et al. (2007), which found similar trends of increasing gas yields and decreasing char yields as a function of higher temperatures.

TABLE 7: Elemental composition of oil obtained from leather shoe waste.

Components	Oil (wt. %)
Nitrogen	8.33
Carbon	69.64
Hydrogen	8.57
Sulfur	1.16
Oxygen [b]	12.98

[b] *By difference.*

TABLE 8: Comparison of HHVs for leather pyrolysis oil, other waste pyrolysis oils and conventional fuels.

Fuel type	HHVs (MJ/kg)	Reference
Leather oil	33.6	Present study
Biomass derived pyrolysis oils		
Softwood craft lignin	30.04	(Ben and Ragauskas, 2011)
Softwood barks (Raw pine, Douglas-Fir and Pine)	25.3-26.7	(Ben et al., 2019)
Wood and agricultural residues	16.0-19.0	(Zhang et al., 2007)
Wood-derived bio-oil	17.0	(Meier et al., 2013)
Pine/spruce wood	16.4-17.6	(Chiaramonti et al., 2007)
Low-grade coal	18	(Dinçer and Zamfirescu, 2014)
Conventional oils		
Diesel	45.7	(Channiwala and Parikh, 2002)
Gasoline	47.3	(Channiwala and Parikh, 2002)

A visual representation of the gas yield distribution as a function of temperature and hold time is shown in Figure 5. The increase in the gas yield can be correlated to factors including the fragmentation of the longer chained condensable volatile molecules and the sublimation of the char to permanent gases. Holding time had a less significant influence on gas yield in comparison to processing temperature. A possible explanation for this is because gas flow, heating rate and residence time of the hot condensable volatiles have a greater influence on the fragmentation of heavy molecules to light molecules in comparison to holding time. In addition, another influential factor was the fairly rapid reaction during pyrolysis which meant that even at lower hold times pyrolysis was near completion, which influenced the gas yield distribution. The response surface in Figure 5 reveals that the correlation between variables and the gas yield is less significant in comparison to trends found in the solid and liquid yields response surface. The variability in the gas yield correlating to an increase in temperature and hold time is supported by results found by Yilmaz et al. (2007). In the study by Yilmaz, a final temperature increase from 450 to 600°C caused an increase in gas yield from 17 to 23 wt.% similar to this study. Similarly, Marcilla et al. (2012) observed that gas yields tended to rise with an increase in process temperature.

3.3 Gas chromatography-mass spectrometry analysis

The results of the GC-MS analysis of leather shoe waste are presented in this section. Each of the liquid fractions from the CCD pyrolysis experiments was analyzed using the GC-MS. In total, nine liquid yields were analyzed with an initial and repeated run to ensure the replicability of findings. The general trends are discussed to provide a concise synopsis of the types of compounds present in the liquid fraction.

The results of the GC-MS analysis show a complex spectrum of liquid products from leather shoe waste. The ten major compounds identified in each of the experiments are summarized in Table 9. The main compounds identified in each of the experiments were italicized in Table 9 to emphasize their significance. The majority of the detected compounds correspond to nitrogen derivatives, which is related to the protein content of the leather shoe waste (Font et al., 1999, Sethuraman et al., 2014, and Kluska et al., 2019). The major compounds identified across GC-MS runs are 9-Octadecenamide, (Z)-; Octadecanamide, 9-Octadecenoic acid, 1,2,3-propanetriyl ester; n-Heptadecanol-1 and 13-Docosenamide. It is noteworthy that 9-Octadecenamide, (Z)-; 9-Octadecenoic acid, 1,2,3-propanetriyl ester; and 13-Docosenamide are isomers since there is a different positioning of the functional group at position 9 and 13, respectively, instead of the normal position. It is important to take note of isomers given the differences in the arrangement of atoms within the molecule, despite the similarity in the molecular formula.

On average, the chromatograms of the liquid yield identified between 100-150 different peaks. The spectrum of compounds formed were complex, most of which were attributed to protein decomposition. As an example, Table 10 shows the list of compounds identified by the GC-MS analyzer from pyrolytic liquid yield at 550°C with a hold time of 10 minutes. The detected compounds in the liquid yield correspond to the chromatogram peaks depicted in Figure 6. Each peak in the chromatogram represents a compound present in the sample. The x-axis of the chromatogram represents the retention time(min), and the y-axis represents the detector response and hence the peaks of the different compounds. The motivation for presenting the results of only one of the chromatograms and tables is because there was minimal discrimination between the composition of the liquid sample yields, and a summary of the significant compounds is depicted in Table 9. The similarity index (SI) values for each peak are also presented in Table 10, according to the mass spectra libraries used. SI compares the query mass spectra with the reference mass spectra via spectrum matching and hence indicates the degree of certainty of the identified compound (Wei et al., 2014). Approximately 41% of the peaks in Table 10 present SI values greater than 90%. The relatively high SI values, therefore, suggest that there was a high level of certainty amongst the identified compounds.

The main types of compounds identified in the sample were grouped based on their structure. Table 11 depicts the percentage of compounds classified according to their composition. The main group of compounds present in

TABLE 9: GC-MS chromatogram main compound list for the different pyrolytic liquid fractions.

Pyrolytic liquid fractions	Compound name	Retention time (min)
Yield 1 (450°C; 5min)	Oleanitrile	30.42
	9-Octadecenoic acid, 1,2,3-propanetriyl ester	31.24
	Octadecanamide	31.51
	N-Methyldodecanamide	31.71
	Cyclobutane, 3-hexyl-1,1,2-trimethyl-, cis-	31.84
	Triethylene glycol monododecyl ether	32.11
	9-Octadecenamide, (Z)-	33.04
	Octadecanamide	33.23
	9-Octadecenamide, N,N-dimethyl-	33.55
	Pyrrolidine, 1-(6-methyl-1-oxooctadecyl)-	35.08
Yield 2 (650°C; 5 min)	Phosphonic acid, (p-hydroxyphenyl)-	16.32
	Caprolactam	21.28
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.31
	n-Heptadecanol-1	30.42
	Hexadecanamide	31.44
	Coumarin-3-carbonitrile, 6-methyl-	31.66
	1,8-Diazacyclotetradecane-2,9-dione	32.64
	9-Octadecenamide, (Z)-	33.03
	9-Octadecenamide, (Z)-	33.08
	Octadecanamide	33.23
Yield 3 (450°C; 15min)	(1H)Pyrrole-2-carbonitrile, 5-methyl-	20.98
	Phenol, 2-undecyl-	21.06
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.24
	n-Heptadecanol-1	30.42
	Octadecanamide	31.43
	Phenol, 4,4'-(1-methylethylidene)bis-	31.75
	Benzeneacetic acid, 4-pentadecyl ester	31.87
	9-Octadecenamide, (Z)-	33.01
	9-Octadecenamide, (Z)-	33.06
	Octadecanamide	33.20

Yield 4 (650°C; 15min)	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-	27.64
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.25
	Oleanitrile	30.44
	6-Octadecenoic acid, (Z)-	31.31
	Octadecanamide	31.54
	9-Octadecenamide, (Z)-	33.09
	13-Docosenamide, (Z)-	33.14
	Octadecanamide	33.28
	N-Methyldodecanamide	33.35
	9-Octadecenamide, N,N-dimethyl-	33.57
Yield 5 (550°C; 10min)	Aniline	15.22
	Caprolactam	21.09
	1-Octadecanol	28.38
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyr	29.25
	n-Heptadecanol-1	30.40
	Octadecanamide	31.44
	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(	31.87
	Triethylene glycol monododecyl ether	32.09
	9-Octadecenamide, (Z)-	33.05
	Octadecanamide	33.19
Yield 6 (409°C; 10 min)	Caprolactam	20.92
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.20
	1-Hexadecanol	30.41
	9-Octadecenoic acid, 1,2,3-propanetriyl ester	31.26
	Octadecanamide	31.53
	9-Octadecenamide, (Z)-	33.04
	Octadecanamide	33.23
	9-Octadecenamide, N,N-dimethyl-	33.55
	9-Octadecenoic acid (Z)-, 2-butoxyethyl ester	35.41
	Cholesta-3,5-diene	40.02
Yield 7 (691°C; 10 min)	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.28
	Oleanitrile	30.45
	Hexadecanenitrile	30.62
	6-Octadecenoic acid, (Z)-	31.40
	Octadecanamide	31.63
	N-Methyldodecanamide	31.69
	1H-Isoindole-1,3(2H)-dione, 2-(2-propynyl)-	31.77
	13-Docosenamide, (Z)-	33.16
	Octadecanamide	33.32
	9-Octadecenamide, N,N-dimethyl-	33.58
Yield 8 (550°C; 17min)	Oleanitrile	30.39
	Octadecanamide	30.82
	N-Methyldodecanamide	31.01
	6-Octadecenoic acid, (Z)-	31.33
	Octadecanamide	31.56
	N-Methyldodecanamide	31.64
	D-Mannohexadecane-1,2,3,4,5-pentaol	31.70
	Cyclopropanecarboxylic acid,pentadecyl ester	32.03
	9-Octadecenamide, (Z)-	32.87
	13-Docosenamide, (Z)-	33.03
Yield 9 (550°C; 3min)	Phenol, 2-methyl-	17.33
	1H-Indene, 1-methylene-	19.56
	Caprolactam	21.08
	Naphthalene, 2-methyl-	21.57
	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo	29.20
	n-Heptadecanol-1	30.34
	Octadecanamide	31.37
	9-Octadecenamide, (Z)-	32.93
	9-Octadecenamide, (Z)-	32.98
	Octadecanamide	33.21

TABLE 10: Peak Report TIC.

Peak #	R Time	Area %	Formula	A/H Name	SI (%)
1	11.767	0.20	$C_6H_{11}N$	Hexanenitrile	95
2	13.692	0.21	C_6H_9N	1H-Pyrrole, 2,5-dimethyl-	92
3	15.224	1.79	C_6H_7N	Aniline	96
4	15.380	0.64	C_7H_5N	Benzonitrile	95
5	15.870	0.61	$C_6H_7O_4P$	Phosphonic acid, (p-hydroxyphenyl)-	96
6	15.932	1.62	C_6H_6O	Phenol	96
7	16.000	0.34	$C_7H_{11}N$	1H-Pyrrole, 2-ethyl-4-methyl-	88
8	16.181	0.50	$C_5H_6N_2$	2-Aminopyridine	95
9	16.458	0.92	$C_{10}H_{16}$	D-Limonene	95
10	16.560	0.22	$C_8H_{18}O$	1-Hexanol, 2-ethyl-	88
11	16.786	0.14	C_9H_9Cl	1H-Indene, 1-chloro-2,3-dihydro-	95
12	17.369	1.15	C_7H_8O	Phenol, 2-methyl-	97
13	17.415	0.27	C_7H_9N	p-Aminotoluene	92
14	17.476	0.40	C_7H_9N	p-Aminotoluene	98
15	17.856	1.04	C_7H_8O	p-Cresol	95
16	17.935	0.51	$C_6H_8N_2$	2-Pyridinamine, 3-methyl-	90
17	18.067	0.36	C_8H_7N	Benzonitrile, 4-methyl-	96
18	18.240	0.24	$C_8H_{10}O$	Phenol, 2,5-dimethyl-	92
19	18.560	0.17	$C_7H_{12}O$	1-Heptyn-4-ol	74
20	18.689	0.24	$C_8H_{18}O_2$	1-Butanol, 4-butoxy-	92
21	18.725	0.18	C_8H_7N	Benzyl nitrile	92
22	19.095	0.32	$C_8H_{10}O$	Phenol, 2,4-dimethyl-	89
23	19.521	0.71	$C_7H_{10}N_2$	Pyridine, 2-aminomethyl-6-methyl-	70
24	19.581	0.53	$C_{10}H_8$	Naphthalene	98
25	19.695	0.43	$C_9H_{17}NO$	Octane, 1-isocyanato-	78
26	20.414	0.33	C_9H_9N	Benzenepropanenitrile	96
27	20.459	0.18	$C_8H_{10}Cl_2$	Cyclohexene, 1-chloro-4-(1-chloroethenyl)-	88
28	20.684	0.32	$C_9H_{12}O$	Phenol, 3-(1-methylethyl)-	92
29	21.088	7.76	$C_6H_{11}NO$	Caprolactam	94
30	21.362	0.26	$C_{11}H_{10}$	Naphthalene, 2-methyl-	90
31	21.604	0.65	$C_{11}H_{10}$	Naphthalene, 2-methyl-	91
32	22.017	0.72	$C_5H_8N_2O_2$	2,4-Imidazolidinedione, 5,5-dimethyl-	69
33	22.640	0.20	$C_9H_{16}O_2$	Bicyclo[3.3.1]nonane-2,9-diol, exo-anti-	67
34	22.731	0.12	C_9H_9N	1H-Indole, 6-methyl-	94
35	23.692	0.30	$C_{12}H_{26}O$	1-Dodecanol	94
36	23.811	0.15	$C_{12}H_{24}BNO$	(hexahydro-2H-azepin-2-onato-N1,O2)bis(1-methylethyl)-, (t-4)-	73
37	25.055	0.20	$C_5H_4N_4O$	1H-Imidazo(4,5-d)pyridazin-7-ol	78
38	25.400	0.37	$C_8H_{18}O_2$	1-Butanol, 4-butoxy-	80
39	25.497	0.12	$C_8H_7NS_2$	Benzothiazole, 2-(methylthio)-	85
40	26.160	0.44	$C_{16}H_{30}Cl_2O_2$	Dichloroacetic acid, tetradecyl ester	81
41	26.603	0.18	$C_{14}H_{30}O_2$	Ethanol, 2-(dodecyloxy)-	91
42	26.694	1.28	$C_{11}H_{10}N_2O$	Furaldehyde phenylhydrazone	75
43	26.894	0.95	$C_{10}H_{14}N_2O_3$	3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	84
44	26.965	0.34	$C_{10}H_{14}O$	Benzene, (1-methylpropoxy)-	64
45	27.110	0.12	$C_{10}H_8N_2O$	3-Phenoxypyridazine	77
46	27.210	0.53	$C_{10}H_{14}N_2O_3$	3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	72
47	27.403	0.32	$C_{17}H_{31}F_3O_2$	Trifluoroacetic acid, pentadecyl ester	91
48	27.470	0.47	$C_{14}H_{29}Br$	2-Bromotetradecane	77
49	27.560	1.07	$C_{11}H_{24}O$	Undecanol-4	77
50	27.620	1.36	$C_7H_{10}N_2O_2$	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-	87
51	27.780	0.20	$C_{15}H_{22}N_2O_4$	2,6-Piperidinedione, 1,1'-(1,5-pentanediyl)bis-	73
52	28.181	0.11	$C_{16}H_{22}O_4$	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	89
53	28.377	2.42	$C_{18}H_{38}O$	1-Octadecanol	87
54	28.572	0.31	$C_{15}H_{29}N$	Pentadecanenitrile	94
55	28.941	0.47	$C_8H_{12}O_3$	6-Hydroxy-9-oxa-bicyclo[3.3.1]nonan-3-one	69
56	29.145	0.41	$C_{11}H_{18}N_2O_2$	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	75
57	29.246	3.37	$C_{14}H_{22}N_2O_2$	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	93

