CO-PROCESSING

Material recovery of the mineral fraction from Refuse-Derived Fuels in the cement industry

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Fundación Laboral del Cemento
y el Medio Ambiente

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About CEMA Foundation

Fundación Laboral del Cemento y el Medio Ambiente (Cement and Environment Labour Foundation; hereinafter, CEMA Foundation) is a joint state-wide organisation that is tripartite in nature, which comprises the cement employer's association OFICEMEN and the two largest trade unions in the industry, CCOO del Hábitat and UGT FICA, Federación de Industria, Construcción y Agro.

CEMA Foundation is a pioneering initiative in the European cement industry, which works in the areas of sustainability, occupational risk prevention and circular economy.

TABLE OF CONTENTS

1 INTRODUCTION

The study **"Co-Processing: Material Recovery of the Mineral Fraction from Refuse-Derived Fuels in the Cement Industry"** has been promoted by Fundación Laboral del Cemento y el Medio Ambiente (Cement and Environment Labour Foundation; hereinafter, CEMA Foundation). Its principal aim is to determine the percentage of material recycling, establishing the mineral content to be found in six of the main types of alternative fuels utilised in the cement industry: Refuse-Derived Fuels from Municipal and Industrial sources, Animal Meal, Wood Waste, End-Of-Life Vehicles and Sewage Sludge.

Within the framework of CEMA Foundation, a joint work group was set up by technicians in the cement groups that form part of OFICEMEN and by technicians from the trade unions CCOO del Hábitat and UGT FICA, with a view to considering, drawing up and conducting the study concerned.

This technical report has been prepared by the Instituto Español del Cemento y sus Aplicaciones (Spanish Institute of Cement and Its Applications; hereinafter IECA) and by the Universidad Politécnica de Madrid (UPM) as a result of the collaboration agreement signed by CEMA Foundation and the above-mentioned University. The document contains the results obtained from the waste analyses carried out by LOEMCO (Official Laboratory for Testing Construction Material), for the six types of waste mentioned.

CEMA Foundation would like to give special thanks to all the cement manufacturing plants, which made available all the waste samples required to conduct the analyses included in this study.

2 BACKGROUND

"Co-processing" is the combination of simultaneous material recycling and energy recovery from waste in a thermal process, which results in replacing natural mineral resources and fossil fuels such as coal and petroleum products. Directive 2018/851, of 3h May 2018 amending Directive 2008/98/EC on waste, expressly states that "The Commission shall assess co-processing technology that allows the incorporation of minerals in the co-incineration process of municipal waste. Where a reliable methodology can be found, as part of this review, the Commission shall consider whether such minerals may be counted towards recycling targets".

The concept of "co-processing", is also consistent with the Spanish Circular Economy Strategy known as "Circular Spain 2030", approved in June 2020, whose goals amongst others are, to reduce by 30% the domestic consumption of materials in relation to the GDP and to reduce waste generation by 15% when compared to the volumes generated in 2010.

In this sense, the best technically-recorded example of simultaneous recovery, both materially and from an energy perspective in the Spanish cement sector, concerns end-of-life tyres. The high calorific value of rubber is used to replace fuels (energy recovery) and the inert components (mainly iron and aluminium), as replacements for raw materials (material recovery). Therefore, in the document "ELT co-processing study in cement plants", prepared in 2017 by the two collective systems of extended producer liability for end-of-life tyres, SIGNUS and TNU, with the collaboration of the Gómez Pardo Foundation, OFICEMEN and CEMA Foundation, the contribution made by recycled material is calculated as being 24.66% when end-of-life tyres are co-processed in a cement plant kiln. Along the same lines, in April 2018, the French Ministry of Ecological Transition informed ALIAPUR (the French ELT collective management system) that as from 2018, 23.75% could now be calculated as material recovery.

On an international level, several countries have already included in their legislation an express mention to co-processing. The first was Chile, by virtue of Decree 29 in 2013, establishing emission standards for incineration, co-incineration and co-processing, which states the following textually:

"That is why it is necessary to include the term 'co-processing' in the cement sector, it being used to refer to the recovery of material and energy in the clinker production process".

Another example is to be found in Portugal, where the National Environment Agency (APA) has accepted the co-processing methodology and accepts that twofold utilisation is made of energy and material obtained from waste; proof of this is that in Article 111 of Decreto-Lei 102-D/2020, on the general waste-management system, taxes are adjusted in accordance with the verified recycling of materials that come from co-processed waste.

Finally, the latest mention of co-processing can be found in the Décret relatif aux déchets, à la circularité des matières et à la propreté publique, referring to the circular nature of materials and public ownership, passed on 8 March 2023, in the Walloon Region of Belgium, which states the following in Chapter 3, Section 1 and Art. 30,3°: "promouvoir, favoriser et soutenir des innovations en matière de valorisation, notamment toute opération de valorisation consistant en une combinaison simultanée de recyclage et de récupération d'énergie à partir d'un flux de déchets dans un procédé de traitement thermique visant la fabrication de produits" (to promote, enhance and sustain innovations in matters concerning recovery, especially all operations involving recovery where there is a simultaneous combination of recycling and retrieving energy from an inflow of waste in the process of heat treatment from the manufacture of products).

In the above context, the purpose of this report is to provide a detailed account of the contribution to material recycling made by of other types of waste habitually used in the cement industry, in addition to the example already given regarding ELTs.

This technical information is considered to be of vital Importance when it comes to positioning waste co-processing in cement plants as an option in the EU's waste management hierarchy beyond mere energy recovery.

2.1. APPROACH TO THE STUDY

LOEMCO and the Higher Technical School of Mining Engineering of the Polytechnical University of Madrid (UPM) helped to prepare the study, together with the laboratories of the cement group plants, which provided the samples, all of which was overseen and coordinated by CEMA Foundation.

The main aim of the study is to establish the recycling index[1] of the 6 main types of waste used as alternative fuels in Spanish cement plants, by applying a methodology that is recognised by the European Union.

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1   Recycling Index (RI), see Section 2.1.2.

2.1.1. Selection of the types of waste

The waste was selected taking into account the following criteria:

- Current aggregated consumption and potential future consumption. Proportion relative to the consumption of each type.
- Potential recycling index rates and relative knowledge concerning them within the sector.

The selection of the types of waste is summarised in the following figure. The column on the right refers to the number of samples of each type collected.

	RDF (Municipal) from municipal sources and RDF (Industrial) from industrial sources Consumption 2021: 341,085 t Potential amount : >1,000,000 t/year	8+23
	Animal Meal, AM Consumption 2021: 341,085 t Potential amount: >130,000 t/year	11
	Sewage Sludge, SS Consumption 2021: 14,442 t Potential amount: >100,000 t/year	7[2]
	End-Of-Life Vehicles, ELV Consumption 2021: 34,309 t Potential amount: >70,000 t/year	8
	Wood Waste, WW Consumption 2021: 44,769 t Potential amount: 150,000 t/year	6

Figure 1. Types of waste selected

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2   Shipments in two batches, 4 in January and 3 in February 2022.

2.1.2. Determination method

The Recycling Index is based on the methodology proposed in the paper[3]*Determination of the material-recyclable share of SRF during co-processing in the cement industry,* published in Resources, Conservation & Recycling in 2020.

The methodology described in the paper is based on determining the Recycling Index, as a percentage of the contribution of the mineral fraction in the ash in the fuel utilised to manufacture cement in accordance with the following formula:

$$R - index_9[\% (d)] = \frac{AC}{100} * \frac{c_{Al_2O_3} + c_{CaO} + c_{Fe_2O_3} + c_{K_2O} + c_{MgO} + c_{Na_2O} + c_{SO_3} + c_{SiO_2} + c_{TiO_2}}{10000}$$

where the sums c_1, c_2 and c_n, in the numerator, are the fractions in weight of the different oxides contained in the ash fraction in the waste concerned. The formula shows 9 oxides.

The way of deciding which oxides can be considered in the formula, has been extended in time within the[4] ISO/TC 300 WG5, which is the committee responsible for drawing up Standard ISO CD 4349 *Solid Recovered Fuels. Determination of the Recycling-Index for Co-Processing.* There are two possibilities: 9 and 4 oxides. Both possibilities[5] have been considered in this study.

Standard ISO CD 4349 establishes a series of steps to be followed when determining the Recycling Index (RI).

First of all, determine the ash content in the way indicated in Spanish Standard[6] UNE- EN-ISO 21656.

And, secondly, determine the element content and the consequent oxides by means of two analysis techniques: X-ray fluorescence spectrometry (XRF) or inductively coupled plasma optical emission spectroscopy (ICP).

The oxide analyses were carried out using the XRF[7] technique, and some samples were compared by means of ICP. Moreover, a comparison took place utilising the EN 196-2[8] method to establish the SO_3.

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3   Determination of the material-recyclable share of SRF during co-processing in the cement industry. S.A. Viczek, A. Aldrian, R. Pomberger, R. Sarc. Resources, Conservation & Recycling 156 (2020) 104696.
4   ISO - ISO/CD 4349 - Solid recovered fuels — Method for the determination of the Recycling-Index
5   A complete account of the oxides considered can be found in Section 4
6   UNE-EN ISO 21656:2021 Solid recovered fuels. Determination of the ash content
7   The SO_3 analysis was conducted by ICP
8   UNE-EN 196-2. Cement test methods. Chemical analysis of cements.

3 SAMPLE TREATMENT & ANALYSIS

The following sections show not only the activities involved in receiving, encoding and sending the samples to the laboratory, but also how they were treated by LOEMCO (Official Laboratory for Testing Construction Material).

3.1. SENDING AND ENCODING SAMPLES

Eight cement groups contributed to the selection and sending of the samples used in the plants, following the sample-taking protocol devised for the purpose and in compliance with the following criteria:

• The samples shall be selected by provider, taken at the place closest to the supply, stockpile, silo or even the lorry, making sure samples from different sources are not mixed.
• The samples shall be split in order to obtain maximum representativity in the 5 kg of sample sent.
• The samples shall be packed, sealed, labelled and sent to CEMA Foundation, for encoding and shall be sent anonymously, to guarantee complete confidentiality, and subsequently shall be sent to the LOEMCO laboratory, which will be responsible for their treatment and analysis.

3.2. TREATMENT OF SAMPLES

CEMA Foundation received and encoded a total of 63 waste samples, most of which were received during January, except for 3 sludge samples, which were received in February 2022.

The samples were sent to the laboratory in plastic drums of different sizes or in plastic sacks, all of which were correctly sealed and none of which showed any signs of sample loss.

The steps described in Spanish Standard UNE-EN 15443:2011 Solid Recovered Fuels. Methods for the preparation of the laboratory sample, were followed in order to obtain the portion of each sample so it could be analysed.

The first section of Spanish Standard UNE-EN 15410 Solid Recovered Fuels. Method for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti), states that the X-Ray fluorescence (XRF) technique is valid for establishing the main elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and their oxides. The purpose of the preliminary step that the Standard describes here is to calcinate a subsample that is representative of each solid recovered fuel (SRF), with a view to obtaining standardised ash, so that it can subsequently be analysed by XRF.

The first stage in the preparation process was to obtain a subsample of approximately 1 kg that was representative of the original sample received. At a second stage, this subsample was used to extract a sample for representative analysis, which was to be the one that was processed at the third and final stage for calcination and the subsequent analysis of the resulting ash.

The instructions described in Chapter 8 of Spanish Standard UNE-EN 15443 concerning the splitting of samples were followed at the first stage. It was possible to split the samples of Sludge, Wood Waste and Animal Meal with a slot splitter. The RDF and ELV samples had to be split by using a stacking cone and split, because the shape and size of the particles in these materials made it difficult to split them with slot splitters.

Great care was invariably taken to ensure all the samples were standardised, including those samples that had a fines content at the bottom of the drum or sack.

All the subsamples that were representative of each waste sample were weighed, then dried for 24 h at 100 °C, to establish their moisture content and so that the second stage could be carried out with dry samples. It was possible to split the Animal Meal and Sludge samples in the chemistry laboratory until 100 g were contained as the portion for analysis.

The subsamples that are representative of RDF (Municipal), RDF (Industrial), Wood Waste and ELV needed to be cut and ground to obtain a portion of 100 to 300 g for analysis.

The ring and ball mills that the laboratory utilises to prepare conventional samples, were not good enough to obtain a final portion for analysis that was sufficiently representative, so blenders and household coffee grinders were used to achieve a uniform grain size for all of them. This meant that the process was long and costly where many of the samples were concerned.

The ELV samples are made up of large particles up to approximately 100 mm and of more diverse materials, such as plastics, rubber, textiles, pieces of end-of-life tyres (ELT), etc., so they could not be cut with blenders or grinders. In the case of the ELVs, a representative subsample of the original sample was weighed as a whole before each individual particle was weighed. A portion of each particle proportional to its relative weight in the whole sample was cut with a knife, this portion being determined on the basis of the relative weight of each particle in the subsample total. A portion weighing about 200 g was prepared for calcination.

The portions thus obtained for analysis were calcinated at 550 °C, as indicated in Section 5 of Spanish Standard[9] UNE-EN 15410.

The material (ash) resulting from each calcination process was ground again with a vibratory ring mill until all of it passed through a 100 μm sieve. The samples originally received and thus prepared were held to be free of their organic part, so the ash consisted exclusively of the mineral part.

Once the samples were prepared, they were packed into self-sealing plastic envelopes and put into plastic containers with a lid.

