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D1.2 – Report on chemical leaching process performances and obtained biocoal quality at pilot scale

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EXECUTIVE SUMMARY

Steel sector decarbonization is a key challenge for the EU Green deal targets. BioRECAST proposes a "New and improved steelmaking technique", reusing EAF waste-heat for the on-site conversion of residual biomass into biocoal and sustainable bioenergy, to be used as alternative sustainable fuels for steelmaking process, increasing the sustainability of EAF process. BioRECAST addresses the research objective: "New, sustainable and low-carbon steelmaking and finishing techniques". The project also aims to the research objective "Decarbonization and Modernization of steel sector", of the European Green Deal Communication". The project work plan includes: biocoal production tests in a 100 kg/h plant, biocoal industrial tests in EAFs; pyrogas combustion trials and design of new pyrogas burner to be used in EAFs, and the executive design based on two industrial case studies of a new integrated pyro-EAF steelmaking plant. As a first step, BioRECAST identified a set of biowaste samples commonly produced in urban, industrial and rural areas, potentially suitable for biocoal production to be used in Electric Arc Furnaces. The present report includes the description of the pilot scale leaching trials, performed on the raw char produced by slow pyrolysis tests, already reported in the Deliverable D1.1. The results of this report will be used to identify the biowaste streams to be processed at large scale in the task 1.3.

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1 Introduction

1.1 Scope of the deliverable

In tasks 1.1., 8 types of biowaste stream were selected and processed by slow pyrolysis at lab and pilot scale, producing several samples of chars. As a result of task 1.2 four biowaste samples were selected for pilot scale trials: Agronomic digestate, agricultural lignocellulosic residues, sewage sludge, and organic fraction of municipal solid waste (OFMSW). As shown in the Deliverable D1.1., the identified biowaste streams presented high inorganic content, reaching the highest values in dry sewage sludge (> 30% db). For this reason, processing biowaste streams by slow pyrolysis led to obtain chars with good stability and reduced H/C ratio, but with an increased amount of ash (between 25 and 59% db). The high concentration of inorganics such as K, Ca, P, Mg reduced the total carbon content and the calorific value of the chars, limiting the application as coal substitute in the Electric Arc Furnaces. This deliverable, and the related task 1.3., investigated the benefits of performing acid leaching on the so produced chars, so that to remove most of the inorganics and improve the char quality, obtaining steel-grade biocoals. The tests have been performed using a pilot chemical leaching unit, able to process up to 4 kg of biocoal, designed and operated by RE-CORD. As a result, a high ash extraction efficiency was obtained, increasing the carbon content in all chars produced by pilot scale pyrolysis. The deliverable shows the mass balance of the tests, and the quality of the obtained biocoals.

1.2 Introduction to chemical leaching

Leaching, also known as solid-liquid extraction, consists in the separation of components from a solid material using a leaching solution. The chemical leaching process is widely applied in minerals and fertilisers industry, to extract inorganics from ores, such as phosphate rocks and alumina. Moreover, the process is commonly used in the fossil coal industry to reduce the ash content and to purify it from mineral matter and sulphur (S), representing an effective technique to improve coal quality. In fact, the presence of ash and sulphur in the coal is the cause of emissions, and of reactions that impacts on environment and on the steel quality. Moreover, ashes reduce the calorific value of coal and make its transport more expensive. The main elements which can be found in coals are silicon (Si), aluminum (Al) and iron (Fe), with lesser amounts of oxides of calcium (Ca), magnesium (Mg), potassium(K), sulphur (S), titanium (Ti), and phosphorus (P) [1]. Minor or trace elements of Ni, Zn, Cd, Pb, Cr [2] have been also identified. Several studies proved that an efficient coal demineralization is obtained by chemical leaching method [1] which can be performed with mixed reagents and in multiple steps, using alkali and acid reagents. The most commonly used inorganic chemicals are alkalis (NaOH, Na_2CO_3, CaO, $Ca(OH)_2$, KOH) and mineral acids (such as HCl, HNO_3, H_2SO_4) [2]. In addition, oxidizing agents have been used by some researchers, such as H_2O_2, and $Fe_2(SO_4)_3$ [2]. Every process uses different inorganic agents (acids, alkalis and other chemicals) and has its own advantages and disadvantages and target components. Acid leaching has the most significant effect on the demineralization of coal. In fact, acids react with most of minerals, such as carbonates, Fe_2O_3, phosphates and sulfides, even if they do not dissociate the clay-bearing minerals [1]. Acid leaching target elements are metal ions because they result soluble in acid environment. In fact, at low pH, cations are exchanged with protons, hence metal hydroxides are dissolved, and metals are removed from coal. For this reason, single acid leaching is widely used to remove ash from coal, and acids represent the most effective chemicals for demineralisation. Single acid leaching using HNO_3, or HCl can be effective on phosphates, carbonates and sulphates, with the advantage of inorganic acids quite low cost. On the other hand, many inorganics are simultaneously present in coal, and not all of them can be removed by the same acid. HCl is effective on phosphates, carbonates, sulphates (associated to Ca, Mg, Fe, Al, K, Ti) but is ineffective on silicates, some aluminosilicates and pyrites [2]. H_2SO_4 is not effective on calcium oxides, as it forms not soluble calcium sulphates. HF can remove almost all minerals, except pyrites, which can be instead separated by HNO_3 in high concentration [2]. However, the use of HF is usually not recommended because of the strict safety measures and to the high cost. Using strong acids can also bring to other issues, such as