58	29.346	1.26	C11H18N2O2	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	86
59	29.517	0.20	C16H34O3	Diethylene glycol monododecyl ether	90
60	30.105	0.28	C11H18O2	2-Propanone, 1-(1-cyclohexen-1-yl)-3-ethoxy-	59
61	30.174	0.21	C18H36O	9-Octadecen-1-ol, (Z)-	96
62	30.403	3.16	C17H36O	n-Heptadecanol-1	92
63	30.507	0.25	C17H32O2	7-Hexadecenoic acid, methyl ester, (Z)-	73
64	30.595	0.36	C14H27N	Tetradecanenitrile	85
65	30.677	0.70	C7H9N5O	1-[3-Pyridyl]-3-amidine urea	65
66	30.793	0.12	C22H46O2	Ethanol, 2-(eicosyloxy)-	89
67	31.011	0.81	C7H9NO2	Ethyl 2-cyanocrotonate	75
68	31.095	0.63	C13H14N2	Benzenamine, 4,4'-methylenebis-	88
69	31.145	1.53	C18H38S	1-Octadecanethiol	87
70	31.439	8.69	C18H37NO	Octadecanamide	90
71	31.647	1.14	C13H27NO	N-Methyldodecanamide	81
72	31.741	2.07	C15H16O2	Phenol, 4,4'-(1-methylethylidene)bis-	75
73	31.869	2.71	C11H18N2O2	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	62
74	32.093	2.14	C18H38O4	Triethylene glycol monododecyl ether	88
75	32.265	1.33	C26H52	Cyclohexane, 1,4-didecyl-	76
76	32.405	1.11	C19H28O2	m-Toluic acid, undec-2-enyl ester	77
77	32.525	1.25	C12H22N2O2	1,8-Diazacyclotetradecane-2,9-dione	90
78	32.625	0.73	C22H46O2	Ethanol, 2-(eicosyloxy)-	91
79	32.725	0.81	C18H18O2	4,4'-Diallyloxydiphenyl	55
80	33.050	11.86	C18H35NO	9-Octadecenamide, (Z)-	88
81	33.194	3.84	C18H37NO	Octadecanamide	95
82	33.370	1.17	C14H16N2O2	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)-	79
83	33.445	0.57	C13H27NO	N-Methyldodecanamide	88
84	33.625	1.27	C20H39NO	9-Octadecenamide, N,N-dimethyl-	77
85	33.790	0.56	C22H38O2	Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester	78
86	33.874	0.56	C18H38O4	Triethylene glycol monododecyl ether	89
87	34.051	0.74	C24H50O	n-Tetracosanol-1	83
88	34.574	0.87	C20H42O5	Tetraethylene glycol monododecyl ether	91
89	34.721	1.01	C10H18O3	1,3-Dioxolan-4-one, 2-(1,1-dimethylethyl)-5-(1-methylethyl)-, (2S-cis)-	75
90	35.292	0.44	C16H34O3	Diethylene glycol monododecyl ether	87
91	36.075	0.21	C36H58	15,17,19,21-Hexatriacontatetrayne	57
92	36.154	0.43	C18H38O4	Triethylene glycol monododecyl ether	90
93	36.838	0.43	C10H18O3	1,3-Dioxolan-4-one, 2-(1,1-dimethylethyl)-5-(1-methylethyl)-, (2S-cis)-	75
94	36.933	0.64	C18H34O7	2,2'-(2,2'-Oxybis(ethane-2,1-diyl)bis(oxy))bis(ethane-2,1-diyl) dipentanoate	75
95	37.136	0.30	C20H42O5	Tetraethylene glycol monododecyl ether	88
96	37.636	0.31	C22H39NO	Pyrrolidine, 1-(1-oxo-10-octadecynyl)-	66
97	38.272	0.57	C26H54O8	Heptaethylene glycol monododecyl ether	92
98	39.542	0.54	C18H38O4	Triethylene glycol monododecyl ether	88
99	39.835	0.41	C30H61Br	Triacontane, 1-bromo-	72
100	39.985	1.02	C27H44	Cholesta-3,5-diene	94

the liquid fraction are compounds containing nitrogen or nitrogen and oxygen atoms in their structure. This finding is consistent with studies by Marcilla et al. (2012) and Kluska et al. (2019), which also identified nitrogenated compounds as the main group of compounds from the analysis of liquid fraction from leather pyrolysis. The percentage of nitrogenated compounds in this study were, however, significantly lower in comparison to the study by Marcilla. The justification for this difference is because this study utilized slow pyrolysis in comparison to fast pyrolysis in the study by Marcilla et al. (2012). This is an important factor to consider as it influences the liquid product composition. The second major group found in the liquid fraction was oxygenated compounds (containing ketones, aldehydes, alcohols, and acids), followed by aromatics, phenols, alkanes, and alkenes, and lastly, sulfur-containing compounds. The compound distribution found in this study exhibit similarities to those reported by Fang et al. (2018).

Based on the composition of the liquid fraction, it would be useful for the following applications. The abundance of NH_2 groups present in the liquid fraction makes it potentially valuable for the production of fertilizers (Marcilla et al., 2012). According to Yilmaz et al. (2007), the liquid yield can additionally be useful as a chemical feedstock or a fuel after retreatments such as hydrogenation, Fischer–Tropsch synthesis, or stream cracking. Some of the main compounds from the liquid chemistries including Octadecanamide and 13-Docosenamide have useful applications as adhesives and sealant chemicals, anti-adhesive agents, as well as lubricants and or surface agents (NCBI, 2020a., and NCBI, 2020b). According to Getachew et al. (2016), oleamides may present industrial applications such as lubricants,

TABLE 11: Liquid yield compound classification.

Classification type	Percentages of compounds (%)
N or N/O compounds	40
O compounds	35
Alkanes and alkenes	9
Aromatics	6
Phenols	6
S compounds	2
	100

(N or N/O = compounds containing N or N and O; O compounds = compounds containing oxygen; alkanes and alkenes=hydrogen and carbon compounds; aromatics = aromatics; phenols = phenol and its derivates; S compounds =compounds containing sulfur)

corrosion inhibitors and slip agents. Specific compounds, such as pyrrole and its derivatives, can be useful as intermediates in the synthesis of pharmaceuticals, perfumes, agrochemicals, and dyes (Marcilla et al., 2012, and Kaur et al., 2017). To achieve the applications for leather footwear pyrolysis products it is necessary to consider that processing would be required in order to improve the product quality through purifying, refining and upgrading the products.

A limitation of pyrolysis in this study, and in general, is that it relies on an external energy supply to reach its processing temperatures, which is often derived from non-renewable sources. Future leather pyrolysis studies should therefore consider solar assisted pyrolysis to overcome this obstacle by prioritizing the utilization of solar energy for thermochemical processing (Morales et al., 2014, and Weldekidan et al., 2018).

4. CONCLUSIONS

This study investigated whether leather from post-consumer footwear could be pyrolyzed using gram-scale (fixed-bed) and microgram-scale (TGA) pyrolysis reactors. The distribution of the product fractions proved that leather footwear pyrolysis was viable under the given conditions. It was shown through an examination of pyrolysis product distribution and characterization that leather footwear has waste recovery potential, hence contributing to the overall aim of the study.

The results of this study showed that pyrolysis temperature has a significant effect on the product yields. According to the results obtained, the liquid yield was maximized within the temperature range of 550-650°C (Max= 54 wt.%). The solid yield decreased substantially from 43 wt.% to 25 wt.% with an increase in the reactor temperature. The solid yield indicated the completion of leather footwear pyrolysis at 650°C since a constant value of approximately 25 wt.% was reached. This was verified since the solid yield remaining corresponded to the fixed carbon and ash proportions characterized in the leather sample. There was a general increase of gas yields as a function of higher temperatures and longer residence times, explained by decreasing char yields in the leather sample.

The pyrolysis product yields were characterized, and the char yield revealed that it may be suitable as a solid fuel due to its high calorific value (25.55 MJ/kg). A wide distribution of pyrolytic compounds were presented in this study, with nitrogenated derivatives forming the major group from the liquid yield. Based on the composition of the liquid yields, potential applications include use in the production of fertilizers, use as a chemical feedstock and use in the pharmaceutical industry. In addition, some of the main compounds found present potential industrial applications including use as adhesives, sealant chemicals, anti-adhesive agents, lubricants, and surface agents. Due to the composition of the pyrolysis product yields, however, it is necessary to consider retreatment before application to remove impurities. The pyrolysis oil presented a gross calorific value higher than biomass derived pyrolysis oils and low-grade coal. This indicated its potential as an energy source or fuel. It can therefore be concluded that the leather pyrolysis oils present a more valuable source of energy than some biomass pyrolysis oils.

Future work should investigate the quantitative aspect of the compounds present in the pyrolysis yields. This would further substantiate the potential for reuse applications and the viability of recovering these materials from leather footwear in practice.

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REFERENCES

Al Arni, S. (2018). Comparison of slow and fast pyrolysis for converting biomass into fuel. Renewable Energy, 124, 197-201. https://doi.org/10.1016/j.renene.2017.04.060

Albers, K., Canepa, P., & Miller, J. (2008). Analyzing the Environmental Impacts of Simple Shoes (Masters). University of Santa Barbara.

Arabiourrutia, M., Lopez, G., Artetxe, M., Alvarez, J., Bilbao, J., & Olazar, M. (2020). Waste tyre valorization by catalytic pyrolysis – A review. Renewable And Sustainable Energy Reviews, 129, 109932. https://doi.org/10.1016/j.rser.2020.109932

Aylón, E., Fernández-Colino, A., Murillo, R., Navarro, M., García, T., & Mastral, A. (2010). Valorisation of waste tyre by pyrolysis in a moving bed reactor. Waste Management, 30(7), 1220-1224. https://doi.org/10.1016/j.wasman.2009.10.001

Aziz, M., Rahman, M., & Molla, H. (2018). Design, fabrication and performance test of a fixed bed batch type pyrolysis plant with scrap tire in Bangladesh. Journal Of Radiation Research And Applied Sciences, 11(4), 311-316. https://doi.org/10.1016/j.jrras.2018.05.001

He, B.J., Zhang, Y., Yin, Y., Funk, T.L., & Riskowski, G.L. (2000). OPERATING TEMPERATURE AND RETENTION TIME EFFECTS ON THE THERMOCHEMICAL CONVERSION PROCESS OF SWINE MANURE. Transactions Of The ASAE, 43(6), 1821-1825. https://doi.org/10.13031/2013.3086

Baniasadi, M., Tugnoli, A., Conti, R., Torri, C., Fabbri, D., & Cozzani, V. (2016). Waste to energy valorization of poultry litter by slow pyrolysis. Renewable Energy, 90, 458-468. https://doi.org/10.1016/j.renene.2016.01.018

Bañón, E., Marcilla, A., García, A., Martínez, P., & León, M. (2016). Kinetic model of the thermal pyrolysis of chrome tanned leather treated with NaOH under different conditions using thermogravimetric analysis. Waste Management, 48, 285-299. https://doi.org/10.1016/j.wasman.2015.10.012

Basu, P. (2018). Biomass gasification, pyrolysis and torrefaction (3rd ed., pp. 479-495). Elsevier.

Ben, H., & Ragauskas, A. (2011). NMR Characterization of Pyrolysis Oils from Kraft Lignin. Energy & Fuels, 25(5), 2322-2332. https://doi.org/10.1021/ef2001162

Ben, H., Wu, F., Wu, Z., Han, G., Jiang, W., & Ragauskas, A. (2019). A Comprehensive Characterization of Pyrolysis Oil from Softwood Barks. Polymers, 11(9), 1387. https://doi.org/10.3390/polym11091387

Channiwala, S., & Parikh, P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel, 81(8), 1051-1063. https://doi.org/10.1016/s0016-2361(01)00131-4

Chiaramonti, D., Oasmaa, A., & Solantausta, Y. (2007). Power generation using fast pyrolysis liquids from biomass. Renewable And Sustainable Energy Reviews, 11(6), 1056-1086. https://doi.org/10.1016/j.rser.2005.07.008

Chrobot, P., Faist, M., Gustavus, L., Martin, A., Stamm, A., Zah, R., & Zollinge, M. (2018). Measuring fashion: Environmental impact of the global apparel and footwear industries study. Full report and methodological considerations. Lausanne: Quantis.

Chowdhury, Z., Ahmed, T., Antunes, P., & Paul, H. (2018). Environmental Life Cycle Assessment of Leather Processing Industry: A Case Study of Bangladesh. Journal- Society Of Leather Technologists And Chemists, 102. Retrieved 11 November 2020, from.

Czajczyńska, D., Nannou, T., Anguilano, L., Krzyżyńska, R., Ghazal, H., Spencer, N., & Jouhara, H. (2017). Potentials of pyrolysis processes in the waste management sector. Energy Procedia, 123, 387-394. https://doi.org/10.1016/j.egypro.2017.07.275

Demirbas, A. (2016). Calculation of higher heating values of fatty acids. Energy Sources, Part A: Recovery, Utilization, And Environmental Effects, 38(18), 2693-2697. https://doi.org/10.1080/15567036.2015.1115924

Dinçer, I., & Zamfirescu, C. (2014). Advanced power generation systems. Elsevier.

Dhyani, V., & Bhaskar, T. (2018). A comprehensive review on the pyrolysis of lignocellulosic biomass. Renewable Energy, 129, 695-716. https://doi.org/10.1016/j.renene.2017.04.035

Fang, C., Jiang, X., Lv, G., Yan, J., Lin, X., Song, H., & Cao, J. (2018). Pyrolysis characteristics and Cr speciation of chrome-tanned leather shavings: influence of pyrolysis temperature. Energy Sources, Part A: Recovery, Utilization, And Environmental Effects, 41(7), 881-891. https://doi.org/10.1080/15567036.2018.1520366

Filho, A., Lange, L., de Melo, G., & Praes, G. (2016). Pyrolysis of chromium rich tanning industrial wastes and utilization of carbonized wastes in metallurgical process. Waste Management, 48, 448-456. https://doi.org/10.1016/j.wasman.2015.11.046

Font, R., Caballero, J., Esperanza, M., & Fullana, A. (1999). Pyrolytic products from tannery wastes. Journal Of Analytical And Applied Pyrolysis, 49(1-2), 243-256. https://doi.org/10.1016/s0165-2370(98)00117-x

Fyvie, E. (2018). Trash revolution: Breaking the Waste Cycle. Kids Can Press, Limited.

Gao, N., Quan, C., Liu, B., Li, Z., Wu, C., & Li, A. (2017). Continuous Pyrolysis of Sewage Sludge in a Screw-Feeding Reactor: Products Characterization and Ecological Risk Assessment of Heavy Metals. Energy & Fuels, 31(5), 5063-5072. https://doi.org/10.1021/acs.energyfuels.6b03112

Getachew, P., Getachew, M., Joo, J., Choi, Y., Hwang, D., & Hong, Y. (2016). The slip agents oleamide and erucamide reduce biofouling by marine benthic organisms (diatoms, biofilms and abalones). Toxicology And Environmental Health Sciences, 8(5), 341-348. https://doi.org/10.1007/s13530-016-0295-8

Godinho, M., Birriel, E., Marcilio, N., Masotti, L., Martins, C., & Wenzel, B. (2011). High-temperature corrosion during the thermal treatment of footwear leather wastes. Fuel Processing Technology, 92(5), 1019-1025. https://doi.org/10.1016/j.fuproc.2010.12.025

Gottfridsson, M., & Zhang, Y. (2015). Environmental impacts of shoe consumption: Combining product flow analysis with an LCA model for Sweden (Masters). Chalmers University of technology.

Guda, V., Steele, P., Penmetsa, V., & Li, Q. (2015). Fast Pyrolysis of Biomass: Recent Advances in Fast Pyrolysis Technology. In A. Pandey, M. Stöcker, T. Bhaskar & R. Sukumaran, Recent Advances in Thermochemical Conversion of Biomass (pp. 177-211). Elsevier. Retrieved 12 November 2020, from.

He, X., Liu, Z., Niu, W., Yang, L., Zhou, T., & Qin, D. et al. (2018). Effects of pyrolysis temperature on the physicochemical properties of gas and biochar obtained from pyrolysis of crop residues. Energy, 143, 746-756. https://doi.org/10.1016/j.energy.2017.11.062

Hedberg, Y., Lidén, C., & Odnevall Wallinder, I. (2015). Chromium released from leather – I: exposure conditions that govern the release of chromium(III) and chromium(VI). Contact Dermatitis, 72(4), 206-215. https://doi.org/10.1111/cod.12329

Hirvonen, P. (2017). The potential of waste tyre and waste plastics pyrolysis in Southern Savonia region (Masters). Lappeenranta University of Technology.

Islam, M., Islam, M., Mustafı, N., Rahim, M., & Haniu, H. (2013). Thermal Recycling of Solid Tire Wastes for Alternative Liquid Fuel: The First Commercial Step in Bangladesh. Procedia Engineering, 56, 573-582. https://doi.org/10.1016/j.proeng.2013.03.162

Januszewicz, K., Klein, M., Klugmann-Radziemska, E., & Kardas, D. (2016). Thermogravimetric analysis/pyrolysis of used tyres and waste rubber. Physicochemical Problems Of Mineral Processing, 53, 802–811. https://doi.org/doi:10.1515/cpe-2017-0028.

Jo, J., Kim, S., Shim, J., Lee, Y., & Yoo, Y. (2017). Pyrolysis Characteristics and Kinetics of Food Wastes. Energies, 10(8), 1191. https://doi.org/10.3390/en10081191

Joseph, K., & Nithya, N. (2009). Material flows in the life cycle of leather. Journal Of Cleaner Production, 17(7), 676-682. https://doi.org/10.1016/j.jclepro.2008.11.018

Kaur, R., Rani, V., Abbot, V., Kapoor, Y., Konar, D., & Kumar, K. (2017). Recent synthetic and medicinal perspectives of pyrroles: An overview. Journal Of Pharmaceutical Chemistry & Chemical Science, 1, 17-32. Retrieved 12 November 2020, from.