3.3. ANALYSIS OF SAMPLES

The 63 samples prepared by LOEMCO in the way described above until the ash was obtained for each one of the RDFs[10], were then sent for analysis to a laboratory accredited as required by ISO/IEC 17025:2017 so they could be analysed by XRF or ICP[11].

Once the results obtained by XRF had been analysed, it was decided that a sample representative of each type of Refuse-Derived Fuel should also be analysed using the inductively coupled plasma optical emission spectroscopy technique (ICP), so a total of 6 samples were analysed in this way. The aim of this further analysis was not only to check the effects of the analysis technique on the results originally obtained by XRF[12], but also to confine the variabilities observed when analysing some oxides.

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9   UNE-EN 15410:2012. Solid recovered fuels. Method for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si and Ti)
10   Refuse-Derived Fuels.
11   A complete account of the analysis techniques is given in 3.3.1 and 3.3.2.
12   In the case of SO_3, the comparison is between ICP and the method contained in EN-196-2, because it is an analysis commonly used in the assessment of cement compliance

3.3.1. X-ray fluorescence spectrometry (XRF)

The X-ray fluorescence technique enables the user to measure the wavelength and the light intensity (X-rays) emitted by the atoms for each element agitated in the sample. The sample is irradiated with a primary X-ray beam using an X-ray tube, causing the emission of fluorescent X-rays with characteristic radiation energy for every element contained in the sample. This allows the researcher to know what elements are contained in the sample and their concentration.

One portion of each sample coming from SRF is melted with a flux that also contains an oxidising agent. The mixture is poured into a platinum mould and the disk that forms is analysed with the XRF equipment. The XRF analysis is supplemented together with an ignition loss at 1,000 °C. The resulting data from both determinations are combined to present a complete account of the elements contained in each ash sample.

This analysis technique is used to calculate the main oxides in every element (Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, Na_2O, SO_3, SiO_2 and TiO_2) by determining the elements present in the ash samples of all the SRFs analysed; this is done by establishing what elements are contained in each ash portion.

3.3.2. Inductively coupled plasma optical emission spectroscopy (ICP)

Inductively coupled plasma optical emission spectrometry (ICP-OES), is another multi-element analysis technique that can determine and quantify the elements that are covered by Spanish Standard UNE-EN 15410. Inductively coupled plasma (ICP) is a source of ionisation that, together with an optical emission spectrophotometer (OES), constitutes the ICP-OES equipment.

In this case, the portion of sample must be in a liquid state before it can be analysed by the ICP equipment. The liquid state is achieved by mixing with a flux, the portion of each ash that has been prepared, and melting it in a kiln at 1,000 °C. The molten mass is then cooled and dissolved with acid.

The liquid sample is poured continuously into the ICP equipment nebulisation system, forming an aerosol that is conveyed to the plasma torch by Argon gas. The high temperature of the plasma causes the analytes to be atomised and ionised, generating the atomic emission spectra of characteristic lines. The spectra are dispersed by the diffraction network and the light-sensitive detector is responsible for measuring the intensities of each line. The equipment software relates these intensities to each element and its concentration.

As is the case with XRF, the concentration of every oxide is calculated from each particular element concentration.

4 RESULTS

The graph that appears below shows the different sample types analysed from a total of 63.

Number of samples

			23		
8	7	11		8	6
ELV, End-Of-Life Vehicles	SS, Sewage Sludge	AM, Animal Meal	RDF, Refuse-Derived Fuel (Industrial)	RDF, Refuse-Derived Fuel (Municipal)	WW, Wood Waste
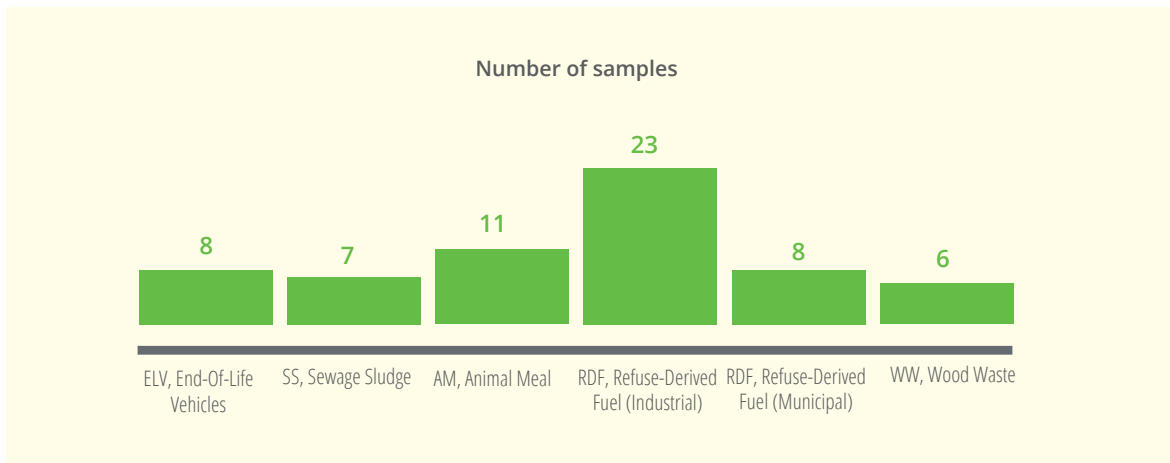
Figure 2. Types of waste analysed

The Recycling Index is calculated on the basis of the contribution made by 9 oxides from the ash fraction in the fuel. Standard ISO CD 4349 enables this calculation to be carried out with the 9 above-mentioned oxides or with only 4, the latter being indicated in green in the following table.

Table 1. Oxides to be considered

Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	SiO_2	TiO_2

The comparison between the results considering 4 or 9 oxides can be seen in Section 5.

The results that are shown below have been calculated with 9 oxides determined using the XRF technique.

All the oxides shown in Table 1 appear in the clinker, so their contributions are absolutely necessary for the manufacture of Portland clinker. A complete account of the clinker composition, including additional oxides such as Manganese Oxide, Mn2O3 and SO3 can be found in Table 4.3 of the reference bibliography used in this study[13].

4.1. ASH ANALYSIS

First of all, the ash has to be determined. The ash content by type of waste can be seen in the following graph.

% ash, average data

Figure values:
- ELV, End-Of-Life Vehicles: 26.2
- SS, Sewage Sludge: 33.5
- AM, Animal Meal: 21.3
- RDF, Refuse-Derived Fuel (Industrial): 13.1
- RDF, Refuse-Derived Fuel (Municipal): 9.3
- WW, Wood Waste: 7.9
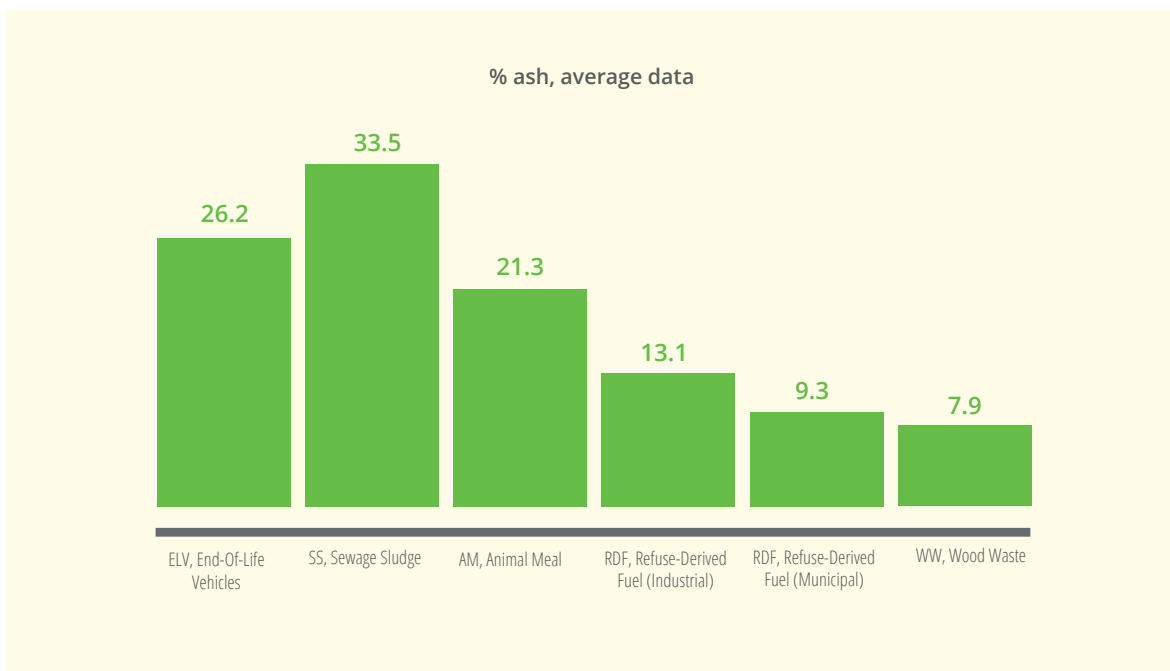
Figure 3. Ash content per type of waste

The ash content varies on the basis of the type of waste. The ash content in Sewage Sludge and End-Of-Life Vehicles ranges from 27 to 32%, whereas the content in the two types of RDF and Wood Waste is less than 15%.

The individual ash data per type of waste can be seen in the following figure below.

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13   Cement Chemistry. HFW Taylor, Thomas Telford, 1990

% Ash, End-Of-Life Vehicles

Label	Value
ELV-06-01-2022	30.5
ELV-06-02-2022	16.7
ELV-06-03-2022	51.5
ELV-06-04-2022	17.7
ELV-10-01-2022	15.7
ELV-10-02-2022	13.7
ELV-07-01-2022	32.2
ELV-07-02-2022	32.1

% Ash, Animal Meal

Label	Value
AM-02-01-2022	20.9
AM-02-02-2022	20.9
AM-07-01-2022	18.6
AM-07-02-2022	23.4
AM-05-01-2022	16.3
AM-05-02-2022	20.2
AM-09-01-2022	18.4
AM-09-02-2022	19.4
AM-09-03-2022	30.9
AM-10-01-2022	21.5
AM-10-02-2022	23.4

% Ash, Sewage Sludge

Label	Value
SS-03-01-2022	40.4
SS-05-01-2022	38.8
SS-05-02-2022	38.9
SS-07-01-2022	18.5
SS-09-01-2022	31.9
SS-09-02-2022	33.5
SS-09-03-2022	32.5

% Ash, Refuse Derived Fuel (Industrial)

Label	Value
RDFI-06-01-2022	8.1
RDFI-06-02-2022	14.8
RDFI-02-01-2022	8.1
RDFI-02-02-2022	4.1
RDFI-03-01-2022	11.1
RDFI-09-01-2022	16.1
RDFI-09-02-2022	18.7
RDFI-09-03-2022	18.7
RDFI-09-04-2022	16.1
RDFI-09-05-2022	16.0
RDFI-09-06-2022	10.6
RDFI-09-07-2022	9.4
RDFI-09-08-2022	2.5
RDFI-09-09-2022	12.0
RDFI-09-10-2022	11.4
RDFI-09-11-2022	14.4
RDFI-10-01-2022	33,3
RDFI-07-01-2022	13.1
RDFI-07-02-2022	15.1
RDFI-07-03-2022	17.1
RDFI-07-04-2022	14.4
RDFI-07-05-2022	12.8
RDFI-05-01-2022	3.3

% Ash, Refuse Derived Fuel (Municipal)

Label	Value
RDFM-11-01-2022	3.9
RDFM-11-01-2022	8.8
RDFM-07-01-2022	11.3
RDFM-07-02-2022	11.4
RDFM-07-03-2022	14.4
RDFM-07-04-2022	7.1
RDFM-07-05-2022	10.4
RDFM-07-06-2022	7.1

% Ash, Wood Waste

Label	Value
WW-03-01-2022	16.6
WW-03-02-2022	2.8
WW-07-01-2022	14.4
WW-05-01-2022	2.6
WW-05-02-2022	3.2
WW-10-01-2022	7.9

