Retrofitting Equipment for Efficient Use of Variable Feedstock in Metal Making Processes - REVaMP

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Variability in material and energy feedstock assessed for the different use cases

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Dissemination level

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CO	Confidential, only for members of the consortium (incl. the Commission Services)	☐

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The REVaMP project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869882.

1. About REVaMP

The main objective of the project "Retrofitting Equipment for Efficient Use of Variable Feedstock in Metal Making Processes" (REVaMP) is to develop, adapt and apply novel retrofitting technologies to cope with the increasing variability and to ensure an efficient use of the feedstock in terms of materials and energy.

For this purpose, existing metal production plants shall be retrofitted with appropriate sensors for scrap analysis and furnace operation. Furthermore, the selection of the optimal feedstock in terms of material and energy efficiency shall be improved by application of appropriate process control and decision support tools. Also, a solid scrap preheating system operated with waste derived fuel shall increase the energy efficiency of the melting processes. To monitor and control the process behaviour in an optimal way, model-based software tools will be developed and applied.

The retrofitting solutions will be exemplarily demonstrated within three different use cases from the metal making industry, namely electric and oxygen steelmaking, aluminium refining and lead recycling. The performance of the different technologies will be assessed, and the benefits will be evaluated in terms of economic and ecological effects, as well as cross-sectorial applicability in other process industries.

2. Introduction and Summary

This deliverable D1.1, "Variability in material and energy feedstock assessed for the different use cases", is included in the work package WP 1 "Analysis of variable feedstock to identify challenges for retrofitting" of the project.

This report provides the results on the study performed to characterize the material and energy feedstock of steel, aluminium and lead furnace charges, including new or alternative inputs. The study includes, but is not limited to, the following issues:

- Analysis of variability of scrap types available or new arising in market
- Study of new wastes and alternative charge materials regarding its economic usability
- Define elements of interest to detect & quantify (tramp elements, valuable alloying elements…)
- Establish metal refining/alloying (micro-addition) requirements

Besides these general issues, for each use case some individual tasks of material feedstock analysis were defined:

BFI, SID and AMB analysed the variability in the feedstock for the steelmaking use case. The requirements for the steelmaking process with respect to scrap composition in terms of undesired tramp elements (Cu, Sn, P, …) and desired alloy elements (Mn, Cr, Ni, …) were defined. Also, the metallic yield of the different scrap types was analysed. Scrap types with high variability in composition were highlighted.

EUT and GRU assessed the inefficiencies in the current production process due to the variability in composition of the Aluminium metal chip feedstock for the aluminium use case.

The analysis was focused in:

- Al scrap and metal chip types available or new arising in market (sizes, composition and common contaminants).
- Definition on requirements of common and alternative Al high-grade alloys (desired alloying elements, as well as impurities admitted).

The variability of the energy feedstock was analysed by REF and AZT with focus on:

- Evaluation of available waste derived fuel (WDF) mixes with fuel characterisation
- Definition of aluminium scrap preheating requirements

In this task, REF characterised the polymeric fraction of automotive shredder residue (ASR, light and heavy fractions), a usual rejection fraction after the metal extraction process of other recycling companies integrated in the the Otua Group, as fuel for a pre-heating system for aluminium scrap:

- Sampling and characterization of the polymeric fractions of ASR (especially, the heavy ASR fraction). The definition of its fuel properties allows to establish the needs of previous treatments required by the material to be used as WDF (size reduction, sieving, format…), evaluating its economic costs, as well as the productive capacities required to the treatment system to be implemented.
- Estimation of the polymeric fraction of ASR available to meet the characteristics and capacities of treatment.
- Optimisation of polymeric fraction of ASR to be used as WDF to overcome characteristics that would affect the performance of the combustion facility:
  - Chemicals in composition which could damage the pre-heater and/or cause oxidation or nitriding reactions. X-ray sensors were considered to separate them from the ASR flow (e.g. PVC sorting).
  - Size reduction and sieving to narrow down the size distribution, to facilitate fuel feeding and combustion

  The aim was to achieve a composition and size of WDF that reduces processing costs derived from size reduction and material sorting, maximising energy recovery for aluminium preheating.

Once the WDF preparation was defined, the material was characterized regarding its fuel properties and behaviour during thermal degradation, by performing proximate analysis and net calorific value measurements, as well as several thermal analyses at lab scale (TGA, evolution of LOI with temperature). Experiments in a research combustion reactor were designed to investigate at a larger scale the combustion products at different temperature and WDF/O_2 ratios and the effect of the WDF heterogeneous composition on deviations of the heat flow. (N.B.*: The execution of those experiments was delayed by COVID-19 situation and the runs were re-scheduled for the period of mid of September to end of November 2020*).

On the other hand, the scrap-preheating requirements were studied, considering:

- Achievable reduction of melting time in rotary furnace
- Content of volatile impurities and moisture of scrap, alloy composition and physical form (shape, size) of scrap

CAR and EXI studied current and new waste materials available on the market to analyse its lead percentage and its applicability as charge material for lead production.

3. Steelmaking material feedstock variability assessment

3.1. Electric steelmaking at Sidenor

The fundamental raw material at the electric steelmaking plant of Sidenor is steel scrap from three different origins:

- Post-consumer scrap: Scrap metal recovery or old scrap from the demolition of the metal structure of old industrial buildings, obsolete machinery, railway and naval scrap, used cars and appliances, etc. (Grades B, C, D and E)
- Pre-consumer scrap: Industrial or new scrap that is generated in processing industries that use steel as raw material in its various forms, in their manufacturing processes. (Grades A, C, F and H)
- Internal recoveries: Scrap generated along the steelmaking process itself, in melt shops, rolling mills and other processes inside Sidenor premises. (Grades G, H, I, J and K)

Pre-consumer scrap is usually very clean in its chemical composition and its variability is lower compared to post-consumer scrap. However, its use is mainly limited due to the high price steel qualities. Well managed, internal recoveries can also provide a stable chemical composition that can lead to huge savings on ferroalloys additions at the secondary metallurgy. Note that some scrap grades at Sidenor come from 2 different origins and are mixed in the scrap yard previous to being charged to the furnace.

As a preparatory step to the development of a scrap charge optimization in WP2, all scrap grades handled at Sidenor's scrap yard have been characterized hereunder.

3.1.1. Characterization of steel scrap grades and its variability

A series of linear regressions were performed based on 2019 data, with the objective of visualizing statistically the variability of the 11 scrap grades currently used at Sidenor during a whole year.

The result is shown in a series of graphs (Figure 1-9), each one showing the composition of each scrap grade regarding the important elements to be controlled for steel production optimization. The element contents and the metallic of the different Grades are shown in the diagrams relative to the mean value of Grade A (=Ref.), the deviation is given in percent in absolute terms.

As it can be easily identified through these graphs, scrap grade G is highly unstable in all the elements, however, it is not consumed in big amounts so its overall influence on final liquid steel composition is small. Regarding scrap cleanness, a highly consumed grade such as D is of vital importance to be well characterized at any moment, as its high content in Cu and P is highly detrimental for steel quality. On the other hand, grades A, B and C (as expected) have proven to be the cleanest in all the elements, being a very stable source of Fe.

3.1.1.1. Copper (Cu)

Copper is one of the most important elements to have under control when designing the scrap mix to be charged in the electric arc furnace. All the copper introduced in the steelmaking process comes with the scrap and cannot be removed from the steel in a later process stage.

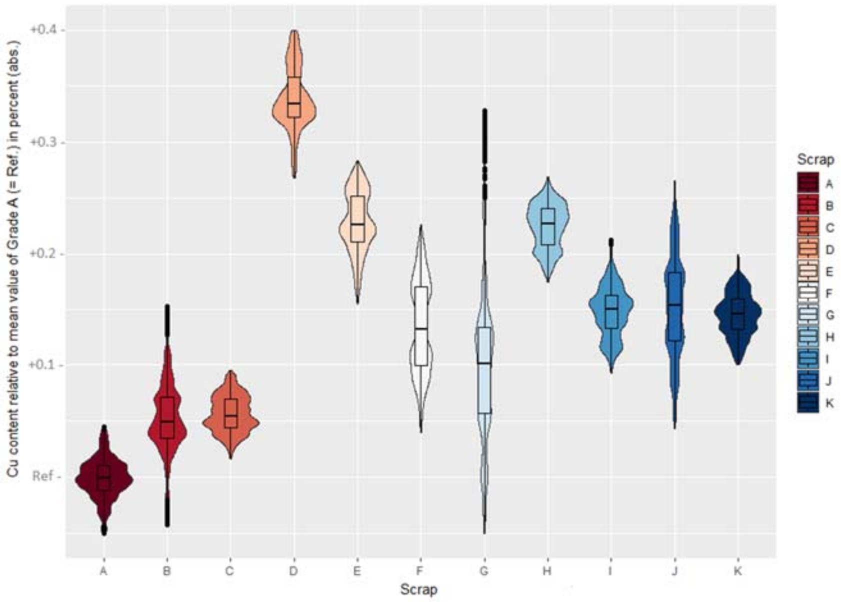


Figure 1. Copper content variability by scrap type at Sidenor.

3.1.1.2. Tin (Sn)

Tin comes with scrap as a common protective layer. Although it comes in a lower concentration compared to copper, it is also a detrimental element that comes with scrap and leads to “Hot shortness” defects.

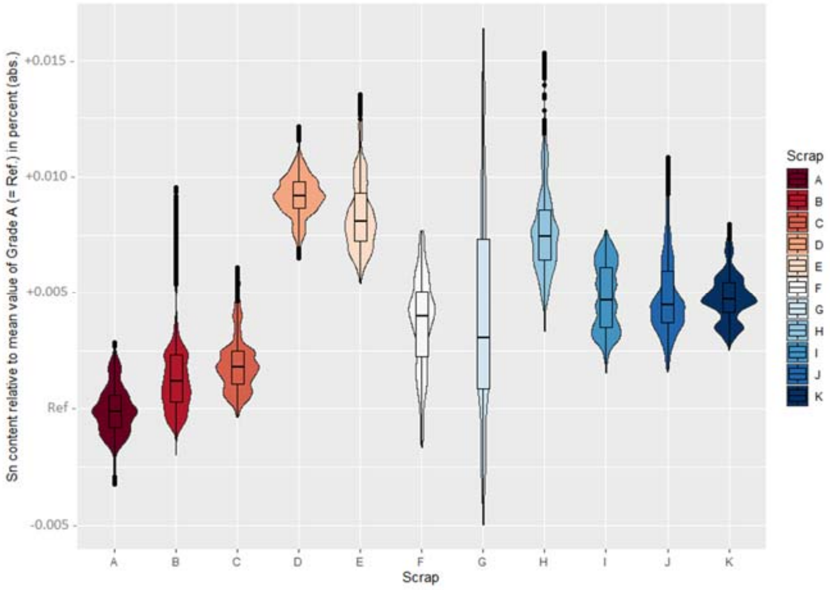


Figure 2. Tin content variability by scrap type at Sidenor.

3.1.1.3. Manganese (Mn)

Manganese is the most commonly used alloying element for steel production, besides Carbon. It provides significant hardening by solid solution and greatly improves hardenability. Due to its low price compared to other alloying elements, it is not of economic interest for charge optimization. A certain amount of the manganese oxidizes in the furnace, therefore this graph just gives a general indication on which scraps contribute more in Mn content.

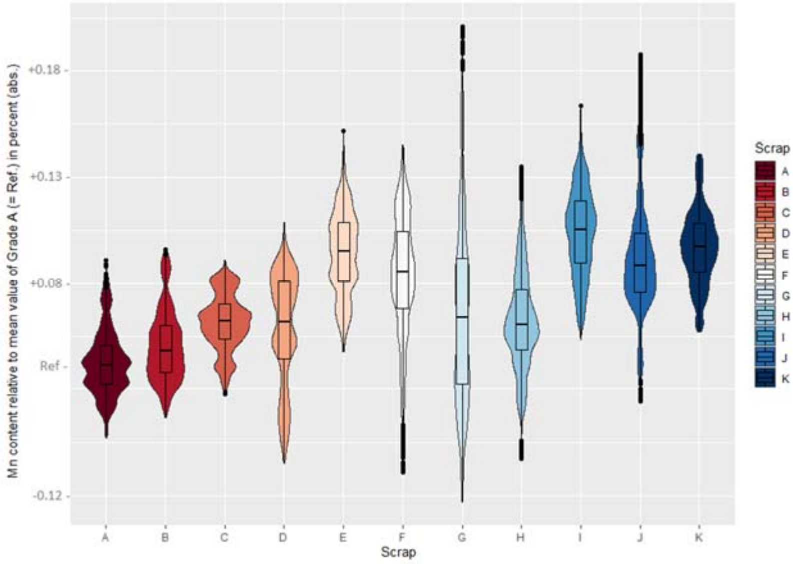


Figure 3. Manganese content variability by scrap type at Sidenor.

3.1.1.4. Chromium (Cr)

Chromium is one of the most commonly used alloying elements due to its hardenability properties and secondary hardening by carbides formation. Like for Mn, a certain amount oxidizes and is transferred to the EAF slag.

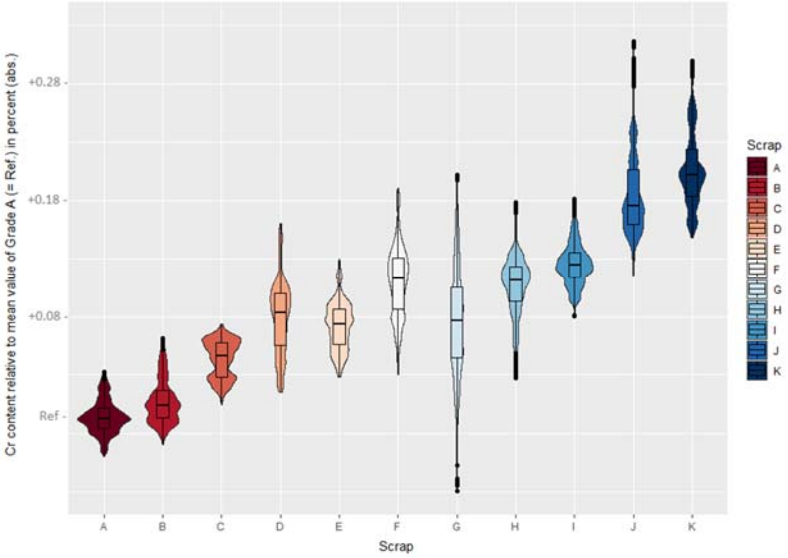


Figure 4. Chromium content variability by scrap type at Sidenor.

3.1.1.5. Nickel (Ni)

Commonly used in combination with other alloying elements (Cr, Mo, V, etc.), Ni increases toughness and reduces cracks and quenching distortions. Its high price compared to Cr requires a good characterization on the internal recovery from the scrap. Different to Cr or Mn, Ni is not oxidized during the EAF process.

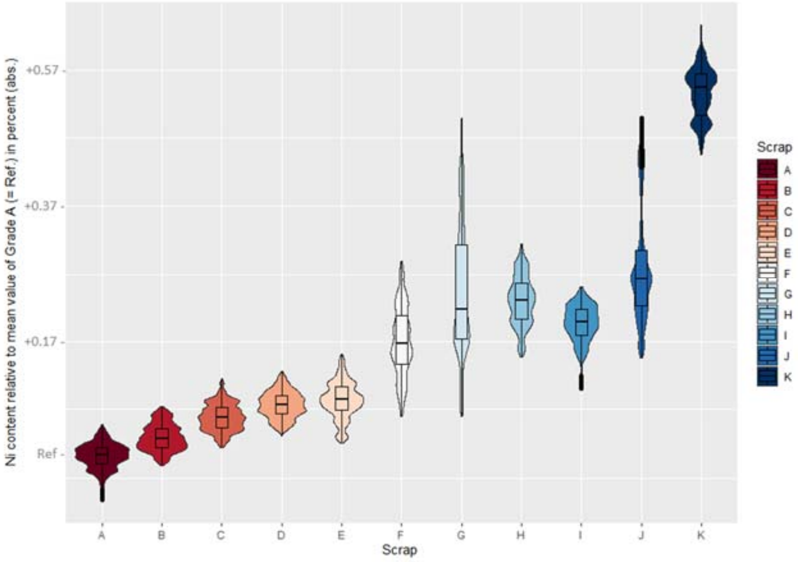


Figure 5. Nickel content variability by scrap type at Sidenor.

3.1.1.6. Molybdenum (Mo)

Molybdenum shows a stronger effect in improving hardenability than Cr and Ni. It also forms more stable carbides that improves secondary hardening. Mo is commonly used for case hardening steel grades and quenching and tempering grades and has a higher price than both Cr and Ni.

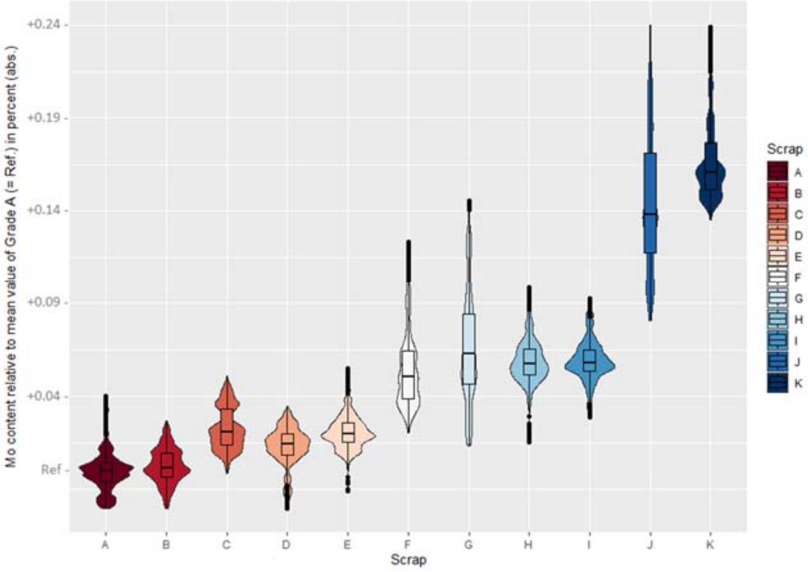


Figure 6. Molybdenum content variability by scrap type at Sidenor.

3.1.1.7. Sulphur (S)

Sulphur is normally considered as a detrimental element. Due to its low solubility in the steel it tends to form sulfides with a low melting point and embrittlement effect at high temperature. It can be removed in the secondary metallurgical process stage, but a scrap charge optimization to minimise Sulphur input by scrap may help to increase productivity reducing the time required for desulphurization.

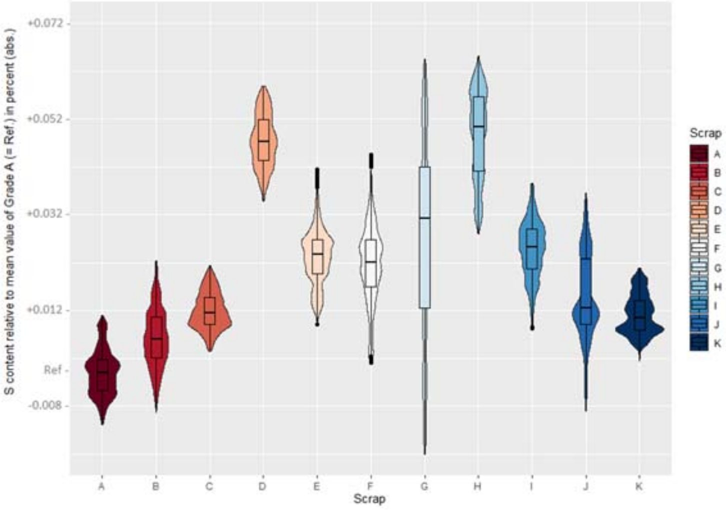


Figure 7. Sulphur content variability by scrap type at Sidenor.

3.1.1.8. Phosphorous (P)

Phosphorous is also considered as a detrimental element. It can only be removed under the oxidizing conditions provided during the refining stage at the electrical arc furnace process. Since the steel sample used for scrap characterization regressions is taken during this stage where dephosphorization takes place, the values are not as representative as the ones obtained for the other elements. However, it gives a general indication on what scrap grades provide more P to the steel bath.

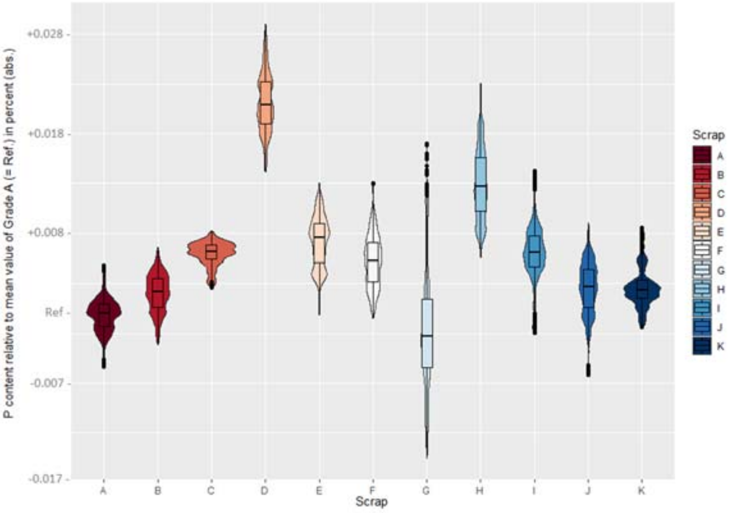


Figure 8. Phosphorous content variability by scrap type at Sidenor.