Kluska, J., Ochnio, M., Kardaś, D., & Heda, Ł. (2019). The influence of temperature on the physicochemical properties of products of pyrolysis of leather-tannery waste. Waste Management, 88, 248-256. https://doi.org/10.1016/j.wasman.2019.03.046

Kolomaznik, K., Adamek, M., Andel, I., & Uhlirova, M. (2008). Leather waste—Potential threat to human health, and a new technology of its treatment. Journal Of Hazardous Materials, 160(2-3), 514-520. https://doi.org/10.1016/j.jhazmat.2008.03.070

Lopez, G., Alvarez, J., Amutio, M., Mkhize, N., Danon, B., & van der Gryp, P. et al. (2017). Waste truck-tyre processing by flash pyrolysis in a conical spouted bed reactor. Energy Conversion And Management, 142, 523-532. https://doi.org/10.1016/j.enconman.2017.03.051

Marcilla, A., León, M., García, Á., Bañón, E., & Martínez, P. (2012). Upgrading of Tannery Wastes under Fast and Slow Pyrolysis Conditions. Industrial & Engineering Chemistry Research, 51(8), 3246-3255. https://doi.org/10.1021/ie201635w

Meier, D., van de Beld, B., Bridgwater, A., Elliott, D., Oasmaa, A., & Preto, F. (2013). State-of-the-art of fast pyrolysis in IEA bioenergy member countries. Renewable And Sustainable Energy Reviews, 20, 619-641. https://doi.org/10.1016/j.rser.2012.11.061

Mia, A., Murad, W., Ahmad, F., & Uddin, K. (2017). Waste Management & Quality Assessment of Footwear Manufacturing Industry in Bangladesh: An Innovative Approach. International Journal Of Engineering Management, 7. Retrieved 11 November 2020, from.

Mkhize, N., Sithole, B., & Ntunka, M. (2015). Heterogeneous Acid-Catalyzed Biodiesel Production from Crude Tall Oil: A Low-Grade and Less Expensive Feedstock. Journal Of Wood Chemistry And Technology, 35(5), 374-385. https://doi.org/10.1080/02773813.2014.984079

Morales, S., Miranda, R., Bustos, D., Cazares, T., & Tran, H. (2014). Solar biomass pyrolysis for the production of bio-fuels and chemical commodities. Journal Of Analytical And Applied Pyrolysis, 109, 65-78. https://doi.org/10.1016/j.jaap.2014.07.012

Murugan, S., Ramaswamy, M., & Nagarajan, G. (2008). The use of tyre pyrolysis oil in diesel engines. Waste Management, 28(12), 2743-2749. https://doi.org/10.1016/j.wasman.2008.03.007

National Center for Biotechnology Information. (2020a). PubChem Compound Summary for CID 31292, Octadecanamide. Pubchem.ncbi.nlm.nih.gov. Retrieved 27 September 2020, from https://pubchem.ncbi.nlm.nih.gov/compound/Octadecanamide.

National Center for Biotechnology Information. (2020b). PubChem Compound Summary for CID 8214, 13-Docosenamide, (13Z)-. Pubchem.ncbi.nlm.nih.gov. Retrieved 27 September 2020, from https://pubchem.ncbi.nlm.nih.gov/compound/13-Docosenamide_-_13Z.

Olazar, M., Lopez, G., Amutio, M., Elordi, G., Aguado, R., & Bilbao, J. (2009). Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. Journal Of Analytical And Applied Pyrolysis, 85(1-2), 359-365. https://doi.org/10.1016/j.jaap.2008.10.016

Perondi, D., Scopel, B., Collazzo, G., Silva, J., Botomé, M., & Dettmer, A. et al. (2016). Characteristics of Pyrolysis Products from Waste Tyres and Spent Foundry Sand Co-Pyrolysis. Progress In Rubber Plastics And Recycling Technology, 32(4), 213-240. https://doi.org/10.1177/147776061603200403

Pham, X., Piriou, B., Salvador, S., Valette, J., & Van de Steene, L. (2018). Oxidative pyrolysis of pine wood, wheat straw and miscanthus pellets in a fixed bed. Fuel Processing Technology, 178, 226-235. https://doi.org/10.1016/j.fuproc.2018.05.029

Portuguese Shoes. (2018). World Footwear Yearbook: Intelligence to drive your business. Portuguese Shoes.

Rodrigues, R., Marcilio, N., Trierweiler, J., Godinho, M., & Pereira, A. (2010). Co-Gasification of Footwear Leather Waste and High Ash Coal: A Thermodynamic Analysis. In The 27th Annual International Pittsburgh coal conference. Istanbul. Retrieved 12 November 2020, from.

Ronsse, F., van Hecke, S., Dickinson, D., & Prins, W. (2012). Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. GCB Bioenergy, 5(2), 104-115. https://doi.org/10.1111/gcbb.12018

Sethuraman, C., Srinivas, K., & Sekaran, G. (2013). Double Pyrolysis of Chrome Tanned Leather Solid Waste for Safe Disposal and Products Recovery. International Journal Of Engineering Research, 4. Retrieved 11 November 2020, from.

Sethuraman, C., Srinivas, K., & Sekaran, G. (2014). Pyrolysis coupled pulse oxygen incineration for disposal of hazardous chromium impregnated fine particulate solid waste generated from leather industry. Journal Of Environmental Chemical Engineering, 2(1), 516-524. https://doi.org/10.1016/j.jece.2013.10.006

Sharuddin, S., Abnisa, F., Daud, W., & Aroua, M. (2016). A review on pyrolysis of plastic wastes. Energy Conversion And Management, 115, 308-326. Retrieved 11 November 2020, from.

Sørum, L., Grønli, M., & Hustad, J. (2001). Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel, 80(9), 1217-1227. https://doi.org/10.1016/s0016-2361(00)00218-0

Staikos, T., Rahimifard, S., Heath, R., & Haworth, B. (2006). End-of-life management of shoes and the role of biodegradable materials. In Proceedings of the 13th CIRP international conference on Life Cycle Engineering (LCE) (pp. 497–502). Bardos; Loughborough: Centre for Sustainable Manufacturing and Recycling Technologies (SMART). Retrieved 12 November 2020, from.

Wei, X., Koo, I., Kim, S., & Zhang, X. (2014). Compound identification in GC-MS by simultaneously evaluating the mass spectrum and retention index. The Analyst, 139(10), 2507-2514. https://doi.org/10.1039/c3an02171h

Weldekidan, H., Strezov, V., & Town, G. (2018). Review of solar energy for biofuel extraction. Renewable And Sustainable Energy Reviews, 88, 184-192. https://doi.org/10.1016/j.rser.2018.02.027

Xiao, R., & Yang, W. (2013). Influence of temperature on organic structure of biomass pyrolysis products. Renewable Energy, 50, 136-141. https://doi.org/10.1016/j.renene.2012.06.028

Yılmaz, O., Cem Kantarli, I., Yuksel, M., Saglam, M., & Yanik, J. (2007). Conversion of leather wastes to useful products. Resources, Conservation And Recycling, 49(4), 436-448. https://doi.org/10.1016/j.resconrec.2006.05.006

Zhang, Q., Chang, J., Wang, T., & Xu, Y. (2007). Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion And Management, 48(1), 87-92. https://doi.org/10.1016/j.enconman.2006.05.010

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THE POSSIBILITY OF SECONDARY RESOURCE RECOVERY DURING WASTE DISPOSAL SITE RECLAMATION

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ABSTRACT

Nowadays, Russian waste management policies demand the closure and elimination of dumpsites and landfills historically located in the vicinity of populated areas, with no reference to geological and hydrological conditions. Landfill mining is one of the technical solutions for old dumpsite reclamation. The unique feature of this study is the application of an integrated scenario approach in the evaluation of landfill mining projects. This approach is based on a scenario matrix that compares costs and revenues for each scenario, depending on resource and technological capabilities on the one hand, and prevailing economic conditions on the other. It was revealed that for large dumpsites the cost of landfill mining project with waste excavation and redisposal, using landfill soil material, and the recovery of secondary raw materials is several times higher than the cost of baseline dumpsite reclamation. This study shows that implementation of landfill mining projects is feasible for relatively small dumpsites with a low object base area load. The age of a landfill, among the other parameters, has an impact on the economic efficiency of landfill mining project. According to the study the older the landfill is, the higher the content of landfill soil and the lower the amount of secondary raw materials available. As a result, the efficiency and cost of sorting technologies for soil material and secondary raw materials are key factors that determine the economic feasibility of landfill mining during waste disposal site reclamation. Within each scenario, the factors that most influence the total cost are identified.

1. INTRODUCTION

Throughout its history in Russia, the system of waste management has been based on setting up disposal sites, most of which have been open dumps. Current waste management policies in the Russian Federation (FZ, 1998; ZK, 2001; FZ, 2002) demand closure and elimination of these waste disposal sites. When an old dump or a landfill is situated on an inappropriate area of land, the entire volume of waste must be excavated and redisposed on a sanitary MSW landfill. It is self-evident that the originally designed capacity of sanitary landfills was not intended to accommodate significant amounts of solid waste excavated from old dumps. The fact that the capacity of landfills currently in operation will be exhausted earlier than planned, significantly limits the implementation of Russian dump elimination programs. In this situation, one of the technical solutions for old dump waste reclamation using waste redisposal is landfill mining.

The history of landfill mining began in 1953, when the first project was implemented at a test site near Tel Aviv, Israel (Ortner et al., 2014; Burlakovs et al., 2017). The main goal of the project was to extract soil material, which was later used to improve the fertile properties of the soil. In Europe, the first landfill excavation project was undertaken in Germany in 1993 at the Bürghof test site in Baden-Württemberg. The project's aim was to assess the technical and economic feasibility of excavation and further processing of waste with a significant shelf life. In Europe, additional landfill excavations were also carried out in Italy, the Netherlands, Austria, Sweden, Finland, Switzerland, Estonia, and Latvia (Sormunen et al., 2008; Krook et al., 2012; Spooren et al., 2013; Ortner et al., 2014; Wolfsberger et al, 2015a; Maul, Pretz, 2016; Bhatnagar et al., 2013; Bhatnagar et al., 2017; Dāce, Bendere, 2017; García López et al., 2018). Projects in the USA and Canada were implemented mainly in 1980-1990 to separate high-calorie fraction (alternative fuel) for energy production (Ortner et al., 2014). In Asia, landfill excavation projects were set up in China, India, Sri Lanka, South Korea, and Thailand. Most of them were aimed at evaluating extracted materials for composting potential (Zhao et al, 2007; Ortner et al., 2014; Weng

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et al., 2015). They also assessed the quality and quantity of fine fraction (Mönkäre et al., 2016; Somani et al., 2018; Parrodi et al., 2018), metals (Wagner, Raymond, 2015), and waste for secondary fuel recovery (Siddiqui et al., 2017). Furthermore, a number of projects focused on land reclamation for economic development (Van Passel et al, 2013; Danthurebandara et al., 2014; Wolfsberger et al, 2015b; Hermann et al., 2015; Rechberger, Fellner, 2016; Hermann et al., 2016; Särkkä et al., 2018; Pastre et al., 2018).

In general, there are several reasons to set up landfill mining projects: the extraction of materials with recycling potential; the extraction of materials suitable for energy recovery; the recovery of soil material; and land reclamation (ISWA WG Landfill, 2013; Greedy, 2016). Given the cost of primary resources in Russia, it is generally hardly feasible to embark on landfill mining projects for the extraction of material and energy resources from waste. Nevertheless, landfill mining at open dumps and old landfills is viable and applicable in three circumstances: (1) when a large number of illegal dumps situated on an inappropriate piece of land must be excavated and waste must be redisposed on a sanitary landfill, (2) when urban areas are surrounded by old dumps and landfills which are "growing" into the cities; so these disposal sites have to be eliminated due to the ban on placing such sites in populated areas, and (3) when existent MSW disposal sites are resued to conserve land resources. Today, the most promising direction is the elimination of old MSW disposal sites located illegally near towns.

A typical example for Russia is waste disposal sites in the Perm region (Figure 1).

In the past, the sites for landfills were chosen randomly in the vicinity of populated areas with no reference to the geological and hydrological conditions of the area. As a result, almost every town in the region has its own waste disposal site, often located in a forest or a ravine. In most cases, the area does not exceed one hectare (Figure 2) and most sites are at the stage of active emission formation due to their age (Figure 3).

The transition to modern waste management systems in the Perm region and in the Russian Federation requires the elimination or reclamation of old waste disposal sites. The practice of implementing projects in this area shows that the cost of MSW disposal site reclamation in the Perm region varies from €25,000 to €65,000 per 1 hectare (Savelev, 2016; Sliusar, 2019).

Additionally, in most regions, there is a large number of landfills with small disposal site areas. In these cases, it is cheaper to export and dispose waste at a sanitary landfill rather than reclaim an existing site. Considering the capacity limitations of sanitary landfills and the cost of waste re-

Population – 2.6 mill. people
Area – 160 thous. sq. km
MSW generation – 250 kg/capita/year

	Landfills	Dumpsites
Active, units	32	525
Closed, units	5	104
Total square, ha	205.7	812.21
Total waste amount, Mt	5,078	13,371

FIGURE 1: Number and capacity of MSW disposal sites in the Perm region, Russia.

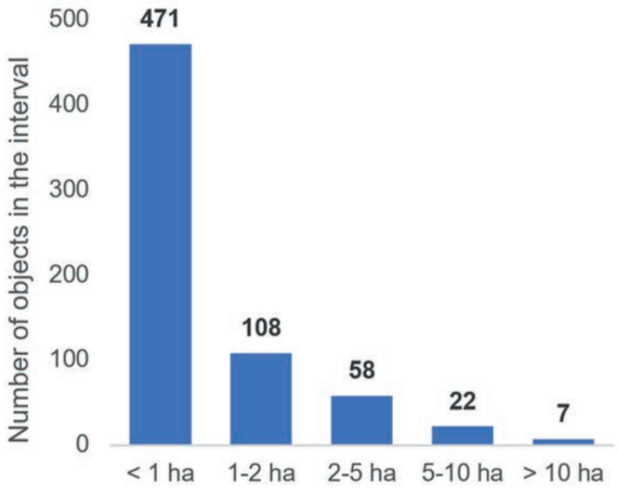


FIGURE 2: Waste disposal sites by site area (Perm region, Russia as an example).

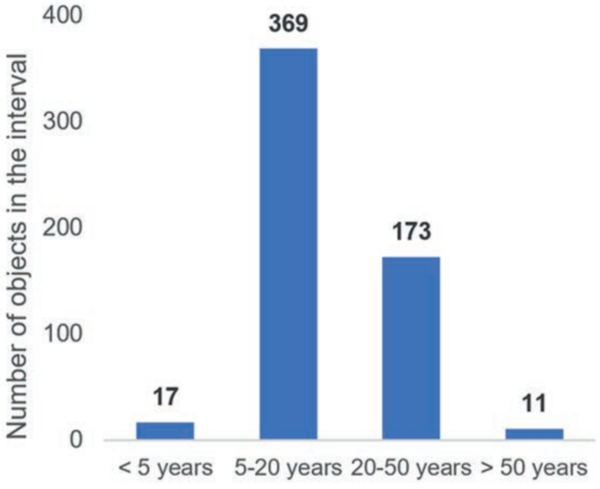


FIGURE 3: Waste disposal sites by age (Perm region, Russia as an example).

landfilling, the issue of extracting material resources and reducing the volume of disposed waste is a pressing one.

Interest in the topic is confirmed by a significant number of studies on the economic feasibility of landfill mining projects. Some researchers consider the ecological expediency of extracting material resources (Bhatnagar et al., 2013; Danthurebandara et al., 2017), while several other projects evaluate the possibility of using fine fraction waste materials for intermediate and final covering at landfills (Sormunen et al., 2013; Mönkäre et al., 2016. Further studies consider using fine fraction as filling material for land leveling or construction of embankments (Parrodi et al., 2018).

In terms of a project's economic efficiency, more attention should be paid to the extraction of metals (Wolfsberger et al., 2015a; Wolfsberger et al., 2015b; Wagner, Raymond, 2015), the recycling of coarse fractions (Bhatnagar et al., 2013), and the integration of WtE plants into landfill mining projects. However, other researchers have focused on integrated economic efficiency, arguing that total costs (cost of land freed, reduction of environmental load, sale of secondary raw materials (SRM)) are important decision-making factors for the implementation of such projects (Spooren et.al., 2013).