Figure 4. Individual data concerning the ash content

It can be seen by using graphs that the ash-content variability within one single type of waste is by no means depreciable; this question is analysed in detail later. 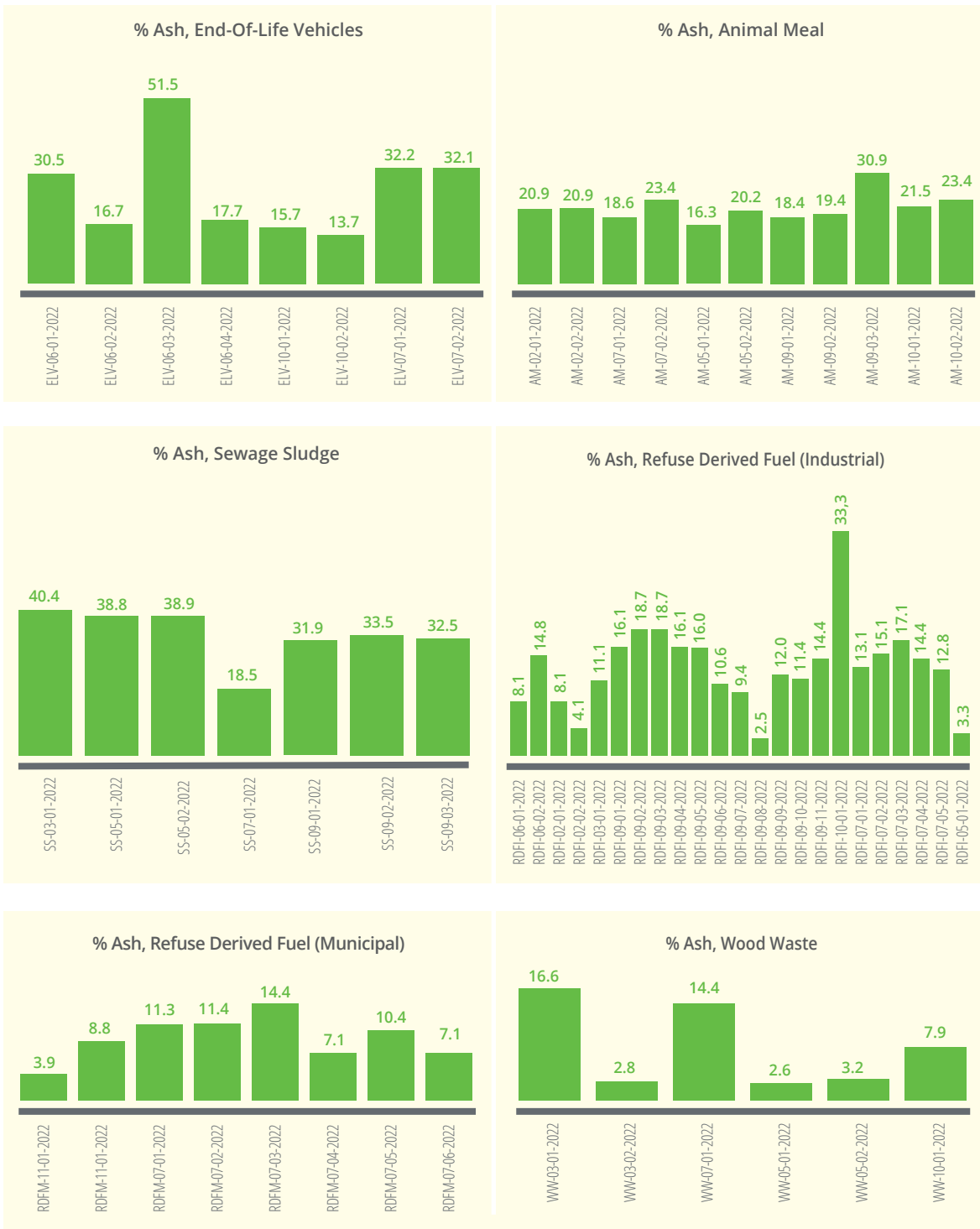Furthermore, the ranges of composition between the percentages of ash found are compatibles with the figures analysed in the scientific literature (6.1% - 33.8%).

The Recycling Index is directly correlated with the ash content, so the ash content is an indicator of what the RI will be in relative terms, for each type of waste considered. The correlation can clearly be seen in the following diagram:
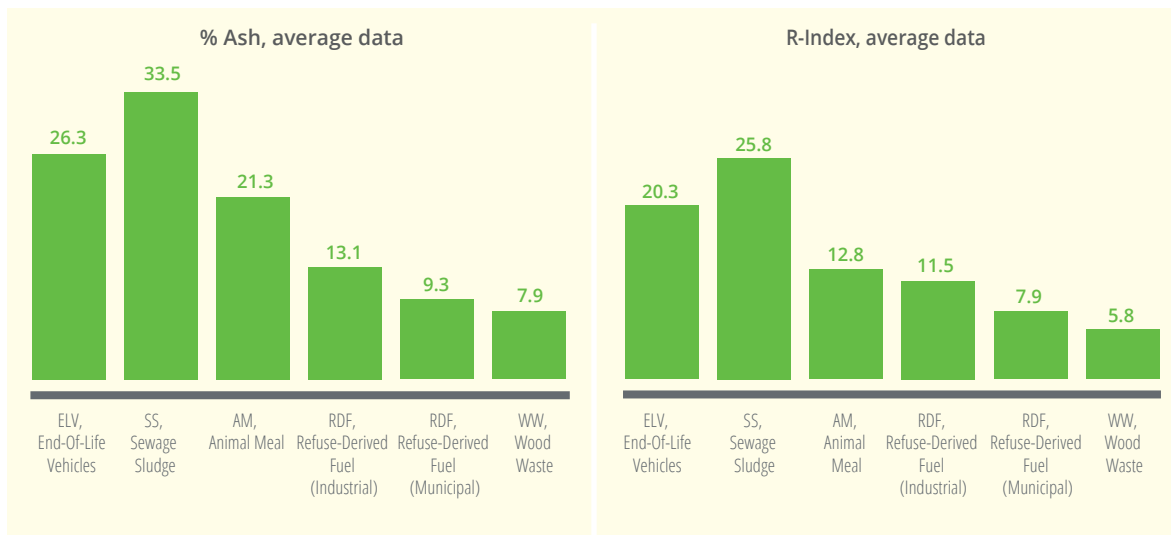
Figure 5. Correlation between ash content and RI

The ash content in the dry sample has been included in the results tables under the term Ash, for each refuse type and for each sample.

The values of the oxides contained in the ash and RI will be analysed separately in the following sections, for each one of the refuse groups.

Along general lines, an analysis of the data shows not only the variety of results that it has been possible to obtain, but also how this variety relates to the variability of the samples. The variability obtained can be caused by one or more of the following:

• Different ash content in the sample. This can generally by due to a greater fines content in the form of solid refuse in the sample.
• A potentially different classification of the refuse in its category or by apparent refuse mixtures.

- A clearly perceived visual differentiation in the samples, whether this owing to their grain size or the differences in in their composition and nature.

Such observable differences will be discussed and presented throughout the report. These samples showing a greater variability correspond to different suppliers, and, thus, to different sources and treatment methods at each one of the supplying plants. Every refuse type has acceptance criteria established at every plant, and these are accounted for basically by the fact that there are different suppliers and by being within the ranges of the defined acceptance criteria. That is to say, the variabilities found in the study are accepted as realities intrinsic to the refuse and its management system.

The analysis by refuse type is conducted below.

4.2. END-OF-LIFE VEHICLES

The oxide values measured by X-ray fluorescence[14] (XRF), ash content and Recycling Index (RI), are shown in the following table. In this table and the subsequent ones, the sample in blue is the one that has been repeated using the ICP technique. A comparison between these two techniques is made in Section 5.1.

Table 2. Values for the samples from End-Of-Life Vehicles

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	ASH (%)	RI
ELV-06-01-2022	Plant 5.1	1,76	20,10	3,61	0,25	2,33	0,46	2,18	11,57	0,94	30,51	**13,18**
ELV-06-02-2022	Plant 5.1	5,79	23,10	4,25	0,33	10,40	0,71	2,16	31,63	2,57	16,68	**13,50**
ELV-06-03-2022	Plant 5.1	6,88	14,20	19,35	0,82	3,19	3,47	0,96	35,91	1,22	51,49	**44,28**
ELV-06-04-2022	Plant 5.1	6,01	17,00	8,91	0,49	7,14	0,95	2,68	39,33	1,20	17,73	**14,84**
ELV-10-01-2022	Plant 9.1	4,24	21,20	6,72	0,30	2,58	0,27	4,68	35,78	1,48	15,65	**12,09**
ELV-10-02-2022	Plant 9.1	3,74	15,90	1,72	0,32	11,55	0,48	5,47	30,05	1,23	13,65	**9,62**
ELV-07-01-2022	Plant 6.1	8,78	17,75	15,82	1,43	3,29	1,60	1,70	31,60	1,28	32,17	**26,78**
ELV-07-02-2022	Plant 6.1	10,60	17,70	15,63	1,40	3,00	1,75	1,54	33,13	1,34	32,14	**27,67**

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14   The SO_3 determinations were taken by ICP, and this applies to all the types of waste.

Three different result patterns emerge in graph form. In dark orange, there is a sample with a greater Recycling Index than the rest. In dark green, there are samples apparently mixed with RDF. The samples in yellow have been identified as plastics shredder samples.

R-Index, End-Of-Life Vehicles

Sample	Value
ELV-06-01-2022	13.2
ELV-06-02-2022	13.5
ELV-06-03-2022	44.3
ELV-06-04-2022	14.8
ELV-10-01-2022	12.1
ELV-10-02-2022	9.6
ELV-07-01-2022	26.8
ELV-07-02-2022	27.7
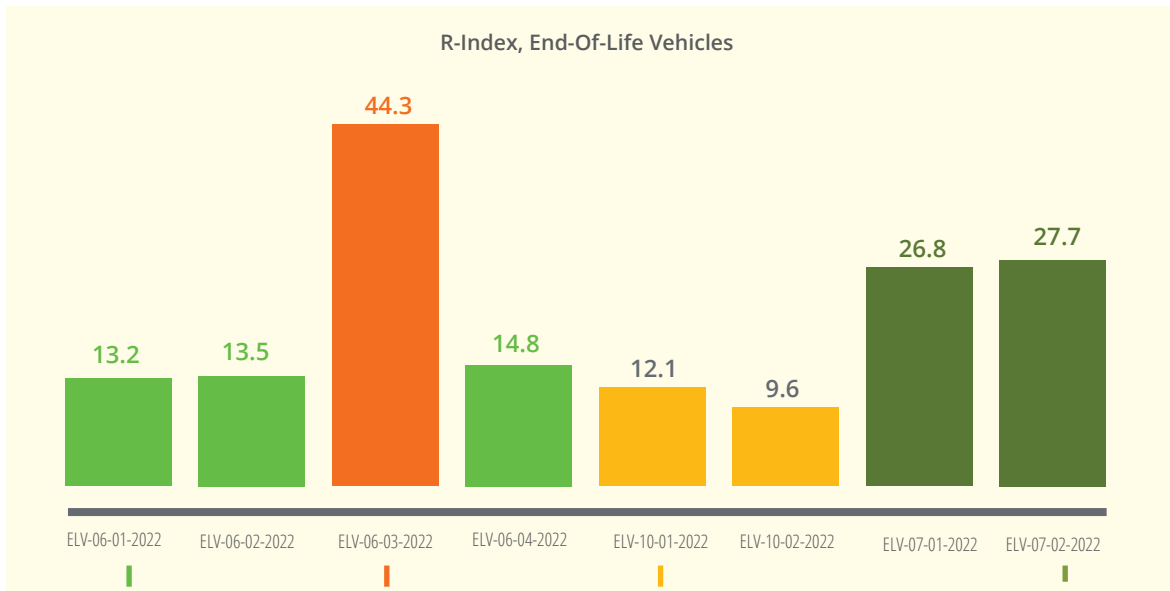
Figure 6. RI results for End-Of-Life Vehicles (ELV)

Figure 7. Images of the End-Of-Life Vehicles (ELV) samples

Sample ELV-06-03-2022 has a much greater ash content value than the rest of the sample components. From a visual perspective it is a sample that is significantly different from the rest. The sample is the second one in the photographs shown in Figure 7, and it appears to have a much higher fines content. The plastics shredder sample is the last one on the right in the above photographs.

Figure 8. Variability affecting individual results and typical variation affecting the determinations

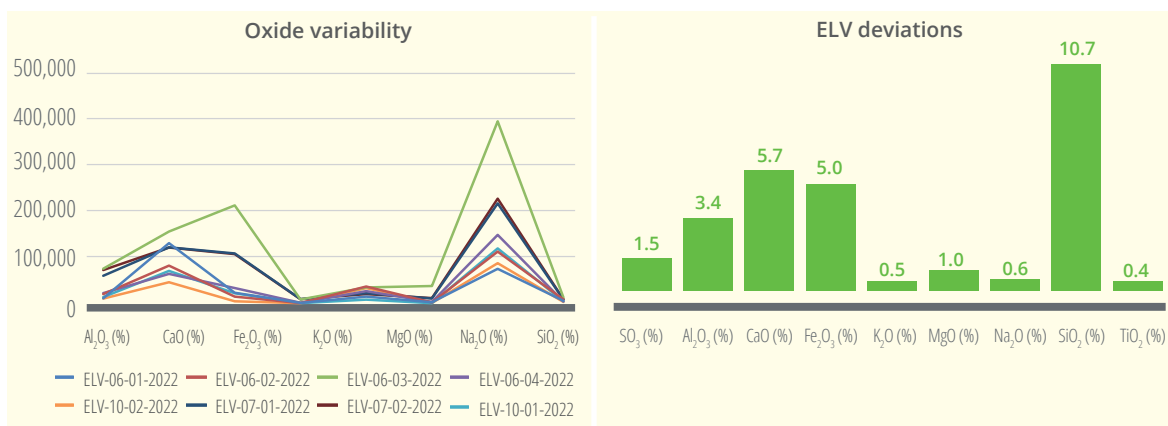The oxide analyses show that there is very little dispersion, except in the case of silicon oxide, whose deviation is greater than for the rest of the oxides. The dispersion analyses will all be examined together later.

Taking all the data as a whole, it was decided to repeat the value that could be regarded as atypical, and to do so using the ICP analysis technique. The results were repeated satisfactorily, RI values of 43.9 being obtained by XRF and 42.26 by ICP. The values found for the oxides were likewise very similar, see the first graph in Section 5.1.

4.3. SEWAGE SLUDGE

The oxide values measured by means of X-ray fluorescence (XRF), ash content and Recycling Index (RI), are shown in the following table.