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oxidation reactions for volatile coals, and alteration of the coal structure and properties. As an alternative, alkali leaching can be performed. The effect of alkalis on coal is the conversion of silicates and aluminosilicates of ash into sodium silicates (sodalite, sodium aluminosilicate). Alkali reagents have high affinity towards coal minerals and the ability to penetrate the interior coal matrix [3]. The hydroxyl ions in the alkali leaching solution have high affinity to clay bearing minerals, hence alkali attack into the major minerals [3]. Ash content and S con be reduced by CaO and $Ca(OH)_2$, which is not corrosive for equipment and is cost affordable. NaOH and KOH are effective, but with much higher costs.

Alkali-acid leaching results very effective, removing more than 90% of ash with just two steps, but excessive use can hinder coal structure, leach organic compounds, and result in very high process costs. At specific concentration and leaching temperatures, organo-chemical structure of coal is not affected by chemical leaching, explaining why this treatment is very attractive. The reduction of mineral matter in coal by chemical leaching is quantified by the degree of demineralization (D.D) [2]:

$$D.D.(\%) = (Ash\ in\ feed\ coal - Ash\ in\ leached\ coal)/(Ash\ in\ feed\ coal) \cdot 100 \quad (1)$$

According to literature, the degree of demineralisation, and that can be varied in function of the required coal demineralisation:

- Chemical type: different chemicals have different target inorganics,
- Chemical concentration: the higher the chemical concentration in the leaching solution, the higher the demineralisation. But experimental results [3] show that up a certain concentration demineralisation rates slow down.
- Temperature: higher temperatures favour the process kinetics, resulting in higher demineralisation.
- Contact time: an increase of the contact time leads to a higher demineralisation.
- Chemical to coal ratio: if a higher quantity of leaching agent is used, demineralisation is improved.
- Coal particles dimension: if coal particles are dimensionally reduced, the contact surface increases and the process is more effective.
- Mixing velocity: it favours the phases contact and represents a parameter to be optimized for energy consumption reasons.

To apply the process on industrial scale, the value of these parameters must be optimized: first, because there can be optimum values of the parameters to be identified; second, because the process must be economically affordable, hence the operating costs and, thus, the chemicals consumption, should be limited in function of the desired demineralisation degree.

2 Methodology

2.1 Materials characterization and pretreatment

2.1.1 Pretreatment

All the char samples have been milled before leaching. Milling has been performed with the aid of a knife milling unit Retsch SM 300, while the drying was carried out in an oven ArgoLab TCN 200.

Figure 1: Milling unit and oven used for samples pretreatment

2.1.2 Laboratory analysis

The characterization of the different char selected has been performed with the aid of different instruments and methodologies to determine proximate and ultimate composition as well as their calorific values. Proximate analysis aimed at the definition of moisture content, ash content, and volatile matter. Ash and volatiles were determined by a LECO TGA701 thermo-gravimetric analyzer. The ash content of the selected materials has been determined at 550 °C (ash 550) and 710 °C (ash 710); volatiles have been determined as the fraction lost by heating at 900°C for 2 hours.