Additionally, there are diverse approaches to conducting analysis. For some authors, the effectiveness of a project includes the entire value chain (Jonce et al., 2012). Others use a comparative approach by analyzing costs when applying different waste treatment technologies (Danthurebandara et al., 2017). There are also various ways to record income from landfill mining projects. Some financial models include only direct income, while others also take indirect earnings into account, such as the sale of a land plot at a higher cost, secondary land use, and taxes (Winterstetter et al., 2015; Wolfsberger et al., 2016).

The key difference in the current study is the application of an integrated scenario approach in determining the expediency of landfill mining projects based on a scenario matrix.

This method allows researchers to compare the costs and profits of each scenario, depending on resources, technological capabilities, and limitations on the one hand, and prevailing economic conditions on the other. The principal advantage of an integrated scenario-based approach is the increased economic feasibility of assessing project implementation technology based on cost and income data. In addition, the model allows for a sensitivity analysis and parameter selection, value changes that have the greatest impact on the total cost

2. MATERIALS AND METHODS

2.1 Description of objects

Assessment of the economic efficiency of secondary resource extraction in the course of reclamation works was carried out at two closed waste disposal sites:

- Object A: A dumpsite with an area of 12.4 hectares. The volume of waste accumulated at the dumpsite was 550,000 m^3. The landfill was in operation from 1957-2015.
- Object B. A dumpsite with an area of 2.4 hectares. The dump is located in a wooded area on the slope of a river, in a water protection zone. It was opened in 1972 and closed to waste reception in 2010. The total amount of accumulated waste at the site was about 30,000 m^3.

Objects with different areas were chosen due to differing efficiency in space exploitation. The average waste load was 4.4 m^3/^{m2} and 1.1 m^3/m^2 at sites A and B respectively.

Both properties belong to local municipalities and are located in commercially unappealing areas. Given that the objects were built many years ago, they do not have the type of modern "green" infrastructure (impermeable liners, drainage system, gas collection system, etc.) that ensures proper environmental protection. The nearest sanitary landfill where the waste can be redisposed is at a distance of 20 km in both cases.

The data on the composition of stored waste was obtained from studies of similar waste mass (Sliusar et al., 2014; Sliusar, 2016) located in the same region, and considering the age of the waste disposal site (Table 1).

2.2 Scenario matrix description

A matrix of scenarios is at the core of an integrated approach to the assessment and justification of the feasibility of landfill mining projects.

It allows researchers to assess an object in two dimensions. The first dimension consists of a total cost assessment for four scenarios based on the resources, as well as the technological capabilities and limitations of the object of study. The second dimension includes an evaluation of three scenarios – baseline, optimistic, and pessimistic – based on the economic potential of the object of study and the economic situation in the market. The two dimensions of a scenario matrix are considered below.

2.2.1 Dimension 1. Landfill mining project scenarios based on resources, technological capabilities and limitations, and ecological requirements of the object

Scenario 0 (S0). According to Russian legislation (GOST,2015; SP, 201) on the closure of landfills for exploitation, dumpsites are required to complete several procedures, such as waste flattening, passive degassing system installation, laying out clay and vegetation soil materials, followed by land coverage. The thickness of the soil layers depends on the future prospects of using the site, whereas the choice of grass mixture composition depends on local conditions. This scenario is used most commonly in Russian practice, as it requires minimal technical equipment and does not involve waste redisposal. This is the basic option when conducting a feasibility study.

Scenario 1 (S1). If a landfill is located in an unsuitable territory, waste should be excavated and redisposed on the nearest sanitary landfill. Scenario 1 includes the following costs: waste excavation, transportation of the entire waste mass over a 20 km distance, vacated land plot design and biological reclamation with soil vegetation and land cover.

Scenario 2 (S2) assumes that excavated waste is screened on a mobile screen with landfill soil separation. Studies (Zaytseva, 2006; Armisheva, 2008) have shown

TABLE 1: Mean value and standard deviation (in brackets) of component and fractional composition of excavated waste.

Material type	Average object age, years			
	1 – 5	6 - 15	16 -30	> 30
Glass	9.3 (5.6)	6.8 (3.1)	6.5 (3.1)	4.5 (3.0)
Stone	11.1 (9.0)	17.2 (7.1)	12.0 (6.8)	11.3 (4.7)
Metals	2.1 (1.9)	1.1 (1.1)	2.7 (3.1)	3.1 (3.5)
Wood	8.4 (6.3)	6.0 (2.6)	10.8 (5.6)	9.5 (10.5)
Polymers	25.9 (9.9)	13.1 (6.9)	10.3 (9.5)	4.2 (5.9)
Textiles	6.1 (5.5)	5.6 (6.5)	4.2 (5.9)	0.8 (0.8)
Paper	8.9 (7.6)	2.6 (2.8)	1.8 (3.0)	1.1 (2.6)
Soil materials	23.7 (13.4)	46.6 (9.5)	50.6 (6.8)	64.0 (12.8)
Other	4.5 (3.7)	1.0 (0.7)	1.0 (0.8)	1.4 (1.4)
< 20 mm	32.6 (14.1)	56.3 (10.7)	58.2 (6.5)	70.3 (12.5)
20-50 mm	14.2 (6.0)	13.1 (4.4)	10.6 (4.0)	9.2 (3.8)
50-100 mm	14.3 (4.7)	11.5 (2.8)	10.1 (2.4)	6.2 (3.0)
> 100 mm	39.0 (16.6)	19.1 (9.1)	21.0 (9.5)	14.2 (10.0)

that the characteristics of disposed mass fine fraction are close to those of technogenic soils. In such cases, it is assumed that the recovered landfill soil will be used on the site for land reclamation.

Scenario 3 (S3) also provides for fine fraction separation and its application on the site. In addition, a mobile sorting complex located in close proximity to the site selects SRM (metals, plastic waste and glass). The rest of the waste is transported to a sanitary landfill for subsequent redisposal.

Scenario 4 (S4) is based on recovery and further use of the waste energy fraction (Polygalov et al., 2019). Excavated waste is sifted on a screen, and energy fractions of waste are collected at a sorting facility located next to the landfill site. In the process of sorting out the energy fraction, the heat of waste combustion per working mass increases by 2-3 times (Table 2). When calculating the heat of waste fuel combustion, the contamination of excavated components was taken into account.

2.2.2 Dimension 2. Landfill mining project scenarios based on the economic potential of the object and the economic situation in the market

The feasibility evaluation of MSW disposal reclamation / liquidation scenarios is based on the following initial data sources:

- Earthworks cost (site planning work, upper reclamation layers, fertile soil layers, waste mass degassing) is estimated from federal price reference books (SBCP, 2001).
- Waste transportation and redisposal are calculated from average market prices in the region.Prices were obtained from the tariff documents published by the Ministry of Tariff Regulation and Energy in the Perm region (Ministry, 2020);
- Sorting materials (fine fraction and recycled materials) cost is calculated from similar facilities and includes equipment rental, along with operating and personnel costs. Prices were obtained upon request of a commercial offer from the equipment owner companies;
- Retail price for recovered secondary resources is set as the lowest in the region due to their low quality (Vtorsyryo159, 2020; Permmakulatura, 2020; Metallpunkt, 2020).

Feasibility evaluation of secondary resources extracted and used during the reclamation and liquidation works is carried out based on the factors in Table 3. Some factors are constant values, such as the operation of equipment, and the cost of soil materials. Other factors, such as waste redisposal cost, recycled waste recovery distance, recycling rate, and SRM cost on the market vary depending on external economic conditions, waste age, recoverable material quality, and sorting technology efficiency. These factors form the basis for three scenarios of dimension 2: baseline, pessimistic and optimistic.

The baseline landfill mining scenario of dimension 2 implies an economic assessment for selected properties

TABLE 2: Calorific value of excavated waste.

Age of landfilling, years	Untreated waste		Energy components (waste fuel)	
	Mass, %	Calorific value (on working mass), MJ/kg	Mass, %	Calorific value (on working mass), MJ/kg
1-5	100	7.08	23.4	10.94
6-15	100	3.49	13.0	8.42
16-30	100	2.95	12.9	8.17
> 31	100	1.73	7.4	6.90

TABLE 3: Factors affecting MSW sites reclamation / disposal economic effect.

Impact factor	Baseline scenario	Pessimistic scenario	Optimistic scenario
Site works (waste excavation, territory layout, etc.)	Cost is based on landfill design project		
Waste mass density	Fixed		
Waste density after sorting	Fixed		
Waste redisposal	561 ₽/t	Cost increase	Free
Waste transport to a redisposal site (distance)	20 km	Depends on the distance to the next site	
Landfill soil selection percentage	30 % (mass)	“young” mass	“old” mass
Polymer selection percentage	10 % (масс)	“old” mass	“young” mass
Glass selection percentage	3 % (mass)	“old” mass	“young” mass
Metal selection percentage	5 % (mass)	“old” mass	“young” mass
Energy component sorting	8 % (mass)	“old” mass	“young” mass
Cost of fine fraction sorting	₽0.5 thous./t	Depends on the type of equipment	
Cost of secondary material sorting	₽1.45 thous./t	optical sorting	manual mobile sorting
Polymer price	₽3 thous./t	Market decline / low quality SRM	Market growth / high quality SRM
Metal price	₽3.5 thous./t	Market decline / low quality SRM	Market growth / high quality SRM
Glass price	₽2 thous./t	Market decline / low quality SRM	Market growth / high quality SRM
Cost of soil material	Fixed		

at current prices. The assessment determines the technological operations and technical parameters that contribute most to the cost of the baseline scenario.

Optimistic and pessimistic scenarios for landfill mining projects suggest a deviation of the baseline impact factors to the positive or negative side. Factors such as landfill soil extraction and SRM percentage depend on the age of the disposal site and the type of excavated waste processing technology. The prices for SRM and waste sorting operations vary according to the waste treatment and disposal market situation. The data obtained is necessary for analyzing existing situations and forecasting conditions under which the implementation of scenarios will be most economically expedient.

3. RESULTS AND DISCUSSION

Material balances of landfill site reclamation are based on two types of data: the composition of waste (Table 1) and the effectiveness of sorting for soil fraction, SRM, and energy components. Figure 4 presents the results of the material flow analysis for the object.

Technically, Scenario 0 (standard reclamation) and Scenario 1 (waste redisposal) are the easiest to execute. However, at the same time, the environmental load in these scenarios decreases slightly, and the resources deposited in the waste are not used.

Landfill mining projects (Scenarios 2 and 3) engage part of the excavated waste into economic circulation, thereby partially covering the excavation and reclamation costs. Studies (Armisheva, 2008; Armisheva et al., 2013) show that landfill soil excavated from old sites can be used as reclamation material to substitute technical soil. Thus, in Scenarios 3 and 4, the volume of redisposed waste can be reduced by 20-60% (mass.) when excavating young and old disposal sites (in pessimistic and optimistic scenarios respectively).

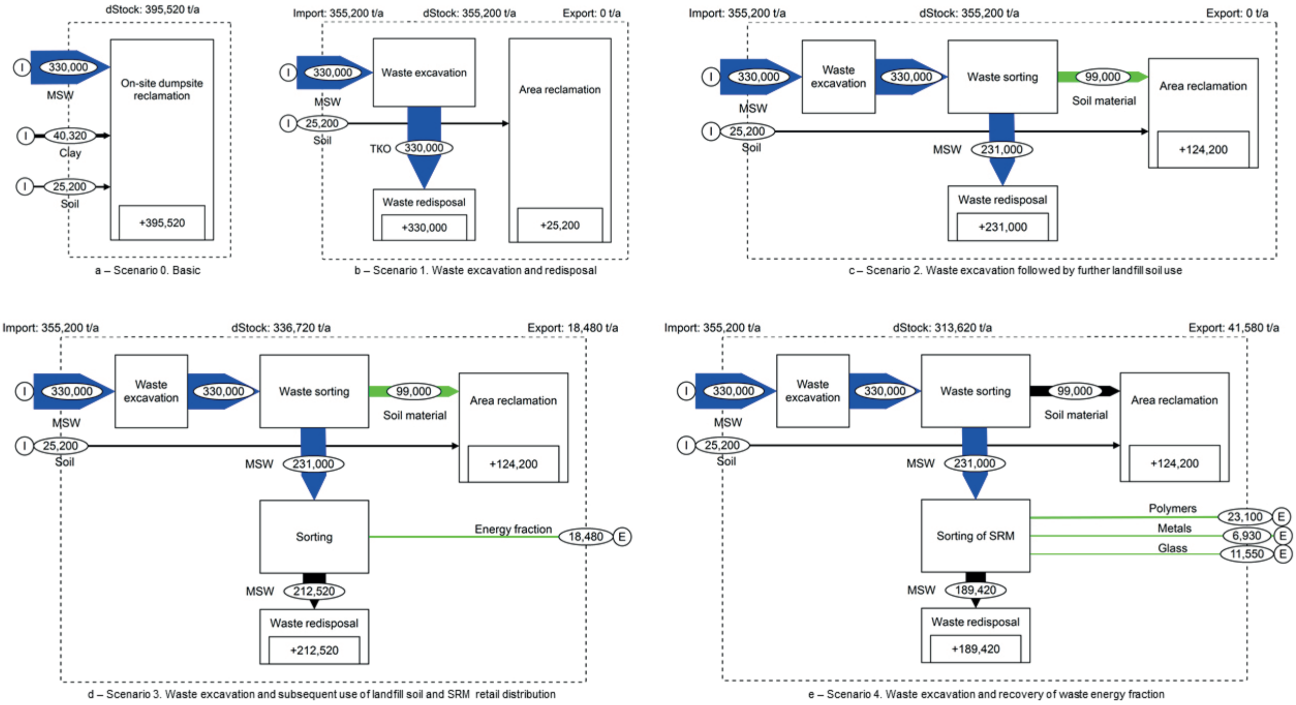
Scenario 4 (the extraction of SRM) is the most promising scenario since it can provide additional revenue from the sale of excavated SRM (polymer, glass, metal), yet the efficiency of SRM extraction and sorting depends heavily on the waste moisture content at the disposal site. In addition, the price of recycled materials on the market is subject to change and the cost of waste sorting amounts to 50% of the total project cost.

Figure 5 presents the breakdown of the cost of work under all scenarios (S0-S4) for objects A and B in three versions: baseline, optimistic and pessimistic.

The cost calculation for Scenarios S0-S4 has the same structure. The costs and revenues for all scenarios (S0-S4) for objects A and B are presented in Figure 6 and 7 respectively.

A more preferable scenario for the dumpsite with a higher object base area load per square meter is scenario S0 (for object A, this value is 4.4 m MSW / m^2) (Figure 5) due to the large volume of waste to be excavated. That being said, with a low load on the landfill base (for object B, this value is 1.25 m MSW / m^2), the cost of scenario S0 in the basic version is comparable to the cost of work under scenarios S1-S2. This provides an opportunity for cost optimization to ensure the possibility of extraction and further recovery of resources deposited in the waste.

In fact, the cost of scenarios S1-S3 (waste removal, excavation using landfill soil, excavation with extraction of SRM) for large objects with a higher object base area load per square meter exceeds the cost of the baseline scenario (scenario S0) even with the most optimistic course of



a – Scenario 0. Basic

b – Scenario 1. Waste excavation and redisposal

c – Scenario 2. Waste excavation followed by further landfill soil use

d – Scenario 3. Waste excavation and subsequent use of landfill soil and SRM retail distribution

e – Scenario 4. Waste excavation and recovery of waste energy fraction

FIGURE 4: Material balance of landfill mining process for object A: a – Scenario 0. Basic; b – Scenario 1. Waste excavation and redisposal; c – Scenario 2. Waste excavation followed by further landfill soil use; d – Scenario 3. Waste excavation and subsequent use of landfill soil and secondary raw material retail distribution; e – Scenario 4. Waste excavation and recovery of waste energy fraction.

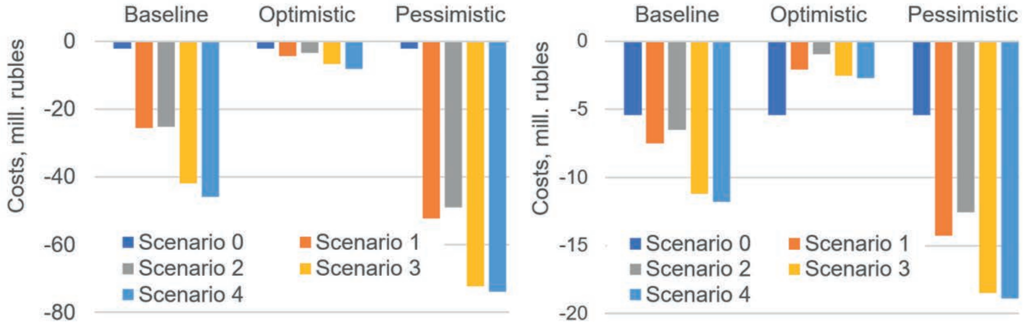


FIGURE 5: Costs for Scenarios S0-S4.

events. At the same time, landfill mining projects (scenarios S1-S3) on relatively small objects with a low base area load per square meter become economically viable in the optimistic scenario when compared to the baseline version. For such sites, it makes economic sense to optimize costs of landfill mining projects in order to reduce the negative impact on the environment.