Table 3. Values for the samples of Sewage Sludge (SS)

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	Ash	RI
SS-03-01-2022	Plant 2.1	12.20	22.70	11.68	1.82	3.63	0.97	3.60	24.95	0.88	40.38	**33.28**
SS-05-01-2022	Plant 4.1	11.51	22.10	10.98	1.86	3.84	1.09	4.98	21.84	0.95	38.79	**30.70**
SS-05-02-2022	Plant 4.1	11.74	22.70	10.85	1.92	3.87	1.11	4.14	22.44	0.98	38.87	**31.00**
SS-07-01-2022	Plant 6.1	9.99	22.00	9.59	2.67	4.97	1.80	3.11	15.16	0.88	18.49	**12.97**
SS-09-01-2022	Plant 8.4	9.81	23.30	13.04	1.78	3.95	1.06	1.14	21.14	1.03	31.92	**24.34**
SS-09-02-2022	Plant 8.4	10.06	21.60	10.52	1.90	3.51	1.11	5.37	22.06	0.95	33.51	**25.83**
SS-09-03-2022	Plant 8.4	13.93	11.95	18.91	1.53	2.62	0.61	3.42	15.14	0.69	32.54	**22.38**

The ash content, and thus the recycling indexes, are uniform, except in the case of the sample encoded as SS-07-01-2022. By checking the appearance of this sample, the fact that it is fibrous, in the form of small worms of sludge, means that it is rather different from the powdery appearance of the rest of the samples. This sample is the third one in the photographs shown in the following image.

Figure 9. Fibrous samples can be seen on the left and powdery samples can be seen on the right
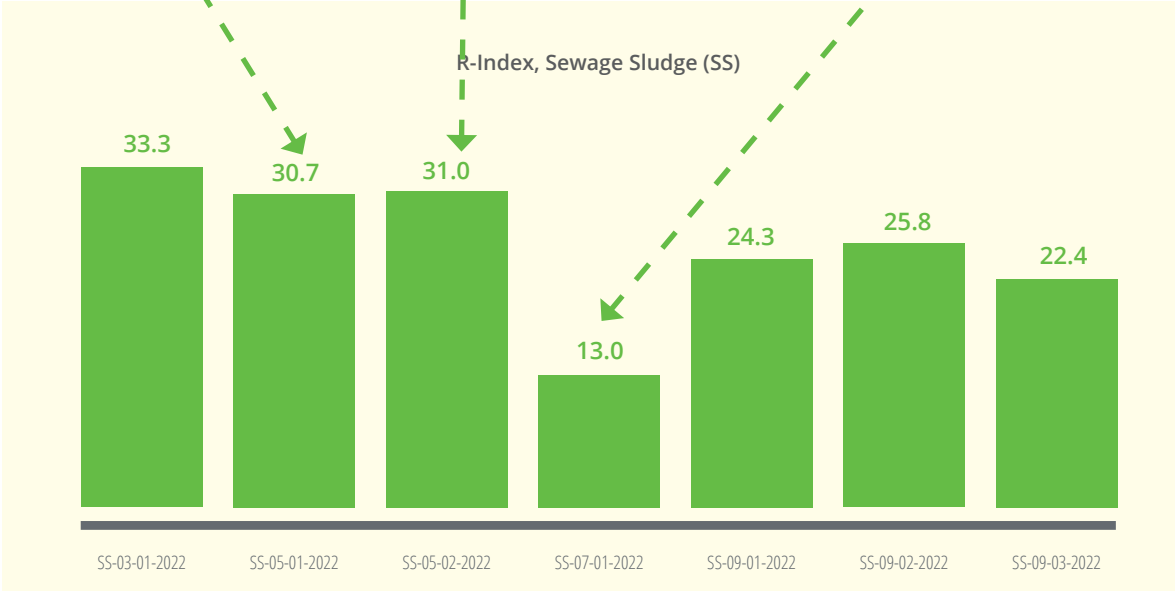

Figure 10. RI for Sewage Sludge (SS)

In graph form, it can be seen that the values obtained are fairly uniform for all the samples, the highest recycling indexes being for the group in the range of 30 to 35%.

4.4. ANIMAL MEAL

The oxide values measured using X-ray fluorescence (XRF), ash content and Recycling Index (Rl), are shown in the following table.

Table 4. Values for the Animal Meal (AM) samples

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	Ash (%)	RI
AM-02-01-2022	Plant 1.1	0.88	40.90	0.63	5.00	1.49	4.63	1.15	6.76	0.08	20.89	**12.85**
AM-02-02-2022	Plant 1.1	0.32	47.00	1.02	3.67	1.31	3.10	0.73	3.54	0.03	20.94	**12.72**
AM-07-01-2022	Plant 6.2	0.42	40.50	3.76	5.19	1.51	4.31	0.68	3.99	0.02	18.55	**11.20**
AM-07-02-2022	Plant 6.3	0.41	45.50	0.75	3.32	1.22	4.02	0.72	3.79	0.06	23.39	**13.98**
AM-05-01-2022	Plant 4.2	0.67	40.50	0.90	6.27	1.68	4.96	0.62	5.60	0.03	16.30	**9.98**
AM-05-02-2022	Plant 4.2	0.72	41.10	1.87	4.36	1.56	4.51	1.21	5.66	0.04	20.23	**12.35**
AM-09-01-2022	Plant 8.1	0.71	40.10	0.55	5.37	1.58	4.52	0.77	5.89	0.40	18.43	**11.04**
AM-09-02-2022	Plant 8.1	1.13	42.70	1.06	3.84	1.40	4.02	0.75	7.25	0.12	19.43	**12.10**
AM-09-03-2022	Plant 8.1	0.04	49.60	0.23	1.60	1.30	2.84	0.43	0.97	0.01	30.90	**17.62**
AM-10-01-2022	Plant 9.2	0.85	40.30	0.72	4.80	1.44	4.28	0.97	6.32	0.06	21.51	**12.85**
AM-10-02-2022	Plant 9.1	0.99	41.40	0.84	3.63	1.10	3.51	0.58	6.72	0.11	23.41	**13.78**

Very uniform values are found for the RI with the exception of Sample 9, where the ash percentage is slightly higher (30.9% compared to an average of 21.27%).
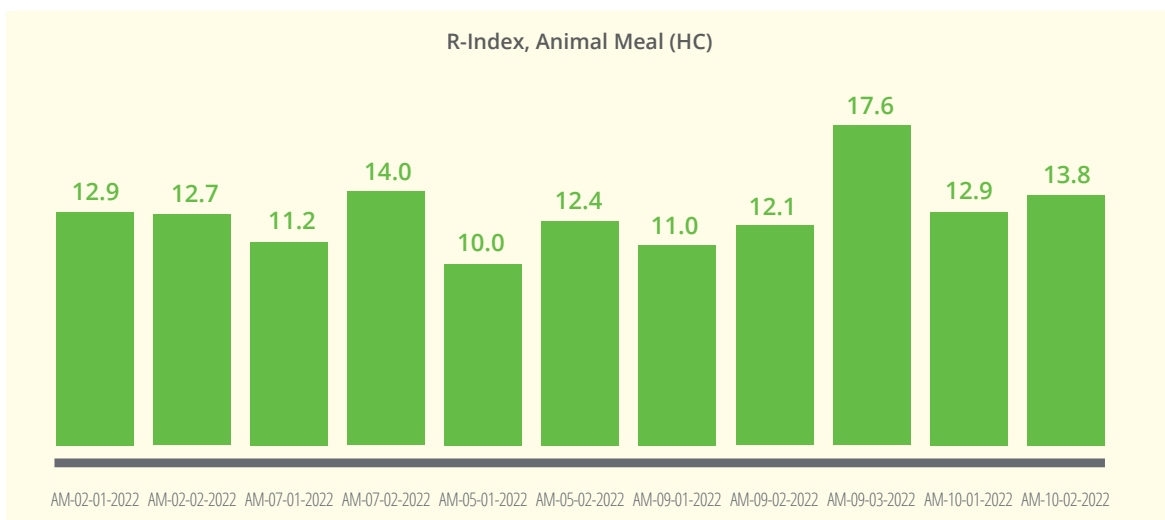

Figure 11. RI values for Animal Meal (AM)

An analysis of the main statistical data for the oxides yields bounded variation and deviation ranges except in the case of calcium oxide.

Table 5. Statistics for the analysis of oxides in Animal Meal (AM)

	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	ASH (%)
MAX	1.13	49.60	3.76	6.27	1.68	4.96	1.21	7.25	0.40	30.90
MIN	0.04	40.10	0.23	1.60	1.10	2.84	0.43	0.97	0.01	16.30
AVG.	0.65	42.69	1.12	4.28	1.42	4.06	0.78	5.14	0.09	21.27
DEV.	0.32	3.22	0.97	1.26	0.17	0.66	0.24	1.87	0.11	3.83
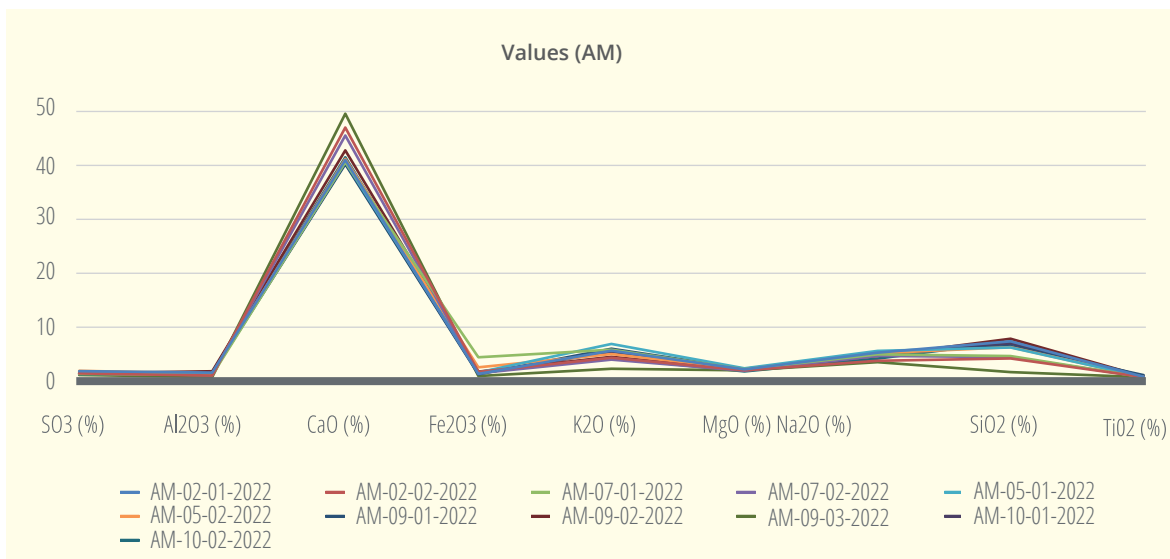
It can be seen in the graph that the individual sample results for all the oxides are the same. The CaO contents are the greatest in relative terms for this type of waste.

4.5. REFUSE-DERIVED FUEL (INDUSTRIAL)

The oxide values measured using X-ray fluorescence (XRF), ash content and Recycling Index (RI), can be seen in the following table.

Table 6. Values for the Refuse-Derived Fuel (Industrial) samples

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	Ash (%)	Rindex
RDFI-06-01-2022	Plant 5.1	69,59[15]	16,85	2,72	1,35	1,35	7,94	1,01	29,54	4,23	7,98	**10,72**
RDFI-06-02-2022	Plant 5.1	9,00	21,10	7,36	1,98	2,04	1,74	0,98	40,08	1,48	14,80	**12,64**
RDFI-02-01-2022	Plant 1.1	10,07	24,20	13,95	2,00	3,07	2,53	1,74	23,03	3,22	8,06	**6,72**
RDFI-02-02-2022	Plant 1.1	13,19	24,10	7,32	2,79	3,16	3,20	1,32	24,09	3,91	4,09	**3,38**
RDFI-03-01-2022	Plant 2.1	10,36	30,70	2,26	1,24	2,18	3,49	2,44	21,47	2,28	11,09	**8,26**
RDFI-09-01-2022	Plant 8.2	12,75	21,70	2,32	1,32	2,89	6,08	1,19	38,19	1,78	16,10	**14,14**
RDFI-09-02-2022	Plant 8.2	5,68	19,05	6,20	1,26	4,13	2,74	2,82	25,27	13,20	18,73	**14,74**
RDFI-09-03-2022	Plant 8.2	24,82	14,60	15,98	0,89	2,12	3,66	0,93	29,18	3,06	18,69	**17,84**
RDFI-09-04-2022	Plant 8.3	30,90	26,00	3,36	0,88	2,03	2,45	4,11	20,14	3,78	16,13	**14,54**
RDFI-09-05-2022	Plant 8.3	27,16	26,20	8,21	0,92	1,90	2,71	3,66	21,34	3,70	16,01	**14,85**
RDFI-09-06-2022	Plant 8.1	43,75	23,00	6,67	1,18	2,14	2,73	1,98	14,35	4,01	10,62	**10,50**
RDFI-09-07-2022	Plant 8.1	16,27	34,10	2,43	0,87	1,70	1,89	2,41	29,48	3,39	9,41	**8,58**
RDFI-09-08-2022	Plant 8.1	14,17	17,10	2,73	1,72	2,37	3,16	2,91	23,55	22,90	2,50	**2,22**
RDFI-09-09-2022	Plant 8.1	16,77	24,00	2,04	1,77	1,95	2,67	1,05	31,73	4,43	11,94	**10,28**
RDFI-09-10-2022	Plant 8.1	15,50	23,10	4,34	3,69	1,74	2,40	1,66	28,34	3,40	11,41	**9,93**
RDFI-09-11-2022	Plant 8.1	7,24	36,70	2,70	0,91	2,26	2,00	2,65	23,62	2,63	14,35	**11,31**
RDFI-10-01-2022	Plant 9.2	9,14	13,50	20,08	0,81	2,07	4,55	0,79	34,16	1,62	33,26	**28,83**
RDFI-07-01-2022	Plant 6.3	5,86	33,60	1,20	1,35	1,89	5,70	1,15	16,50	7,96	13,14	**9,85**
RDFI-07-02-2022	Plant 6.2	13,50	27,20	3,55	1,85	2,61	5,13	1,38	32,57	2,71	15,05	**13,60**
RDFI-07-03-2022	Plant 6.2	12,13	27,30	3,91	1,50	2,10	4,52	1,64	26,41	2,87	17,08	**13,98**
RDFI-07-04-2022	Plant 6.3	7,76	33,00	1,85	1,45	1,62	5,34	2,05	15,10	7,53	14,41	**10,82**
RDFI-07-05-2022	Plant 6.3	25,04	30,70	5,37	0,78	1,72	2,64	1,89	9,85	9,76	12,77	**11,07**
RDFI-05-01-2022	Plant 4.2	6,74	28,00	0,98	9,31	2,65	10,00	1,97	7,30	0,71	3,31	**2,46**