Ultimate analysis enabled to determine carbon, hydrogen, nitrogen, sulfur, and chlorine contents in the material. The concentration of C, H, N and S was conducted by a CHN-S analyzer (LECO TruSpec CHN and LECO TruSpec S). The oxygen content was calculated as per UNI EN ISO 18125:2018 according to the following equation:

$$O = 100 - Ash\ 550 - C - H - N - S \quad (2)$$

Where C, H, N, S represent elements' weight fraction converted on a dry basis. The chlorine content was determined by means of a bomb calorimeter (LECO AC500) pre-treatment and an ion chromatography system (Metrohm 883 Basic IC plus). The higher heating value (HHV) of the feedstock was determined analytically by a bomb calorimeter (LECO AC500).

Fixed carbon represents the recalcitrant fraction of total carbon, i.e. the non-volatile carbon share. Fixed carbon percentage is determined by subtracting ashes and volatiles percentage from total mass, being then defined on a dry basis:

$$Fixed\ carbon\ \left(\%\ \frac{m}{m}\ d.b.\right) = 100 - (Ash\ 710 + volatiles) \quad (3)$$

The concentration of metals and other inorganics in both the liquid and solid specimens was determined after pretreating the solid sample by microwave assisted mineralization system Milestone Start D, thereafter samples have been analyzed by mean of plasma atomic emission spectroscopy (MP-AES, by Agilent 4200 MP-AES). For digesting the solid substrate, the samples have been treated either with aqua regia, or hydrofluoric acid.

2.1.3 Normative reference

The normative references of the analysis are summarized in Table 3.

Table 3. Normative references

Parameter	Normative
Moisture	UNI EN ISO 18134-2:2017
Volatiles	UNI EN ISO 18123:2016
Ashes	UNI EN ISO 18122:2016
Fixed carbon (calculation)	UNI EN ISO 1860-2:2005
C, H, N	UNI EN ISO 16948:2015
S (solid matrix)	ASTM D4239-14
Cl	UNI EN ISO 16994:2017
O (calculation)	UNI EN ISO 16993:2017
Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, V, Zn	UNI EN ISO 16967:2015/UNI EN ISO 16968:2015
HHV	UNI EN ISO 18125:2018
LHV (calculation)	UNI EN ISO 18125:2018
pH	ASTM E70-24
Water content	ASTM E203-08
Coversion factor wet basis/dry basis (calculation)	UNI EN ISO 16993:2017

2.2 Description of the chemical leaching pilot unit

During the research activity, a pilot chemical leaching unit was designed and assembled, so that to validate the process in real environment with commercial equipment. The equipment consists in the following components:

a stainless steel AISI 316 L tank of 70 litres capacity, externally heated by a hot water jacket and stirred with a double helicoidal blade with a maximum speed of 300 rpm;

- An electric control panel;
- Electric resistance to heat the hot water in the jacket;
- An Iwaki acid dosing pump for the injection of the reagent;
- A water boiler to provide hot water for the process;
- A piston pump of 10 bar nominal pressure to send the solid-liquid slurry to the filterpress;
- A filter press in stainless steel AISI316 equipped with 5 plates and a maximum capacity of 2.5 litres;
- A stirred buffer tank of 40 litres capacity.

The plant can operate with up to 50 litres net capacity (Figure 17) at temperature up to 85°C with organic acids as well as HNO_3, and H_2SO_4 at concentration of up to 10 % in the solution. No hot acid solutions containing HCl can be processed in the plant.

Figure 2. Picture of the chemical leaching unit developed and installed at REC PARK

2.2.4 Methodology of chemical leaching tests

The char obtained at pilot scale was processed by chemical leaching at pilot scale. The chemical leaching procedure adopted for pilot scale tests includes the following steps:

- Char grinding in a knife mill down to less than 250 microns,
- Heating water to the desired temperatures by electric boiler
- Switch on the heating jacket with hot water recirculation and add hot water in the reactor,
- Dosage of solid from the hole placed on the head of the reactor,
- Activation of the mixer at the desired velocity,
- Closure of the reactor,
- Dosage of the acid with the dosing pump,
- Stirring and heating for 1 hour residence time,
- Open the discharge valve and activate the piston pump to send the slurry to the filterpress until the reactor was empty,
- Collect the leachate (process liquid) in HDPE tanks,
- Charge hot wáter in the reactor
- Open the discharge valve and activate the piston pump to flush the hot wáter to the filterpress and wash the char cakes.
- Collect the washing water in HDPE tanks,
- Flux dry air in the filterpress top hole to dry the cakes
- Open the filterpress and collect the washed biocoal cakes
- Dry the biocoal cakes at 105 °C for > 16 hours.