3.1.1.9. Metallic Yield

In the particular case of metallic yield characterization, there are many other variables involved: Fe losses with exhaust dust and slag, other elements oxidation like C and Cr, liquid steel leaving through the slag door, etc. Additionally, the amount of liquid steel generated per heat is not a straightforward mass balance, since there is a certain amount of liquid steel remaining inside the furnace. Therefore, mass balances are just reliable enough when involving the whole production cycle (approximately a week), which reduces highly the amount of available data.

The result is a not so good regression. However, it is clear that some grades are cleaner (both regarding residual elements and steriles) than others.

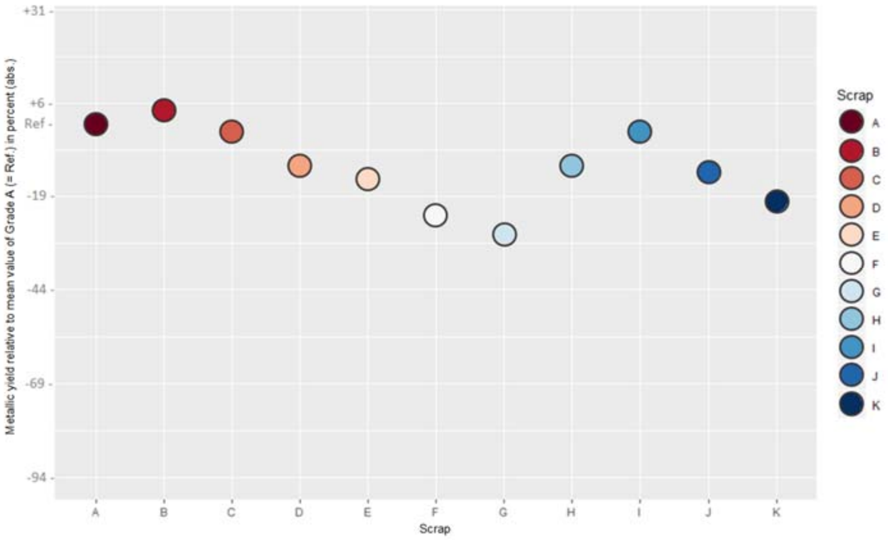


Figure 9. Metallic yield by scrap type at Sidenor.

3.1.2. Definition of tramp and valuable alloying elements requirements

The production at Sidenor is characterized for being very heterogeneous in terms of the chemical composition of its products, being highly dependent on client demand.

During 2019, 390 different grades were produced, with amounts ranging from just 1 to 250 heats per grade. It is important to notice that even for one steel grade, there are significant differences in the chemical composition requested by different clients. Therefore, it is not of interest to set general requirements for a few family grades since the optimization won't really be optimal.

A charge mix optimization should be performed according to the following two main requirements on each heat:

Copper upper limit

This is known to be the most restrictive value when calculating a scrap mix. A Cu value exceeding the upper limit may require the whole heat to be scrapped in the worst-case scenario. This is due to the impossibility of removing the Cu excess by any means during the steelmaking process.

Nickel and Molybdenum lower limit

The scrap charge should be optimized so that Ni and Mo content in the scrap are mostly used for Ni and Mo containing steel grades. These alloying elements are adjusted according to the lower limit requirements of each heat, focusing on the optimization of the costs, as it is not technically necessary that Ni and Mo contents exceed the lower limits during the EAF melting process. The final composition adjustment can be done in the following secondary metallurgy processes, i.e. in the ladle furnace.

The following diagram shows the chemical composition requirements of these 3 elements for the heats produced during 2019.

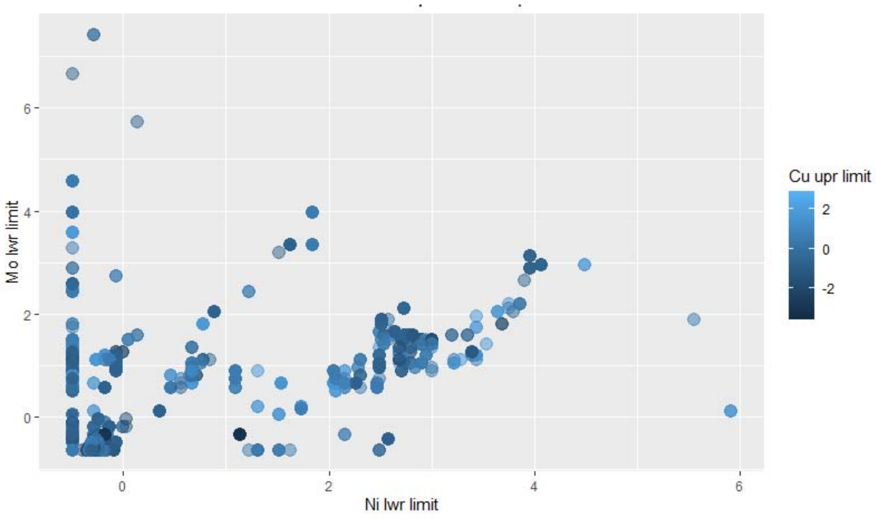


Figure 10. Chemical composition requirements of steels grades at Sidenor.

Note: Values have been standardized, i.e. centred to the mean and rescaled with standard deviation.

As can be seen in the graph above, there is no clear clustering for Cu upper limit and Ni and Mo lower limit requirements per heat. The objective will be to maximize the use of high Ni and Mo scrap grades (mostly internal recoveries) when there is a Ni and Mo lower limit requirement above 0.

3.1.3. Other charge materials available in the market

The following scrap grades are used sporadically when market prices are found compelling.

- Pig iron:
  Coming from the BF, it has a high Carbon content (around 4%), and a considerable amount of Si (around 0.5%), which requires a higher oxygen consumption during melting and an early charge into the furnace (usually with 1st scrap basket) to avoid longer processing times for complete decarburization.
- High Briquetted Iron (HBI):
  It is characterized by a very low residual content. However, it tends to break and originate fines, which results in a lower yield.
- Railroad ferrous scrap:
  Similar to other scrap currently used but with lower and stable residuals.

3.2. Oxygen steelmaking at ArcelorMittal Bremen (AMB)

Like at the electric steelmaking plant of Sidenor as described in Chapter **Fehler! Verweisquelle konnte nicht gefunden werden.**, the scrap types used at AMB can be separated into three groups:

- Post-consumer scrap (types 3, 5, 8 and 9)
- Pre-consumer scrap (types 4, 6, 7 and 19)
- Internal recoveries (types 2 and 10 to 18)

In contrast to the electric steelmaking plant of Sidenor, in the oxygen steelmaking process at AMB only around 20 % of the material charged into the BOF converter is made up by scrap. The remaining 80 % consists of hot metal from the blast furnace, whose composition is analysed for every single heat and is therefore known with good accuracy.

In purpose of optimizing the scrap mix the goal is to maximize the amount of post-consumed scrap due to the low price. The limitations come from the high amounts of tramp elements and their high, and most importantly, unpredictable variability. Therefore, adding clean, but expensive Pre-consumer scrap and Internal recoveries is necessary. For the internal recoveries, most scrap types provide a stable chemical composition. The limitations for those are the availability, and especially for the oxidic recoveries their influence on the energy balance.

3.2.1. Characterization of steel scrap grades and its variability

In order to determine the composition and the metallic yield of the scrap types used at AMB, a data set of 325 heats containing

- analysis and mass of the charged scrap types,
- analysis and mass of the hot metal,
- analysis and mass of tapped steel,
- analysis and mass of the slag

were used in a multiple regression analysis. No statistically significant statements could be made for three scrap types due to insufficient frequency of use, so that in the following the results are only given for 18 scrap types.

Similar to Sidenor, a total of 8 elements were examined, whose content in the produced steel grades is of particular interest. Based on a global optimization calculation, the most probable element content was determined for all scrap types (shown as "global opt." in the following diagrams). In order to quantify the different variability or statistical significance of the determined element content for the different scrap types, additionally a probability distribution was determined, which is shown as a vertical symmetrical histogram in the diagrams. For better comparability the expected value ("mean") and the "median" of each probability distribution are marked in the diagrams. Since the composition of the charged hot metal is known from a heat-individual lab analysis, it is not shown in the respective diagrams. It occurs only in the diagram for the metallic yield, where the hot metal is marked as feedstock No. 01. Thus, the numbering of the scrap types begins with 02 in all diagrams.

The scrap types with an average mass fraction in the charge of more than 3 % (scrap no. 7, 8, 10, 17, 19) show clearly compact distributions for all elements and are less susceptible to outliers. In contrast, scrap types with an average input fraction of less than 1% (scrap no. 3, 12, 14, 16) show significantly more frequent outliers far outside a compact core. Broad distributions therefore do not necessarily have to be an indication of a fluctuating quality of the scrap type but may also or partly be the result of increased statistical sensitivity due to low input masses.

The post-consumer scrap types (3, 5, 8 and 9) show a significantly high contamination with Copper and Tin: the three types with the highest Cu content and the two with the highest Sn content are post-consumer scrap types.

3.2.1.1. Manganese (Mn)

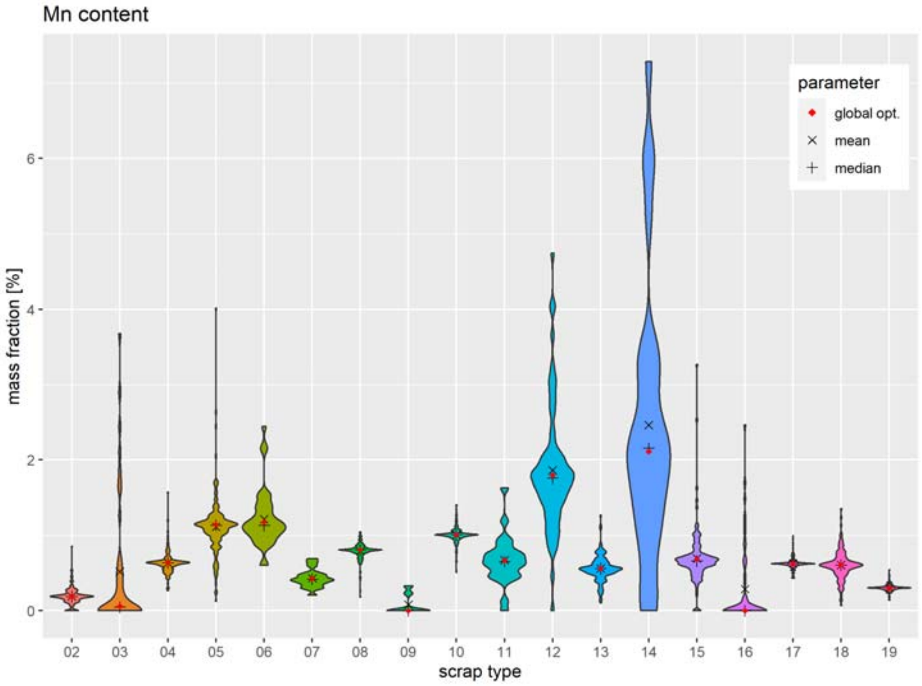


Figure 11. Manganese content variability by scrap type at AMB.

3.2.1.2. Phosphorus (P)

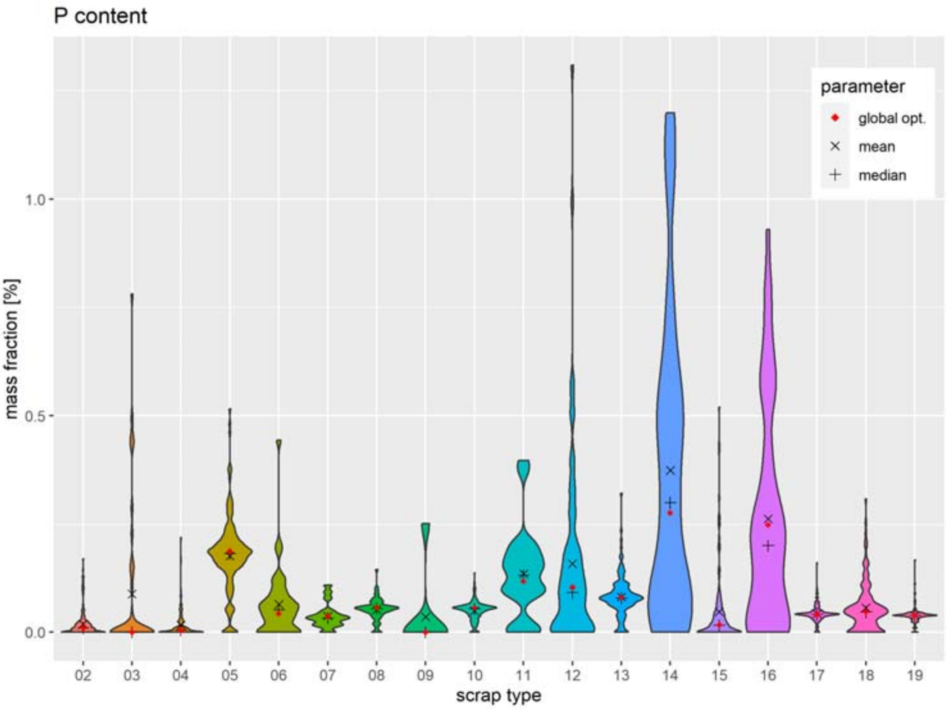


Figure 12. Phosphorous content variability by scrap type at AMB.

3.2.1.3. Sulphur (S)

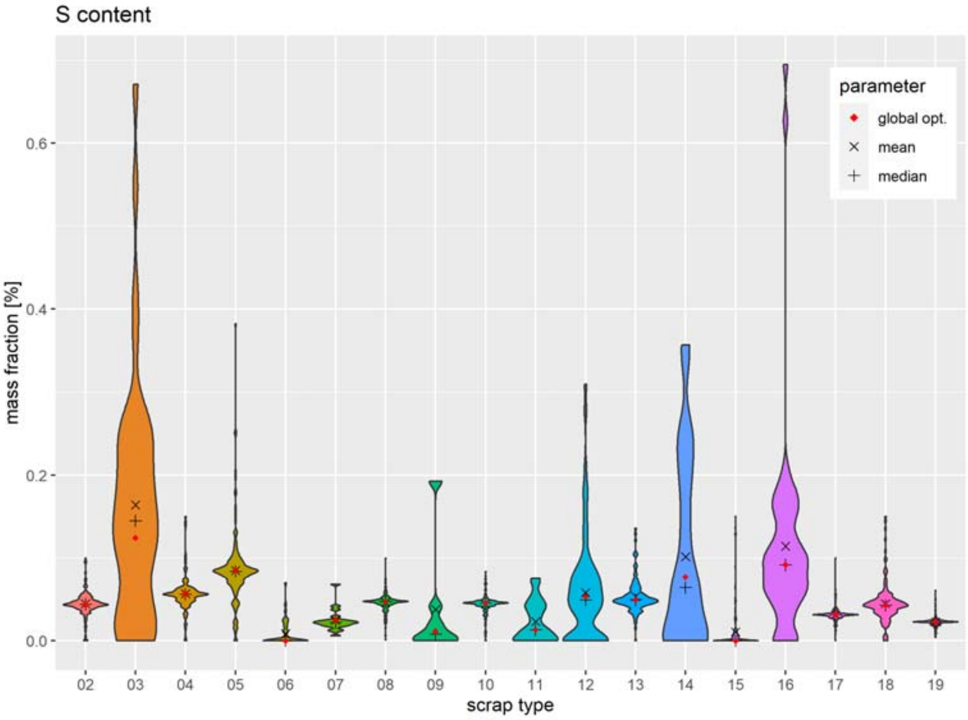


Figure 13. Sulphur content variability by scrap type at AMB.

3.2.1.4. Chromium (Cr)

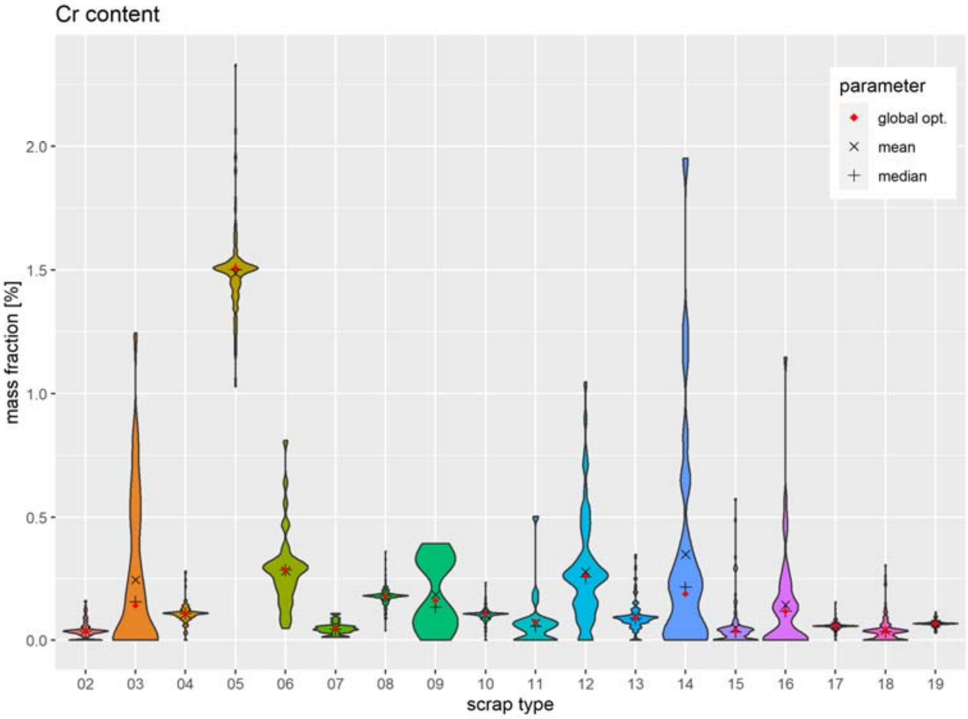


Figure 14. Chromium content variability by scrap type at AMB.

3.2.1.5. Copper (Cu)

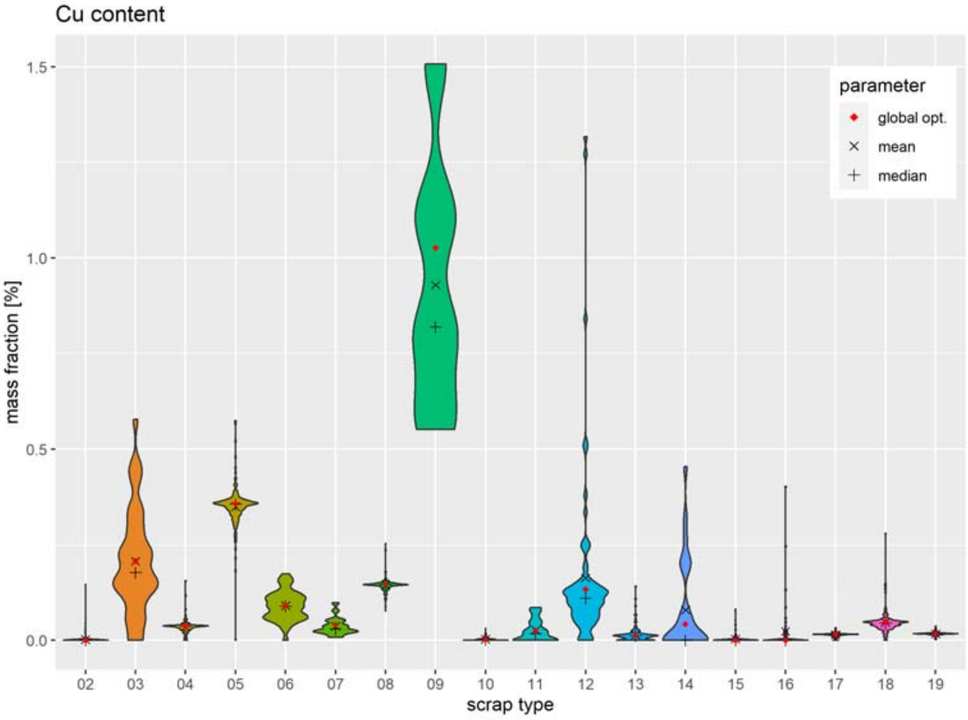


Figure 15. Copper content variability by scrap type at AMB.

3.2.1.6. Nickel (Ni)

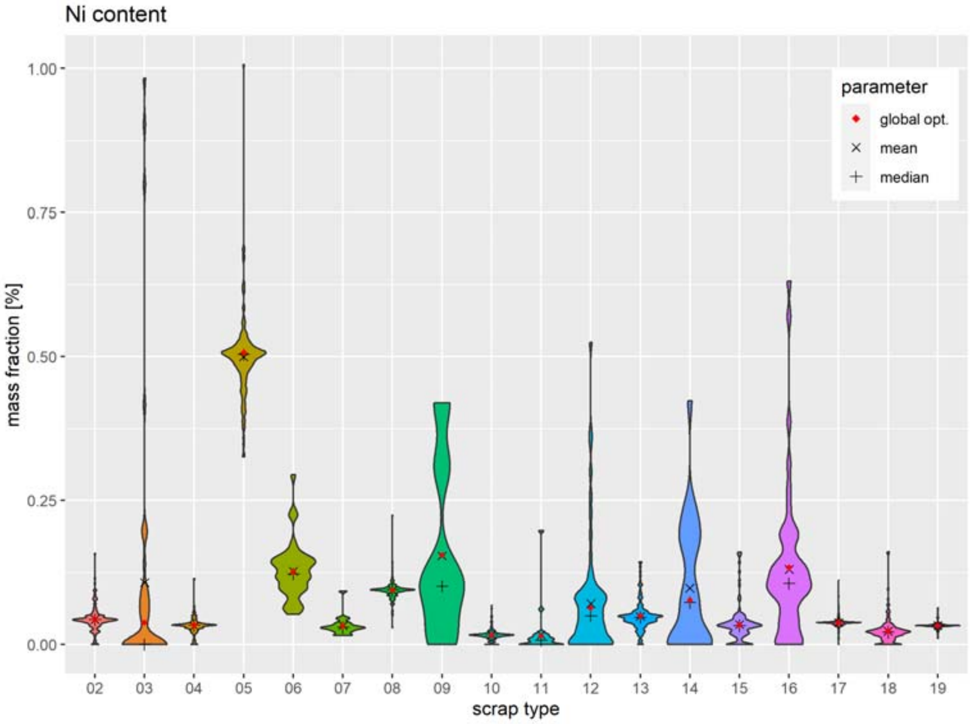


Figure 16. Nickel content variability by scrap type at AMB.