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15   This value of 69% for Al2O3 is completely out of keeping with the calibration line adjusted for oxide values of 15 to 16% at the most. Moreover, this sample's loss due to calcination was negative by 14.41%; this means that instead of losing mass, the sample gained mass owing to oxidation during the pearling process, which would require the tablet preparation process to be carried out in an inert atmosphere.
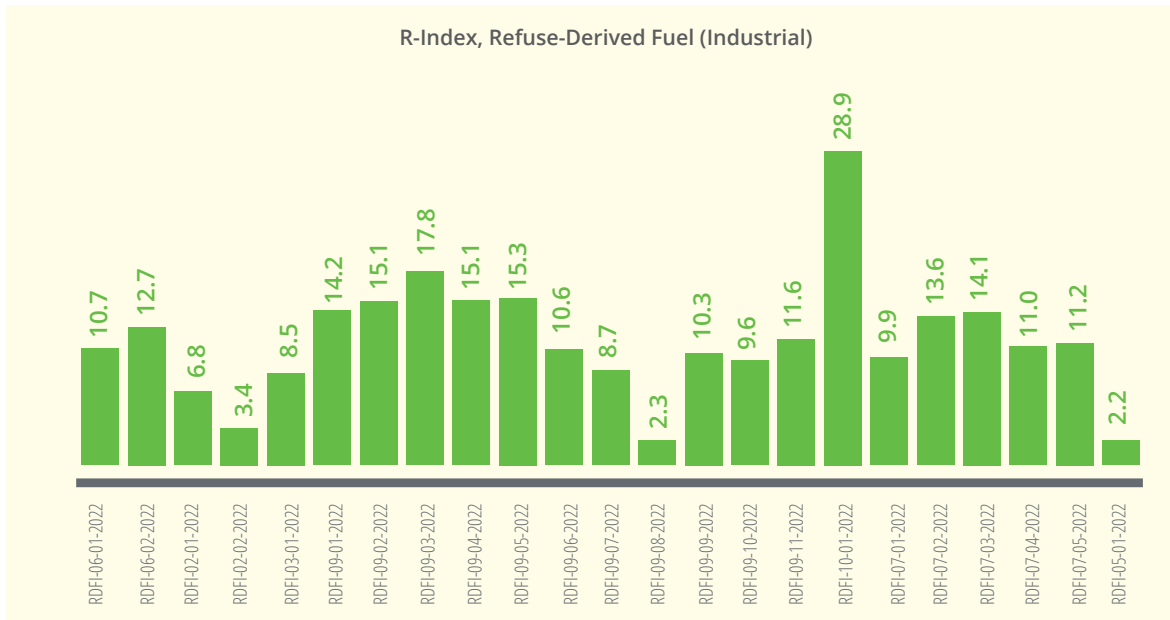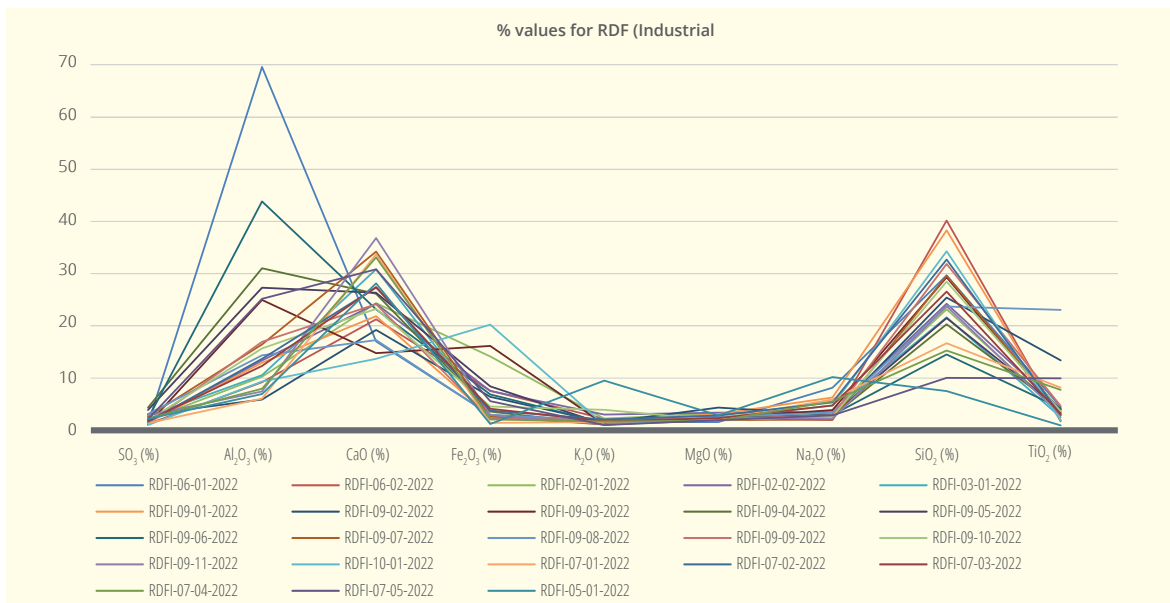
Figure 12. RI for the Refuse-Derived Fuel samples of industrial origin (RDFI)

The variability of the results is acceptable in view of the intrinsically heterogeneous nature of the waste. In the case of Sample 10, the percentage of ash is appreciably higher (33.26% when compared to an average of 13.8%).

A high variability was observed in the determination of Al2O3 for this group of samples. However, the repetition of Sample RDFI-09-11-2022, whose analysis using XRF yielded a result of 7.24% of Al203, gave a result of 7.22% when using ICP. That is to say, when determining this oxide, the percentual variation between the two techniques is less than 1%, so we must attribute that variability to the nature of the samples themselves.

The appearance of the two samples is shown below. The sample with a high Al2O3 content can be seen on the right, and ash, on the left. In the latter case, the amount of fine-particle material is common among other types of waste with a higher ash content.

Figure 13. Refuse-Derived Fuel samples of industrial origin (RDFI)

Appearance of the set of RDF (Industrial) samples. Nevertheless, despite their heterogeneity nature, the samples do share a common composition pattern, which is broken on occasions by their grain size, or, in the case of the photograph in the bottom right-hand corner, with an apparent mixture of biomass.

Figure 14. Other Refuse-Derived Fuel samples of industrial origin (RDFI)

4.6. REFUSE-DERIVED FUEL (MUNICIPAL)

The oxide values measured using X-ray fluorescence (XRF), ash content and Recycling Index (RI), can be seen in the following table.

Table 7. Values for the Refuse Derived Fuel of Municipal origin samples

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	Ash (%)	Rindex
RDFM-11-01-2022	Plant 10.1	19,11	32,20	2,14	0,90	2,80	1,50	2,16	18,88	16,85	3,89	**3,75**
RDFM-11-02-2022	Plant 10.1	37,05	21,10	1,85	0,56	4,11	1,42	3,05	19,98	7,70	8,80	**8,52**
RDFM-07-01-2022	Plant 6.2	11,69	32,80	4,25	2,22	2,69	4,39	4,25	15,42	3,29	11,25	**9,12**
RDFM-07-02-2022	Plant 6.1	10,40	31,30	2,11	2,15	2,83	3,05	3,89	15,70	4,56	11,36	**8,63**
RDFM-07-03-2022	Plant 6.1	9,47	23,20	7,58	1,43	2,88	3,06	1,97	31,64	1,92	14,37	**11,95**
RDFM-07-04-2022	Plant 6.1	10,30	29,30	2,19	2,66	3,32	7,39	3,91	17,94	7,26	7,05	**5,94**
RDFM-07-05-2022	Plant 6.1	9,17	36,00	6,00	2,54	3,36	3,82	2,98	18,74	4,86	10,44	**9,13**
RDFM-07-06-2022	Plant 6.1	9,47	26,80	2,86	2,50	4,64	6,94	3,45	18,15	8,91	7,06	**5,91**

A high variability was found for Samples RDFM-11-02-2022 and RDFM-07-03-2022, when it came to determining aluminium oxide and silicon oxide.

The analysis was repeated with ICP for the first of these, a value of 37.05% being yielded by XRF and a value of 35.40% being yielded by ICP. With respect to silicon oxide, the value by XRF was 19.98%, and by ICP it was 19.35%; these percentages are considered to be within the expected margins.
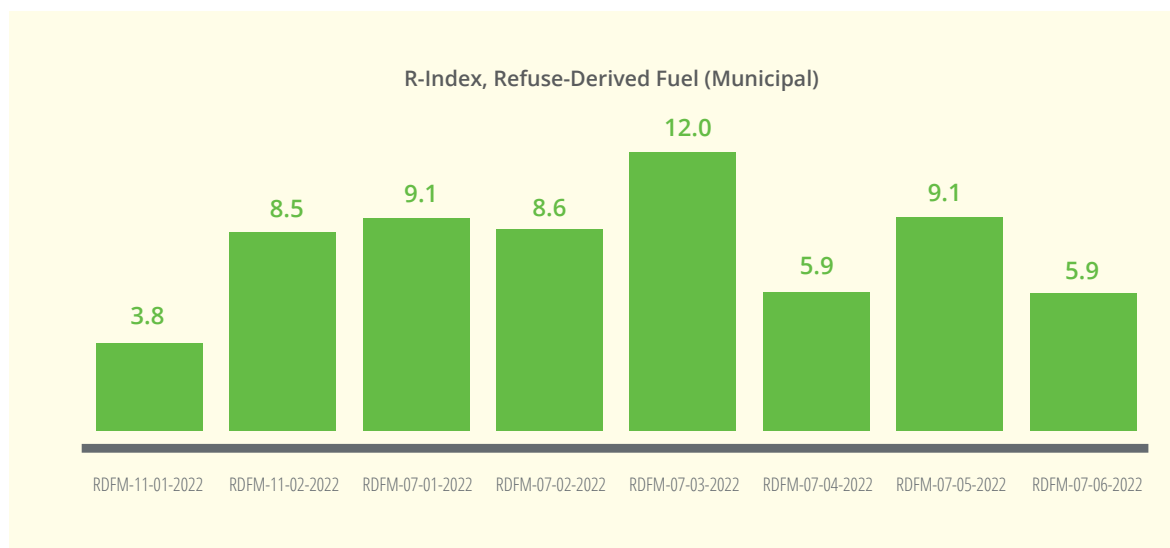

Figure 15. RI values for Refuse-Derived Fuels of Municipal origin (RDFM)

It is useful to see what the RDF (Municipal) samples look like when compared to the RDF (Industrial) samples. Once again, despite the heterogeneous nature of the waste, the pattern is clearly recognisable, as can be seen in the following images.

Figure 16. Appearance of the Refuse-Derived Fuel of Municipal origin samples (RDFM)

4.7. WOOD WASTE

The oxide values measured by X-ray fluorescence (XRF), ash content and Recycling Index (RI), are shown in the following table.