2.2.5 Performance indicators

The performances of the leaching tests were evaluated by two indicators. The first is the degree of demineralization (DD), which expresses the percentage of extracted ash against the initial content in the processed char, under the assumption that no other compounds besides ashes leach out from the solid:

$$D.D.(\%) = \frac{ash\ char{,}i\ (\%\ d.b.) - ash\ char{,}f\ (\%\ d.b.)}{ash\ char{,}i\ (\%\ d.b.)} \quad (3)$$

Where ash *char,i* is the ash content (710 °C) in the recycled coal, and ash *char,f* is the ash content (at 710 °C) in the produced char. The second indicator is the element extraction efficiency (*EE,l*), which expresses the percentage of extracted element against the initial content of the element in the processed char:

$$EE,l\,(\%) = 100 - \frac{E\ LBC,f\ (mg/kg) \times My}{E\ BC,i\ (mg/kg)} \cdot 100 \qquad (4)$$

Where:

- *E LBC*, f is the concentration of the i-element in the biocoal after leaching (mg/kg d.b.),
- *My* is the solid mass yield (%d.b.) of the leaching process
- *E BC,i* is the i-element concentration in the processed char (mg/kg d.b.)

The *E LBC*, f and the E *BC,I* was determined by MP-AES, in mg/kg

3 Results of chemical leaching tests

3.1 Description of processed raw chars

After the slow pyrolysis tests, performed in a pilot unit and described in the Deliverable D1.1, four chars were obtained:

- CR-SS: Raw char from sewage sludge
- CR-AGW: Raw char from straw
- CR-AGD: Raw char from digestate
- CR-OFMSW: Raw char from Organic fraction of municipal solid waste

These chars have been processed by chemical leaching in the above-described leaching plant. The raw chars have been characterized, as reported in Table 4.

Table 4. Proximate, ultimate analysis and calorific value of processed raw chars

Parameter	Unit	CR-SS	CR-AGW	CR-AGD	CR-OFMSW
Moisture	%, wb	0.56	1.18	0.73	1.89
Volatiles	%, db	17.4	12.20	12.06	18.12
Ashes (550)	%, db	58.4	28.55	35.89	45.69
Fixed C	%, db	24.3	60.93	52.80	40.23
C	%,db	31.7	64.3	56.8	45.9
H	%,db	1.38	2.0	1.6	1.3
N	%,db	4.8	1.3	1.5	2.5
S	%,db	0.26	0.1	0.3	0.2
Cl	%,db	0.76	0.5	0.5	1.9
O	%,db	2.77	4.9	4.1	8.4
O:C	mol/mol	0.06	0.058	0.054	0.138
H:C	mol/mol	0.50	0.374	0.335	0.339
HHV	MJ/kg, db	12.7	24.4	20.9	16.4

As reported in Table 4, all raw char present a relatively low carbon content (between 31.7 and 64.3 % db). The reason stays in the high concentration of ashes, between 28.55 % in CR-AGW and 58.4 % in CR-SS. The high ash concentration has a direct impact on the calorific value, and on the applicability of these chars in the furnaces.

Moreover, Table 5 shows that, all chars contain harmful elements which can reduce the performances as reducing agents at high temperatures, and also reduce the steel quality. In fact, CR-SS, CR-AGD and CR-OFMSW contain all high concentrations of phosphorus (1.5-4 %db), while high concentration of alkali elements, such as potassium, are found in CR-AGW, CR-AGD, and CR-OFMSW.

Table 5. Characterisation of inorganic elements

Parameter	Unit	CR-SS	CR-AGW	CR-AGD	CR-OFMSW
Al	mg/kg db	15442	4080	1579	1284
Ba	mg/kg db	336	121	94	138
Ca	mg/kg db	21561	15594	33591	93247
Cd	mg/kg db	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Co	mg/kg db	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Cr	mg/kg db	164	12	10	48
Cu	mg/kg db	647	9	70	96
Fe	mg/kg db	89462	2131	3638	3135
K	mg/kg db	9022	31075	39404	23275
Mg	mg/kg db	4771	4121	20207	8808
Mn	mg/kg db	350	210	425	375
Na	mg/kg db	3253	4203	5331	15427
Ni	mg/kg db	33	b.d.l.	b.d.l.	b.d.l.
P	mg/kg db	39835	3580	26787	16123
Pb	mg/kg db	136	b.d.l.	b.d.l.	b.d.l.
Si	mg/kg db	72704	66311	36021	24396
Ti	mg/kg db	2754	b.d.l.	139	293
V	mg/kg db	37	4	8	4
Zn	mg/kg db	1500	b.d.l.	288	109

Each char was leached to remove the harmful inorganics and improve the properties of the biocoal.