The main costs of scenario S1-S3 (Figure 6-7) are connected with waste redisposal on a sanitary landfill and sorting excavated waste (scenarios S2-S3). Scenario S3 (excavation with the extraction and sale of SRM) should be considered. Though its implementation will significantly reduce the environmental impact compared to other scenarios, the additional costs of sorting SRM several times decrease the revenue from their sale, which makes implementation economically inexpedient.

Thus, the total costs of scenarios S1-S3 (with waste removal, excavation of landfill soil, and excavation with SRM recovery) are lower than the total costs of the baseline scenario S0, even for an optimistic course of events. For this reason, the urgent question is which costs of technological operations and technical processes should be reduced in order to reduce the total costs of each scenario?

The cost calculations enable the identification of factors that contribute most to the economic efficiency of a landfill mining project if the most significant parameters change by 1% (Table 4).

For scenarios S1 and S2, one of the most significant parameters is the cost of waste disposal on a nearby sanitary landfill. If fraction is removed from waste and retuned to economic use, it can reduce the amount of recycled waste and consequently its cost.

Scenarios S2 and S3 also include the cost of sorting the fine fraction and SRM from excavated waste, which increases the total cost of implementation. However, this can be controlled and reduced by choosing an optimal

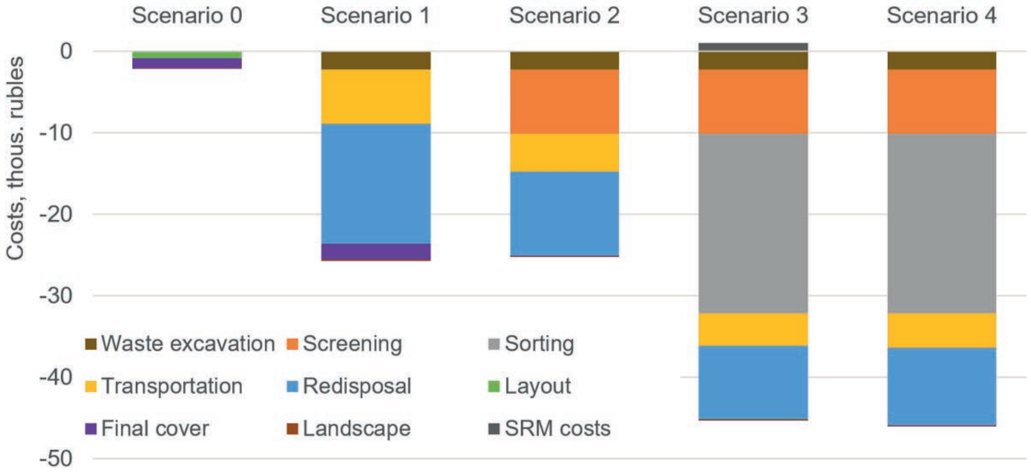


FIGURE 6: Cost and revenue analysis for reclamation / liquidation of MSW disposal site (object A, baseline scenario).

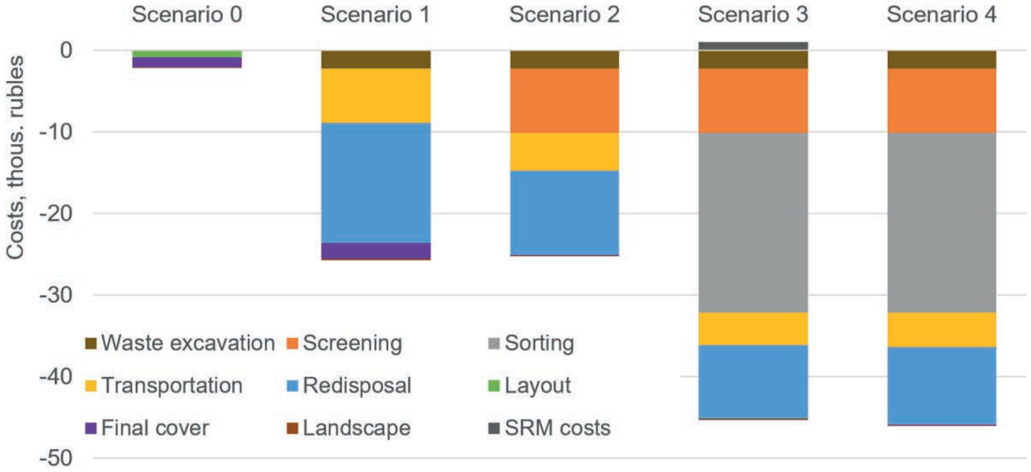


FIGURE 7: Cost and revenue analysis for reclamation / liquidation of MSW disposal (object B, baseline scenario).

technological sorting line, optimizing sorting line operating modes, and installing high-performance equipment. These steps will reduce the cost of work in Scenarios 2-3 (the optimistic scenario), while maximizing the use of the resources deposited in the waste disposal mass.

In the scenarios considered, one of the most significant parameters is the cost of waste disposal on a nearby sanitary landfill. It raises the urgent issue of maximizing fraction removal from waste and returning it into economic circulation.

Another important factor is the cost of sorting the excavated fines fraction and SRM. This variable can be controlled by choosing the optimal technological sorting line, optimizing the operating modes of the sorting lines, or by using high-performance equipment to reduce the sorting cost. In an optimistic scenario, the improved factor can reduce the cost of work in scenarios 2 and 3, while maximizing the use of the resources in the deposited waste.

Total costs are slightly sensitive to the cost of technological operations and technical processes for objects of various sizes, so the conclusions remain true for objects A and B.

4. CONCLUSIONS

Based on the studies presented in this article, the decision to extract resources during reclamation of closed waste disposal sites should be carried out while taking into account the environmental requirements along with the technical and economic characteristics of the processes.

The study shows that for large dumpsites with a higher object base area load per square meter, the cost of reclamation with waste excavation and redisposal, using landfill soil material, and the recovery of SRM is several times higher than the cost of basic dumpsite reclamation. On the other hand, implementation of landfill mining projects is feasible for relatively small dumpsites with a low object base area load per square meter. In these cases, it makes economic sense to optimize costs so as to reduce the negative impact on the environment.

There are many factors that affect the economic performance of a landfill mining project in unique ways. Firstly, the age of a landfill is one of the parameters that has an impact on the environmental and economic efficiency of

TABLE 4: Factors of influence when implementing the scenario-based approach.

Impact factor	Factor significance	
	Object A	Object B
Scenario 1. Landfill mining	Relative divergence	
Waste transportation to disposal site	0.26%	0.23%
Waste reburial	0.57%	0.50%
Scenario 2. Landfill mining with utilization of fine fraction		
Fine fraction sorting	0.31%	0.31%
Waste transportation to disposal site	0.18%	0.18%
Waste disposal	0.41%	0.40%
Scenario 3. Landfill mining with extraction of secondary materials		
Fine fraction sorting	0.19%	0.18%
Secondary material sorting	0.52%	0.50%
Waste transportation to disposal site	0.10%	0.09%
Waste disposal	0.21%	0.20%
Secondary material sale	-0.08%	0.04%
Scenario 4. Waste excavation and recovery of waste energy fraction		
Fine fraction sorting	0.17%	0.17%
Secondary material sorting	0.48%	0.48%
Waste transportation to disposal site	0.09%	0.09%
Waste disposal	0.21%	0.20%
Energy fraction sale	0	0

the project. The study results show that the older the landfill is, the higher the content of landfill soil and the lower the amount of SRM available. This is due to the changes in composition of the incoming disposal waste (low proportion of polymers, glass and metals in 20-30 year old waste and a sharp increase of polymers in newer waste), as well as waste decomposition and formation of landfill soil, which is similar to man-made soils.

The efficiency and cost of sorting technologies for soil material and SRM are key factors that determine the economic feasibility of landfill mining during waste disposal site reclamation. The efficiency of the sorting process is linked directly with the quality of the excavated waste. The quality of excavated materials, and as a result the possibility of selecting them from disposal waste, drops significantly in the first 5 years of waste mass. Low volumes of recoverable secondary materials do not cover the high cost of their extraction. Nonetheless, as waste ages, the proportion of soil materials grows, and the quality approaches the quality of technogenic soils. This allows the use of soil materials as a substitute for natural soils during land reclamation and the deployment of deferred resources which improves the economic performance of the process.

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REFERENCES

Armisheva (2008). In Russian: Армишева Г.Т. (2008). Рекуперация ресурсов при захоронении твердых бытовых отходов // Диссертация на соискание ученой степени кандидата технических наук. Пермский государственный технический университет. Пермь, – 2008. – 179 с [Armisheva G.T. Rekuperacija resursov pri zahoronenii tverdyh bytovyh othodov [Resource recovery in the disposal of municipal solid waste] // Dissertacija na soiskanie uchenoj stepeni kandidata tehnicheskih nauk. Permskij gosudarstvennyj tehnicheskij universitet. Perm'. – 2008. – 179 p.]

Armisheva, G., Sliusar, N., & Korotaev, V. (2013). Briefing: Urban-mining of landfills. Proceedings of Institution of Civil Engineers: Waste and Resource Management, 166(4). https://doi.org/10.1680/warm.12.00025

Bhatnagar, A, Kaczala, F., & Kriipsalu, M. (2013). Closing the Life Cycle of Landfills-Landfill Mining in the Baltic Sea Region for future, presented at Linnaeus Eco-Tech 2012, November, 2012. http://lnu.se/polopoly_fs/1.78199!SESSION 7 LANDFILL MINING.pdf

Bhatnagar, A., Kaczala, F., Burlakovs, J., Kriipsalu, M., Hogland, M., & Hogland, W. (2017). Hunting for valuables from landfills and assessing their market opportunities A case study with Kudjape landfill in Estonia. Waste Management and Research, 35(6), 627–635. https://doi.org/10.1177/0734242X17697816

Burlakovs, J., Kriipsalu, M., Klavins, M., Bhatnagar, A., Vincevica-Gaile, Z., Stenis, J., … Hogland, W. (2017). Paradigms on landfill mining: From dump site scavenging to ecosystem services revitalization. Resources, Conservation and Recycling, 123(July), 73–84. https://doi.org/10.1016/j.resconrec.2016.07.007

Dāce, E., & Bendere, R. (2017). Landfill Mining in Latvia, presented at Linnaeus Eco-Tech 2017. https://doi.org/10.15626/eco-tech.2012.011

Danthurebandara, M., Van Passel, S., Vanderreydt, I., & Van Acker, K. (2014). Assessment of environmental and economic feasibility of Enhanced Landfill Mining. Waste Management, 45, 434–447. https://doi.org/10.1016/j.wasman.2015.01.041

FZ (1998). In Russian: Федеральный закон "Об отходах производства и потребления" от 24.06.1998 N 89-ФЗ [Federal Law 89-FZ, dated 26 Jun. 1998, "On industrial and munisipal waste"]

FZ (2002). In Russian: Федеральный закон "Об охране окружающей среды" от 10.01.2002 N 7-ФЗ [Federal Law 7-FZ, dated 10 Jan. 2002, "On environmental protection"]

García López, C., Küppers, B., Clausen, A., & Pretz, T. (2018). Landfill Mining: a Case Study Regarding Sampling, Processing and Characterization of Excavated Waste From an Austrian Landfill. Detritus, 2(1), 29. https://doi.org/10.31025/2611-4135/2018.13664

Greedy, D. (2016). Landfilling and landfill mining. Waste Management and Research, 34(1), 1–2. https://doi.org/10.1177/0734242X15617878

GOST (2015). In Russian: ГОСТ Р 56598-2015. Ресурсосбережение. Обращение с отходами. Общие требования к полигонам для захоронения отходов [GOST R 56598-2015. Resursosberezhenie. Obrashchenie s othodami. Obshchie trebovaniya k poligonam dlya zahoroneniya othodov [Resources saving. Waste treatment. Technical requirements for specially engineered landfill]]

Hermann, R., Baumgartner, R. J., Vorbach, S., Ragossnig, A., & Pomberger, R. (2015). Evaluation and selection of decision-making methods to assess landfill mining projects. Waste Management and Research, 33(9), 822–832. https://doi.org/10.1177/0734242X15588586

Hermann, R., Wolfsberger, T., Pomberger, R., & Sarc, R. (2016). Landfill mining: Developing a comprehensive assessment method. Waste Management and Research, 34(11), 1157–1163. https://doi.org/10.1177/0734242X16657610

Jones, P. T., Geysen, D., Tielemans, Y., Van Passel, S., Pontikes, Y., Blanpain, B., Hoekstra, N. (2013). Enhanced Landfill Mining in view of multiple resource recovery: A critical review. Journal of Cleaner Production, 55, 45–55. https://doi.org/10.1016/j.jclepro.2012.05.021

ISWA Landfill Working Group Key Issue Paper: Landfill Mining. URL: http://www.iswa.org/index.php?eID=tx_iswaknowledgebase_download&documentUid=3224

Krook, J., Svensson, N., & Eklund, M. (2012). Landfill mining: A critical review of two decades of research. Waste Management, 32(3), 513–520. https://doi.org/10.1016/j.wasman.2011.10.015

Maul, A., & Pretz, T. (2016). Landfill Mining from the processing perspective – a view on mass balance and output streams. https://doi.org/10.13140/RG.2.1.4245.4800

Metallpunkt (2020). In Russian: Пункты приема вторсырья [Recyclable materials point]. Available at: https://metallpunkt.ru

Ministry (2020). In Russian: Министерство тарифного регулирования и энергетики Пермского края [Ministry of tariff regulation and energy of the Perm region]. Available at: http://mtre.permkrai.ru

Mönkäre, T. J., Palmroth, M. R. T., & Rintala, J. A. (2016). Characterization of fine fraction mined from two Finnish landfills. Waste Management, 47, 34–39. https://doi.org/10.1016/j.wasman.2015.02.034

Ortner, M. E., Knapp, J., & Bockreis, A. (2014). Landfill mining: Objectives and assessment challenges. Proceedings of Institution of Civil Engineers: Waste and Resource Management, 167(2), 51–61. https://doi.org/10.1680/warm.13.00012

Parrodi J.C.H., Höllen, D, Pomberger, R. (2018). Characterization of fine fractions from landfill mining: a review of previous investigations. Detritus, V. 02, 46-62. https://doi.org/10.31025/2611-4135/2018.13663

Pastre, G., Griffiths, Z., Val, J., Tasiu, A. M., Camacho-Dominguez, E. V., Wagland, S., & Coulon, F. (2018). A Decision Support Tool for Enhanced Landfill Mining. Detritus, 01(i), 91–101. https://doi.org/10.26403/detritus/2018.5

Permmakulatura (2020). In Russian: ПермМакулатура. Available at: http://kartona.net

Polygalov, S. Ilinykh, G., Sliusar, N., Korotaev, V., Rukavishnikova I. (2019). Challenges and opportunities for energy recovery from municipal solid waste in the Russian Federation. WIT Transactions on Ecology and the Environment, Vol. 222, 131–143. DOI: 10.2495/EQ180131

Rechberger, H., & Fellner, J. (2016). Development of a resource classification framework for old landfills in Flanders (Project RECLAF). In: Proceeding "SUM2016, 3rd Symposium on Urban Mining", 23-25 May 2016, Bergamo, Italy.

Särkkä, H., Kaartinen, T., Hannus, E., Hirvonen, S., Valjus, T., Dino, G. A., … Coulon, F. (2020). Investigation of Municipal Solid Waste (MSW) and Industrial Landfills As a Potential Source of Secondary Raw Materials. Detritus, 01, 83–90. https://doi.org/10.26403/detritus/2018.3

Savelev (2016). In Russian: Савельев А.А. Оценка и обеспечение геоэкологической устойчивости массивов твердых коммунальных отходов для строительно-хозяйственного освоения: дис. … канд. техн. наук. – Самара, 2014. – 323 с. [Savelev A.A. Ocenka i obespechenie geoekologicheskoj ustojchivosti massivov tverdyh kommunal'nyh othodov dlya stroitel'no-hozyajstvennogo osvoeniya [Assessment and provision of geoecological stability of municipal solid waste arrays for construction and economic development] // Dissertacija na soiskanie uchenoj stepeni kandidata tehnicheskih nauk. Samarskii gosudarstvennyj tehnicheskij universitet. Samara. – 2016. – 323 p.]