Table 8. Values for the Wood Waste (WW) samples

		Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)	Ash (%)	Rindex
WW-03-01-2022	Plant 2.1	6,45	33,00	3,46	1,84	2,80	0,68	0,97	24,29	1,08	16,61	**12,39**
WW-03-02-2022	Plant 2.1	5,40	20,80	4,58	3,59	3,52	4,35	2,82	27,36	8,53	2,84	**2,30**
WW-07-01-2022	Plant 6.4	5,52	24,10	2,92	1,72	2,29	2,76	2,69	38,87	2,55	14,42	**12,03**
WW-05-01-2022	Plant 4.1	5,13	21,80	6,23	3,48	3,97	4,71	2,64	28,72	8,35	2,55	**2,17**
WW-05-02-2022	Plant 4.1	5,22	24,20	4,21	3,54	3,87	3,54	2,12	27,01	8,47	3,18	**2,61**
WW-10-01-2022	Plant 9.1	0,97	8,29	0,70	15,00	3,60	3,25	1,55	6,17	0,07	7,94	**3,14**

In graph form it is obvious that there are differences between the two subpopulations in the sample, which are distinguished by their different R-Indexes, the former being about 2% and the second being about 12%. These differences can also be seen clearly in Figure 18, where the sample shows the presence of earthy fines with a different colour.
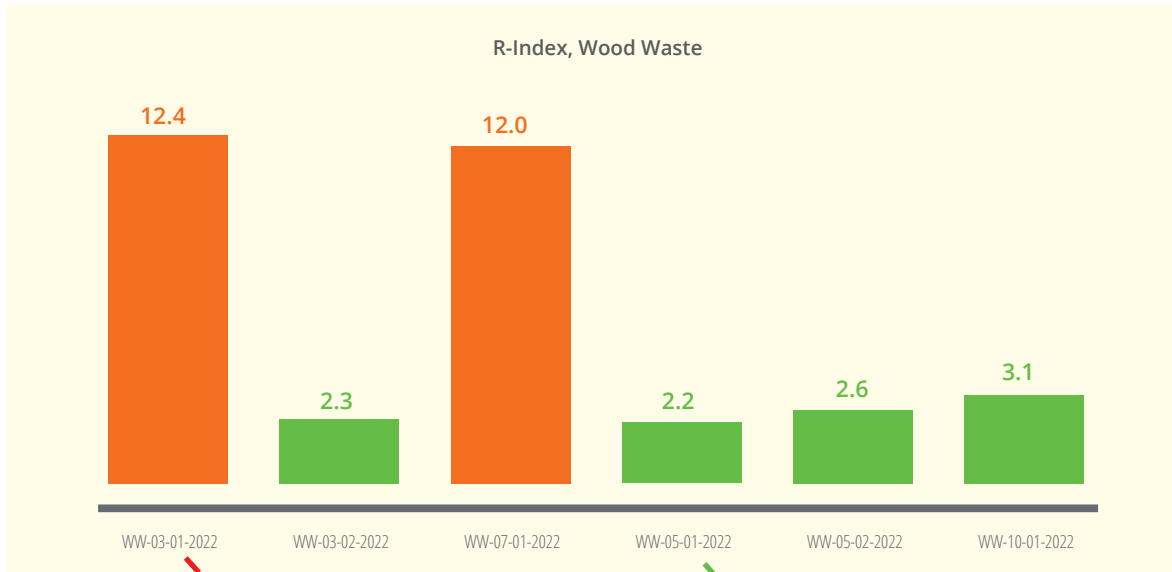
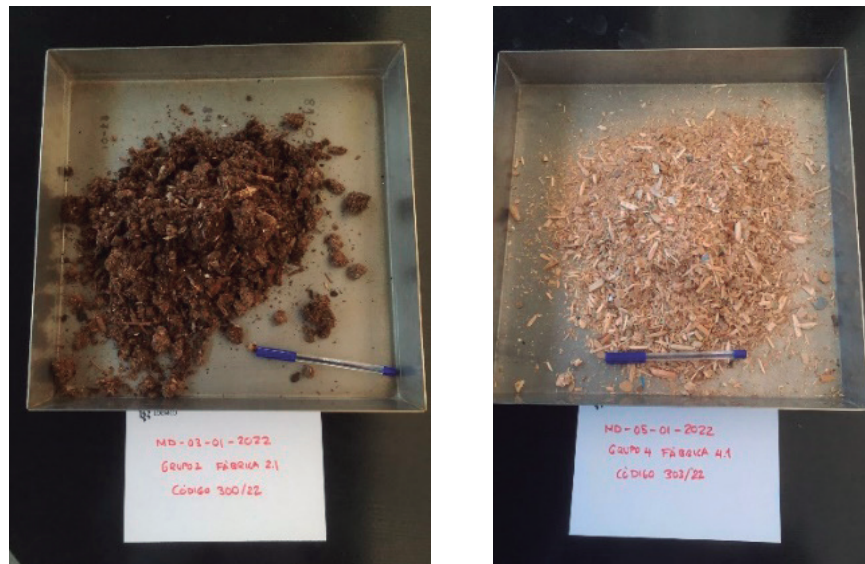**Figure 17. RI for the samples of Wood Waste (WW)**

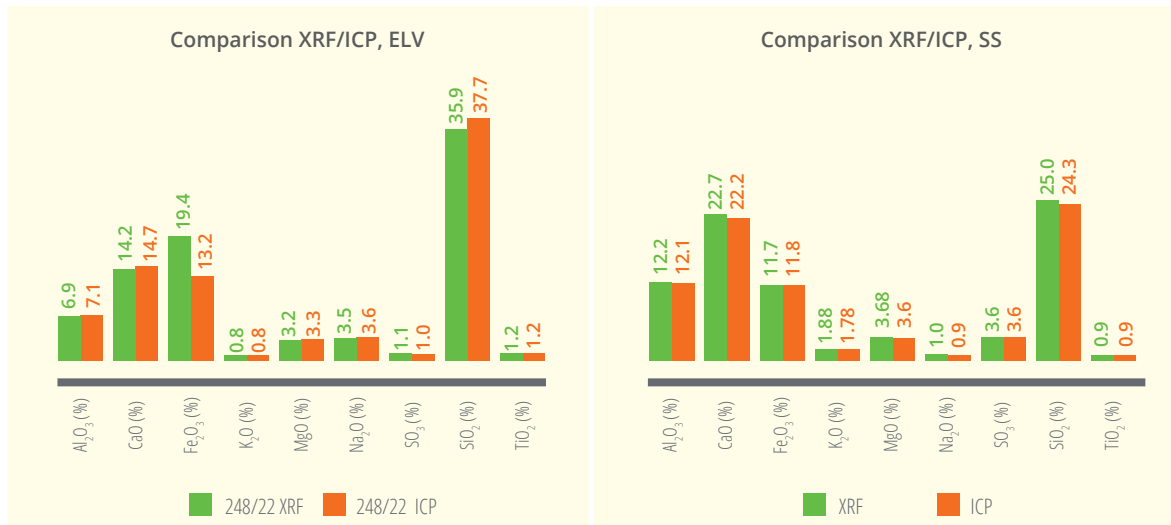**Figure 18. Appearance of the Wood Waste samples**

5 SENSITIVITY ANALYSIS

5.1. VARIABILITY OF THE ANALYSES

How the repetitions using ICP have confirmed the preliminary analyses by XRF has already been explained in the section concerned, where it is also indicated that the possible dispersion of values for a particular oxide can be accounted for by the actual variability of the samples.

The following image is inserted with a view to providing a complete account of the comparison between some XRF results, and some ICP results. It shows the analysis of individual oxides with the two techniques[16]. Note that the comparison has been made for the samples which have yielded the greatest data dispersions for a particular determination. No discrepancies were found in the determinations following the two methods.

Comparison XRF/ICP, ELV

	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)
248/22 XRF	6.9	14.2	19.4	0.8	3.2	3.5	1.1	35.9	1.2
248/22 ICP	7.1	14.7	13.2	0.8	3.3	3.6	1.0	37.7	1.2

Comparison XRF/ICP, SS

	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)
XRF	12.2	22.7	11.7	1.88	3.68	1.0	3.6	25.0	0.9
ICP	12.1	22.2	11.8	1.78	3.6	0.9	3.6	24.3	0.9

16   When determining the SO_3, the comparison is between ICP and the determination method included in EN 196-2. This determination is used very frequently in cement determination, so the latter method is considered to be the benchmark.
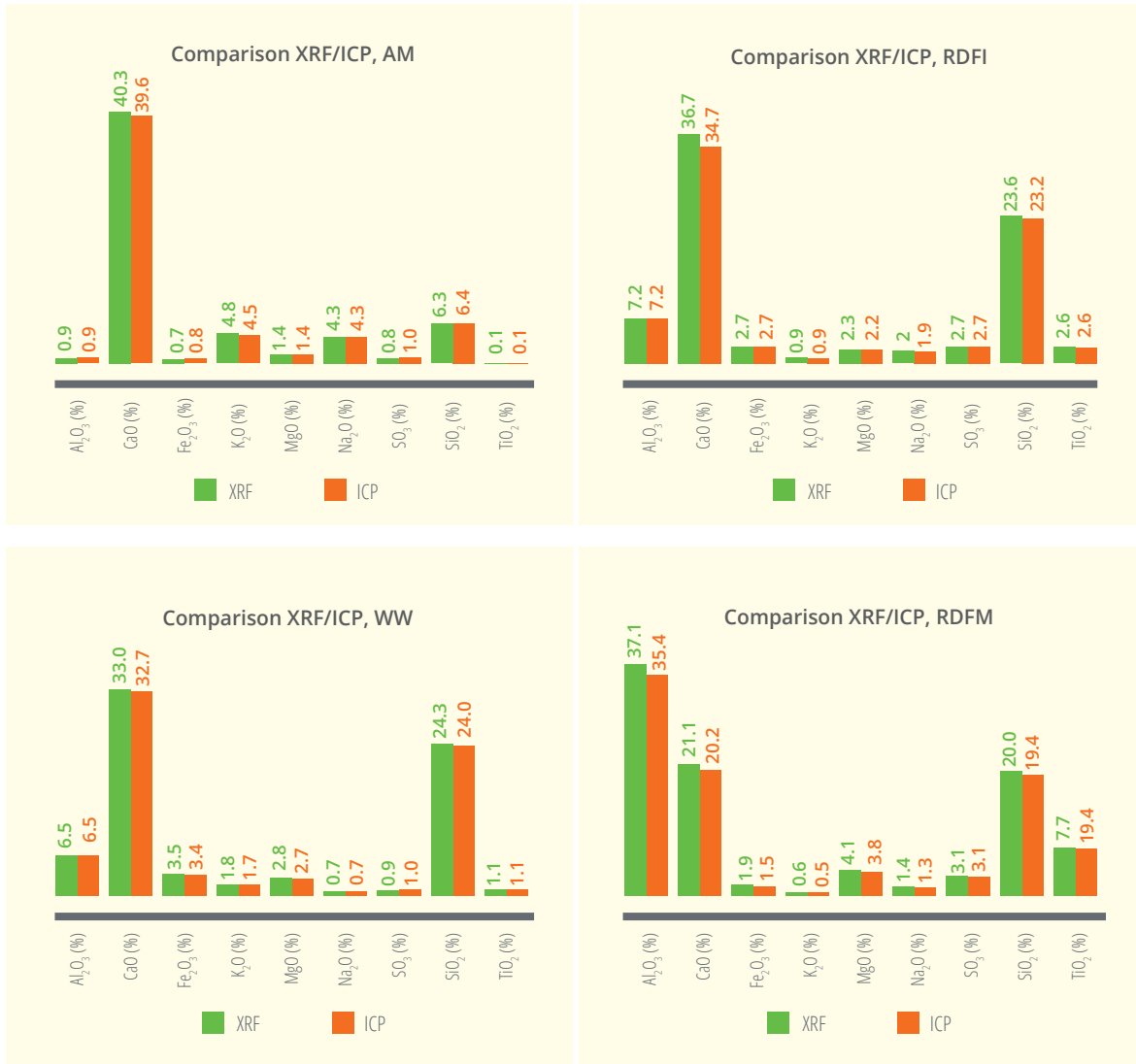
Figure 19. Analysis of oxides using two techniques

Firstly, different compositions of oxides can be detected depending on the type of waste. Calcium, Aluminium and Silicon are the most abundant oxides. Secondly, it can be observed that the test results for all the oxides are very close, those yielded by ICP being a few tenths below those yielded by XRF.

The results of the comparison are shown in numerical form in the following table.

Table 9. XRF and ICP data

	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)
248/22 XRF	6,88	14,20	19,35	0,82	3,19	3,47	1,10	35,91	1,22
248/22 ICP	7,14	14,70	13,20	0,83	3,33	3,63	0,96	37,70	1,24
254/22 XRF	12,20	22,70	11,68	1,82	3,63	0,97	3,59	24,95	0,88
254/22 ICP	12,10	22,20	11,75	1,74	3,56	0,89	3,60	24,30	0,88
267/22 XRF	0,85	40,30	0,72	4,80	1,44	4,28	0,80	6,32	0,06
267/22 ICP	0,90	39,60	0,76	4,50	1,41	4,23	0,97	6,39	0,06
284/22 XRF	7,24	36,70	2,70	0,91	2,26	2,00	2,71	23,62	2,63
284/22 ICP	7,22	34,70	2,71	0,85	2,22	1,94	2,65	23,20	2,55
293/22 XRF	37,05	21,10	1,85	0,56	4,11	1,42	3,11	19,98	7,70
293/22 ICP	35,40	20,20	1,54	0,51	3,83	1,28	3,05	19,35	7,60
300/22 XRF	6,45	33,00	3,46	1,84	2,80	0,68	0,86	24,29	1,08
300/22 ICP	6,52	32,70	3,36	1,72	2,74	0,68	0,97	24,00	1,08

The results are now shown in graph form for the RI determinations utilising the two techniques for the selected samples[17].
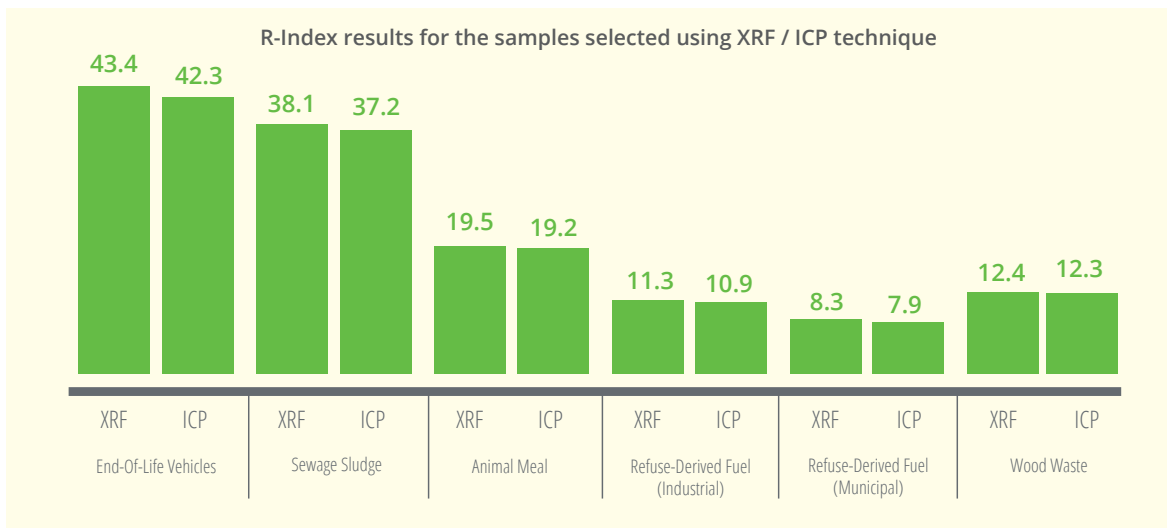

Figure 20. Results for RI using the two XRF and ICP techniques, respectively for the same samples

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17   It must be remembered that these samples ARE NOT representative of their population.