3.2 Chemical leaching of raw char from Sewage Sludge

3.2.1 Tests conditions

Raw char from sewage sludge was processed by chemical leaching adopting the following conditions.

Table 6. Chemical leaching conditions adopted for CR-SS

TEST CONDITIONS	Unit	Value
acid:char ratio	$^{m}/_{m}$	0.55
liq:char ratio	$^{m}/_{m}$	10
Acid	-	HNO_3
Temperature	°C	75
time	h:min:sec	02:00:00
Washing water:char ratio	$^{m}/_{m}$	10

The test was then performed with the below quantities

Table 7. Quantities processed in the leaching reactor

Material	Unit	Value
Char	kg	4.0
Process water	kg	36.6
Wash water	kg	40.0
Dosed acid	kg	3.51
Temperature dosage process water	°C	80
Liquid:char (eff., process)	$^{m}/_{m}$	10.0
Temperature dosage wash water	°C	80

3.2.2 Tests results

The acid leaching brought to extract 64% of the inorganics, obtaining a solid mass yield of 55 % wt db. In summary, 2.2 kg of biocoal were obtained. The pictures of the biocoal and of the process liquid are shown below.

Figure 3. LIquids and solid obtained from the leaching test

The composition of the biocoal (CL-SS) is reported below.

Table 8. Composition of the Biocoal „CL-SS“

Parameter	Unit	CL-SS
Volatiles	%, db	19.5
Ashes (815)	%, db	37.6
Fixed C	%, db	43.0
C	%,db	42.0
H	%,db	1.5
N	%,db	6.6
S	%,db	0.1
Cl	%,db	0.36
O	%,db	12.3
O:C	mol/mol	0.221
H:C	mol/mol	0.425
HHV	MJ/kg, db	16.3
LHV	MJ/kg, db	16

Table shows a higher carbon content, which increased of 32.5%, from 31.7 %db to 42.0 % db, and a reduced ash content, decreased to 36.6 % db. The calorific value increased of 34%, passing from 12 to 16 MJ/kg. The biocoal obtained, was also classified by Van krevelen, as shown in Figure 4.