3.2.1.7. Molybdenum (Mo)

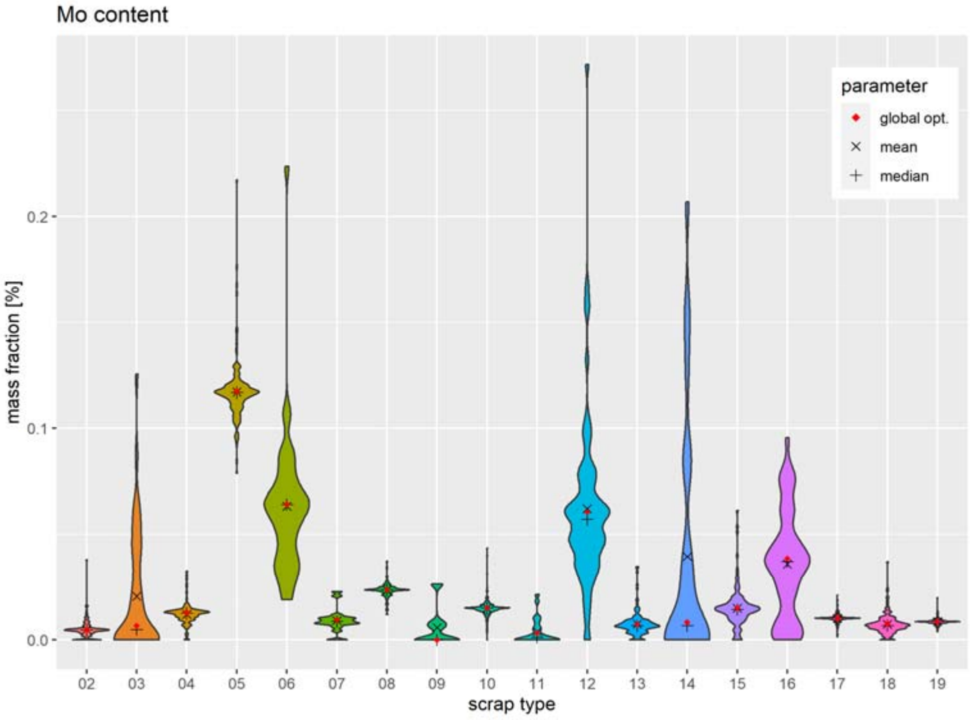


Figure 17. Molybdenum content variability by scrap type at AMB.

3.2.1.8. Tin (Sn)

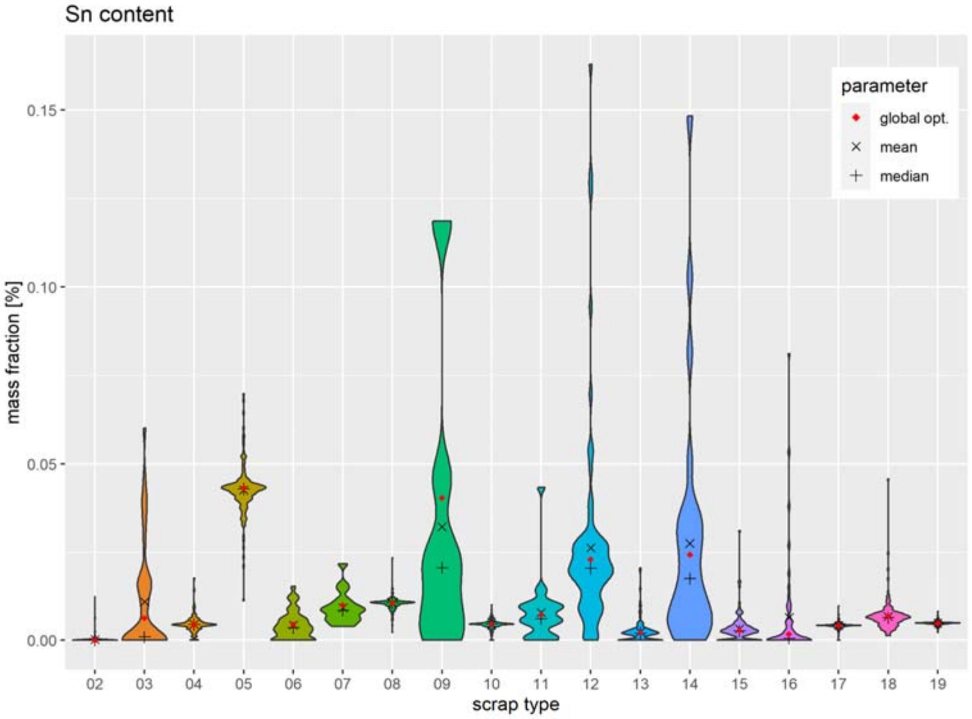


Figure 18. Tin content variability by scrap type at AMB.

3.2.1.9. Metallic Yield

As expected, the results for metallic yield show a high value with low spread for the hot metal (No. 01). Of the scrap types, only Nos. 5, 6 and 12 show similarly high values, while for most scrap types the metallic yield lies between 70 % and 90 %. The broad distribution for scrap types 3, 14 and 16, which cover the full range, is likely to be the effect of a lack of statistical robustness because of the low mass fraction in the heats of less than 1% on average of the scrap types in question.

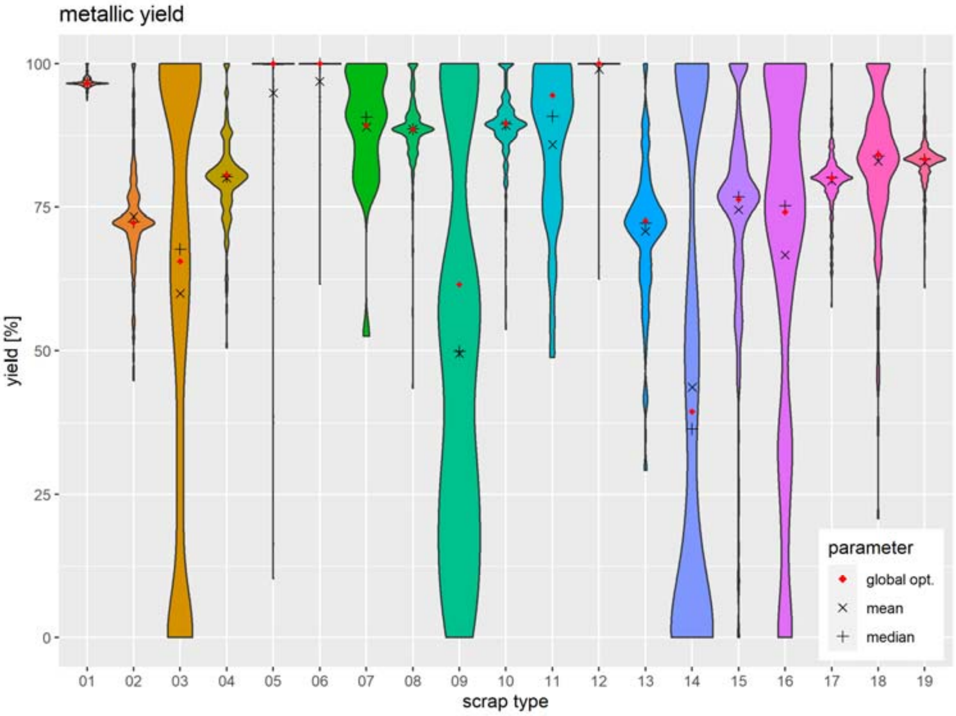


Figure 19. Metallic yield by scrap type at AMB.

3.2.2. Definition of tramp and valuable alloying elements requirements

While all in Chapter 3.2.1.1 - 3.2.1.8 described elements are important to fulfill the quality requirements, elements like Manganese, Phosphorus and Sulphur can be limitedly controlled during the steelmaking process. However, Sulphur, being removed during a certain secondary metallurgical process, that is not applicable for all steel qualities, must be monitored and controlled within the scrap mix optimization.

Elements like Copper, Chromium, Nickel, Molybdenum and Tin cannot be sufficiently or not at all removed from the steel during the processes. Therefore, they have to be strictly limited already in the phase of charge mix selection.

Thus, having the highest variability in post-consumer scrap types, the most important tramp elements to monitor are Copper, Chromium and Nickel. Their single contents and the sum of those three determine the quality of the product. Molybdenum and Tin being just as important as the aforesaid three but showing a much lower variability in the analysed scrap types.

Another restraint for the scrap mix optimization is the influence on the energy balance. Deoxidizing oxidic scrap raises the energy demand and therefore leads to an increase of the hot metal ratio. However, the hot metal ratio is nowadays one of the most important key performance indicators of oxygen steelmaking, especially with regard to CO_2 emissions.

4. Aluminium feedstock variability assessment

4.1. Aluminium material feedstock variability assessment at Grupal Art

Grupal Art is specialized and has the specific equipment for recycling and treating aluminium chips. Therefore, aluminium chips are the main feedstock material used by Grupal Art to obtain their product: aluminium ingots of the different alloys.

As a production protocol, Grupal Art takes samples of each aluminium chip delivery and measures its composition by means of Optical Emission Spectrometry. The chemical composition of the aluminium chips is measured and stored in the company database in order to use the feedstock in the most effective and convenient manner for their daily production.

This deliverable presents the aggregated results for the composition of the aluminium chips measured during the last year (2019), focusing on the most important and concerning elements: Si, Fe, Cu, Mn, Ni, Mg, Cr, Zn, Ti and Pb.

4.1.1. Characterization of aluminium metal feedstock and its variability

Grupal Art classified the aluminium chips received in 2019 from their suppliers in 6 different categories: C1, C2, C3, C4, C5 and C6.

The composition values are presented as relative values taking as reference the median of C6 category composition, as C6 is the category with a globally lower content and lower dispersion of the different elements.

4.1.1.1. Silicon (Si)

Silicon is not a big concern in terms of impurity for Grupal Art, as all the casting alloys have at least 5 % of Si. Actually, always some amount of Si has to be added to the melt to reach the required concentration. Nevertheless, Si has been also added to the study due to the big amount present in most of the chips, even if it is not of big concern in aluminium casting alloys.

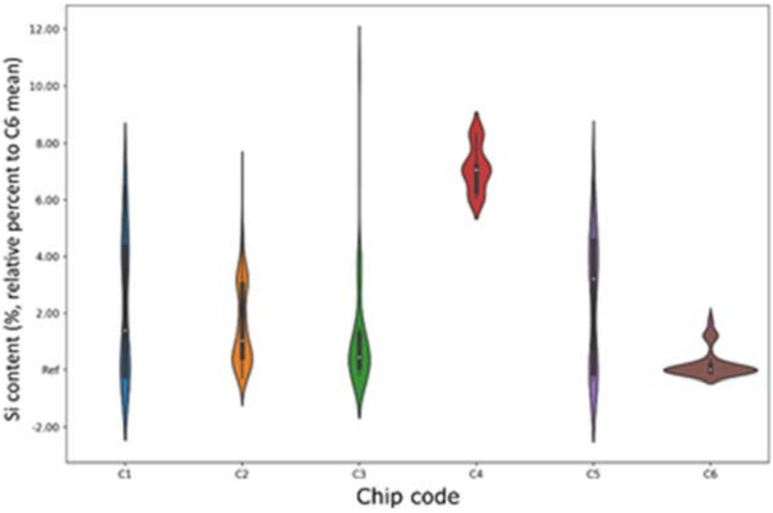


Figure 20. Silicon content variability by chip category at Grupal Art.

4.1.1.2. Iron (Fe)

Iron is the most common impurity present in aluminium alloys, having a detrimental impact in the mechanical properties of the alloy, mainly its ductility. It is frequently mixed with aluminium chips, as aluminium machining tools are typically made from steel. It is critical for high-grade aluminium alloys as they require low Fe levels, below 0.5 % and in some cases even below 0.15 %.

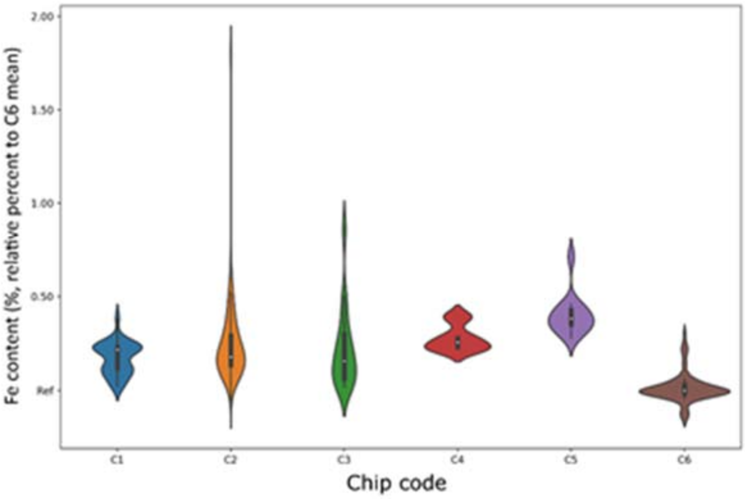


Figure 21. Iron content variability by chip category at Grupal Art.

4.1.1.3. Copper (Cu)

Copper is a common alloying element in aluminium alloys. For this reason, it is quite common to have high concentration of Cu in the aluminium chips feedstock. However, it is important to control the level of this element, as an important number of the alloys produced by Grupal Art do not require Copper.

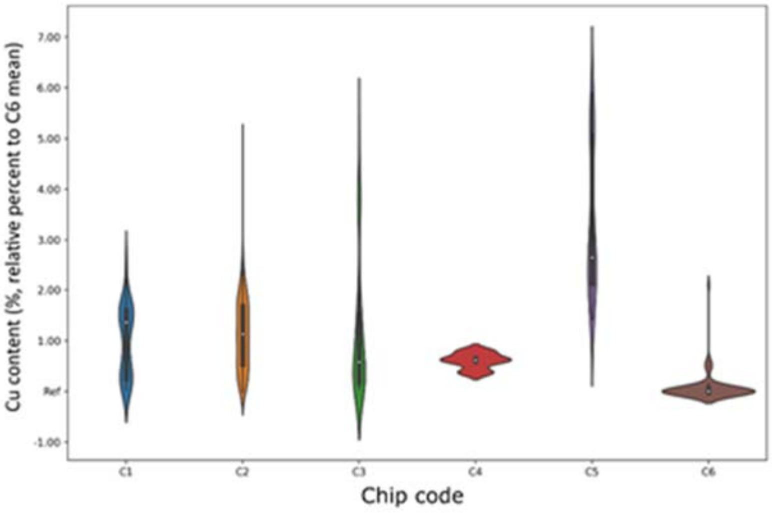


Figure 22. Copper content variability by chip category at Grupal Art.

4.1.1.4. Manganese (Mn)

Manganese is an aluminium alloying element, commonly used in some wrought and casting alloys. Nevertheless, it is considered an impurity in most of the alloys, and therefore its levels should be controlled in order to use Mn rich feedstock to produce those aluminium alloys that actually require it as alloying element.

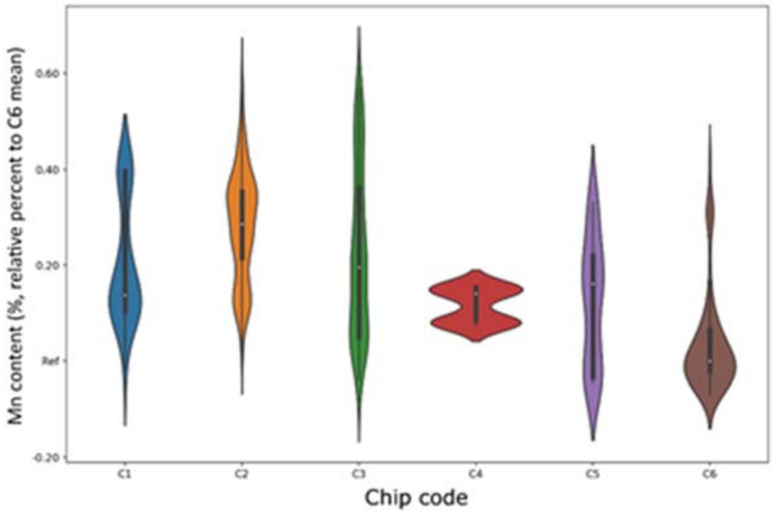


Figure 23. Manganese content variability by chip category at Grupal Art.

4.1.1.5. Magnesium (Mg)

Magnesium is a common aluminium alloying element, used specially in wrought alloys (5xxx and 6xxx series). However, in the casting alloys produced by Grupal Art, the alloying level is much lower. Thus, in some of the alloys magnesium is treated as an impurity and should be kept at a very low level (even below 0.1%).

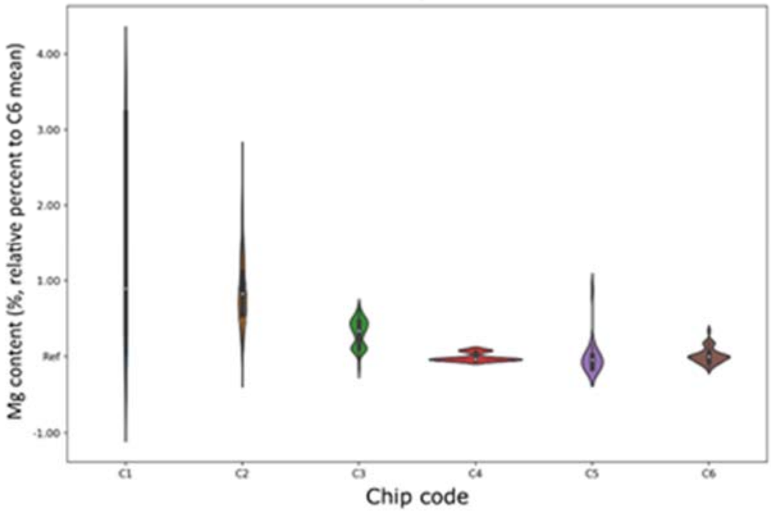


Figure 24. Magnesium content variability by chip category at Grupal Art.

4.1.1.6. Chromium (Cr)

Chromium is considered an impurity in most of the aluminium alloys, especially in casting. However, it is used in some wrought alloys to limit grain growth and/or improve corrosion resistance and can be frequently found in small amounts in some of the aluminium chips. As it is an impurity for all casting alloys produced by Grupal Art, chromium levels should be strictly controlled and kept as low as possible.

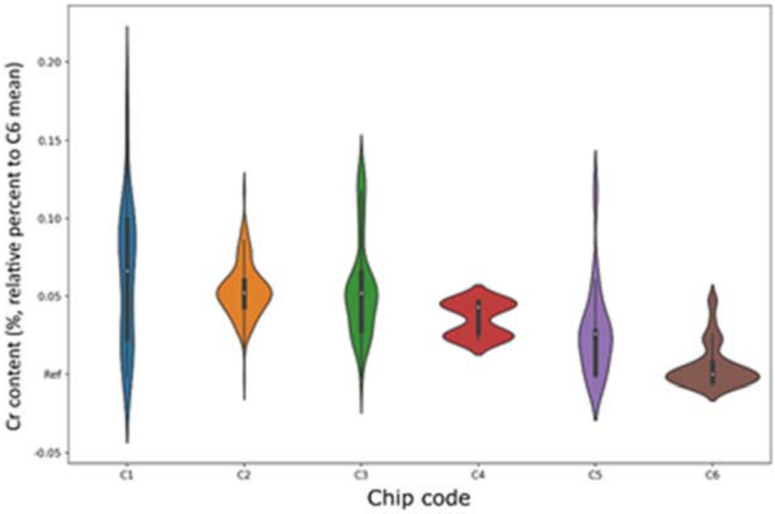


Figure 25. Chromium content variability by chip category at Grupal Art.

4.1.1.7. Zinc (Zn)

Zinc is an element used in large amounts in some aluminium wrought alloys (series 7xxx). It is a common tramp element present in the machining chips and it should be taken into consideration. In casting alloys, such as those produced by Grupal Art, is commonly regarded as an impurity. However, there are some alloys for die casting (such as EN AB-46000 and EN AB-46500) that admit up to 1.2 and 3% of Zn, respectively. Therefore, Zn rich chips should be used in the production of those alloys.