5.2. DETERMINATIONS WITH 4 OXIDES

Finally, it was found out how the results yielded by using 9 oxides vary when compared to the results yielded with 4 oxides. Along general lines, the determinations with 9 oxides give higher RI results. The comparison was made for Sewage Sludge, ELV and RDF (Industrial), as can be seen in the following graphs:
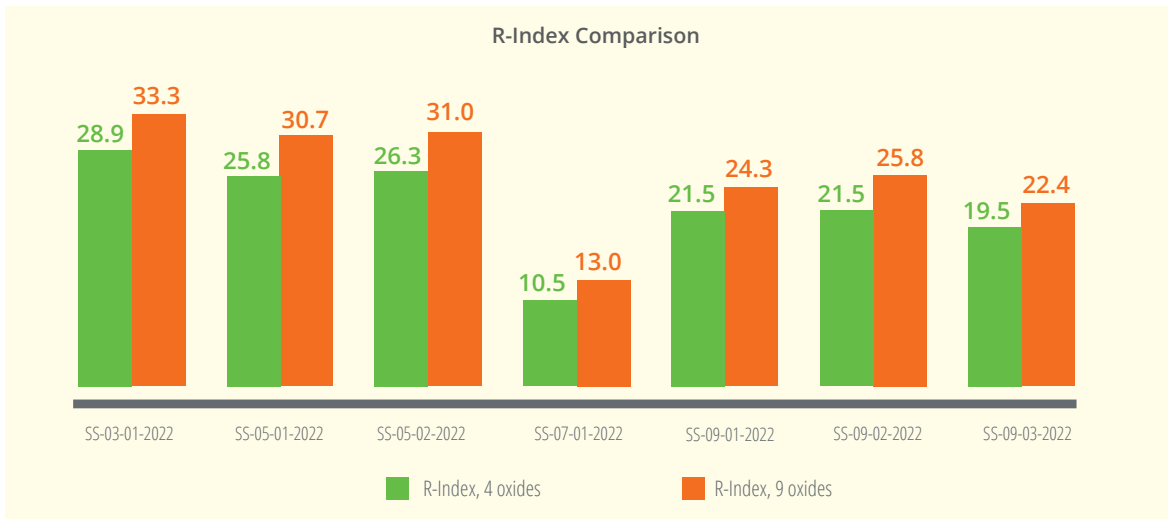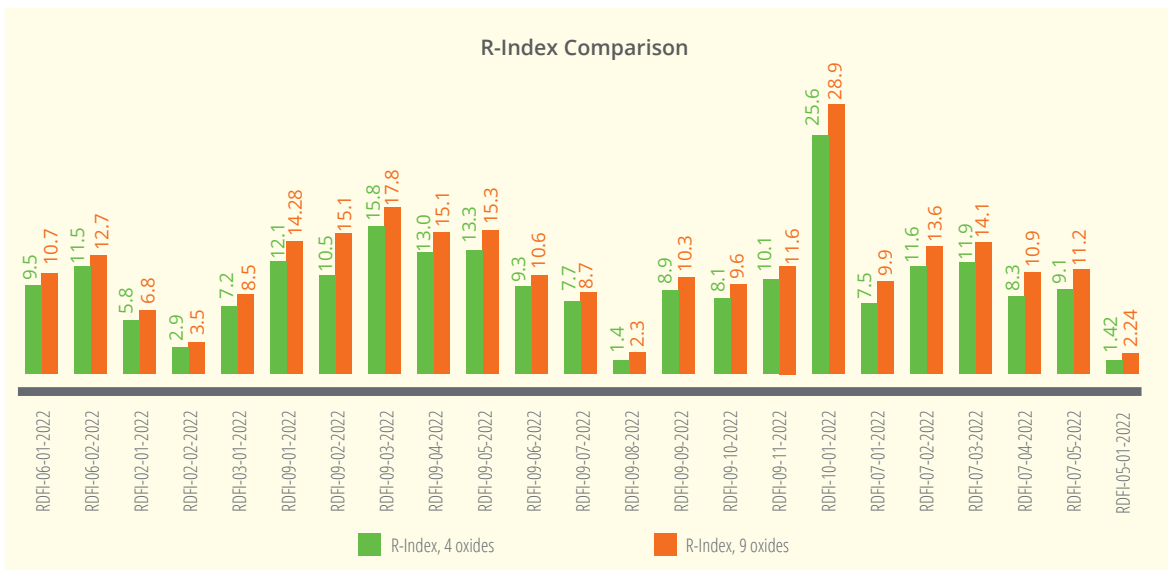

Figure 21. Comparison for Sewage Sludge

Figure 22. Comparison for RDFI

The results of the comparison are shown in numerical form in the following table.

Table 10. Data with 4 oxides and 9 oxides

	RI, 4 OX	RI, 9 OX		RI, 4 OX	RI, 9 OX
SS-03-01-2022	28,89	33,29	RDFI-06-01-2022	9,48	10,74
SS-05-01-2022	25,77	30,70	RDFI-06-02-2022	11,48	12,69
SS-05-02-2022	26,33	31,00	RDFI-02-01-2022	5,74	6,76
SS-07-01-2022	10,49	12,98	RDFI-02-02-2022	2,81	3,40
SS-09-01-2022	21,48	24,34	RDFI-03-01-2022	7,18	8,47
SS-09-02-2022	21,53	25,83	RDFI-09-01-2022	12,07	14,21
SS-09-03-2022	19,50	22,38	RDFI-09-02-2022	10,53	15,05
ELV-06-01-2022	11,30	13,18	RDFI-09-03-2022	15,80	17,80
ELV-06-02-2022	10,81	13,50	RDFI-09-04-2022	12,97	15,11
ELV-06-03-2022	39,31	44,28	RDFI-09-05-2022	13,27	15,34
ELV-06-04-2022	12,63	14,84	RDFI-09-06-2022	9,32	10,60
ELV-10-01-2022	10,63	12,09	RDFI-09-07-2022	7,74	8,71
ELV-10-02-2022	7,02	9,62	RDFI-09-08-2022	1,44	2,26
ELV-07-01-2022	23,79	26,78	RDFI-09-09-2022	8,90	10,31
ELV-07-02-2022	24,77	27,67	RDFI-09-10-2022	8,13	9,60
			RDFI-09-11-2022	10,08	11,58
			RDFI-10-01-2022	25,57	28,84
			RDFI-07-01-2022	7,51	9,88
			RDFI-07-02-2022	11,56	13,62
			RDFI-07-03-2022	11,91	14,07
			RDFI-07-04-2022	8,32	10,91
			RDFI-07-05-2022	9,06	11,21
			RDFI-05-01-2022	1,42	2,24

The average R-Index data per type of waste are shown in Figure 23. There are significant differences.

R-Index, average data per type of waste with determination based on 4 Oxides and 9 Oxides

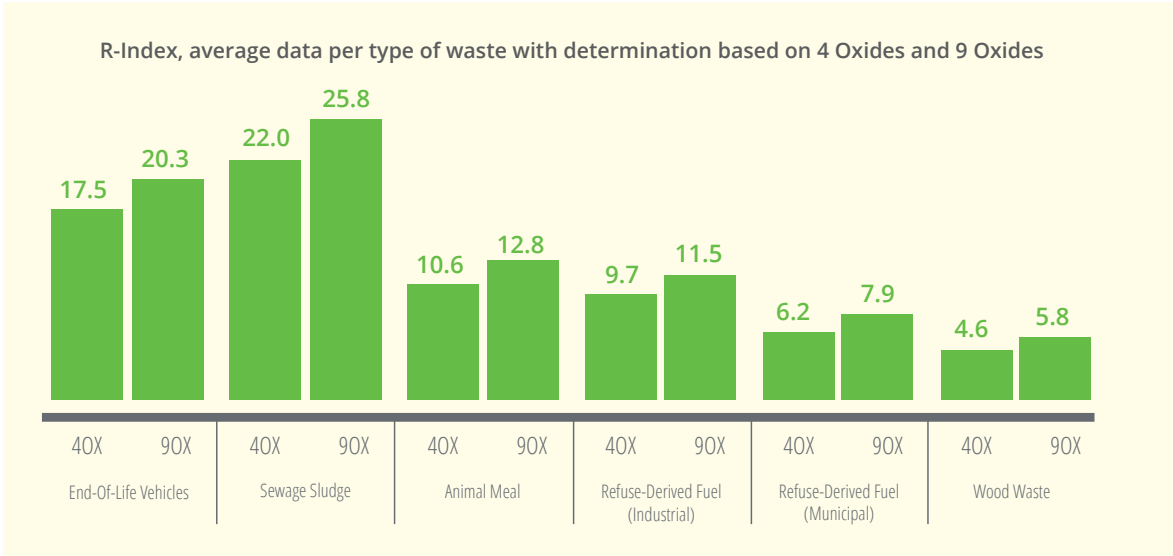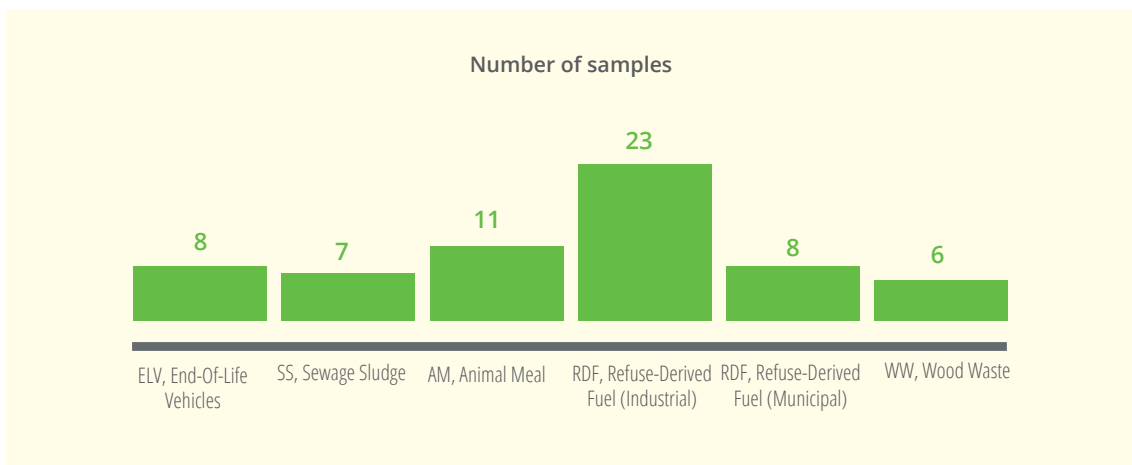|	4OX	9OX
End-Of-Life Vehicles	17.5	20.3
Sewage Sludge	22.0	25.8
Animal Meal	10.6	12.8
Refuse-Derived Fuel (Industrial)	9.7	11.5
Refuse-Derived Fuel (Municipal)	6.2	7.9
Wood Waste	4.6	5.8