SBCP (2001). In Russian: СБЦП 81-2001-03 Справочник базовых цен на проектные работы для строительства "Объекты жилищно-гражданского строительства" [SBCP 81-2001-03 Spravochnik bazovyh cen na proektnye raboty dlya stroitel'stva "Ob"ekty zhilishchno-grazhdanskogo stroitel'stva" [Reference list of basic prices for design work for construction "Objects of housing and civil construction"]]

Siddiqui, F. Z., Zaidi, S., Manuja, S., Pandey, S., & Khan, M. E. (2017). Development of models for prediction of the energy content of disposed MSW from an unsecured landfill. Waste Management and Research, 35(11), 1129–1136. https://doi.org/10.1177/0734242X17725392

Sliusar, N., Zagorskaya, Y., Korotaev, V. (2014). Studies on waste composition of old landfills and dump sites: case study in Perm region, Russia. Deponietechnik 2014. Dokumentation der 9. Hamburger Abfallwirtschaftstage. – Hamburg, 2014.

Sliusar (2016). In Russian: Слюсарь, Н.Н. (2016). Возможности извлечения отложенных ресурсов из массивов захоронения твердых коммунальных отходов. Вестник Пермского национального исследовательского политехнического университета. Прикладная экология. Урбанистика. – 2016. – № 1. – С.63–78. [Sliusar, N. Vozmozhnosty izvlecheniya otlozhennykh resursov iz massivov zakhoroneniya tverdyhk komunalnykh otkhodov [Possibilities for mining of delayed resources on municipal solid waste dumps and landfills] // Vestnik Permskogo nacionalnogo issledovatelskogo politechniceskogo universiteta. Prikladnaya ekologiya. Urbanistika. – 2016. – № 1. – 63–78 p.]

Sliusar (2019). In Russian: Слюсарь, Н.Н. (2019). Теория, методы и технологии обеспечения геоэкологической безопасности полигонов захоронения твердых коммунальных отходов на постэксплуатационном этапе // диссертация на соискание ученой степени доктора технических наук. – Пермь, 2019. – 241 с. [Sliusar N.N. Teoriya, metody i tekhnologii obespecheniya geoekologicheskoj bezopasnosti poligonov zahoroneniya tverdyh kommunal'nyh othodov na postekspluatacionnom etape [Theory, methods and technologies for ensuring geoecological safety of municipal solid waste landfills at the post-operational stage] // Dissertacija na soiskanie uchenoj stepeni doktora technicheskikh nauk. Perm'. – 2019. – 241 p.]SP (2017). In Russian: СП 320.1325800.2017 Полигоны для твердых коммунальных отходов. Проектирование, эксплуатация и рекультивация [SP 320.1325800.2017 Poligony dlya tverdyh kommunal'nyh othodov. Proektirovanie, ekspluataciya i rekul'tivaciya [Polygons for solid communal waste. Projecting, operation and reclamation]]

Somani, M., Datta, M., Ramana, G. V., & Sreekrishnan, T. R. (2018). Investigations on fine fraction of aged municipal solid waste recovered through landfill mining: Case study of three dumpsites from India. Waste Management and Research, 36(8), 744–755. https://doi.org/10.1177/0734242X18782393

Sormunen, K., Ettala, M., & Rintala, J. (2008). Detailed internal characterisation of two Finnish landfills by waste sampling. Waste Management, 28(1), 151–163. https://doi.org/10.1016/j.wasman.2007.01.003

Spooren, J., Quaghebeur, M., Nielsen, P., Machiels, L., Blanpain, B., & Pontikes, Y. (2013). Material recovery and upcycling within the ELFM concept of the Remo case, presented at International Academic Symposium on Enhanced Landfill Mining, 2013, Houthalen-Helchteren, Belgium

Van Passel, S., Dubois, M., Eyckmans, J., De Gheldere, S., Ang, F., Tom Jones, P., & Van Acker, K. (2013). The economics of enhanced landfill mining: Private and societal performance drivers. Journal of Cleaner Production, 55, 92–102. https://doi.org/10.1016/j.jclepro.2012.03.024

Vtorsyryo159 (2020). In Russian: Компания «VТОРСЫРЬЁ». Available at: http://вторсырьё159.рф

Wagner, T. P., & Raymond, T. (2015). Landfill mining: Case study of a successful metals recovery project. Waste Management, 45, 448–457. https://doi.org/10.1016/j.wasman.2015.06.034

Weng, Y., Fujiwara, T., Houng, H. J., Sun, C., Li, W., & Kuo, Y. (2015). Management of landfill reclamation with regard to biodiversity preservation, global warming mitigation and landfill mining: Experiences from the Asia-Pacific region. Journal of Cleaner Production. https://doi.org/10.1016/j.jclepro.2015.05.014

Winterstetter, A., Laner, D., Rechberger, H., & Fellner, J. (2015). Framework for the evaluation of anthropogenic resources: A landfill mining case study - Resource or reserve? Resources, Conservation and Recycling, 96, 19–30. https://doi.org/10.1016/j.resconrec.2015.01.004

Wolfsberger, T., Aldrian, A., Sarc, R., Hermann, R., Höllen, D., Budischowsky, A., … Pomberger, R. (2015). Landfill mining: Resource potential of Austrian landfills - Evaluation and quality assessment of recovered municipal solid waste by chemical analyses. Waste Management and Research, 33(11), 962–974. https://doi.org/10.1177/0734242X15600051

Wolfsberger, T., Nispel, J., Sarc, R., Aldrian, A., Hermann, R., Höllen, D., … Ragossnig, A. (2015). Landfill mining: Development of a theoretical method for a preliminary estimate of the raw material potential of landfill sites. Waste Management and Research, 33(7), 671–680. https://doi.org/10.1177/0734242X15590473

Zaytseva (2006). In Russian: Зайцева Т.А. (2006). Закономерности изменения микробиоценозов на полигонах депонирования твердых бытовых отходов в процессе деструкции органических веществ // диссертация на соискание ученой степени доктора биологических наук. – Пермь, 2006. – 289 с. [Zaytseva T.A. Zakonomernosti izmeneniya mikrobiocenozov na poligonah deponirovaniya tverdyh bytovyh othodov v processe destrukcii organicheskih veshchestv [Changes in microbiocenoses at municipal solid waste landfills in the organic substances destruction process] // Dissertacija na soiskanie uchenoj stepeni doktora biologicheskikh nauk. Perm'. – 2008. – 289 p.]

Zhao, Y., Song, L., Huang, R., Song, L., & Li, X. (2007). Recycling of aged refuse from a closed landfill. Waste Management and Research, 25(2), 130–138. https://doi.org/10.1177/0734242X07074053

ZK (2001). In Russian: Земельный кодекс Российской Федерации от 25.10.2001 N 136-ФЗ [Land code of the Russian Federation 136-FZ, dated 20 Jan. 2001]

Extra contents

COLUMNS AND SPECIAL CONTENTS

This section comprises columns and special contents not subjected to peer-review

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Environmental Forensic

SAMPLING MICROPLASTICS FOR ENVIRONMENTAL FORENSIC APPLICATIONS

Claire Gwinnett [1], Eleanor Harrison [1], Amy Osborne [1], Alberto Pivato [2] and George Varghese [3]

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Microplastics – the new challenge to an environmental forensic expert

Environmental forensics involves the investigation of a diverse range of pollutants that have been accidentally or deliberately released into the environment, to understand their origin and aid the courts in attributing responsibility. For decades, pollutants such as oil and heavy metals, have been the focus of investigation. More recently, emerging pollutants such as plastic waste have become of interest to environmental forensic scientists (Aswini and Varghese, 2020). Plastics have revolutionised our daily lives and have provided significant benefits for many industries; however, although the societal benefits have been immense; there is no doubt that plastic has developed into a considerable environmental problem, resulting in calls for plastics to be classed as a hazardous waste (Rochman et al., 2013a).

The extent of this pollution type is vast; far greater than many other pollutants that are typically investigated by environmental forensic scientists. Only 9% to 12% plastic was recycled or incinerated; and 79% was discharged into the natural environment or landfills (He et al., 2020). Plastic pollution has been found to be present in all of our environmental compartments including atmospheric, terrestrial, marine and freshwater ecosystems. Figure 1 shows the abundant nature of microplastics found on a beach in San Diego. Plastic litter has been found to be present in even the most remote locations on the planet, including the Arctic (Bergmann et al., 2019), and the deep sea (Taylor et al., 2016; Woodall et al., 2014). These plastics pose a problem to aquatic biota in both marine and freshwater environments; mega plastic (>1m) and macro plastic items (2.5cm-1m) cause entanglement, suffocation and starvation and microplastics (<5mm) exposure leads to a reduction in fecundity, reduced ability to remove pathogenic bacteria and lower feeding rates (GESAMP, 2019).


FIGURE 1: Microplastic pollution on San Diego Beach (5-7-18).

Microplastics are released into our environments through a variety of mechanisms, these include both accidental and deliberate release of plastic waste. Primary sources (those which have been deliberately manufactured at this small size, e.g. microbeads in cosmetic products) and secondary sources (formed from the degradation of larger plastic items) transport between environments easily (Arthur, 2008). For example, synthetic fibres are released into the atmosphere through wear and drying of clothes (O'Brien et al., 2020), into water environments via washing (Fontana, G.D, Mossotti, R and Montarsolo, 2020) and into our terrestrial environments via sewage sludge from wastewater treatment plants (Ren et al., 2020). Although microplastics are not a standard contaminant in the remit of an environmental scientist, with other discipline experts from marine science backgrounds taking the lead in these studies, now it is clear that environmental forensic science approaches are beneficial in understanding the source of such contaminants and also in providing robust methods for sampling.

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Microplastic Sampling

The microplastic sampling methods used are dependent on the purpose of sampling and the medium being sampled. Air sampling typically uses air pumps which recover particulates onto filter papers, whereby they are easily recovered for analysis. Although air sampling for microplastics is relatively new, it has adopted approaches from other air pollution sampling techniques.

Sampling water is a little more complex depending on the amount of water being sampled, the depth and the microplastic size fraction being targeted. Water sampling can include volume reduction approaches which employs the use of nets with a given mesh size, such as neuston or manta nets that are towed along the surface (Schönlau et al., 2020) or bongo nets for sampling below the surface (Doyle et al., 2011). Alternatively, grab sampling, aka bulk sampling may be employed, where a given amount of water is collected either by using a container, such as a metal bucket (for surface sampling) or niskin bottle (for below surface sampling - Figure 2) or an in-situ pump. Grab sampling is not size selective unlike the use of any mesh or filters which will only capture samples larger than its mesh/pore size. This typically leads to microplastics smaller than 300 micrometers, (a common mesh size) not being collected (Setälä, 2016), which is problematic when trying to understand the extent of this pollution. A critique of the different methods employed for sampling water for microplastics was completed by Prata et al.

Soil sampling utilises metal augers or steel soil samplers (usually trowels) to obtain samples to a given depth (Yang et al., 2021). Figure 3a shows a metal auger used for soil sampling. Sampling in beach sediments (Figure 1) is carried out by scraping out a small depth of sediments from a definite area. The procedure specified by NOAA (Lippiatt et al., 2013) for sampling of micro-debris from shoreline is often adopted. Figure 3b demonstrates mapping out soil sampling locations along a bank of a river.

FIGURE 2: Water sampling using a niskin bottle along the Hudson River with Staffordshire University (UK) and the Rozalia Project (USA). Photo courtesy of the Rozalia Project.

FIGURE 3a-b: Soil Sampling along the Hudson River with Staffordshire University (UK) and Rozalia Project (USA) Photos courtesy of the Rozalia Project.

A specific strategy should be employed for complex biosolid matrices such as composts, anaerobic digestates and sewage sludges where microplastics are widely found nowadays. These end-of-wastes can be directly used as bio-fertilizers in soils and, therefore, a deep investigation on concentrations of MPs is required to avoid their remission into the biosphere.

Because it is not practicable to separate the MPs and the solid matrix before the sampling phase, the sampling should follow several standards developed specifically for the above cited biosolids. The choice of the approach is determined by the research, technical or forensic question and involves considerations of the hypothesized analyte distribution in the field, potential sources, or final destination.

Microplastic sampling for forensic applications

Sampling of contaminants for the context of the courts, requires robust procedures. In environmental forensic sampling, the integrity and continuity of the sample is paramount. In microplastic research studies, the requirements of court are not currently present but as we move towards gaining source level information from microplastic samples, the need for methods that can stand up to scrutiny in court is required. Regardless of the sample type, they should be secured for transportation in a manner that prevents contamination and loss. However, for many years, microplastic studies did not consider contamination of samples during sampling, transportation or processing, likely leading to the overestimation of microplastics present. Since then, protocols from the forensic science industry for minimising contamination have been adapted for microplastic use (Woodall et al., 2015).

Environmental forensic procedures require full labelling of samples and detailed descriptions of the locations they have been obtained from. GPS coordinates, along with local details such as proximity to cities, roads and wastewater treatment plants is required yet not always gathered. In addition, control samples from potential sources of the pollutant are not regularly recovered, for example, agricultural plastics that may have entered the soil and subsequently nearby water environments. Collection of controls in other environmental forensic sampling is standard and it is likely due to the infancy of the analysis of this new pollutant that the sub-discipline has not evolved enough to start investigating source in a meaningful manner. For environmental forensic scientists and those investigating waste, inclusion of plastic pollution into workflows is likely to increase in coming years.

REFERENCES

Arthur. C., Baker. J., Bamford (2008) International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris, University of Washington Tacoma, Tacoma, WA. Group

Ashwini S. K. & George K. Varghese (2020): Environmental forensic analysis of the microplastic pollution at "Nattika" Beach, Kerala Coast, India, Environmental Forensics, DOI: 10.1080/15275922.2019.1693442

Bergmann, M., Mützel, S., Primpke, S., Mine B. Tekman, M. B., Trachsel, J. & Gerdts, G (2019). White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. Science Advances. 5 (8). pp. eaax1157. Available from: https://advances.sciencemag.org/content/5/8/eaax1157

Doyle, M.J., Watson, W., Bowlin, N.M., Sheavly, S.B (2011)Plastic particles in coastal pelagic ecosystems of the Northeast Pacific ocean, Mar. Environ. Res., 71, pp. 41-52, 10.1016/j.marenvres.2010.10.001

Fontana, G.D, Mossotti, R and Montarsolo, A (2020) Assessment of microplastics release from polyester fabrics: The impact of different washing conditions, Environmental Pollution, Volume 264, https://doi.org/10.1016/j.envpol.2020.113960.

GESAMP. 2019. "Guidelines for the Monitoring and Assessment of Plastic Litter in the Ocean." GESAMP Reports & Studies. Vol. 99.

He, D., Zhang, X., Hu, J., 2020. Methods for separating microplastics from complex solid matrices: Comparative analysis. J. Hazard. Mater. 124640. doi:10.1016/j.jhazmat.2020.124640

Lippiatt, S., Opfer, S., and Arthur, C. (2013) Marine debris monitoring and assessment: Recommendations for monitoring debris trends in the marine environment. NOAA Technical Memorandum NOS-OR&R-46. Available at: http://marinedebris.noaa.gov/sites/default/files/Lippiatt_ et_al_2013.pdf.

O'Brien, S., Okoffo, E.D., O'Brien, J.W., Ribeiro, F.B., Wang, X., Wright, S.L., Samanipour, S., Rauert, C., Toapanta, T.Y.A., Albarracin, R., Thomas, K.V (2020) Airborne emissions of microplastic fibres from domestic laundry dryers, Science of The Total Environment, Volume 747, https://doi.org/10.1016/j.scitotenv.2020.141175.

Prata, J.C., da Costa, J.P., Duarte, A.C., Rocha-Santos, T (2019) Methods for sampling and detection of microplastics in water and sediment: A critical review, TrAC Trends in Analytical Chemistry, Volume 110.

Ren, X., Sun, Y., Wang, Z., Barceló, D., Wang, Q., Zhang, Z., Zhang, Y (2020) Abundance and characteristics of microplastic in sewage sludge: A case study of Yangling, Shaanxi province, China, Case Studies in Chemical and Environmental Engineering, Volume 2, https://doi.org/10.1016/j.cscee.2020.100050.

Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K., Rios-Mendoza, L.M., Takada, H., Teh, S., Thompson, R.C., (2013) Policy: Classify plastic waste as hazardous. Nature. doi:10.1038/494169a

Schönlau, C., Karlsson, T.M., Rotander, A., Nilsson, H., Engwall, M., Bavel, B.V., Kärrman, A (2020) Microplastics in sea-surface waters surrounding Sweden sampled by manta trawl and in-situ pump, Marine Pollution Bulletin, Volume 153, https://doi.org/10.1016/j.marpolbul.2020.111019

Setälä, O., Magnusson, K., Lehtiniemi, M., Norén.F (2016) Distribution and abundance of surface water microlitter in the Baltic Sea: a comparison of two sampling methods, Mar. Pollut. Bull., 110 (2016), pp. 177-183, 10.1016/j.marpolbul.2016.06.065

Taylor, M., Gwinnett, C., Robinson, L. et al. Plastic microfibre ingestion by deep-sea organisms. Sci Rep 6, 33997 (2016). https://doi.org/10.1038/srep33997

Woodall, L. C. et al. The deep sea is a major sink for microplastic debris. Royal Society Open Science 1, doi: 10.1098/rsos.140317 (2014).

Woodall, L.C., Gwinnett, C., Packer, M., Thompson, R.C., Robinson, L.F., Paterson, G.L.J (2015) Using a forensic science approach to minimize environmental contamination and to identify microfibres in marine sediments, Marine Pollution Bulletin, Volume 95, Issue 1, https://doi.org/10.1016/j.marpolbul.2015.04.044.

Yang, J., Li, R., Zhou, Q., Li, L., Li, Y., Tu, C., Zhao, X., Xiong, K., Christie, P., Luo,Y (2021) Abundance and morphology of microplastics in an agricultural soil following long-term repeated application of pig manure, Environmental Pollution, Volume 272, https://doi.org/10.1016/j.envpol.2020.116028.

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Research to Industry and Industry to Research

COMPOST HEAT RECOVERY SYSTEMS – A TOOL TO PROMOTE RENEWABLE ENERGY AND AGRO-ECOLOGICAL PRACTICES

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A recent ENEA Report focussing on the environmental impacts of combustion highlighted how, in recent years, the sector that has contributed most significantly to a worsening of air quality in Italy is that of domestic heating. Indeed, despite the improvements in technology performance, an increase in particulate matter emissions (both PM_{10} and $PM_{2.5}$) has been registered, mainly caused by increased biomass combustion (ENEA, 2017). Compost Heat Recovery Systems (CHRS) are alternative plants for domestic heating that allow the recovery and sustainable use of thermal energy produced during the aerobic biodegradation of biomass waste originating from urban gardening/pruning residues and agricultural/forestry activities. This waste is system fed with organic residues in the absence of combustion processes, thereby preventing PM emissions associated with heat production. Conversely, an aerobic biodegradation process (*aka* composting process) capable of releasing considerable heat and reaching temperatures of up to 65-70°C is adopted. The heat released is recovered by thermal exchangers and used for domestic purposes. Moreover, the more recalcitrant fractions of organic matter that are not readily hydrolysable and therefore not available for microbial oxidation, remain in the compost, which is subsequently returned to the soil. By this means, CHRS are not only sustainable, but also regenerative for the environment. They indeed have the potential to mitigate climate change and achieve a carbon-negative balance once a considerable fraction of the carbon fixed by plants during photosynthesis has been stored in soils as compost and contributed to long-term soil carbon pools. The possibility of storing carbon in soil is an important aspect of CHRS particularly as, according to the Italian Institute for the Environment Protection and Research, approximately 80% of Italian soils feature an organic carbon content lower than 2% (ISPRA, 2008).

Figure 1 shows a conceptual model of the plant.

CHRS provides sustainable energy whilst also yielding effective waste management solutions, thus fully implementing the principles of circular economy with low-profile organic residues and waste being fully valorized and finally returned to the soil. Concomitantly however, the requirements of the blue economy are also met. Gunter Pauli

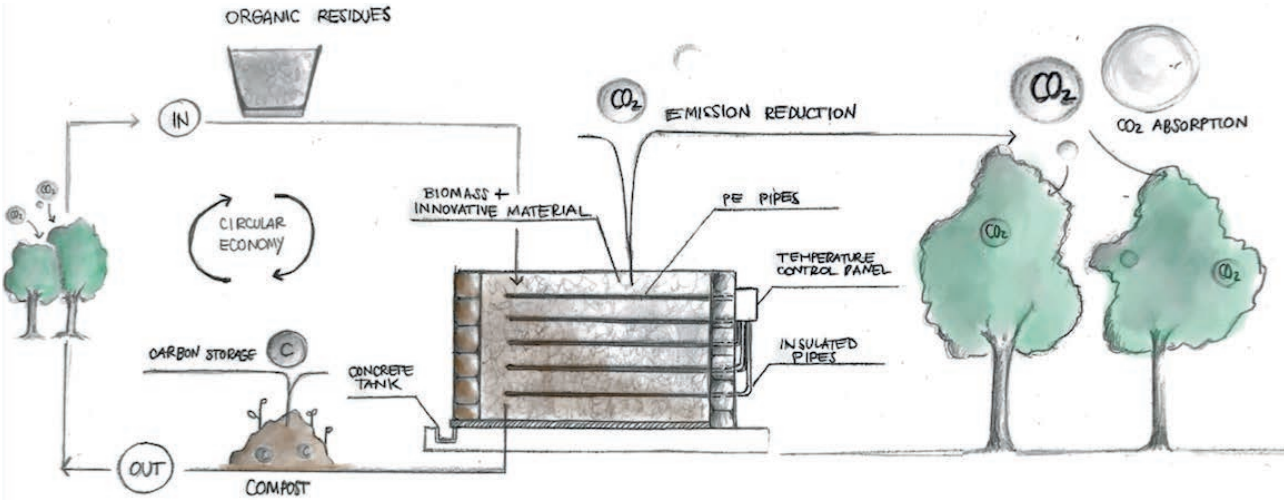

FIGURE 1: Conceptual model of CHRS showing carbon dioxide removal rates, compost production and valorization of organic residues.

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(2010), the founder of the blue economy concept, has underlined how the time has come for societies to move to a pragmatic redesign of the economic system inspired by ecosystems, using locally available resources and transforming one person's waste into another's resource. CHRS comply with these biomimetic principles, which merely improve on a function which occurs naturally in ecosystems to revalorize local residues and regenerate the environment.

1. State of the art of different technologies

Extensive literature reports have been published with regard to well-established composting processes, whilst the literature relating to heat generation and recovery from composting is disjointed and incomplete. This is largely due to the fact that heat recovery from composting processes is frequently achieved on the basis of independent projects conducted by researchers or enterprises in their search for inexpensive energy systems (Zantedeschi, 2018). Rural farmers in ancient China first captured this form of renewable heat over 2000 years ago with the use of hotbeds (Brown, 2014). However, it was only in the 1960s that Jean Pain set up experiments to investigate how this form of heat could be used to heat buildings (Zimmermann, 2020). From the advent of Jean Pain's studies to the 1990s, systems for use in the recovery of energy from composting evolved from conduction-based recovery systems to those using compost vapor stream to capture the latent heat. Accordingly, numerous different configurations have been adhered to worldwide in recovering heat produced during composting processes and exploiting it for the heating of buildings. Four different CHRS configurations are reported and compared below. The main differences relate to the way in which heat exchange is carried out. A comparative analysis between the configurations considered is provided in Table 1.

- Traditional CHRS consists essentially in a heap of raw biomass placed inside a cylindrical container system made of welded iron mesh. The system is insulated with a waterproof membrane and the cylinder surrounded by hay bales; a waterproof bottom membrane allows the leachate produced to be collected and conveyed to a concrete well housing a leachate recirculation pump. The dimensions of traditional CHRS are usually in the range of 35 to 55 m^3, although this may vary (from 25 to 170 m^3, according to Native Power association, https://native-power.de/). The heat generated is recovered by means of spirally-arranged polyethylene pipes fixed on wire mesh at different heights inside the cylinder inside which an exchange fluid flows. Oxygen required by microorganisms is provided using perforated polyvinylchloride pipes placed vertically inside the cylinder promoting aeration by means of a chimney effect (statically). An illustration of the plant scheme is provided in Figure 2.
- The Biologik^R technology differs from traditional CHRS with regard to the type of heat exchanger used. Biologik CHRS does not use polyethylene pipes but rather a metal exchanger inside the biomass pile. The heat exchanger is placed directly inside the body of the plant, reducing heat dispersion and enhancing efficiency of the plant. The related costs are on average much higher than those of a traditional system, due to the presence of the large heat exchanger. The external structure of these systems is comprised of a double iron welded mesh layer inside which homogenously-sized stones are placed for insulation and to allow oxygen to flow statically throughout the body of the plant. The plant is based on a grid base containing gravel and one side of the plant comprises a wood closing wall. Figure 3 provides an illustration of the Biologik CHRS.
- The Condenser Type CHRS facilitates recovery of latent heat by means of vapor condensation. Since the majority of heat released during composting is contained in the latent form of water vapor (Bajiko et al., 2019), to improve the rate of heat recovery a heat exchanger based on condensation of compost vapors may be used. This solution overcomes the problem

TABLE 1: Characteristics and differences between different configurations of CHRS.

Configuration	Feeding material	Process	Aeration system	Insulating system	Heat recovery	Latent heat recovery	Material output	Energy output	References
Traditional CHRS	Woodchip	aerobic	static	Waterproof membrane + hay bales	Polyethylene pipes + exchange fluid	No	compost	Thermal energy	Pain and Pain, 1985 Native Power (https://native-power.de/en/) Biomeiler (https://www.biomeiler.at) associations
Biologik^R	woodchip	aerobic	static	stones	Metal heat exchanger placed inside	No	compost	Thermal energy	Biologik Association (http://www.biologik.it/)
Condenser type	Woodchip, grass, manure	aerobic	static or forced	Waterproof membrane + Hay bales	Low Density Polyethylene pipes + exchange fluid	Yes	compost	Thermal energy	Bajiko et al., 2019
Micro-bioenergy	Woodchip, manure, food waste	hybrid (aerobic + anaerobic)	static	Waterproof membrane + Hay bales	Polyethylene pipes + exchange fluid	No	Compost + digestate	Thermal energy + biogas	Zantedeschi, 2018

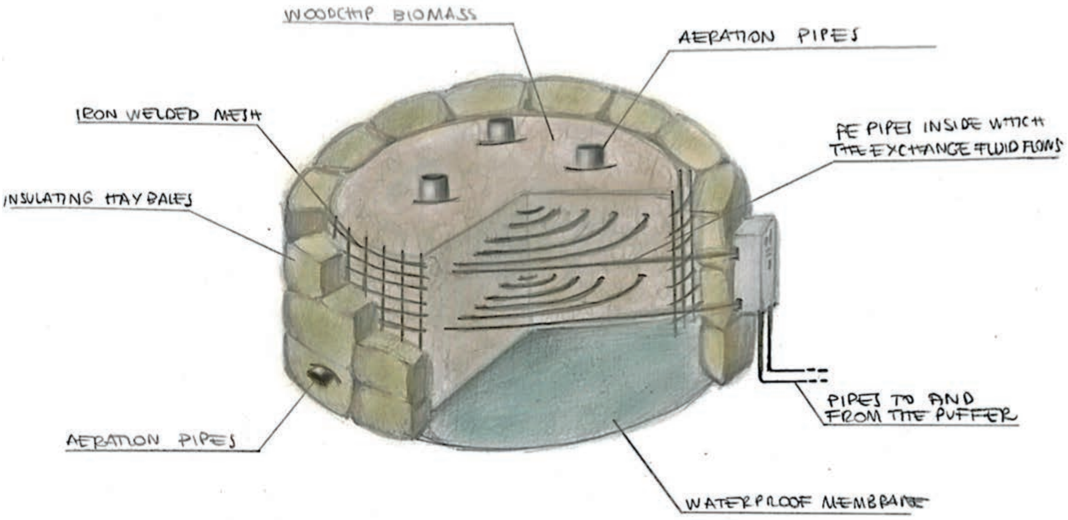

FIGURE 2: Illustration of a traditional CHRS.

of direct heat removal from internal parts of the compost pile that may affect microorganism activity and enhances recovery of the latent heat bound in the liquid-vapor phase. The captured heat is transferred using a heat-carrying medium and the condensed water reused to maintain optimal moisture conditions inside the plant. The heat exchanger is placed on the top of the plant at the end of construction and does not affect the dismantling process. The hot vapor reaches the top by means of natural convection in passively aerated piles, thus highlighting the importance of intensifying the chimney effect. The heat exchanger is made up of Low Density Polyethylene (LDPE) spirally-arranged pipes.

To promote vapor accumulation and condensation on the heat exchanger surface, a cavity is created under the piping system using a wooden lath structure. The aeration pipes are placed vertically but instead of turning up from the top, before the last layer the pipes are folded to exit sideways. A layer of mature compost is placed on top of the plant to act as a biofilter. Figure 4 provides an illustration of a Condenser Type CHRS.

- Microbioenergy involves the installation of an anaerobic digester (micro-biogas plant) inside a traditional CHRS. As anaerobic digestion is an endothermic process, in this configuration, the function of the CHRS is to keep the digester warm whilst providing thermal energy to a building. Microbioenergy yields compost, ther-

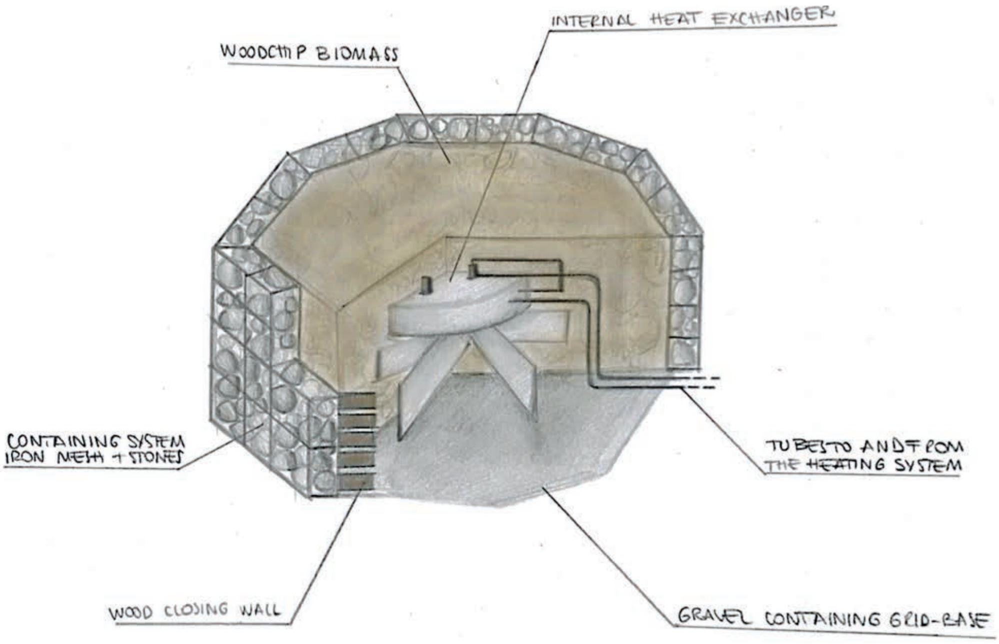

FIGURE 3: Illustration of Biologik CHRS.

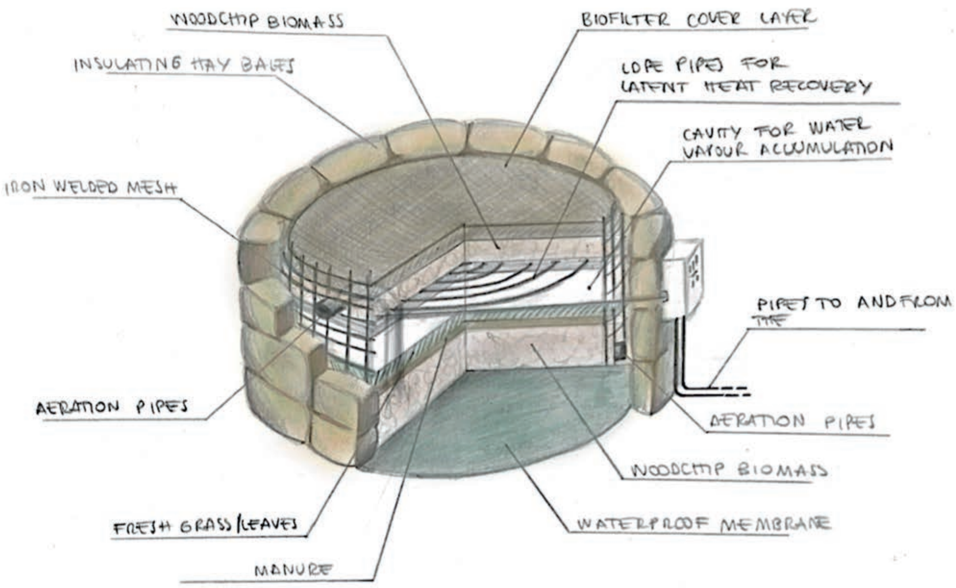

FIGURE 4: Illustration of a condenser type CHRS.

mal energy and biogas. The aerobic part of the plant is fed with woody biomass while the anaerobic part is fed with readily biodegradable organic material (manure and food waste). The dimensions of traditional CHRS and the digester vary and do not feature a linear proportion; generally, CHRS volume is in the classic range of 35 - 55 m^3. Heat is recovered through the traditional polyethylene pipe system. Simultaneously, methane is produced and collected through a biogas outlet pipe in a dedicated tank, compressed and used after desulfurization for many different purposes, including powering a stove or a gas-fueled boiler to produce hot water or sent to a co-generator to produce electric energy.