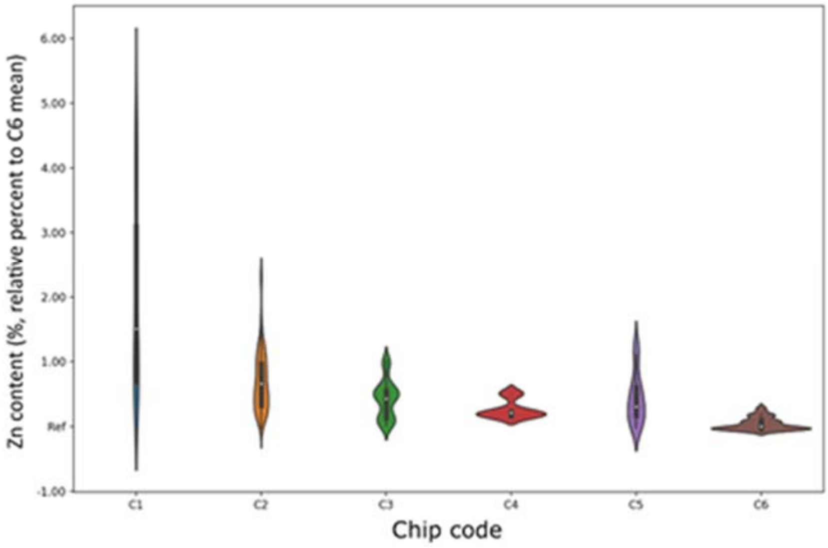


Figure 26. Zinc content variability by chip category at Grupal Art.

4.1.1.8. Titanium (Ti)

Titanium is typically used as grain refiner at low concentrations (below 0.15 %) in both wrought and casting alloys, and is commonly found in aluminium chips at this level. In general, it is not a big concern as most of the alloys produced by Grupal Art accept Ti levels up to 0.2 or 0.25 %. In fact, some alloys improve their mechanical properties with low levels of Ti. For this reason, several Grupal Art costumers demand to have some level of Ti. Therefore, to control its level and use when required can mean an important cost reduction of Ti master alloys.

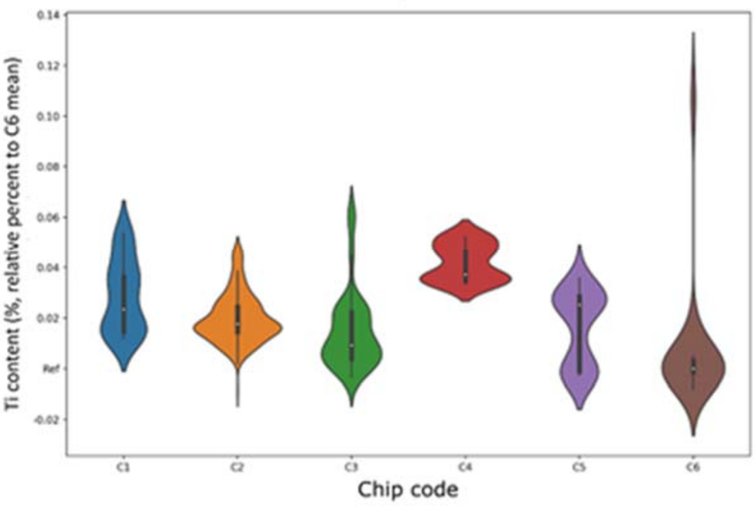


Figure 27. Titanium content variability by chip category at Grupal Art.

4.1.1.9. Lead (Pb)

Lead is an element that is used in some wrought aluminium alloys, at levels of around 0.5%, for improving its machinability. However, Pb is regarded as an impurity in all the casting alloys produced by Grupal Art. In order to be able to keep it below the maximum allowed level, from 0.05 to 0.35 %, it is required to control the aluminium chips rich in Pb and doss them in a controlled manner in different production batches.

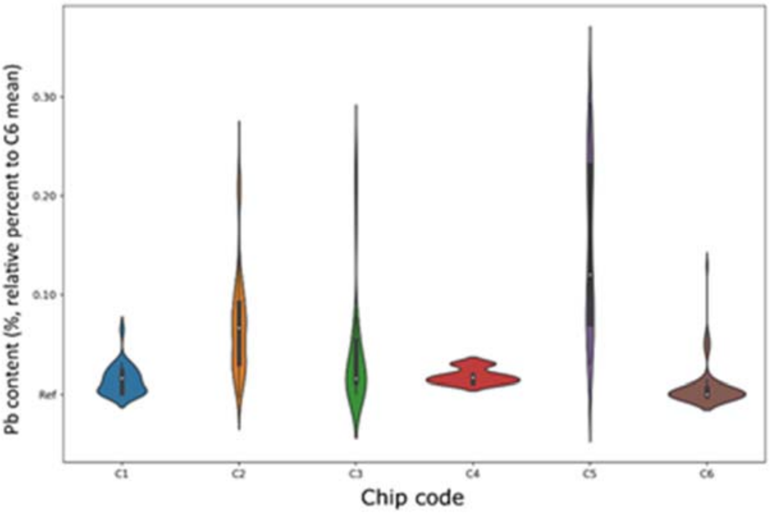


Figure 28. Lead content variability by chip category at Grupal Art.

4.1.2. Requirements of common and alternative Al high-grade alloys

Table 1 presents the aluminium high-grade alloys produced by Grupal Art in 2019, together with new alloys that they are not currently producing, but they are willing to produce after the improvements expected thanks to the REVaMP project. Table 1 also shows the compositional interval established by the corresponding norm for each alloy.

The cells defined with a single value, instead of an interval range, show the elements that are considered impurities for the given alloy and only a maximum amount for the element is established. There is no lower limit for those elements, the lower the composition the better.

All high-grade aluminium alloys for casting require a low level of impurities. To obtain these alloys from aluminium chips is a challenging task. In order to reach the required concentration of Fe, Cu Mn and Zn, it is necessary to have an accurate estimation of the amount of each of those elements present in the aluminium chips used to produce the melt, and to be able to predict the composition of the final mixture.

The demand of high-grade aluminium alloys is increasing over the last years and Grupal Art aims to address this increasing demand. In order to increase the production of these high-quality alloys, it is fundamental to be able to use as maximum as possible the aluminium chips of the groups with higher dispersion in an intelligent way. As can be seen in the composition charts from section 4.1.1, the dispersion of the chemical composition of the chips is considerable, especially in the chips from codes C1, C2, C3 and C5. In order to increase the production of high-grade aluminium alloys it is required to use larger amounts of these feedstock materials in the production. A better chemical characterization of each single batch received is essential to better predict the actual composition of the feedstock materials used to produce the aluminium ingots and to predict their final composition.

Table 1. Target alloy composition of the aluminium high-grade alloys produced and planned to be produced in the future by Grupal Art

Al high-grade alloys													
ALLOY	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Ni**	**Zn**	**Pb**	**Sn**	**Ti**	**Others**	**Al**
EN AB-42000	6,5-7,5%	0,45%	0,15%	0,35%	0,25-0,65%	0,05%	0,15%	0,15%	0,15%	0,05%	0,20%	0,15%	Remainder
EN AB-42100	6,5-7,5%	0,15%	0,03%	0,10%	0,3-0,45%	0,03%	0,03%	0,07%	0,03%	0,03%	0,18%	0,10%	Remainder
EN AB-42200	6,5-7,5%	0,15%	0,03%	0,10%	0,5-0,7%	0,03%	0,03%	0,07%	0,03%	0,03%	0,18%	0,10%	Remainder
EN AB-43000	9,0-11,0%	0,40%	0,03%	0,45%	0,25-0,45%	0,05%	0,05%	0,10%	0,05%	0,05%	0,15%	0,15%	Remainder
EN AB-43100	9,0-11,0%	0,45%	0,08%	0,45%	0,25-0,45%	0,05%	0,05%	0,10%	0,05%	0,05%	0,15%	0,15%	Remainder
EN AB-43200	9,0-11,0%	0,55%	0,30%	0,55%	0,25-0,45%	0,05%	0,15%	0,35%	0,10%	0,05%	0,15%	0,15%	Remainder
EN AB-43400	9,0-11,0%	0,45-0,9%	0,08%	0,55%	0,25-0,5%	0,05%	0,15%	0,15%	0,15%	0,05%	0,15%	0,15%	Remainder
EN AB-43500	9,0-11,5%	0,20%	0,03%	0,4-0,8%	0,15-0,6%	0,05%	0,05%	0,07%	0,05%	0,05%	0,15%	0,15%	Remainder
EN AB-44100	10,5-13,5%	0,55%	0,10%	0,55%	0,10%	0,05%	0,10%	0,15%	0,10%	0,05%	0,15%	0,15%	Remainder
EN AB-44200	10,5-13,5%	0,40%	0,03%	0,35%	0,05%	0,05%	0,05%	0,10%	0,05%	0,05%	0,15%	0,15%	Remainder
EN AB-44300	10,5-13,5%	0,45-0,9%	0,08%	0,55%	0,05%	0,05%	0,05%	0,15%	0,05%	0,05%	0,15%	0,25%	Remainder
EN AB-44400	8,0-11,0%	0,55%	0,08%	0,50%	0,1%	0,05%	0,05%	0,15%	0,05%	0,05%	0,15%	0,15%	Remainder
EN AB-44500	10,5-13,5%	0,45-0,9%	0,18%	0,55%	0,4%	0,05%	0,05%	0,30%	0,05%	0,05%	0,15%	0,25%	Remainder
EN AB-48000	10,5-13,5%	0,60%	0,8-1,5%	0,35%	0,9-1,5%	0,05%	0,7-1,3%	0,35%	0,05%	0,05%	0,20%	0,15%	Remainder

4.2. Aluminium energy feedstock variability assessment at Refial

REFIAL is an aluminium refinery dedicated to the supply of aluminium from secondary smelting. The aluminium refining process at REFIAL is carried out in two melting furnaces (tilting rotary furnaces) and two holding furnaces (reverberatory type). The refinery is also equipped with a pilot rotary furnace for melting sample batches of scrap for composition analysis purposes, in order to select conditions in the industrial furnace to achieve the target metal yield. This pilot rotary furnace will be used in this project, in which a new step is proposed, that consists in heating up the scrap before charging into the melting furnace:

Figure 29. Scheme of the proposed retrofitted process in aluminium refining at REFIAL

Retrofitting of this existing pilot rotary furnace is planned by equipping it with sensors and with a sensorised scrap pre-heater consisting of a Waste Derived Fuel (WDF) combustor (including fuel gas cleaning system), heat exchanger and heated scrap charging system (into the melting rotary furnace).

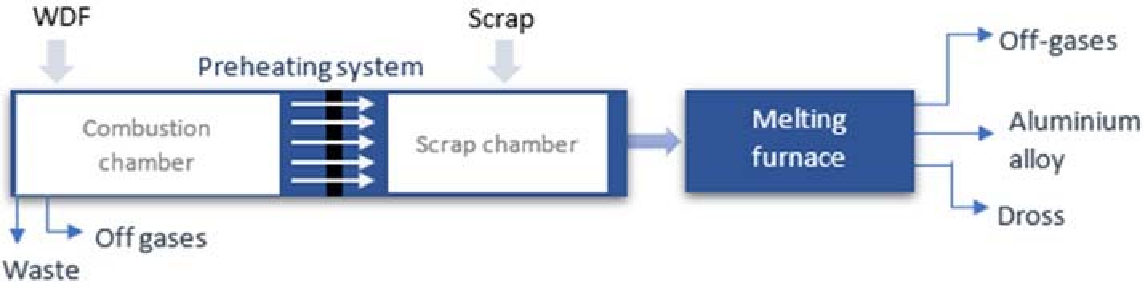


Figure 30. Flowchart of the overall process, with indication of main inputs and outputs

By directing hot fuel gases from the WDF combustor to a heat exchanger, solid aluminium scrap which is to be melted can be heated up, before charging into the melting furnace. Sensor recorded data will be combined and analysed by the algorithms of the monitoring and control system, so that scrap will be charged in the furnace when the pre-heating conditions are met, and the melting process will be then adjusted to the measured values to optimise melt quality and process efficiency.

In REFIAL refinery use case, a polymeric fraction of Automotive Shredder Residue (ASR) is planned to be valorised as fuel for the scrap preheating system. In the recycling process of end-of-life vehicles (ELV) led by another company of the Otua Group, polymeric rejection fractions are generated in important quantities after metals separation. This waste stream is currently not recovered and is landfilled. Considering the specifications established in the European standard EN 15359 for Solid Recovered Fuels (SRF), that polymeric waste reaches calorific values defined for SRF which are currently used in energy intensive industries, such as cement industries.

The present chapter of Deliverable D1.1 deals with the characterization and preparation of waste streams as potential WDF for the scrap-preheating system and with the analysis of variability of the selected alternative fuel, inherent to the heterogeneity in composition and properties intrinsic to any post-consumer waste, and how it impacts on combustion behaviour of WDF. Additionally, the variability of scrap feedstock at REFIAL is discussed.

4.2.1. Evaluation of available waste derived fuel mixes with fuel characterization

Based on historical data (composition, Net Calorific Value (NCV), quantity), two fractions were selected for the study, which are the largest rejected fractions after the metal extraction process of other recycling companies integrating the Otua Group:

- Polymeric fraction of light Automotive Shredder Residue (ASR), also known as “SLF Fluff” (Shredder Light Fraction, SLF).
- Polymeric fraction of heavy ASR (known as Shredder Heavy Fraction, SHF)

These fractions are visualised in Figure 31, with the generated amount for 2019, and the Low Calorific Value (LCV) based on historical data.

Figure 31. Historical data of the selected streams to be analysed in the project

Industrial non-hazardous waste landfill is the usual destination for this material, only a small proportion is used as fuel in energy production facilities. But the net calorific value of both streams is high enough to be considered for preparation of waste derived fuel.

4.2.1.1. Characterization of Polymeric fractions of ASR and its variability

A characterization of representative samples (collected in Jan-Mar 2020) of the selected ASR fractions, i.e. SHF & SLF fluff, was performed, including the analysis of material composition & Chlorine (Cl) content. This study was performed according to the following steps:

- Several representative samples are taken for heavy and light polymeric fraction.
- Manual sorting is performed for each of the chosen samples.
- Each of the separate fractions is sent to an external laboratory to analyze chlorine content and dissolved organic matter (DOM).

The results of the manual sorting of the light (Figure 32) and heavy (Figure 33) polymeric fraction can be seen in the following figures.

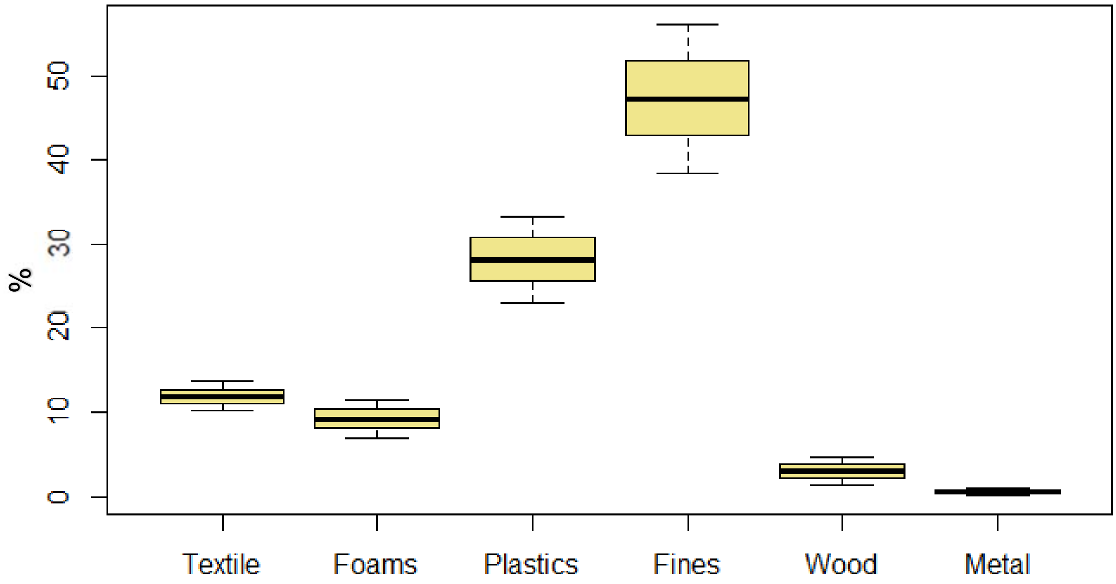


Figure 32. Results of the manual sorting of the light polymeric fraction (SLF fluff).

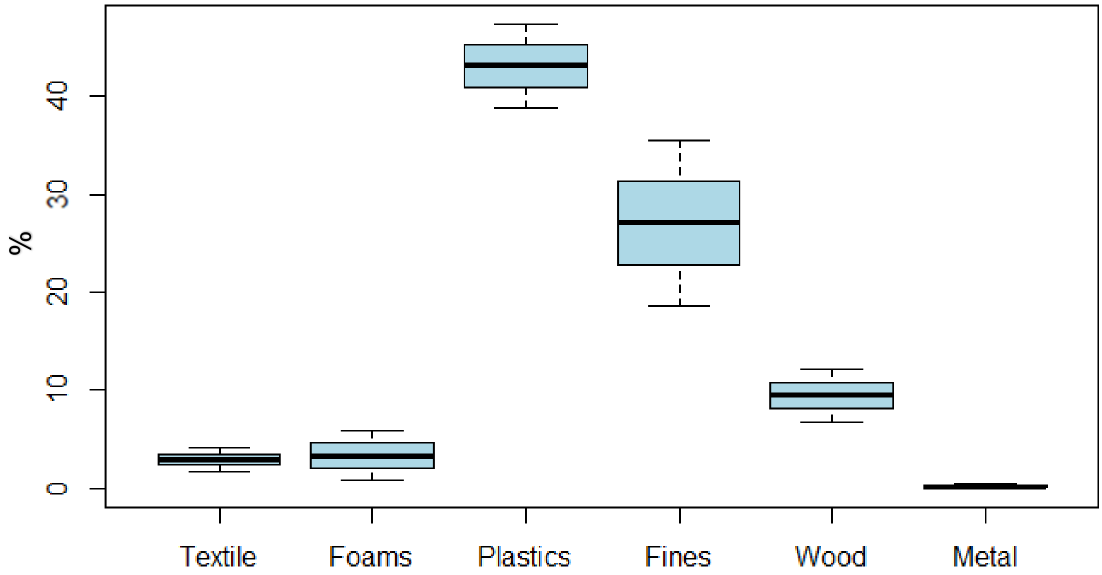


Figure 33. Results of the manual sorting of the heavy polymeric fraction (SHF).

It can be observed that the SHF has a higher content of plastics and a lower content of fines compared to the SLF fluff. In both cases, as this waste is produced in the treatment of automotive residues in which the recovery of metals is performed, the proportion of metals is very low or near to zero.

In order to use this material as a fuel, the halogens content plays an important role in the composition of this waste. For this reason, specific analyses were performed on the chlorine content, the results are shown in Figure 34.

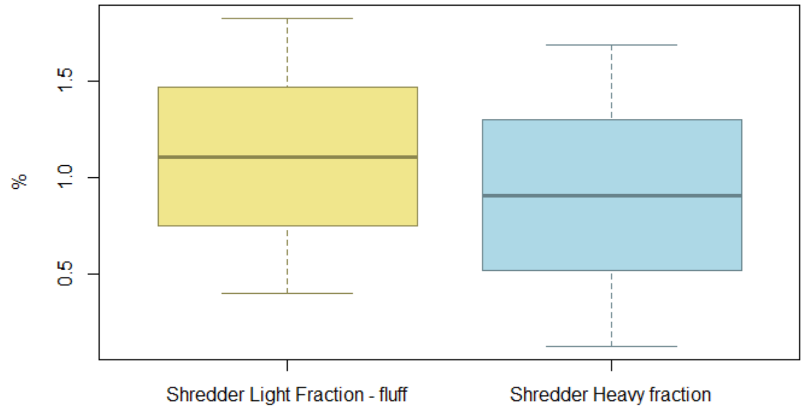


Figure 34. Chlorine content of the waste before treatment- Light (SLF fluff) and heavy (SHF) polymeric fractions.

The chlorine content is quite high in both streams, but it is bigger in the light fraction compared with the heavy fraction. An additional analysis that was performed was the DOM of each waste stream, and it is observed in Figure 35 that the higher content can be found in the light fraction, being even three times higher compared with the heavy fraction.

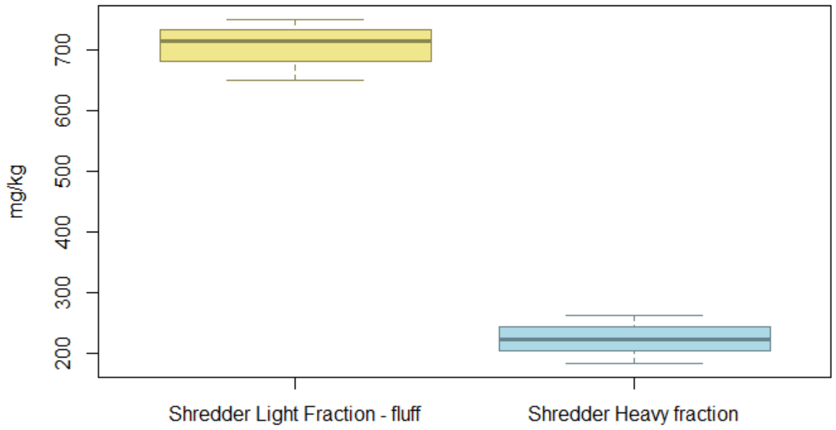


Figure 35. DOM of the waste before treatment - Light and heavy polymeric fractions.

Finally, due to its high net calorific value (based on analysis of historical data) the higher quantity generated (based on data from 2019), the chorine content and the DOM, the polymeric fraction of heavy ASR is chosen as the material for producing waste derived fuel (WDF).