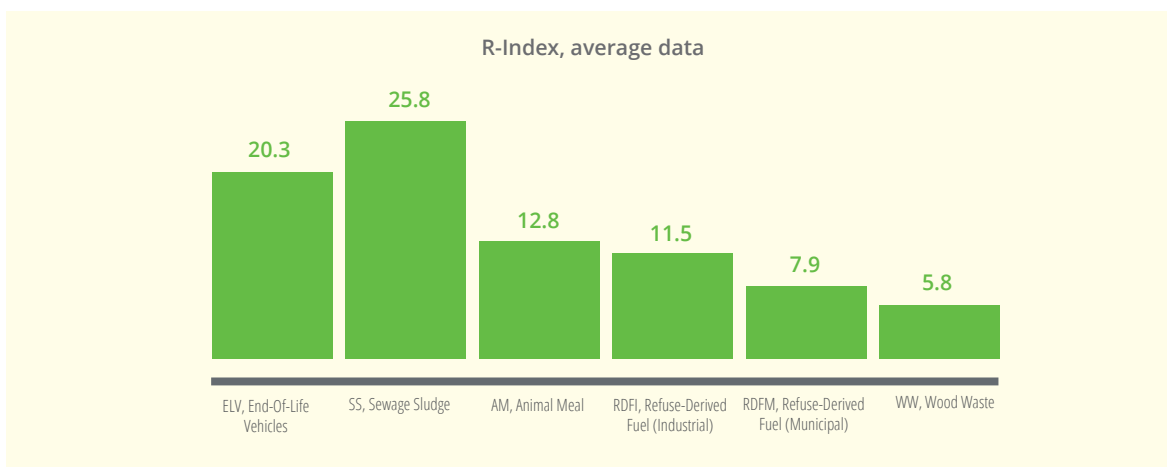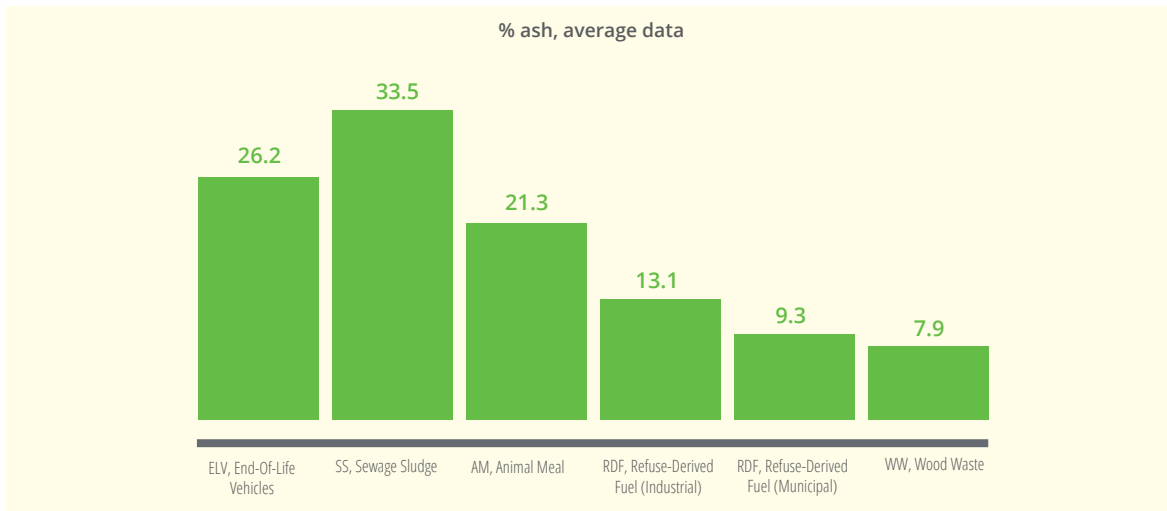**Figure 23. R-Index with 9 OX/4 OX**

6 SUMMARY OF THE RESULTS

- 63 waste samples coming from 8 cement groups were analysed; They were taken from the following types:

Number of samples

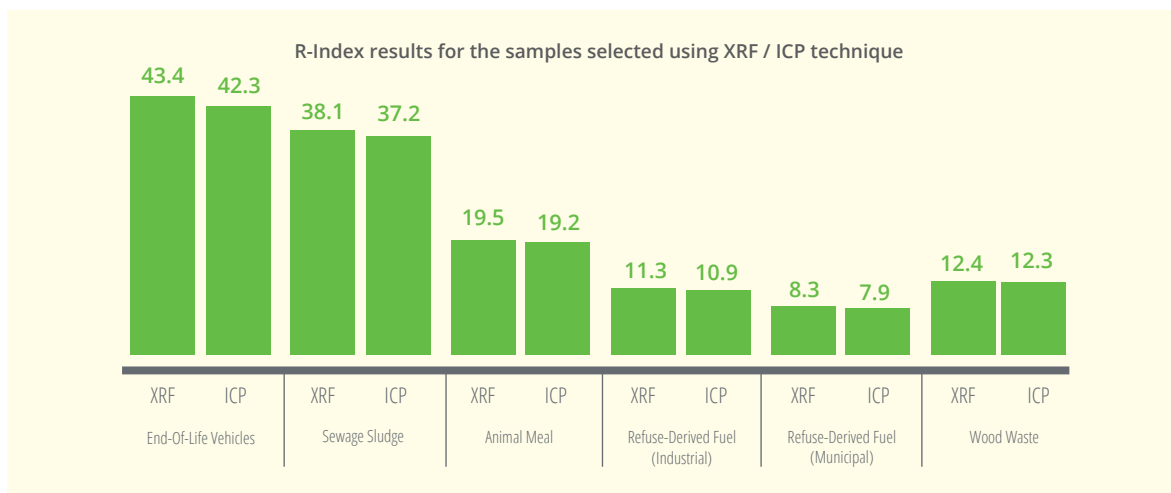|					
8	7	11	23	8	6
ELV, End-Of-Life Vehicles	SS, Sewage Sludge	AM, Animal Meal	RDF, Refuse-Derived Fuel (Industrial)	RDF, Refuse-Derived Fuel (Municipal)	WW, Wood Waste

- All the samples were analysed by XRF (X-ray fluorescence spectrometry). Furthermore, the Inductively Coupled Plasma Optical Emission Spectroscopy technique (ICP) was utilised to conduct an analysis of a further 6 samples, one for each type of waste, in order to check data that were inconsistent for some oxides (which ruled out inconsistencies in the determination) and to check the overall differences in terms of R-Index.
- The results obtained show that there is a direct correlation between the Recycling Index (R-Index) and the ash content, so, in relative terms, the ash content is an indicator of what the R-Index is going to be for each type of waste considered.

% ash, average data

Category	Value
ELV, End-Of-Life Vehicles	26.2
SS, Sewage Sludge	33.5
AM, Animal Meal	21.3
RDF, Refuse-Derived Fuel (Industrial)	13.1
RDF, Refuse-Derived Fuel (Municipal)	9.3
WW, Wood Waste	7.9

R-Index, average data

Category	Value
ELV, End-Of-Life Vehicles	20.3
SS, Sewage Sludge	25.8
AM, Animal Meal	12.8
RDFI, Refuse-Derived Fuel (Industrial)	11.5
RDFM, Refuse-Derived Fuel (Municipal)	7.9
WW, Wood Waste	5.8

- All the values obtained are consistent with the results contained in the scientific literature, not only as regards the ash content, but also the oxide composition and R-Index as shown in Sections 4.1 to 4.7.
- The repetition of these samples using ICP or EN 196-2, has also served to clarify some out-of-range data in relative terms, and has made it possible to have further data to explain and confine the variability found in the analysis of certain parameters, confirming their value more accurately.
- The out-of-range values found, clearly related to the appearance of the samples, when compared to the rest of their group. Even in the case of the RDFs, which initially could appear to be more heterogeneous, clearly observable patterns within their type can be made out, not only where their appearance is concerned but also regarding their chemical composition and ash fraction.
- The determining variable in the R-Index is the ash content that, as it is different for each type of waste, can vary greatly within the same group.

- It is possible to discern common patterns that can be identified visually by type of waste. Furthermore, subgroups can be established where the apparent heterogeneity decreases considerably. These subgroups per type of waste can be associated with different suppliers, which is a matter that must be the subject of a future study.
- There are greater differences in the results obtained for the R-Index, if the calculations are made taking into account 4 oxides or 9 oxides, than the differences found when determining with one analytical method or another, XRF instead of ICP. This can be seen in the following graphs.

R-Index, average data per type of waste with determination based on 4 Oxides and 9 Oxides

17.5	20.3	22.0	25.8	10.6	12.8	9.7	11.5	6.2	7.9	4.6	5.8
4OX	9OX	4OX	9OX	4OX	9OX	4OX	9OX	4OX	9OX	4OX	9OX
End-Of-Life Vehicles		Sewage Sludge		Animal Meal		Refuse-Derived Fuel (Industrial)		Refuse-Derived Fuel (Municipal)		Wood Waste	

R-Index results for the samples selected using XRF / ICP technique

43.4	42.3	38.1	37.2	19.5	19.2	11.3	10.9	8.3	7.9	12.4	12.3
XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP
End-Of-Life Vehicles		Sewage Sludge		Animal Meal		Refuse-Derived Fuel (Industrial)		Refuse-Derived Fuel (Municipal)		Wood Waste	

Moreover, determination with 9 oxides is considered to be more complete, because it includes all the variability of oxides contained in the components that constitute Portland clinker.

7 CONCLUSIONS

The 6 alternative fuels studied: Refuse-Derived Fuels (RDF) of Municipal and Industrial Origin, Animal Meal, Wood Waste, End-Of-Life Vehicles and Sewage Sludge possess a mineral fraction that has been quantified in this technical report. The mineral fraction in those wastes is incorporated into the clinker matrix, replacing the natural raw materials.

The alternative fuels mentioned, apart from replacing part of fossil fuels by means of energy recovery, also replace a certain percentage of natural raw materials, through material recovery, in a joint-operation known as "co-processing".

Until the present time, there has been no standardised methodology that enables the user to accurately assess this material recovery. The development of Standard ISO CD 4349 "Solid Recovered Fuels. Determination of the Recycling-Index for co-processing", has enabled the user to make this assessment, with a representative sample of the six alternative fuels that form part of this study.

Three possible formulas can be utilised to quantify this percentage of material recovery:

- The first, by calculating the percentage of ash contained in the mineral fraction, based on Spanish Standard UNE-EN-ISO 21656 "Solid Recovered Fuels. Determination of Ash Content".
- The second, by calculating a Recycling Index, based on Standard ISO CD 4349, which assesses which oxides contained in the ash fraction are compatible with the oxides that constitute Portland clinker, and make a positive contribution to its benefits as a hydraulic conglomerate. This calculation can made in either of the following two ways:

  - Calculation with 9 oxides constituting the clinker: Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, Na_2O, SO_3, SiO_2 and TiO_2.
  - Calculation with 4 oxides basic constituents of the clinker: Al_2O_3, CaO, Fe_2O_3, and SiO_2.

This study has allocated the following material replacement percentages for the alternative fuels considered, these percentages depending on the methodology used:

Results for recovery of material based on the percentage of ash and Recycling Index (R-Index)
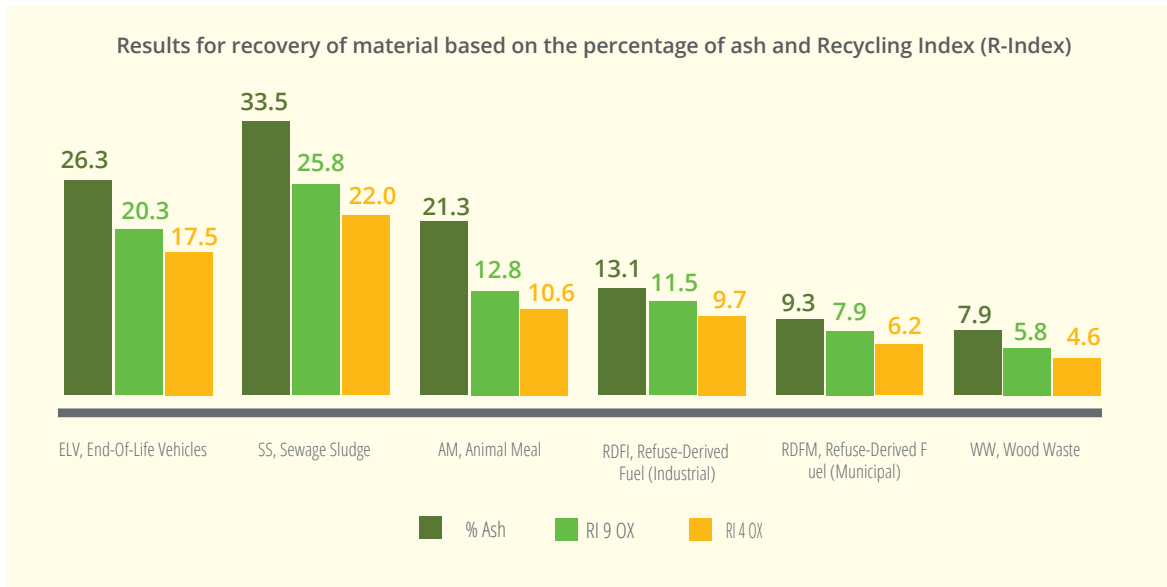
In view of the results obtained, we can state that **this study shows there is a material recovery, which is significant in terms of the percentage of mineral fraction in the fuels.** This mineral fraction is equally significant in quantitative terms when compared to the total amount of raw materials used to produce clinker.

The index that most accurately assesses the magnitude of the Recycling Index is the calculation based on 9 oxides, because it includes all the oxides that provide Portland clinker with its benefits. **That is why the R-Index 9 OX, in accordance with Standard ISO CD 4349** *Solid Recovered Fuels. Determination of the Recycling-Index for co-processing,* **is proposed as the reference method for assessing that indicator.**

Finally, the study brings to light the fact that the alternative fuels share a fairly uniform chemical and visual pattern, even in the case of waste from different suppliers. The pattern can easily be discerned between each type of waste and subtype, which makes it possible to rule out the idea of an apparent heterogeneity attributed *a priori*.

8 REFERENCES

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- *UNE-EN 15410 Solid Recovered Fuels. Method for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti).*
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