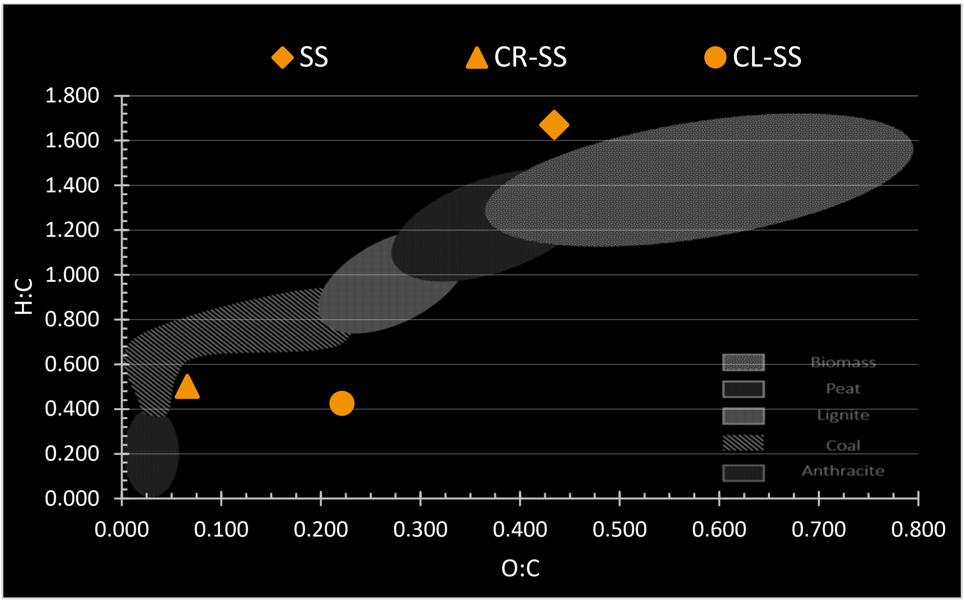


Figure 4. Van krevelen classification of SS, CR-SS and CL-SS

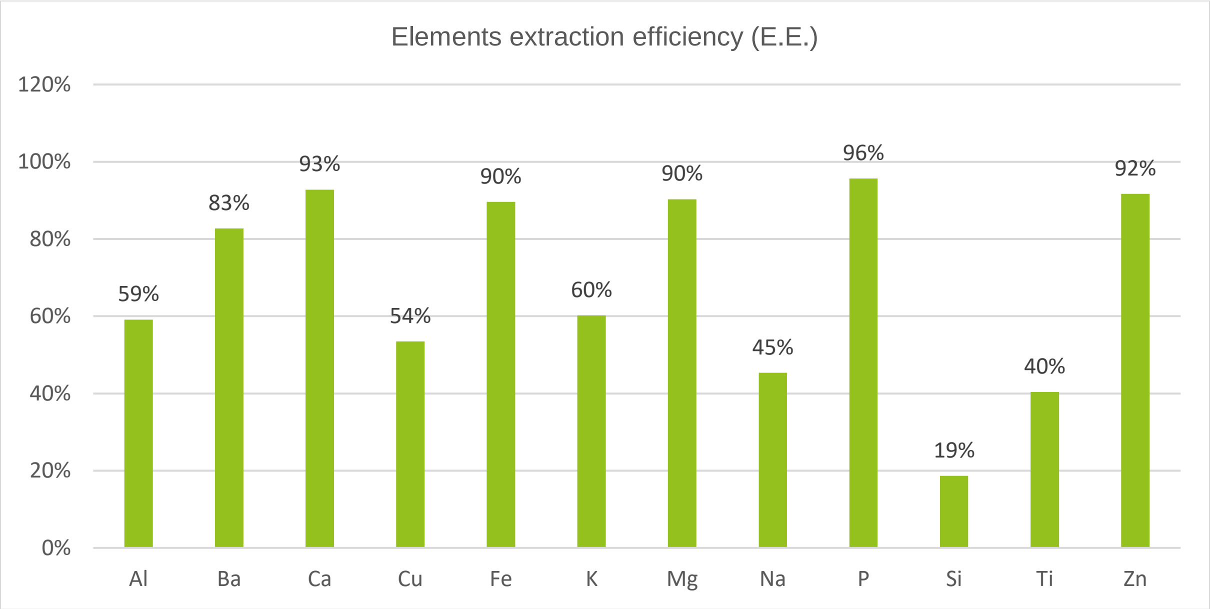
This achievement is due to the extraction of most of inorganic elements, excluding silicon, remaining inert to the process, as shown in the below table.

Table 9. Inorganic elements in CR-S and CL-SS

Element	unit	CR-SS	CL-SS
Al	ppm	15442	11437
Ba	ppm	336	105
Ca	ppm	21561	2832
Cr	ppm	164	101
Cu	ppm	647	545
Fe	ppm	89462	16911
K	ppm	9022	6508
Mg	ppm	4771	840
Mn	ppm	350	66
Na	ppm	3253	3221
Ni	ppm	33	37
P	ppm	39835	3105
Pb	ppm	136	b.d.l.
Si	ppm	72704	107182
Ti	ppm	2754	2977
V	ppm	37	25
Zn	ppm	1500	226

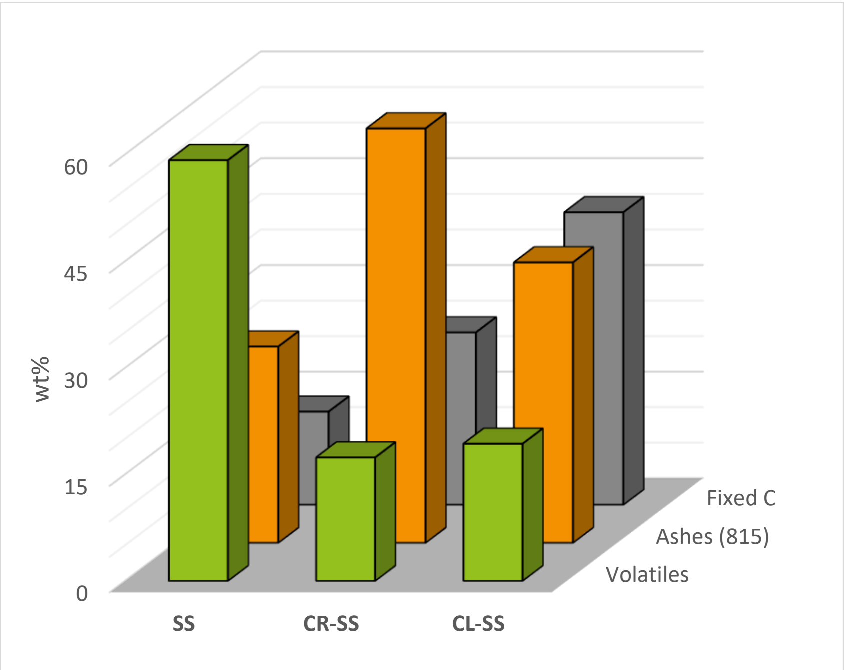
The extraction efficiency of main inorganic elements is reported in the chart below.