Treatment trials have been performed in order to prepare this material to be used as a Waste Derived Fuel, with the following treatments:

- Size reduction: Crushing at different granulometries and sieving.
- Reducing halogen content: Elimination of pieces with halogen content using RX (Transmission) technology.

4.2.1.2. Pre-treatment to obtain Waste Derived Fuel

4.2.1.2.1. Size reduction: Crushing and sieving process

The material is processed in the industrial facilities of Otua Group, being crushed in a knife mill, and sieved in different mesh size (15 and 25 mm). After performing the treatment trials, the selected treatment of SHF is crushing (25 mm) & Sieving (>15 mm), because it induces sufficient conditions to feed the material to the next step of the treatment.

Figure 36. Sieves used in the pre-treatment trials (10, 15 and 25 mm).

4.2.1.2.2. Elimination of pieces with halogen content using RX technology

In this step of the treatment, the pieces with halogen content are removed from the material using X-Ray (Transmission) technology, in order to obtain a WDF ready to be used in the tests. The technical information of the X-ray technology is shown in Table 2.

Table 2. Technical information of the X-Ray technology used in the test.

Operative conditions	
Temperature	4,4-32,2 °C
Radiation level	< 0,5 mR/h in 5 cm.
Speed	150-240 cm/s
Capacity	1,5 kg/cm

This technology has a productive capacity in 2020 of 24.000 t, but it is expected to increase to reach 40.000 t in 2021, with a new operating machine. The main halogen that can be found in this waste stream is chlorine, and the results obtained of the mass balance of chlorine content when processing the material can be seen in Table 3.

Table 3. Mass balance of the processing of material to eliminate halogens (Cl)

Weight of sample	**WDF**		**Rejected material**	
	%	**% Cl**	**%**	**% Cl**
1.108 kg	63,2	0,32	36,8	1,4

Nearly 40 % are rejected in this process, with a halogen content higher than 1%. The rest, more than 60% of the input, is the waste derived fuel obtained, prepared to be tested as a fuel (Figure 37).

Figure 37. Waste derived fuel obtained after processing

After this treatment, the chlorine content has been analysed for several samples, and the chlorine variability in the treated WDF can be seen in Figure 38, being in all cases a content lower than 1%, with a median around 0.5%.

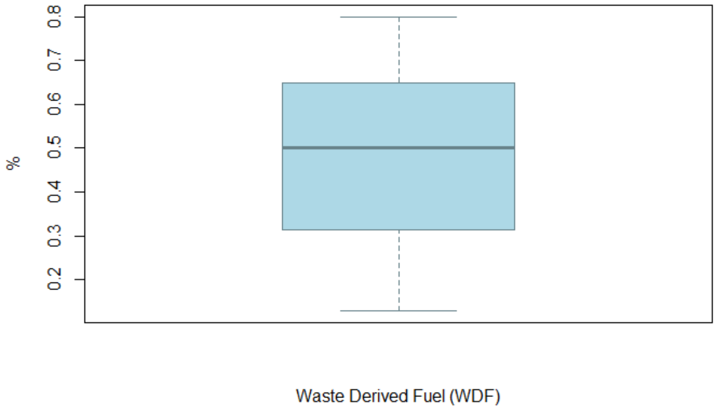


Figure 38. Chlorine variability in the WDF produced

In order to perform a specific analysis of this WDF, a representative sample of the WDF obtained was taken, a small part of that sample is shown in Figure 39.

Figure 39. Representative sample to be analysed with X-Ray.

First of all, the analysis consisted in the main streams that were found in the sample, classifying them into plastics, wood, textile, foam and the rest (Figure 40).

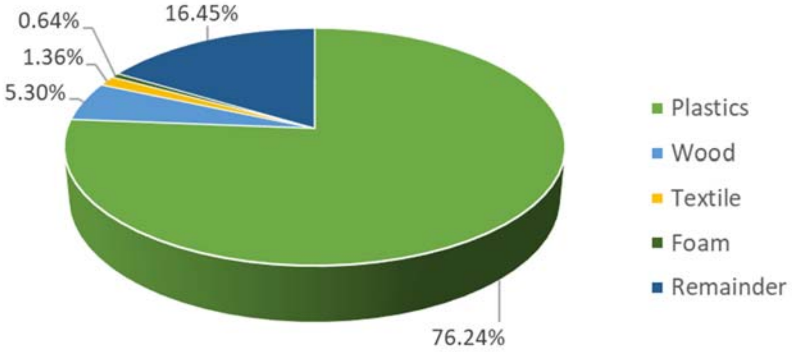


Figure 40. Streams contained in the sample of the Shredder Heavy Fraction

It can be observed that the sample is composed mainly by plastics, with approximately 75%, being 5% wood, 1.5% textile and less than 1% foam. These main streams detected (plastics, wood, textile and foam), were further analysed with X-Ray technology (fluorescence), in terms of chemical content (Cr, Ba, Ti, Cl, Sb, Sn, Cd, Pb, Br, Zn, Cu, Ni, Fe and V). In all the cases, Bi, Se, As, Hg and Au were not detected in none of the streams, in all the samples analysed. The results for the main component of this waste stream, plastics, can be seen in Figure 41.

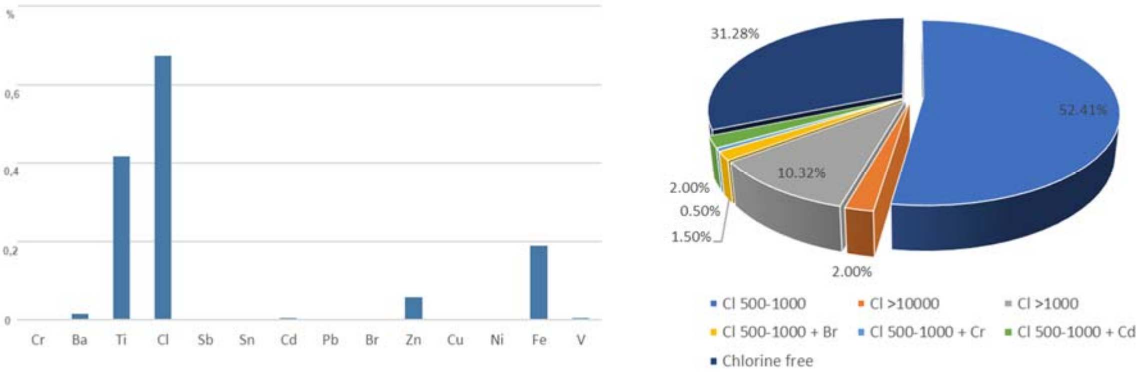


Figure 41. Analysis of plastics for the main elements, and analysis of concentration of chlorine.

The presence of chlorine is clear in plastics, being the [Cl] in the range of 500-1000 ppm in 52.4% of the samples, that increase to 56.4 % if the samples with [Cl] in the range of 500-1000 ppm with the presence of Br, Cr or Cd are taken into account. 31% of the samples were chlorine free, being the remaining 12.6% of the samples the ones with higher chlorine content, being only a 2% the ones with a concentration higher than 10000 ppm (1%).

7.3% of the materials found in the WDF consisted of foam, wood and textile. Chemical analyses were also performed for these materials, and the results can be seen in Figure 42.

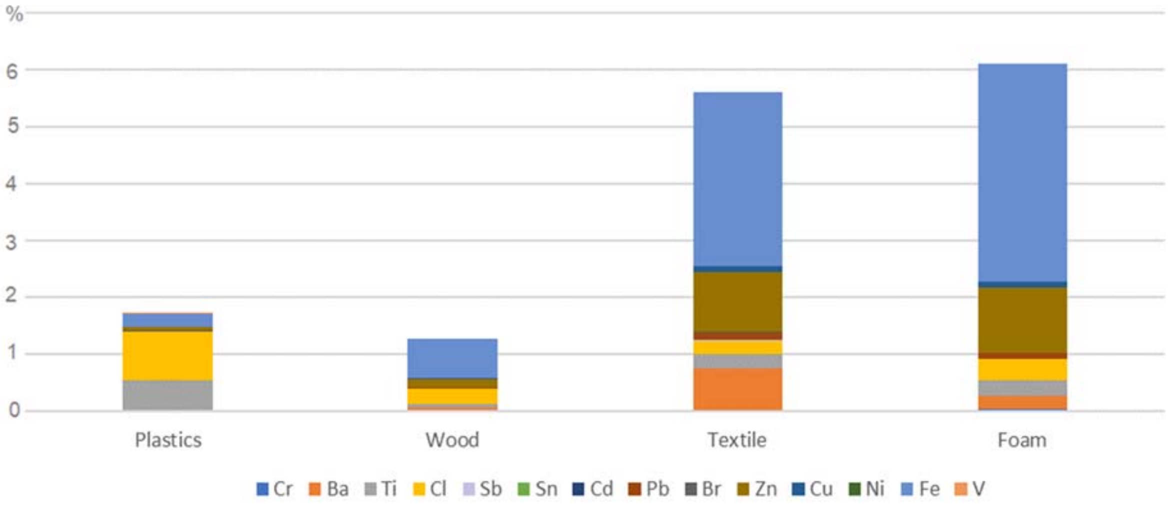


Figure 42. Chemical analysis of elements in the main streams detected in the WDF

In comparison to the plastics stream, the chlorine content present in the other streams is very low, being iron the prevailing element detected. In the case of wood, the elements detected in more quantity were iron, chlorine and Zn. In the case of textile and foam material, the main elements detected were iron, Ba, Zn, chlorine and Ti, with a small quantity of lead. As it was emphasized before, the proportion of these materials in the stream is very low (7,3% of the total), being diluted its concentration in the total of the WDF. Other materials, as Sb, Sn, Cd, Br, Cu, Ni and V were almost negligible, compared with the other elements. In fact, Cd and V were only found in plastics, and Sb only in plastics and textile, in a very low concentration (lower than 0.004%).

4.2.1.2.3. Economic costs of WDF preparation

The cost of the process for conditioning SHF into WDF would amount to 6,70 €/t. Breakdown of the costs: energy (45,31 kWh/t), productive capacity (1,79 t/h) and maintenance (2,77 €/t)

4.2.2. WDF characterization: fuel properties and combustion behaviour

In order to assess the performance of the WDF obtained from upgrading the SHF waste stream, as alternative fuel for the scrap pre-heating system, the following research has been conducted:

- Proximate analysis of fuel and determination of high and low heating values.
- Study of thermal degradation of WDF in inert and oxidative atmospheres at various heating rates, in laboratory thermal analysis equipment (TGA/DSC) and in a combustion research system. Those studies have served to define the range of temperatures for combustion, the evolved gases, char yield and reactivity, ash melting behaviour. Besides, potential hazardousness of the solid residue in combustion chamber has been determined, and the need and conditions of a post-combustion step to destroy persistent organic pollutants in combustion gases to comply with air emissions limits has been investigated.

4.2.2.1. Proximate analysis and calorific value of fuel

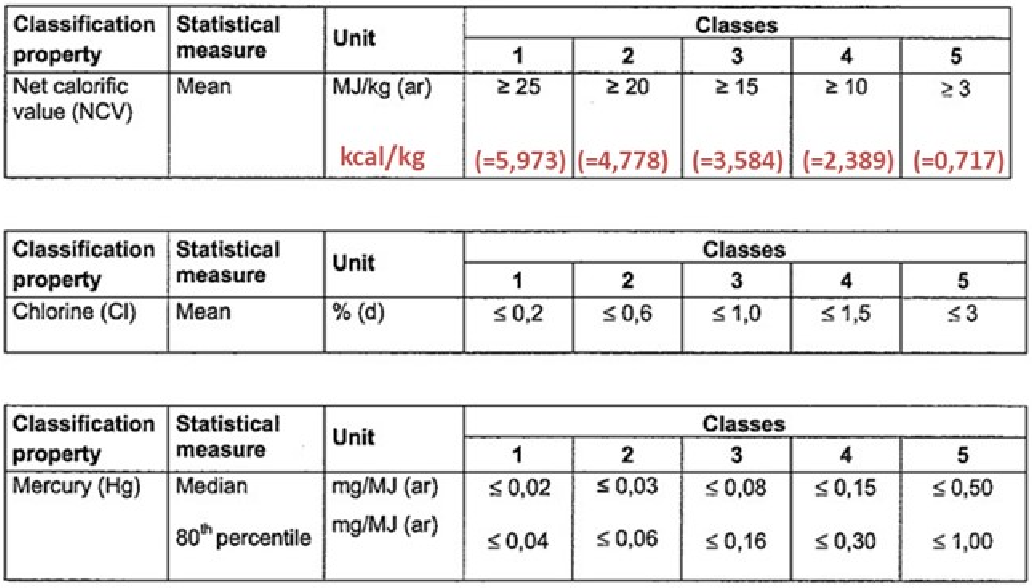
Shredder granulate is made up of plastics (rigid, foams), rubber, textiles, wood and some inert materials as glass, dirt and stones. The contents in PVC and halogenated fire retarded plastics are diminished in the conditioning of the waste to prepare the WDF and, also, some inert materials may be removed from the mix through the comminution and sieving steps. According to several studies (1), net calorific values of rigid plastics fraction of SHF vary between 33 and 40 MJ/kg, depending on concentration of different types of polymers in the mix; the calorific value of textiles ranges from 17 to 27 MJ/kg and is around 26 MJ/kg for foams and about 29 MJ/kg for rubbers. Fines, originated mostly from fragilization of foams and fibrous materials, are a constituent fraction with rather high carbon content, and consequently, calorific value. Lower Heating Values (LHV) for cellulosic (wood) materials are in the 15-17 MJ/kg range. Those materials fractions blended in the SHF can deliver fuels with net calorific values between 28-36 MJ/kg. Other reported calorific values for ASR waste in literature are: 29.3 MJ/kg (2), 29 MJ/kg (HHV) (3), 17.8 MJ/kg (4), and 18.8 MJ/kg (5). Historical data on LHV of ASR fractions recovered in Grupo Otua show values of 24 MJ/kg for SHF and 22 MJ/kg for fluff.

Samples of the WDF prepared from SHF by REFIAL-INATEC have been tested by AZTERLAN for proximate analysis of fuel (analysis that indicates moisture, volatile matter, fixed carbon and ash content of the fuel in terms of percentage by weight) and determination of calorific value (higher and lower heating values). The results obtained are shown below:

- Ash (550 ^{o}C) = 21% (QL= 0,001%)
- Dry matter (ar) = 97,90% (QL=0,1%)
- HHV (*db*)= 27.940 MJ/kg (QL=0,500 MJ/kg)
- LHV (*db*)= = 26.260 MJ/kg (QL=0,500 MJ/kg)

The net calorific value of 26.2 MJ/kg (d) is in line with previous results for that waste stream in Otua Group. Standard EN 15359:2012 (to be superseded by ISO/DIS 21640, currently under development) specifies a classification system for solid recovered fuels (SRF), fuels produced from non-hazardous waste, and a template containing a list of characteristics for the specification of their properties, enabling trade and use of SRF supporting the protection of the environment. Considering the calorific value and the chlorine and mercury contents measured in the WDF characterization at REFIAL, the WDF would be classified as SRF Class code NCV 1; Cl 2; Hg 2 according to standard prEN ISO 21640.

Table 4. Classification for solid recovered fuels in EN 15359:2012 and prEN ISO 21640



Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Net calorific value (NCV)	Mean	MJ/kg (ar) kcal/kg	≥ 25 (=5,973)	≥ 20 (=4,778)	≥ 15 (=3,584)	≥ 10 (=2,389)	≥ 3 (=0,717)

Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Chlorine (Cl)	Mean	% (d)	≤ 0,2	≤ 0,6	≤ 1,0	≤ 1,5	≤ 3

Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Mercury (Hg)	Median	mg/MJ (ar)	≤ 0,02	≤ 0,03	≤ 0,08	≤ 0,15	≤ 0,50
	80th percentile	mg/MJ (ar)	≤ 0,04	≤ 0,06	≤ 0,16	≤ 0,30	≤ 1,00

4.2.2.2. Thermal analysis

The lab study of thermal degradation of WDF in oxidative atmospheres (air) have been performed through thermogravimetric analysis (TGA) of micro-samples and by tracking evolution of weight with temperature in a muffle furnace (Loss on Ignition,). With such heterogenous material as WDF the issue of representativeness of analysis samples (micro size) is crucial. Several options exist to try to overcome that problem, as recommended in the EN/ISO standard methods for SRF characterization. The solution adopted for the characterization of the WDF has been to supplement the laboratory TGA technique with less precise measuring methods that however work on larger samples.

Thermogravimetric analysis (TGA):

Two thermal degradation experiments in air were performed in a thermogravimetric analyser (TA Instruments), that can characterize the mass loss of a sample with time and temperature during a continuous heating process. Approximately 50 mg of a sample were loaded into an alumina crucible for each experiment. The temperature was programmed for running at a range from 25 °C to 950 °C at a heating rate of 10 °C /min, in air atmosphere.

TGA graphical results (Figure 43) indicate three different stages in thermal decomposition, with different mass loss rate: first one in the interval around 250-450 °C, with the highest mass loss rate; second one, up to around 600 °C; third between 600 °C and 725 °C. From that temperature until end of measurements it is still noted a very slow mass loss, probably while the formed chars burn off. Those results are consistent with findings reported in literature (3) (5).

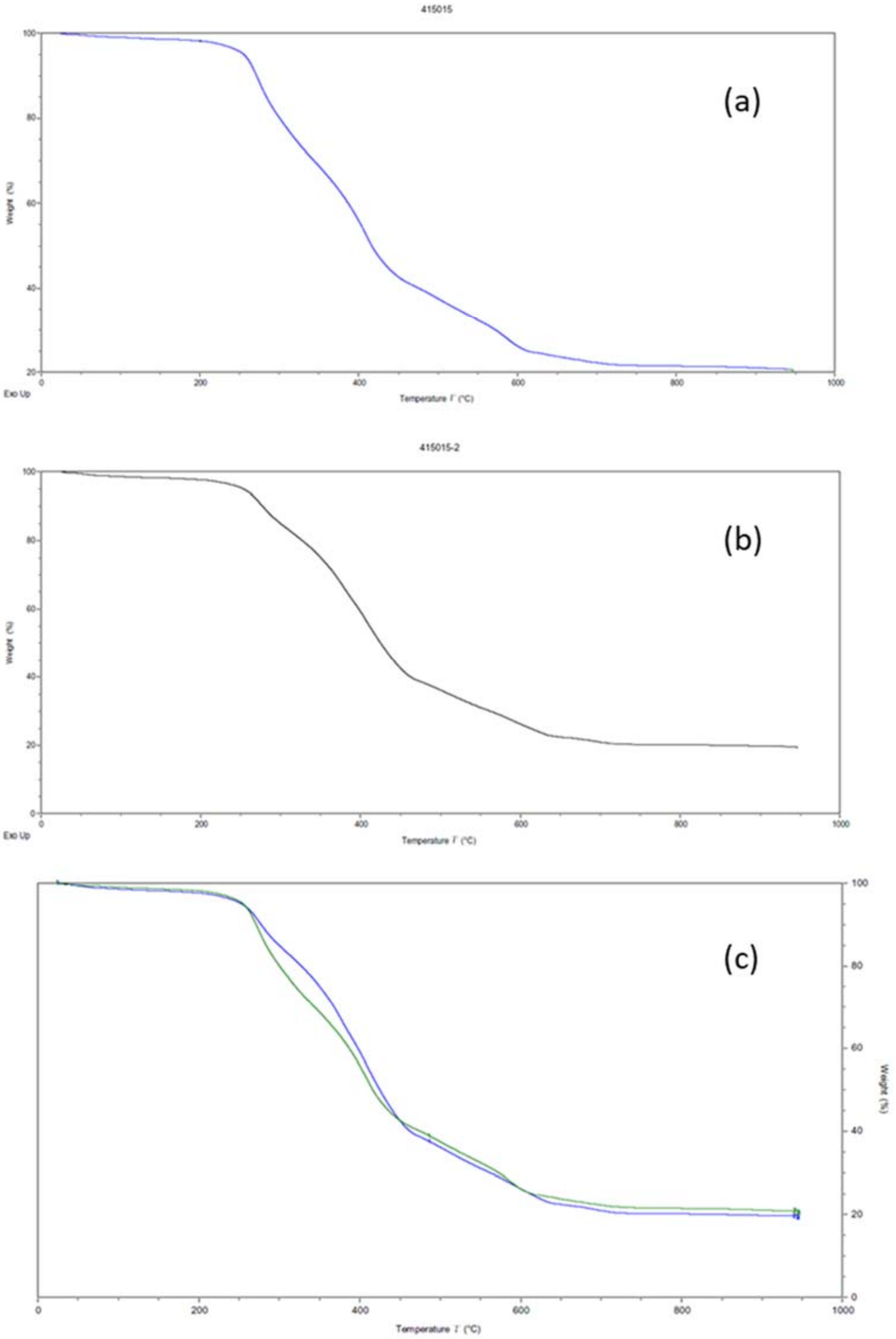
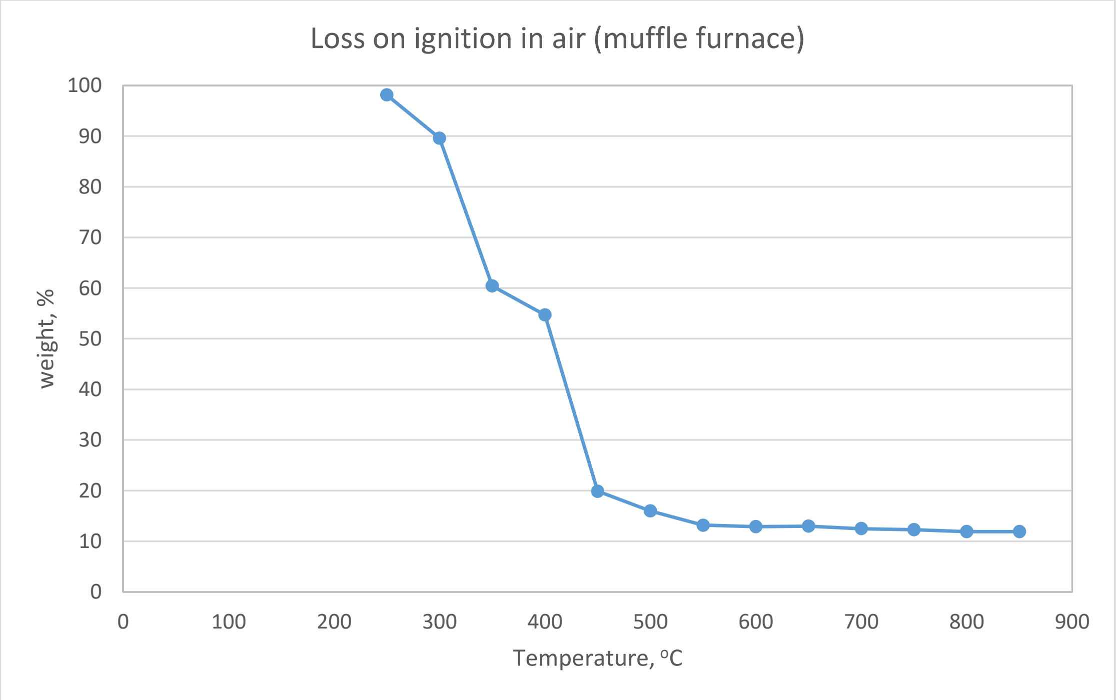


Figure 43. Thermal degradation of WDF in air at 10 °C /min heating rate: sample mass loss ratio vs temperature for two samples of WDF (a, b) and overlay of the two curves (c)

Loss on Ignition (LOI) evolution:

A WDF sample of 3 g weight has been heated in a muffle furnace and the LOI has been measured at various temperatures, by weighing the mass of the sample every 50 ºC, from 250 ºC up to 850 ºC, until constant weight. Results depicted in the figure below show a trend coincident with TGA results, with major mass losses between 250 ºC and 450 ºC and extending up to around 600 ºC.