By means of this configuration both compost and digestate are produced; compost is used directly while the digestate is treated and used in various ways; it may be collected in a septic tank, aged, separated and dried to be used as fertilizer. An illustration of this system is provided in Figure 5.

All these plants are generally connected to a puffer by means of which the recovered heat is distributed between the Underfloor Heating System (UHS) and the Domestic Hot Water (DHW) system of a building. The biomass that undergoes biodegradation in the CHRS is capable of providing adequate levels of thermal energy for approximately one year. After this period, the thermal energy yielded is no longer sufficient and the biomass should be replaced. For this reason, once a year CHRS should be dismantled and rebuilt using new chipped biomass.

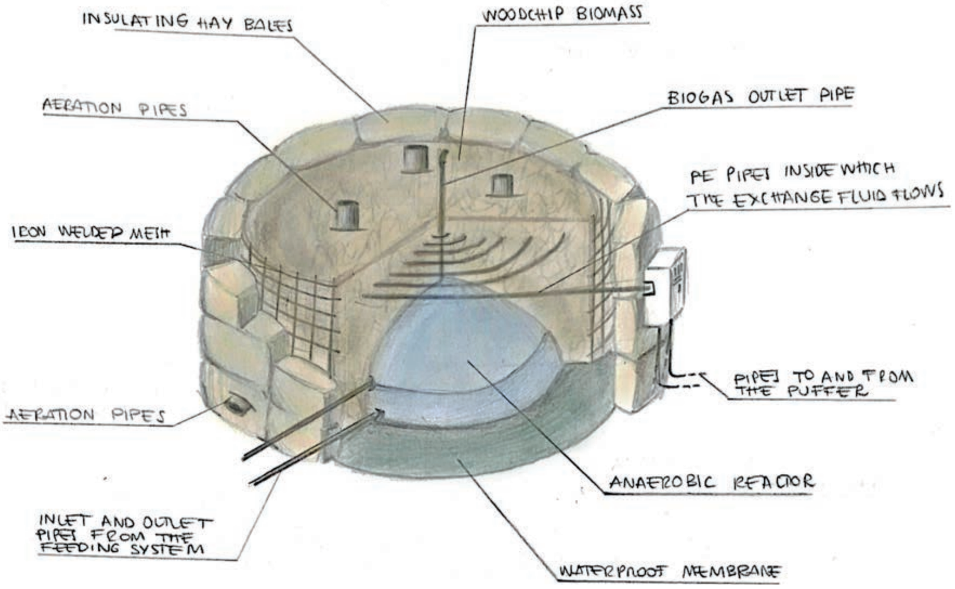

FIGURE 5: Illustration of a Microbioenergy CHRS.

2. Current research activities for the development of CHRS

CHRS is in a position to compete on the market with both traditional and green technologies such as pellet combustor or natural gas condensing boilers and solar thermal panels or geothermal plants, respectively. CHRS features two main advantages over competitors: low investment costs and potentially lower GHG emission balance. On the contrary, the main limitations relate to a need for maintenance (typically once yearly) and high volumes/spaces occupied by the heaps. In order to maximize the advantages and reduce limitations, further research should be conducted to address the following topics:

- Evaluation of CHRS emissions related to the full life cycle by means of a Life Cycle Assessment study.
  CHRS should be compared to other technologies from both economic and environmental viewpoints. Environmental assessment will take into account not only operational life span of the system, but also full life cycle of a CHRS using LCA. Moreover, the potential impact of unwanted emissions on overall carbon balance should be considered. Locally-established anaerobic conditions in ‘dead-zones’ of the heap might lead to release of considerable amounts of methane; emissions of nitrous oxide and ammonia from nitrogen-rich biomass should also be evaluated.

- Evaluation of thermal power output through monitoring of a real-scale CHRS.
  Information relating to the thermal power output of CHRS is based on literature data suggesting an average value of 0.1 kW/m^3 of biomass, depending on different parameters. According to the Native Power association, a traditional plant (volume ranging from 25 to 80 m^3) fed with chipped woody biomass yields an average thermal power output of approx. 0.05 kW/m^3 of biomass. These data reveal how thermal power output is predominantly linked to the dimensions of the plant and the material used to feed the plant. In order to determine more accurate output values, traditional plants should be regulated by means of innovative remote monitoring systems purpose designed for CHRS. These consist in a Wi-Fi control unit connected to measurement probes capable of storing plant functionality parameters on a graphical interface. The objective is to test this innovative device and optimize the same by adding new monitoring probes for the measurement of additional parameters.

- Optimization of plant configuration and thermal energy production processes.
  Currently, CHRS are not a viable solution for use in contexts with low space availability, and have a limited operational life span due to degradation of the biomass; after 12-14 months the plant will need to be dismantled and rebuilt using new biomass. These aspects limit the potential field of installation of a CHRS and increase the costs. Studies are currently being carried out to investigate ways of overcoming these limitations. Potential future developments are represented by the use of innovative support materials featuring electrochemical properties. Use of these materials will be combined with new organic readily biodegradable substrates, implying the installation of an external feeding system and determining a new configuration that could reduce the volumes involved and prolong the operational life span of a plant.

- Implementation of CHRS to boost ecosystem services.
  CHRS are currently being considered for use in the context of Agroforestry (AF) systems, i.e. systems adopted to provide a series of different ecosystem services, including biodiversity enhancement, carbon sequestration, nutrient retention, and soil water retention, whilst maintaining high cash-crop yields (Beillouin et al., 2019). To demonstrate the ability of CHRS to function synergistically with AF systems providing agro-energy by ‘intercepting’ the residual biomass to produce bioheat while contributing to soil carbon and nutrients stocks, real scale plants should be implemented and both the plants themselves and the agroforestry system that feeds them closely monitored.

REFERENCES

Bajko, J., Fišer, J., & Jícha, M. (2019). Condenser-type heat exchanger for compost heat recovery systems. Energies, 12(8). https://doi.org/10.3390/en12081583

Damien Beillouin, Tamara Ben-Ari, David Makoswki. Assessing the quality and results of meta- analyses on crop diversi cation Protocol for systematic review and evidence map. 2018. hal-01815485

Brown, G. (2014). The compost-powered water heater. Wood- stock: The Countryman Press (2017). ISBN: 1581571941.

Pauli, G. (2010). The Blue Economy: 10 Years, 100 Innovations, 100 Million Jobs. Paradigm Publications (2010). ISBN: 9780912111902.

ENEA (2017): Final Report: Impatti energetici ed ambientali dei combustibili nel riscaldamento residenziale. https://www.enea.it/it/seguici/pubblicazioni/pdf-volumi/v2017-impatti-combustibili-nel-riscaldamento.pdf (last access: 22/03/2021)

IPCC (2007): Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team: Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, p. 104.

ISPRA (2008). Il suolo, la radice della vita. Pp. 49-57. http://www.isprambiente.gov.it/files/pubblicazioni/pubblicazionidipregio/suolo-radice/49-57.pdf (last access: 22/03/2021)

Native Power Association website: https://native-power.de/ (last access: 10/03/2021)

Zantedeschi, M. (2018). MICROBIOENERGY®: heat and biogas biomass-fueled generation plant for domestic use. Polytechnic of Milan.

Zimmermann, V. (2020). Energia dai rifiuti: Der Biomeiler - Analisi e ottimizzazione del recupero di calore dal compost come alternativa efficiente dal punto di vista energetico e rispettosa del clima ai generatori di calore convenzionali. Scientific Project, Hochschule Augsburg, University of Applied Sciences.

Pain, J., & Pain, I. (1972). The Methods of Jean Pain - Another kind of garden (J. Pain & I. Pain (eds.); 7th ed.). Ancienne Imprimerie NEGRO. https://www.jean-pain.com/en/mjp.php (last access: 19/03/2021)

Smith, M. M., Aber, J. D., & Rynk, R. (2017). Heat Recovery from Composting: A Comprehensive Review of System Design, Recovery Rate, and Utilization. Compost Science and Utilization, 25(1), S11–S22. https://doi.org/10.1080/1065657X.2016.1233082

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Waste to Art

WASTE TO LIGHT

Ugo Matzuzzi
Guasila, Sardinia, Italy

Ugo Matzuzzi was born sixty years ago in Guasila, a small village in Southern Sardinia.

For years he worked as a carpenter, a trade in which he gained a deep knowledge of the material, respecting it and forging it at his will. Intrigued by the beauty of a series of waste materials and refusing to accept their elimination and neglect, almost for fun, together with his son Davide he started to collect inert wastes of all types and to transform the latter using his skills as an artisan. Completely unrelated pieces originating from totally different paths of existence were combined to give rise to new shapes and forms, primed for a redesigned functionality: the perception of and emanating of light. This has given rise to a series of artistic light fixtures, unique sculptures evoking a world of manifold colours comprised of robotic female forms, ancient warriors, fragments of distant civilisations, of space ships... (Figure 1) Some are imaginary works of fiction which, as an abstract art, assume particular significance in the eyes and propensity of the beholder.

The works created by Matzuzzi are not confined merely to their sculptured or multi-coloured form, but rather gain in significance thanks to an effect of light and shadows, achieving a spiritual contrast reminiscent of the yin and the yang. Two diametrically opposed energies, one light and the other dark, necessary and complementary, with the existence of each interdependent on the other. All objects and all situations connect to this powerful duality, crucial in the life search for an equilibrium fostering the conquest of serenity and wellbeing. An added sentiment for those who view the light sculptures forged by Matzuzzi.

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FIGURE 1: The light sculptures created by Ugo Matzuzzi.

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DETRITUS & ART / A personal point of view on Environment and Art

by Rainer Stegmann

Artists seldom provide an interpretation of their own work; they leave this to the observer. Each of us will have his/her own individual view of a specific piece of art, seeing different contents and experiencing a range of own feelings and emotions. Bearing this in mind, I created this page where you will find regularly selected masterpieces from different epochs and I express my thoughts on what the work conveys to me personally. My interpretation will refer specifically to the theme "Environment". Any comments or suggestions regarding this column should be addressed to stegmann@tuhh.de.

PAUL CÉZANNE / Auvers du Cote´du Valhermeil (1882)

Paul Cézanne (1839-1906) is one of the most influencing artists of his time. He represents the art genre impressionism in its last phase and is a pioneer of expressionism. The beautiful painting of the landscape was created near Auvers, a village north of Paris.

Living in peace with nature is an answer to anthropocentric life and a pre-requisite for a sustainable society. I selected this painting because I think it gives us an idea what it means, "living in peace with nature". The painting by Cézanne shows a cultural landscape with a small village, meadows, agricultural land and forests. The houses "hide" in the landscape and do not look like foreign bodies. Nature and human made fields merge into one unit. The painting conveys a calm, peaceful atmosphere in all its beauty. We may have seen similar landscapes and have enjoyed it, but probably did not "see" it in that intensity as Cézanne is presenting it. He encourages us to look at landscape and nature more intensively.

This work of art was created in 1882 when the world was quite different. We find landscapes like the one on the painting less and less often and we may have to search for them. Today most people live in cities and many villages urbanize. Agriculture has changed being more mechanized and optimised for effectiveness; many forests, shrubs and bushes disappeared.

So what does this art- work may tell us? It can give us an impression of a direction in which agriculture should be transformed, how it may become more "natural". This would also satisfy our wish for more nature in life. With so many more people on earth we cannot turn back time and farm as in the old days, but we can try to make agriculture more ecological. Implementing natural bio-tops as ecological islands in the fields and shrubs around them, using crop rotation and more natural fertilizer may be the way to go. We should make cities greener also by practising urban farming. These changes would help to increase biodiversity, to produce healthier food, reduce emissions and to slow down climate change. In addition ecological farming makes the landscape more beautiful.

Next issue: in my next column I will present a painting from Hubert Robert. Hubert Robert (1733-1808) was a French landscape painter who painted preferably architectural subjects. He is also well known for his drawings.

He travelled with Jean-Honoré Fragonard through Italy where he painted many Roman ruins.

HUBERT ROBERT / Demolition of houses on The Pont au Change (1788).

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WELCOME TO THE 40+ YEARS PERSISTENCE CELEBRATION OF THE WASTE RESEARCH DISCIPLINE AT LULEÅ UNIVERSITY OF TECHNOLOGY, SWEDEN

Anders Lagerkvist and Jurate Kumpiene *

A little retrospective on times passed

Following the so called energy crisis of 1973, there was a political consensus in the Swedish parliament that we should strive to utilize the resources hidden in waste streams better. One of the consequences was the decision to start a new kind of engineering education focusing on waste management and environmental issues.

The program started in 1977 and was called Environmental Planning and Design. None of the major technical universities in the country wanted to have a program focusing on waste, but the recently established university of the far north of Sweden welcomed it. One of the character disciplines was waste management, although it was called Residual Products Technology at the time, following the then politically correct terminology, which emphasized the difference between Residuals and Waste. One problem to begin with was the fact that there were no academics with degrees in this new topic, so recruiting a professor for the chair was troublesome and failed at first.

The initial establishment of the group, especially its courses, but also the first research projects, was headed by Per E O Berg, with a background in sewage sludge treatment at the Sanitary Engineering group at Chalmers and the first Swedish studies on source grouping of household waste. He held the title of Acting Professor.

In 1984 Nils Tiberg, then managing director of a metallurgical byproducts recycling company called Merox was appointed professor and chair of the subject. The research interest of these leaders influenced the focus of research of course, so the initial studies on different aspects of household waste management was replaced by a focus on process industry waste management.

Meanwhile, one in the first group of students, Anders Lagerkvist, started working in the group from 1982 with a focus on biological treatment and landfill technology. The group was small during the first years and working in very diverse areas such as household waste collection, biogas and landfill technology, and metallurgical waste recycling processes. Teaching was a main activity for the group since it was a cornerstone in the master program.

In 1988 the group was identified as a primary Swedish research group on biogas technology, and in particular landfill gas technology, by the Swedish Energy Board and

Field work A Lagerkvist, C Maurice, H Ecke in Umeå, Sweden,1998.

Landfill symposium, Sweden, 1998

1st Intercontinental landfill research symposium - ICLRS, Sweden, 2000

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for a number of years the group got support for capacity building in that area. In the same year a close co-operation with the soil mechanics group of LTU resulted in a spin-off research focus of soil remediation issues. Connected to the landfill research a focus on environmental information management also developed, e g for strategic siting of waste management facilities. The group expanded and reached a size which is similar to the present, but still with few individuals in any particular field of research.

In 2001 Anders Lagerkvist became the chaired professor of the academic discipline and in connection with that the group's name was changed to Waste Science and Technology, following the advice of Grahame Farquhar who was visiting professor for a while in the group. In 2019 Anders was succeeded by Jurate Kumpiene. Today the group consists of researchers at various levels of academic carrier, and adjunct professors from industry and academia worldwide. The research subjects have diversified reflecting the contemporary challenges of the waste management sector and the society. These include, but not limited to, various aspects of waste-to-energy, characterization, treatment and recycling of industrial waste, risk assessment and remediation of contaminated sites, etc.

After all these years one can wonder what has been achieved, apart from a bunch of doctor and master theses, courses given, projects performed, papers published, and so on. We would like to think that the core of what has been achieved is the creation of an academic discipline, with its perspectives and practices, and its established home turf in the waste management world - something that has added to the understanding and knowledge development in the field of Waste Science and Technology.

We are planning to celebrate our anniversary sometime during the late autumn when we hopefully can travel again. Look out for further announcements.

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Field work in landfills. A Lagerkvist, J Kumpiene (left) and L. Andreas (right)

Waste sorting exercises with K. Grennberg, LTU

Waste Science & Technology at PhD graduation ceremony of H. Ecke (left) and C. Maurice (right), 2002

Random Friday afterwork, 2001

R. Cossu and A. Lagerkvist at 3rd ICRLS in Lake Toya, Japan, 2004. Friendship Forever!

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