Graph 1. Extraction efficiency of main inorganic elements



As shown in Graph 1, more than 50 % of Al and Cu is extracted, with a high extraction efficiency (> 90%) for Ca, Fe, P, and Zn. By consequence, the mass is reduced and the concentration of the other non extracted elements, such as Si, is increased. A further comparison between raw sludge, raw char and biocoal is reported in Graph 2.

Graph 2. Proximate analysis and Fixed C in dry sludge, raw char (CR-SS) and biocoal (CL-SS)



Given the strong effect of the leaching process on the ash extraction, with more than 64% of the ash removed from the solid, Fixed C content increases to above 42% from below 30% db.

3.3 Chemical leaching of char from AGD (CR-AGD)

3.3.1 Test conditions

Raw char from digestate was processed by chemical leaching adopting the following conditions:

Table 10. Conditions of AGD chemical leaching test

TEST CONDITIONS	Unit	Value
acid:char ratio	$^m/_m$	0.4
liq:char ratio	$^m/_m$	10
Temperature	°C	75
Acid	-	HNO_3
time	h:min:sec	02:00:00
Washing water:char ratio	$^m/_m$	10
Stirrer velocity	Hz	55

The test was then performed with the below quantities. 4 kg of CR-AGD was milled and processed in the reactor, with 2.4 kg of nitric acid, and 37.5 kg of water.

Table 11. Quantities used for the leaching test

Material	Unit	Value
Char	kg	4.0
Process water	kg	37.54
Wash water	kg	40
Dosed acid	kg	2.46
Temperature dosage process water	°C	80
Liquid:char (eff., process)	$^m/_m$	10.0
Temperature dosage wash water	°C	80

3.3.2 Tests results

The acid leaching brought to extract 70% of the inorganics, obtaining a solid mass yield of 69 % wt db. In summary**, 2.76 kg of biocoal were obtained from 3 kg of raw char**. A picture of the obtained products is reported below

Figure 5. Pictures of liquid and solid obtained from leaching test on AGD

The composition of the biocoal (CL-AGD) is reported below.

Table 12. Composition of the obtained biocoal (CL-AGD)

Parameter	Unit	CL-AGD
Volatiles	%, db	18.7
Ashes (815)	%, db	15.4
Fixed C	%, db	65.9
C	%,db	69.6
H	%,db	1.9
N	%,db	2.7
S	%,db	0.4
Cl	%,db	0.01
O	%,db	9.9
O:C	mol/mol	0.107
H:C	mol/mol	0.330
HHV	MJ/kg, db	26.3

Table 12 shows a higher carbon content, which increased of 22.5%, from 56.8 %db to 69.6 % db, and a reduced ash content, decreased to 15.38 % db. The calorific value increased to more than 26 MJ/kg. The classification of the obtained biocoal in comparison with both raw digestate and raw char is reported in Figure 6.