T, ºC	250	300	350	400	450	500	550	600	650	700	750	800	850
m loss, %	1,87	10,4	39,6	45,3	80,1	84	86,8	87,1	87	87,5	87,7	88,1	88,1

Figure 44. Mass loss ratio of WDF vs temperature, on ignition in a muffle furnace

4.2.2.3. Combustion study

Using WDF in combustion processes in dedicated plants may have several technical and environmental limitations due to formation of residual solid waste (potential hazardousness of ashes; corrosion, fouling and/or slagging phenomena of equipment) and to air emissions (source of greenhouse gases; potentially, furans and dioxins emissions; corrosion of equipment). Those aspects should be taken into account for the design of WDF burner and operation conditions in the pre-heating system.

With the aim of advancing in the knowledge of combustion performance of the WDF, composition of combustion gases and solid waste (bottom ashes) characteristics, a set of combustion experiments have been planned in a research pilot plant of the Chemical and Environmental Engineering Dept. of the University of the Basque Country. The reaction system, consisting of combustor and post-combustor steps, allows feeding up to 2 litres of WDF, operating at different ratios of WDF/air/O_2, continuously measuring temperature of combustion gases and sampling combustion and post-combustion gases for analysis of composition.

The reaction system (Figure 45) consists of a heated tank (combustor) —a batch reactor where solid fuel is loaded and reactant gasses can be fed at different flow rates—, followed by a vertical tubular reactor packed with inert material, where gas leaving the combustion chamber can be, either, maintained at a constant temperature to increase the residence time for completing combustion reactions in the gas phase initiated in the batch reactor, either be heated up to 900 °C to promote thermal decomposition of organic compounds (post-combustor), or be by-passed. The system is equipped with a serial condenser train, which allows the fractional condensation of volatiles of the flue gas and can be used to collect condensates for reaction product analysis. Gas sampling bags are used for sampling the exhaust gas for off-line analysis for light hydrocarbons by gas chromatography (GC). Optionally, real-time measurements of concentration of O_2, CO_2, CO, NO_2, NO, SO_2, HCl and HF in combustion gases can be obtained with the help a portable FTIR gas analyser for stack emission testing, by connecting its sampling system to the outlet of the tubular reactor.

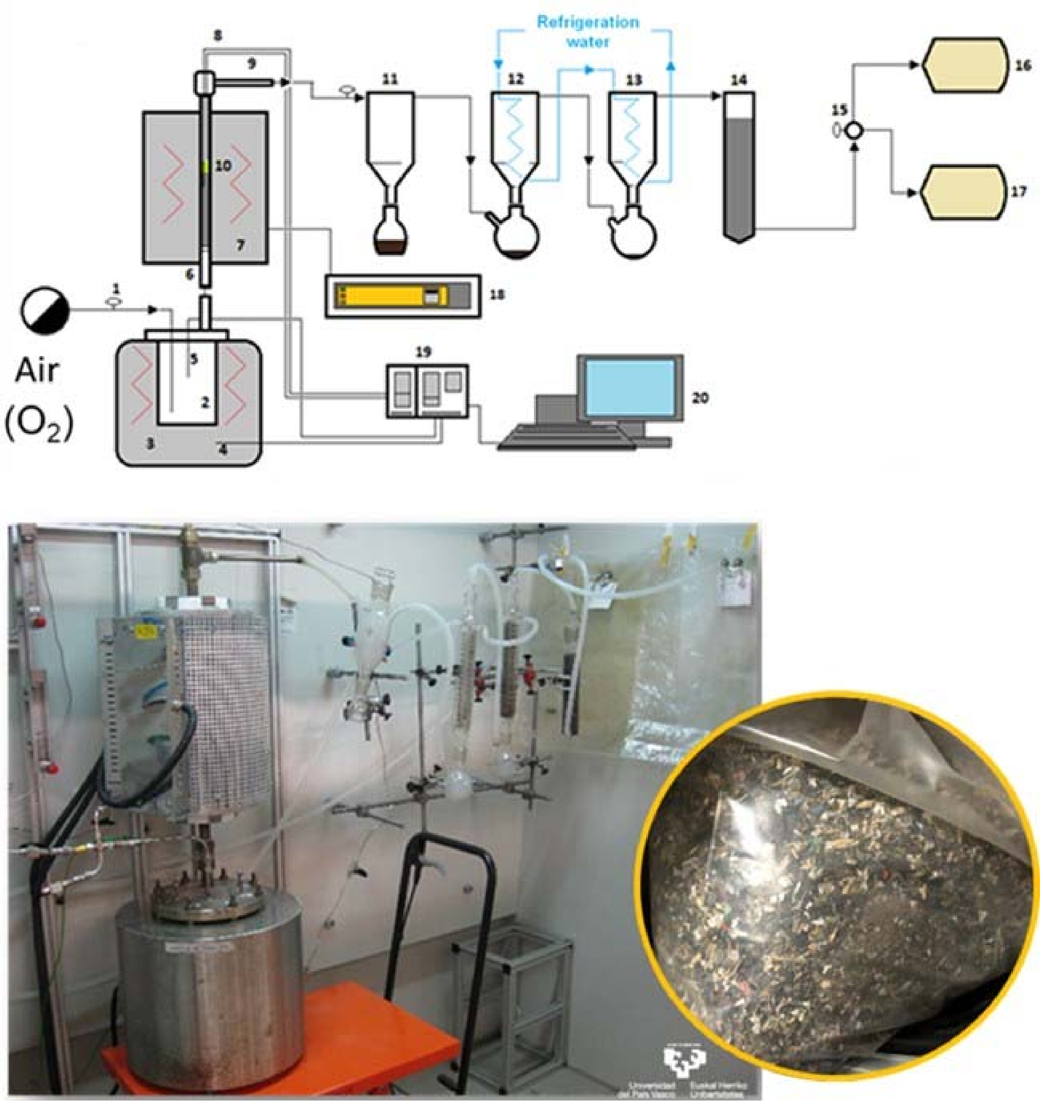


Figure 45. Chemical reaction system and WDF sample used in combustion study. Top image: Process flow diagram of reaction system

Experiments have been designed to run several combustion (+ post-combustion) trials at different atmospheres (oxidative atmospheres with growing O_2 %) and several temperatures (in combustor and in post-combustor). Composition of combustion gas outflow has been analysed, to evaluate conversion achieved and efficacy to comply with air emissions regulations. Solid residue in combustor (bottom ash) after each trial has been characterised, on the one hand to determine char and unburnt contents, and, on the other hand, to assess whether it is non-hazardous or hazardous waste. Observations made about the kinetics and thermodynamics of the combustion process will help in the design of the combustor chamber and heat exchanger of the scrap pre-heating system for the pilot rotary furnace, as well as in selecting operating conditions.

Combustion mechanism - Emissions to air

A first set of experiments was performed to select the operation temperatures and WDF/air ratios in the combustor to achieve the most complete combustion and stable reaction possible. Based on the results of previous TGA and LOI analysis, indicating that most of the thermal degradation in air of the WDF occurred below 600 ^{o}C, mainly between 250 and 450 ^{o}C, several experiments were conducted at varying heating rates of WDF in the tank, up to set points in the interval 500-550 ^{o}C, with different air flow rates (5.5, 4.7 and 3.3 L/min) and changing the temperature at which air was fed into the batch reactor (400 ^{o}C, 250 ^{o}C). In all the experiments 50 g of WDF sample (particle size = 10 mm) were loaded in the batch reactor. It was concluded that WDF needs to be heated from 250 to 550 ^{o}C at low heating rates, while air flow started, and that the residence time of evolved gases should be increased to allow for combustion reaction in the gas phase before venting. To that end, the serial arrangement of the two reactors was required in the experimental set-up, with the packed bed tubular reactor kept at a constant temperature during the tests, in order to increase the residence time of the gas at high temperature and to allow its combustion.

Observed results of that first set of experiments point out that WDF combustion in the batch reactor seems to follow the two-step conversion process of combustion (of biomass, municipal solid waste or coal) in a grate furnace. One first step of heterogeneous gasification, as the solid fuel on the grate is pyrolysed-gasified (devolatilisation and subsequent char oxidation). And then, homogeneous combustion in the gas phase (when burnout of the pyrolytic decomposition and gasification products takes place). That reaction mechanism should be considered in the design of the scrap pre-heating system, to allow for enough residence time of volatilised products in the combustion chamber, so that it is not until their combustion process is finished, that the gases release their heat to the heat exchanger.

After those preliminary tests, it was decided that, for the second set of experiments to be executed, the batch reactor would be heated up to 220 ^{o}C following a 100 ^{o}C/min ramp and after reaching this value, the air/oxygen supply would start and the temperature would be raised up to 550 ^{o}C with a 3 ^{o}C/min ramp.

During the second part of the study, the following combustion conditions have been investigated:

1. Combustion in air, temperature set points: batch reactor T=550 ^{o}C, tubular reactor T=550 ^{o}C
2. Combustion in air, temperature set points: batch reactor T=550 ^{o}C, tubular reactor T=900 ^{o}C
3. Combustion in oxygen, temperature set points: batch reactor T=550 ^{o}C, tubular reactor T=900 ^{o}C
4. Combustion in enriched air (50 vol% O_2), temperature set points: batch reactor T=550 ^{o}C, tubular reactor T=550 ^{o}C

The aim of those experiments has been to evaluate completeness of combustion achieved at different temperatures and using different O_2 contents in the airflow. To check repetitiveness, two repetitions at each set of experimental conditions have been run. In four of the tests carried out, the composition of the exhaust fumes was measured continuously using the FTIR analyser for stack emission testing. This analyser was connected directly to the outlet of the vertical tube reactor. In the remaining tests, the outlet gas was sent to the condenser train and the liquid condensate was collected at the end of each test. As an example, Figure 46 depicts the continuous concentration measurement of some compounds obtained in the gas outflow from the tubular reactor, corresponding to a combustion test carried out with air, T=550 ^{o}C in the batch reactor and T=550 ^{o}C in the vertical tubular reactor.

The FTIR analyser used is calibrated for compliance testing in stacks (emission limits set out in *Directive 2010/75/EU on Industrial Emissions, IED*). However, in the experiments, in the period of highest generation of products during the combustion process, the concentrations of several chemical species have been out of calibration range, exceeding the superior quantification limits shown in Table 5. In the case of organic compounds, high contents seem to confirm pyrolytic products not combusted (i.e., longer residence times are required). It has been noted that HCl concentration in flue gas has been also recurrently out of range —in spite of total Cl content in WFD being below the 1% limit requested to SRF by e.g. cement kilns. That signifies the importance of incorporating flue gas cleaning systems to comply with emission limits and to avoid equipment corrosion problems (*Commission Implementing Decision (EU) 2019/2010 establishing the best available techniques (BAT) conclusions for waste incineration*).

The experiments run in airflow at higher combustion temperatures (900 ^{o}C) in the second reactor seem to have achieved more complete combustion (i.e., burnout of pyrolysis/gasification gases), as higher amount of water was produced and lower oxygen content was detected in the flue gas. Thermal runaway occurred in one of the experiments carried out injecting pure oxygen to the batch reactor, leading to a fast and unstable reaction, with a sudden rise of temperatures in the tank of around 150 ^{o}C. Although reactor heating was controlled in the repetition, the exothermic conversion process was still too fast to allow gases to burnout and an array of organic compounds were observed in the gas outflow. Better results have been obtained with enriched airflow (O_2=50 vol%), in terms of repetitiveness and combustion products in flue gas.

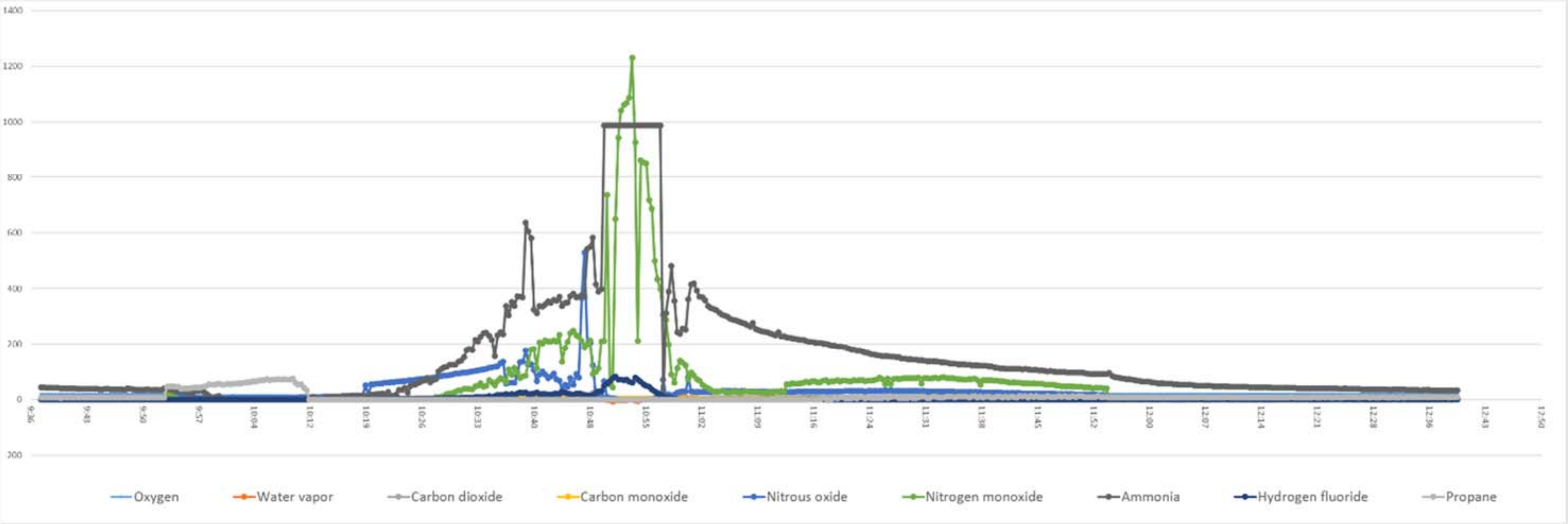
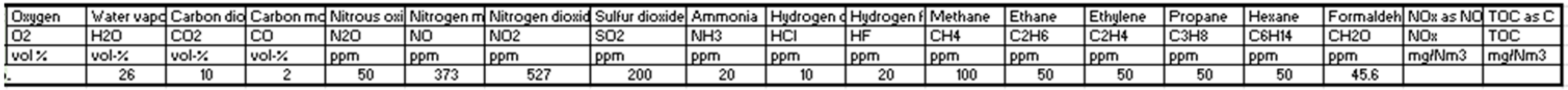


Figure 46. Continuous composition results of gas at the tubular reactor outlet during a combustion test

Table 5. Chemical species determined by FTIR analyser and their superior quantification limits in stack testing calibration range (IED emission limits compliance)



Oxygen	Water vapo	Carbon dio	Carbon mo	Nitrous oxi	Nitrogen m	Nitrogen dioxid	Sulfur dioxide	Ammonia	Hydrogen c	Hydrogen f	Methane	Ethane	Ethylene	Propane	Hexane	Formaldeh	NOx as NO	TOC as C
O2	H2O	CO2	CO	N2O	NO	NO2	SO2	NH3	HCl	HF	CH4	C2H6	C2H4	C3H8	C6H14	CH2O	NOx	TOC
vol %	vol-%	vol-%	vol-%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	mg/Nm3	mg/Nm3
	26	10	2	50	373	527	200	20	10	20	100	50	50	50	50	45.6		

Combustion solid waste (bottom ash)

Taking into account composition of the WFD prepared from the heavy fraction of ASR, any incineration bottom ash obtained in combustion processes would consist of a mineral fraction (inorganic oxides) and a minor fraction of unburnt material (carbonaceous residue, char). Residues from waste (co-)incineration processes are waste subject to Commission Decision 2014/955/EU, in which a List of Waste (LoW) is established that classifies defined waste types as hazardous or non-hazardous. Two entries in that LoW are relevant for bottom ashes from WDF combustion: 19 01 11* – *bottom ash and slag containing hazardous substances* and 19 01 12 – *bottom ash and slag other than those mentioned in 19 01 11*. Consequently, the bottom ash should be tested to check if it shows hazardous properties or if contents of certain substances exceed limit values for maximum concentrations (Annex III of Waste Framework Directive, amended by Commission Regulation (EU) No 1357/2014)).

The amount of bottom ash collected in the batch reactor in the experiments has ranged from 7 to 15 g. This may be due to the heterogeneity of the WDF itself, and to the fact that incomplete combustion of the WDF has occurred differently in the various trials. That amount of ash has been sufficient to perform the ultimate analyses (C. H, N, S) to check the presence of unburnt organic matter, but insufficient for chemical analysis of eluates to determine environmental hazardousness of that solid waste. Therefore, it has been necessary to mix samples of several combustion experiments until obtaining sufficient mass for testing leaching behaviour of the ash.

Regarding unburnt material content in collected bottom ashes, measured C has been below 3 wt% in all the cases, except for the ashes of one of the experiments of combustion in air (higher flow rate) maintained at 550 °C. Less presence of carbonaceous residue in ashes of the combustion processes with oxygen and enriched air has been noticed.

The contents of heavy metals (barium, selenium, molybdenum, zinc, antimony, arsenic, cadmium, copper, chromium, mercury, nickel, lead) and some inorganic anions, such as sulphate, chloride and fluoride, have been determined in eluates obtained at standardised conditions from bottom ash composed samples. Measured average concentrations meet limit values set as criteria for acceptance of non-hazardous waste in landfills (Council Decision 2003/33/EC),

4.2.3. Scrap variability in terms of alloying elements

REFIAL is an aluminium refinery dedicated to the supply of aluminium from secondary smelting, whose facilities are based on the latest technology in aluminium refining for optimum use of the waste treated. The overall process of secondary aluminium manufacturing starts with the scrap collection, and it should be outlined that REFIAL uses in its production process mainly aluminium post consumption, approximately an 85%, produced and characterized in the companies of its business group (Grupo Otua: a metal recycling company). In fact, the key grades of scrap used at REFIAL comes from the processing of waste electrical and electronic equipment (WEEE) and end-of-life vehicles (ELV), like chips, aluminium recovered from shredder waste, or even aluminium utensils. The remaining 15% is post-production aluminium scrap that also arrives characterized at the REFIAL facilities.

Depending on the source from which this aluminium has been recovered (e.g. the type of WEEE or ELV), the composition of the scrap varies. For this reason, REFIAL performs measurements of the composition of scrap directly on reception. The chemical elements analysed in the scrap are related with the standard UNE-EN 1706, that regulate the composition of the casting alloys produced at REFIAL. The key elements to be detected are: Al, Si, Cu, Fe, Mn, Mg and Zn, but also, other elements like Cr, Ni, Pb, Sn and Ti have a specific range of composition that have to be respected, based on the standard. This analysis consists on taking and smelting a representative sample of the scrap, obtaining an ingot and a cylindrical specimen, being the latest tested in an optical emission spectrometer (by spark). Taking into account the results obtained, and with the knowledge of other parameters like moisture, organic content, or the metallurgic yield, among others, the scrap mix required to produce a specific alloy is defined.

REFIAL has classified the aluminium scraps in 9 different categories: A, B, C, D, E, F, G, H, and I. The composition values are presented as relative values taking as reference the median of E, for all the alloying elements analysed.

4.2.3.1. Silicon (Si)

The addition of silicon to aluminum reduces melting temperature and improves fluidity. Silicon additions to aluminum are commonly used for the manufacturing of castings, and it is one of the main alloying elements of the aluminium alloys produced by REFIAL, and for this reason is of high importance to control the content of this element in the melt.

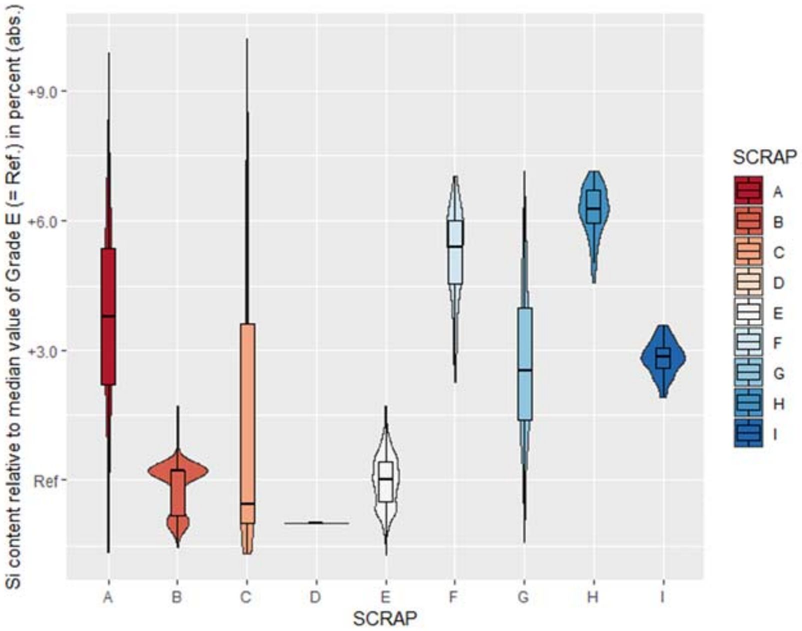


Figure 47. Silicon content variability by scrap type at Refial.

4.2.3.2. Copper (Cu)

The aluminum-copper alloys produced by REFIAL typically contain between 1 to 5% copper, but the range of this alloying element is narrow in most of them. The copper provides substantial increases in strength and facilitates precipitation hardening, and also, the introduction of copper to aluminum can reduce ductility and corrosion resistance.

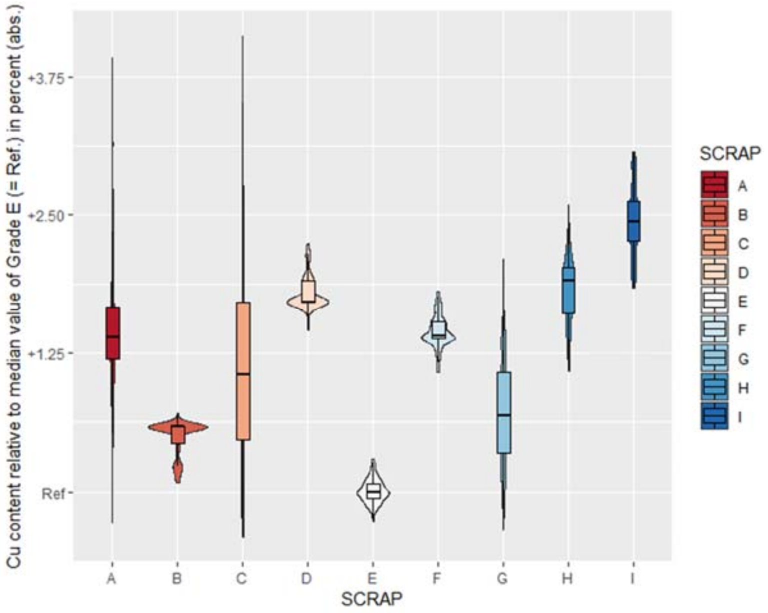


Figure 48. Copper content variability by scrap type at Refial.

4.2.3.3. Iron (Fe)

Iron is the most common impurity found in aluminum, being the maximum limit for the alloys produced by REFIAL lower than 1%. For this reason, it is of high relevance to control the quantity of this metal introduced into the melt.

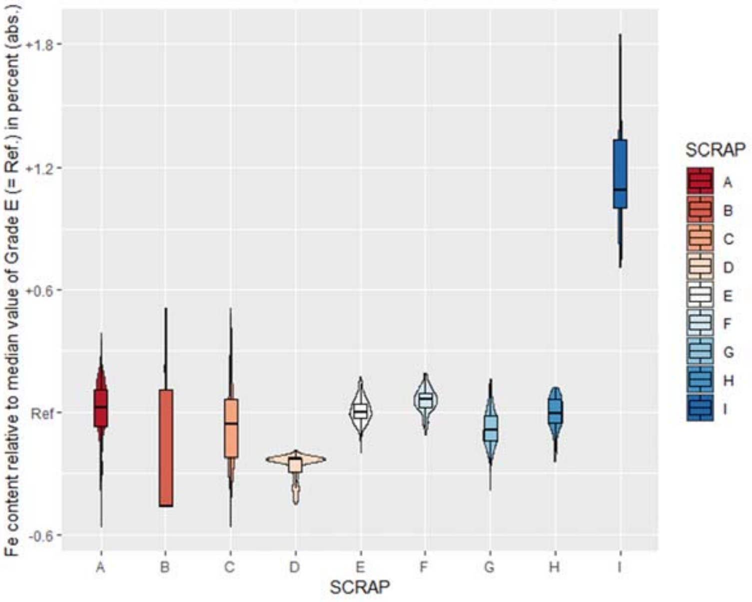


Figure 49. Iron content variability by scrap type at Refial.

4.2.3.4. Manganese (Mn)

The addition of manganese to aluminum increases strength somewhat through solution strengthening and improves strain hardening while not appreciably reducing ductility or corrosion resistance. The maximum quantity of this alloying element in the alloys produced by REFIAL is very low, lower than 1% in all cases.

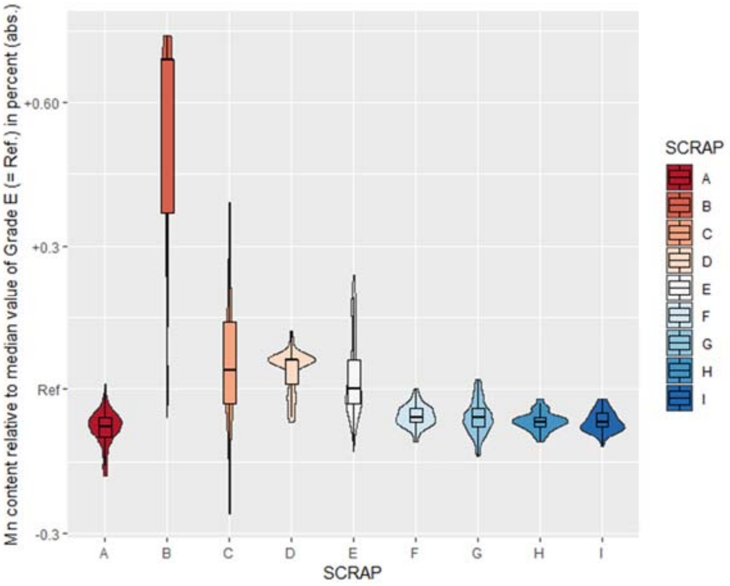


Figure 50. Manganese content variability by scrap type at Refial.

4.2.3.5. Magnesium (Mg)

The addition of magnesium to aluminum increases strength through solid solution strengthening and improves their strain hardening ability. The limits for this alloying element in the alloys produced by REFIAL are low (lower than 2%) and narrow (some of them only have a range of 0.1 between minimum and maximum value of content).

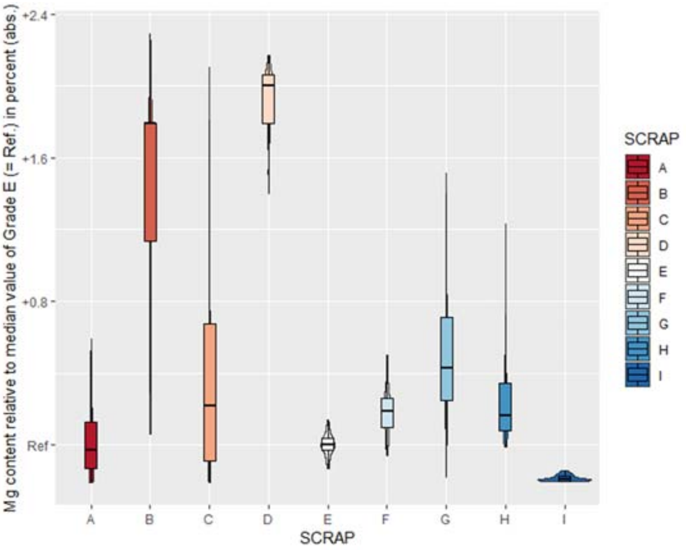


Figure 51. Magnesium content variability by scrap type at Refial.

4.2.3.6. Zinc (Zn)

The addition of zinc to aluminum (in conjunction with some other elements, primarily magnesium and/or copper) produces heat-treatable aluminum alloys of the highest strength. The zinc substantially increases strength and permits precipitation hardening. The maximum level of this element in the alloys produced by REFIAL goes from 0.07 till a maximum of 3.

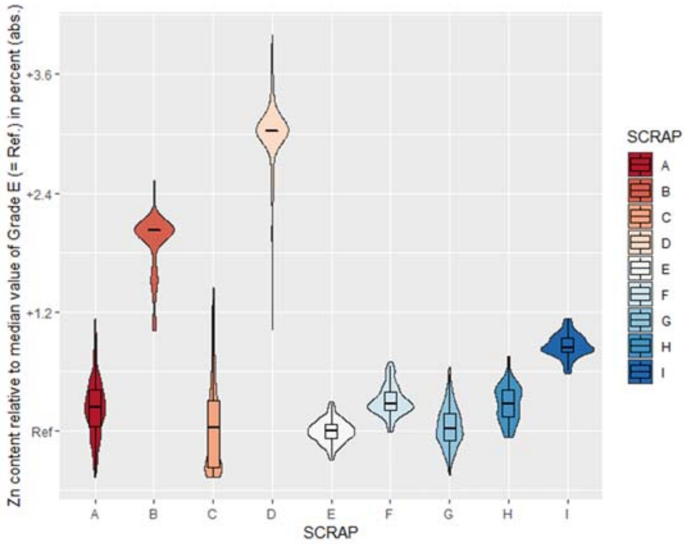


Figure 52. Zinc content variability by scrap type at Refial.

4.2.3.7. Metallic yield

Refial has also analysed the metallic yield of the nine types of scrap selected, and the results based on historical data can be observed in Figure 53.

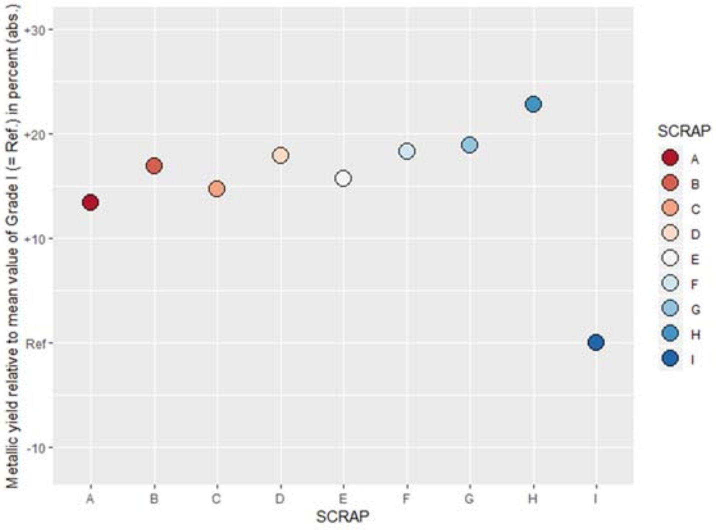


Figure 53. Metallic yield of the selected scrap.

As expected, the metallic yield of most of the scrap types show a high value, lying between 75 % and 90 %. The scrap type I, has a significantly lower metallic yield compared with the rest of the selected types of scrap. This scrap comes from another company of the Otua Group, in order to recover its aluminium content, but due to its low metallic yield is used only in low proportion in the melts.

4.2.4. Definition of aluminium scrap preheating requirements

The motive behind preheating scrap aluminium is to reduce the melting time and thereby increase the energy efficiency. Besides, that step would remove moisture from the metal scrap before it is loaded into the melting furnace, an action that has to be executed to avoid explosions.

The first concept of the pre-heating system proposed in REVaMP is based on two separate chambers

- WDF burner
- Heat exchanger (to avoid direct contact between hot gases and scrap)

Design constraints for the pre-heating system are

- **Dealing with WDF heterogeneity and chemical composition**
    - NCV fluctuations
    - Risk of uncontrolled overheat of the WDF
    - Corrosion, slagging, fouling issues, that could affect the refractory, filters and heat exchanger system
- **Environment issues:**
    - Air emissions: treatment of off-gases from burner
    - Residual waste (char, slag) hazardousness

One important design consideration for the preheating system is the maximum temperature the metal load will reach. The maximum should be below the melting temperature so that metal pieces in the scrap are not led into plastic state. The selection of the temperature to pre-heat the scrap should be a compromise among several factors

- Target reduction of melting time achievable in rotary furnace
- Energy demand in scrap pre-heating (energy delivered by the WDF combustion) and pre-heating time. That would depend on calorific value and combustion kinetics of WDF, but also on aluminium scrap physical-chemical characteristics (Content of volatile impurities and moisture of scrap, alloy composition and physical form (shape, size) of scrap) and heat exchanger design.
- Recovery of heat contained in WDF combustion gases, using convection pre-heaters, might be limited by maintaining low wall temperature, in order to control hot corrosion of equipment and, thus, the preheated combustion air provided by these heat exchangers may be at relatively low temperature (425-315 ^{o}C) (6).

5. Lead material feedstock variability assessment

5.1. Characterization of waste materials on the market for lead production

5.1.1. Characterization of lead scrap variability

Lead is a naturally occurring metal. Its chemical and physical characteristics, such as its malleability, low melting point and resistance to corrosion, make it applicable to a wide range of uses.

The main source of lead scrap for recycling is lead acid batteries. This scrap represents over 90% of the contained lead available for recycling. They are mainly used in cars representing around 85% of the total lead acid battery but there are also several other type in use for emergency power supply, electric cars, load levelling, cattle-grazing, traffic lights, telephones etc.

Other lead scrap materials for recycling include sheaths from telephone and power cable, lead pipe sheet, **weights** (particularly automobile and truck wheel weights and fishing weights), printing metals, ammunition, nodes, residues, dross, sludges and dust.

Lead compound can add durability, opacity and colour to **paint.** As of September 2019, 73 countries have adopted lead paint law to reduce the amount of lead added in paint to 90 ppm, the smallest quantity technically feasible.

Lead shots are the small round pellets of lead used as projectiles in shotguns. Lead is the primary material for **shots and bullets**.

Lead sheet, used in the **construction industry** for roofing and as a radiation shield in the healthcare industry, also has an impressive recycling record. All lead sheet that is manufactured from recycled material, and more than 95% of scrap lead sheet is collected and recycled.

Lead **piping** is less likely to be installed in water distribution systems today because of the public health risk and the availability of alternatives, but some are still used in the chemical industry.

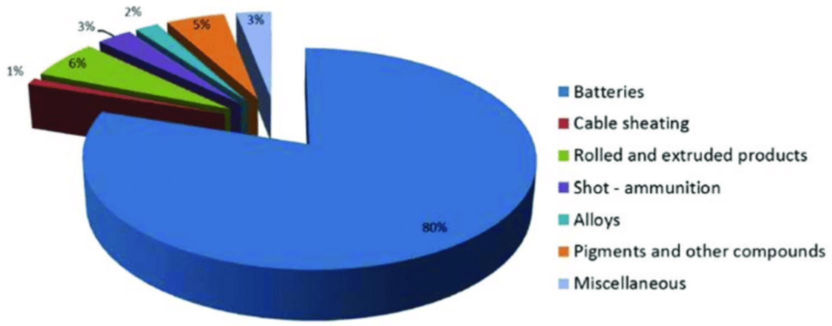


Figure 54. Different end uses of lead in the world

Used lead-acid batteries are the main raw material in secondary lead production. The batteries have a complex composition with a variety of components made of lead (i.e., metallic, oxide or sulphate) and non-lead materials (plastics and electrolyte). Lead and polypropylene (PP) plastics are recyclable components. The next figure illustrates the components in a modern lead-acid battery, their characterisation is described below (from (7)).

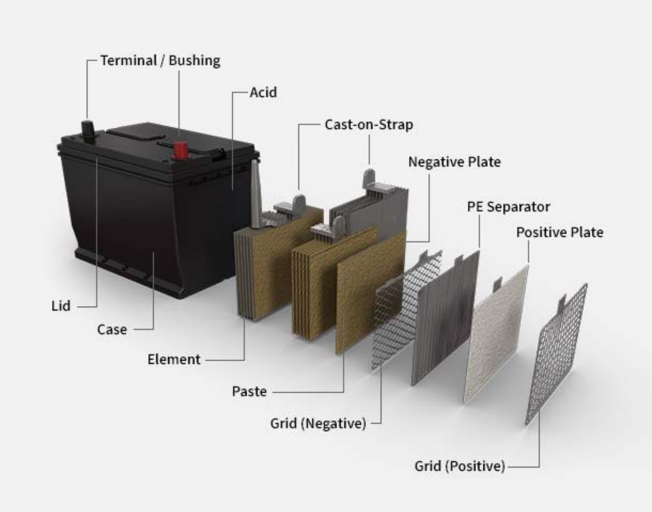


Figure 55. Components in a car battery (Autobatteries, 2018)

- **Battery Terminal/Bushing**: The terminals are connected to the positive strap and the negative strap of the end cells, and are the interfacing point between the battery and the vehicle's electrical system.
- **Battery Acid**: The acid is a high-purity solution of sulfuric acid and water.
- **Cast-on Strap for Batteries**: The cast-on straps are welded to the top of each element to provide an electrical connection to the terminals.
- **Battery Negative Plate**: The negative plate contains a metal grid with spongy lead active material.
- **Battery Separator**: The separator is a polyethylene material that separates the positive plates from the negative plates to provide an efficient flow of electrical current.
- **Battery Positive Plate**: The positive plate contains a metal grid with lead dioxide active material.
- **Lid on Battery**: The lid is made of polypropylene resin and sealed to the battery case.
- **Battery Case**: The case is polypropylene resin, which holds the battery plates, cast-on straps and electrolyte. It's designed to minimize vibration impact and extend battery life.
- **Battery Plates**: The element consists of stacked alternating positive and negative plates. The plates are connected at the top by a cast-on strap that is welded to the plates. The elements fit into the individual cells of each battery.
- **Battery Paste**: The paste is a lead oxide mixture that creates both lead dioxide and sponge lead. It adheres to the positive and negative battery grids.

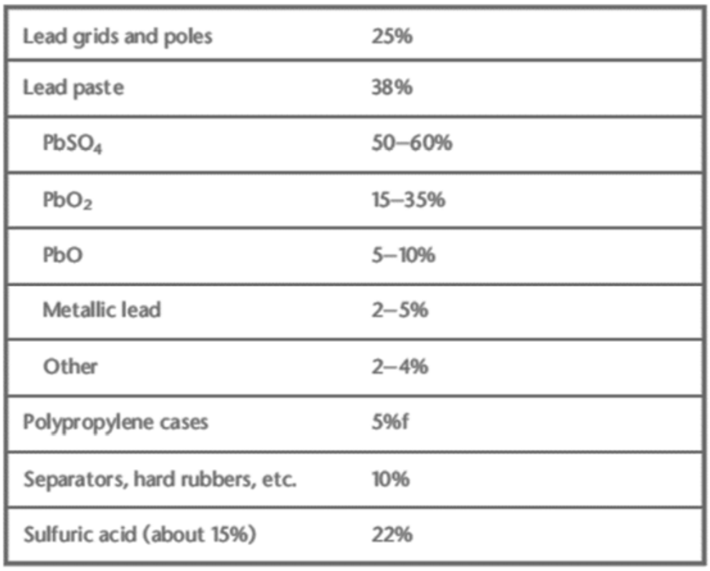
The battery is composed of plates containing paste grids where the paste initially is composed of PbO_2. Lead paste from used batteries contains mainly of lead oxides $PbSO_4$, PbO_2, PbO, lead sulphate and a small amount of metallic lead.

The grids and poles are made of lead alloy, where a small amount of metal is added. The most common additives are antimony, calcium, tin and selenium. The separators are usually made of PVC or polyethylene. The complex composition causes difficulties in subsequent recycling processes.

The recycling process allows to divide the used lead-acid batteries into following four fractions: (1) paste; (2) grids, poles and separators; (3) electrolyte (sulphuric acid solution); (4) casing made of polypropylene. Although the composition of these fractions is currently standardized, meaning that there is not much variation in composition of lead-acid car batteries, if there are variations then they occur in the amount of lead in each of the elements of the battery.

The following table shows the quantity of each of the elements according to (8).

Table 6. Typical content of a lead acid automotive battery



Lead grids and poles	25%
Lead paste	38%
$PbSO_4$	50–60%
PbO_2	15–35%
PbO	5–10%
Metallic lead	2–5%
Other	2–4%
Polypropylene cases	5%f
Separators, hard rubbers, etc.	10%
Sulfuric acid (about 15%)	22%

In the case of the EXIDE plant, the raw material that arrives at the factory comes from two different sources.

The largest amount of raw material comes from external suppliers, around 70%. This raw material arrives at the factory in trucks containing already classified material. Paste is the fundamental raw material, although materials such as metallic ones also arrive, and to a lesser extent, mixed battery elements such as grids, oxides, separators, etc.

The rest, 30% of the raw material comes from its internal suppliers. 90% correspond mainly to used batteries and 10% belong to rejects from the EXIDE group's battery production plants. After the process of breaking the batteries, pastes are obtained in 20% and metallic in 70%.

The paste and the metallic that arrive from the suppliers are analysed in the laboratory, with an Inductively Coupled Plasma Spectroscopy (ICP) to detect the lead content. The paste (Figure 56) usually has an average of 72% lead content and 9% moisture. On the contrary, the metallic (Figure 57) that are separated into lead paste, inert and metallic for analysis, usually have an average content of 92% lead and moisture of 2%.

Variability of both moisture and lead content depends on the raw material supplier. It also influences on the form of presentation of the raw material. For example, it is not the same if the raw material is present whole or crushed.

Due to this variability of the scrap the load in the furnaces depends to a great extent on the experience of the production planner to obtain the most homogeneous yields possible.

Figure 56. Paste or fines

Figure 57. Lead metallic

Figure 58. Pastes or fines

Figure 59. Inert

Figure 60. Lead metallic

The following figures show the laboratory results for different samples of pastes and metals in relation to their moisture and lead content.

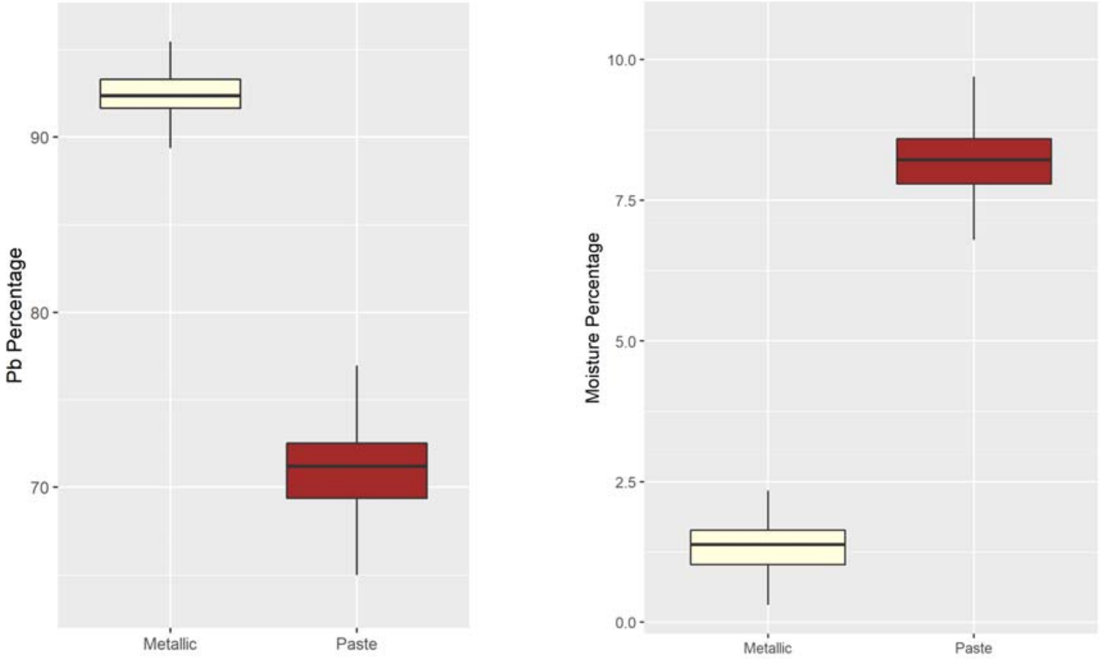


Figure 61. Percentage of lead and moisture in lead paste and metallics

There are other raw materials that come from the outside, such as plates and oxides or by-products of the melting process that are reused as raw materials such as ashes, sludge or fumes. These last raw materials also show variability in terms of lead content as can be seen in the following table.

Table 7. Lead content in different raw materials of the furnace charge

Raw Material	Variability in % Pb
Paste	69-75%
Metallic Lead	88-94%
Plates	60-75%
Hard Ashes	80-82%
Cu Ashes	75-81%
Sb Ashes	84-86%
Sludge	4-11%
Fumes	60-62%

Not only is interesting the characterization of the amount of lead in scrap metal. Knowing the content of each of the lead compounds such as oxides and sulfates can help to determine the amount of fluxes necessary for thermodynamic reactions to take place optimally.

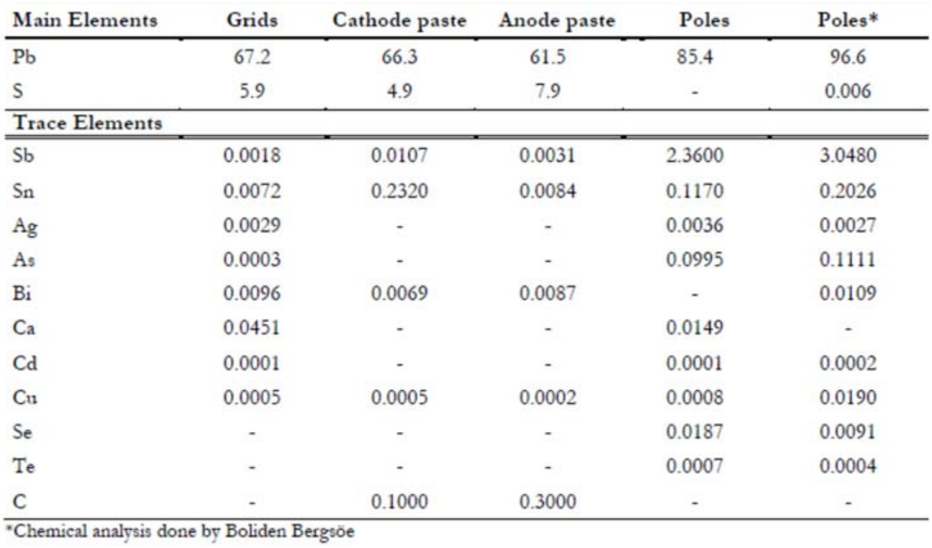
This analysis of these components is not done routinely in company laboratories due to the high cost of resources.

It may also be interesting to determine the composition of other metallic elements, for example antimony, with the aim of obtaining bullion more precise to facilitate the refining process. Some studies (9) have made a more accurate characterization of lead scrap.

Table 8 shows the content of lead and sulphate in lead bearing samples and to reveal the trace elements presents in the samples according to chemical analysis carried out. The highest lead content could be observed in the poles. There was no significant difference between the pastes and grids in terms of lead content which varied from 61.5 % to 67.2 %.

Other elements present in lead scrap such as Sb, As, Bi, Sn, Cu, Ni, Ag, Ca, Se and Te can be analysed for their content. The major trace elements in the poles were antimony (~3 %) and tin (~0.2 %). Analysis of these elements carried out in the EXIDE laboratories can be seen in the section 5.2.

Table 8. Chemical composition of the lead bearing components in %.



Main Elements	Grids	Cathode paste	Anode paste	Poles	Poles*
Pb	67.2	66.3	61.5	85.4	96.6
S	5.9	4.9	7.9	-	0.006
Trace Elements					
Sb	0.0018	0.0107	0.0031	2.3600	3.0480
Sn	0.0072	0.2320	0.0084	0.1170	0.2026
Ag	0.0029	-	-	0.0036	0.0027
As	0.0003	-	-	0.0995	0.1111
Bi	0.0096	0.0069	0.0087	-	0.0109
Ca	0.0451	-	-	0.0149	-
Cd	0.0001	-	-	0.0001	0.0002
Cu	0.0005	0.0005	0.0002	0.0008	0.0190
Se	-	-	-	0.0187	0.0091
Te	-	-	-	0.0007	0.0004
C	-	0.1000	0.3000	-	-

*Chemical analysis done by Boliden Bergsöe

5.1.2. New waste materials on the market for lead production

The demand for battery energy storage will grow in the coming years in sectors such as the automotive industry with new markets such as hybrid electric vehicles, automotive start-stop systems and network energy storage applications at scale.

Lead batteries have continued to be more widely used in automotive and industrial applications and still provide 75 % of global rechargeable energy storages. New technologies have entered the market and lithium-ion (Li-ion) batteries in particular are set to grow substantially in electric vehicles of all types and in energy storage, see Figure 62. Lead batteries, however, represent 75% of the market in MWh because of the large price difference in $/MWh. With the ban on the use of lead in many raw materials such as paints, solder, ammunition, in recent years practically all the use of lead is concentrated in the production of acid batteries. Therefore, lead batteries will continue to be the main raw material for secondary lead recycling factories in the coming years.

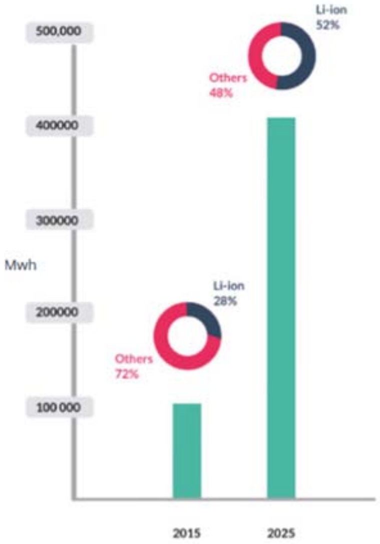


Figure 62 - Growth of battery for energy storage applications (Avicenne – ALABC report, 2018).

5.2. Definition of charge material requirements for lead production

The basic charging of the rotary kiln is lead products from the recycling of batteries. Feedstocks are divided into lead-bearing materials, flux and reductant components. A flow sheet of the secondary lead metallurgy process is shown in Figure 63.

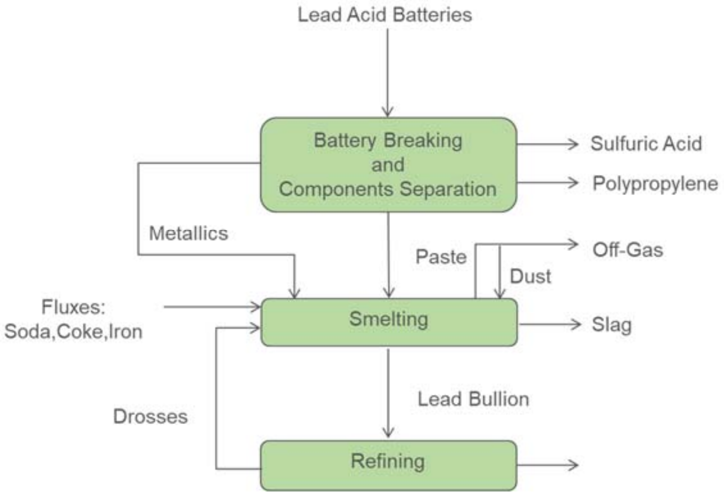


Figure 63. Flowsheet of lead secondary industries for recycling lead-acid batteries.

The main raw material used in the charge of the furnace which size is small, between 1mm to 3 mm, is as follows:

- Lead paste consists mainly of Pb and lead oxides $PbSO4$, $PbO2$, PbO.
- Metallic lead. It´s mainly composed of lead and can contain lead oxides and sulfates. Metallic lead can be alloyed with other elements, mainly antimony. Other compounds like Cu, Zn, Cd and S are as impurities.
- Dross. This comes from the Bullion's refining stage. Dross is primarily composed of lead oxides, metallic lead and lead compounds with antimony.
- Others.

Other materials are added to provide the necessary conditions for obtaining the bullion:

- A carbothermic reducer is used, in this case carbon, which reduces the lead present in the form of $PbSO4$, $PbO2$ and PbO to metallic Pb. Commonly used agents are coke and anthracite.
- The added material for the slag formation is iron which acts as a sulfur collector fixing it and forming FeS, it also fixes the impurities present in the raw materials. Iron can be added as iron or steel production residues, in which it contains a percentage of carbon. This carbon contributes to the reduction and minimizes the melting point of iron.

Both iron and carbon are **reductants** and have a combined effect to produce metallic lead. The difference between these elements is that the iron added to the charge is still present at the end as iron oxide or iron sulphide; while most of the carbon is consumed to produce gaseous products (CO and CO_2).

- Some materials called **fluxes** can be added in order to decrease the melting temperature and viscosity of the slag to facilitate the slag-metal separation, the most common material used as flux is sodium carbonate (Na_2CO_3, soda) and can act on the reactions and contribute to the reduction of the metal compounds and become part of the slag.

The amount of flux and reducing agent added must be carefully controlled:

a) The lack of flux will prevent trapping all the sulphur and the other materials present in the scrap metal, for which reason a large quantity of sulphur oxides will be released;

b) If, on the other hand, a small amount of reducing agent is added, it will not reduce all the lead oxides present in the scrap metal, and the slag will be highly contaminated with lead, which can pose a danger to the environment.

If there is excess carbon in the charge, a portion of the iron that was in the form of FeS or FeO is carbo-thermically reduced to metallic iron or Fe3C, which are solid and increase the viscosity of the slag making the process more poor in recovery of the bullion. Therefore, it is important to optimize the reactants (C, Fe, and Na_2CO_3) to give the highest lead recovery for a given charge.

An example of characterization of the charge material to obtain a bullion lead in an EXIDE furnace is shown in the following table. The amounts of fluxes are calculated in relation to the total charge and the production to the sum of total charge plus fluxes. As can be seen, the components with the highest percentage are paste and metallic ones that contain a high content of Lead. The flux content is usually between 6-8% of the value of the total load by weight introduced in the furnaces.

Table 9. Example of Raw Material Charge in rotary furnace in EXIDE plant.

TOTAL CHARGE					FLUXES			PRODUCTION
Metallic	**Paste**	**Oxides**	**Plates**	**Dross**	**Anthracite**	**Iron**	**Soda**	**Bullion**
49,48%	**33,10%**	**7,32%**	**7.32%**	**2,79%**	**7,49%**	**6,62%**	**6,45%**	**77,84%**

The rotary furnace process takes places at temperatures between 900º and 1000ºC by the combustion of a mixture of natural gas and oxygen. This temperature, necessary for the promotion of chemical reactions, is achieved by means of an oxi-gas burner. During combustion the charge, the reducers and fluxes are heated.

The ratio between oxygen and gas depends on the phases that take place in the furnace. Specifically, four phases are distinguished: organic burning, melting, reduction and casting. Each of these phases takes place at different temperatures, times and oxygen-gas ratios, taking an O_2/Natural gas ratio with an approximate value of 2 to 2.2 depending on the stage of the smelt process.

At the end of the process two products are obtained, the bullion that contains mostly lead and when the charge has high dross content, there is also antimony, and the slag. Slag formation occurs during the melting and reduction stages as a result of the different chemical reactions that occur between the agents and the undesirable impurities or compounds in the final product.

The slag is mainly composed of oxides, such as Na_2O, Na_2CO_3, PbO, FeO and Fe_2O_3. Na_2SO_4 has also been found in slag characterization studies. There may be solid compounds in the slag such as carbon, metallic iron, Fe_3C and Fe_3O_4. The slag from a rotary furnace in general contains also low levels of lead (2-5%).

In the recycling of lead there are other elements that come from batteries and other types of lead scrap, such as, Sb, As, Sn, Cu, Bi, Ag, Ni, Se, Te, Al, Fe and Zn. Generally, the secondary refineries do not remove silver or bismuth from the bullion because the quantities present do not justify the costs of removal. The rest of the elements are eliminated in the refining process depending on the type of final lead alloy that wants to be obtained. The most common products of the refinery process are pure lead and lead-antimony and lead-calcium alloys according to the final required properties of the lead alloy.

The following graph in Figure 64 represents the average percentage of these elements present in the soft lead bullion of different castings produced in the furnaces of the EXIDE plant.

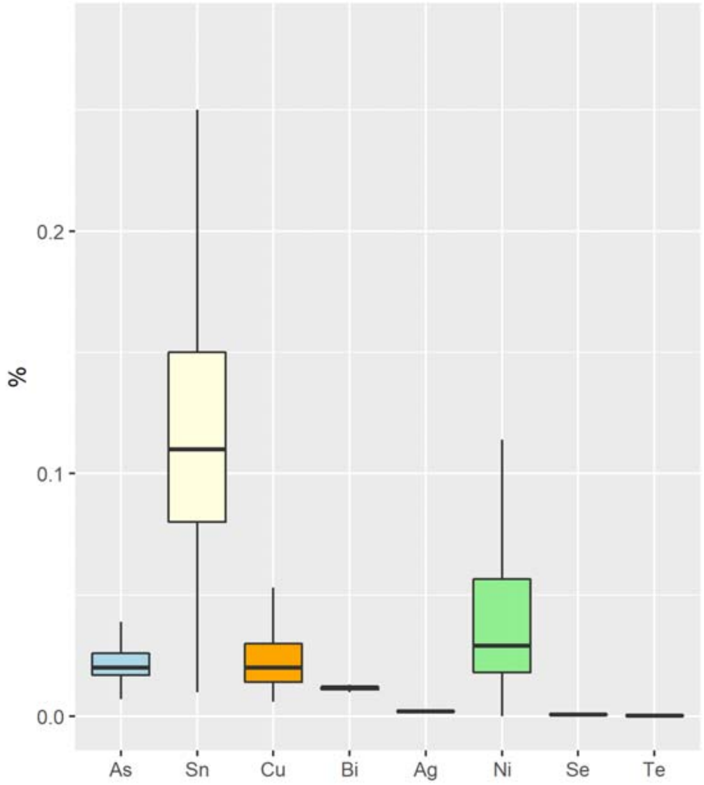


Figure 64. Content for different elements in soft lead bullion castings.

A specific case is antimony, which has a greater variation, since this element can be added as raw material to the furnace in the form of dross to obtain a bullion lead that is subsequently used to obtain a lead-antimony alloy. In these cases, the percentage of antimony in the bullion lead can be up to 8% by weight. In the following graph in Figure 65, on the right the antimony content in castings that are used to obtain pure lead ingots after a refining process is depicted. In the graph on the left the antimony content corresponds to castings that are used to obtain lead-antimony alloys. In the first case, the hard lead bullion obtained has an average antimony content of around 3.83% while the soft lead bullion has an average content of around 0.73%.

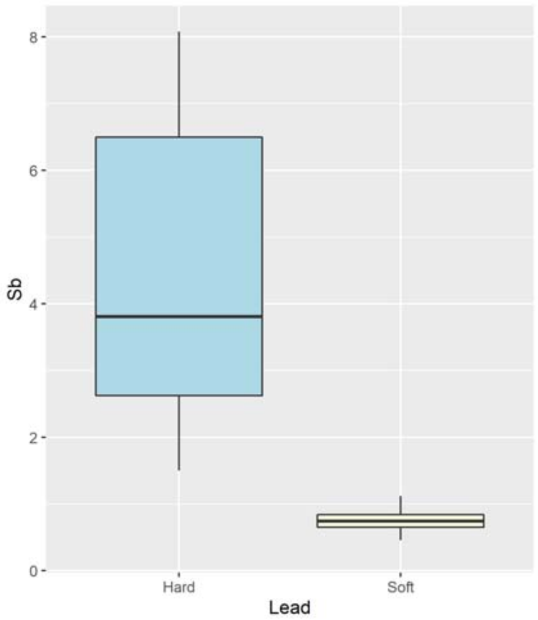


Figure 625. Antimony content for different soft and hard lead bullion castings.

Other aspects to consider that are related to the composition of the charge in the furnaces are the thermodynamic processes that are carried out in the different stages of the melting process. The thermodynamic analysis of the rotary furnace process is rather complex due to the components and phases that must be considered. This means that the loading of material in the furnaces must be carried out optimally to obtain the greatest amount of lead in the bullion and the least in the slag.

To summarise, a better measure of the percentage of lead in the feedstock will lead to a better control of the feed of the furnace, which can be adjusted based on the required properties of the lead alloy to obtain as final product.

For this reason, it is very important to have sensors that allow to measure the variability of the scrap metal that reaches the recycling plants. This is one of the objectives of the REVaMP project to obtain a sensor capable of determining the amount of lead in the paste and the metallic, these being the fundamental raw material in the battery recycling process. It would also be interesting to see how some other parameters affect to the furnace charge, e.g. size distribution.

6. Abbreviations

ar	as received
ASR	Automotive Shredder Residue
BOF	Basic Oxygen Furnace
d	dry
DOM	Dissolved Organic Matter
db	dry basis
DSC	Differential Scanning Calorimetry
EAF	Electric Arc Furnace
ELV	End-of-Life Vehicles
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
HHV	Higher Heating Value
IED	Industrial Emissions Directive
LHV	Lower Heating Value
LOI	Loss on Ignition
LOW	List of Waste
NCV	Net Calorific Value
QL	Quantitation Limit
SHF	Shredder Heavy fraction
SLF	Shredder Light Fraction
SRF	Solid Recovered Fuel
VOC	Volatile Organic Compound
TGA	Thermo-Gravimetric Analysis
WDF	Waste Derived Fuel
WEEE	Waste Electrical and Electronic Equipment

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