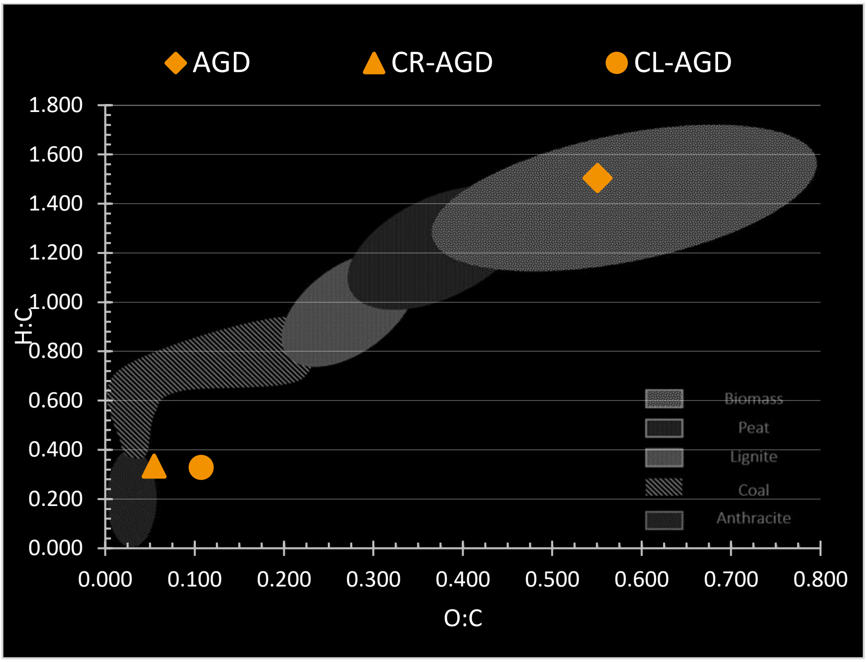


Figure 6. Classification of AGD, CR-AGD and CL-AGD by van krevelen diagram.

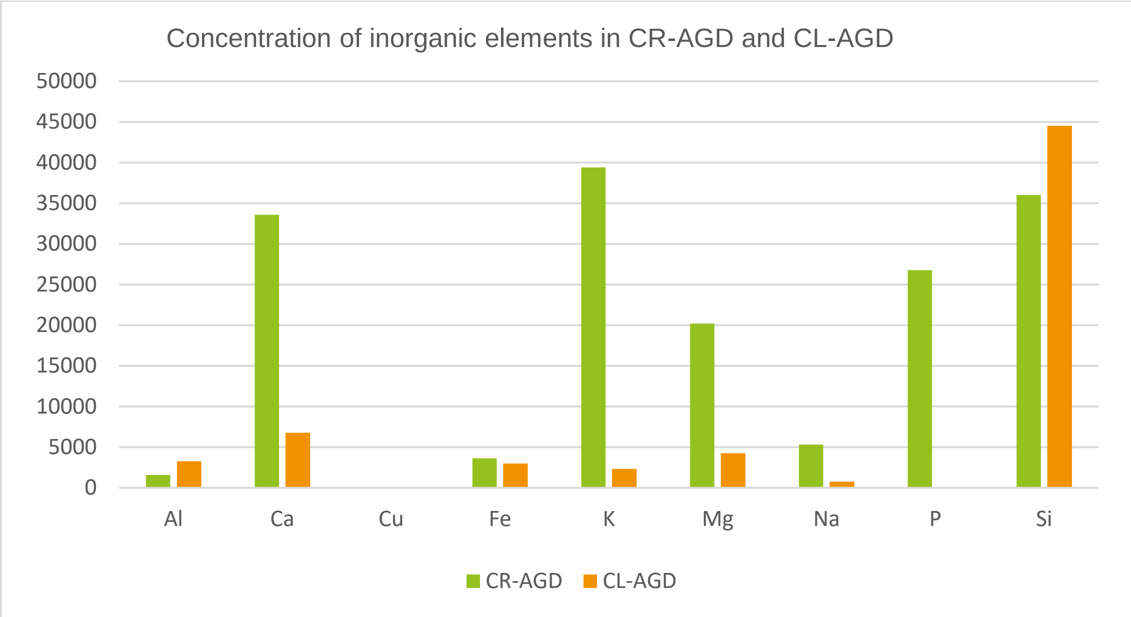
This achievement is due to the extraction of most of inorganic elements, excluding silicon, remaining inert to the process, as shown in the below table.

Table 13. Inorganic elements in CL-AGD after leaching in comparison with CR-AGD

Element	unit	CR-AGD	CL-AGD
Al	ppm	1579	3281
Ba	ppm	94	32
Ca	ppm	33591	6762
Cr	ppm	10	13
Cu	ppm	70	48
Fe	ppm	3638	2979
K	ppm	39404	2307
Mg	ppm	20207	4234
Mn	ppm	425	108
Na	ppm	5331	741
P	ppm	26787	b.d.l.
Pb	ppm	b.d.l.	b.d.l.
Si	ppm	36021	44523
Ti	ppm	139	195
V	ppm	8	6
Zn	ppm	288	98

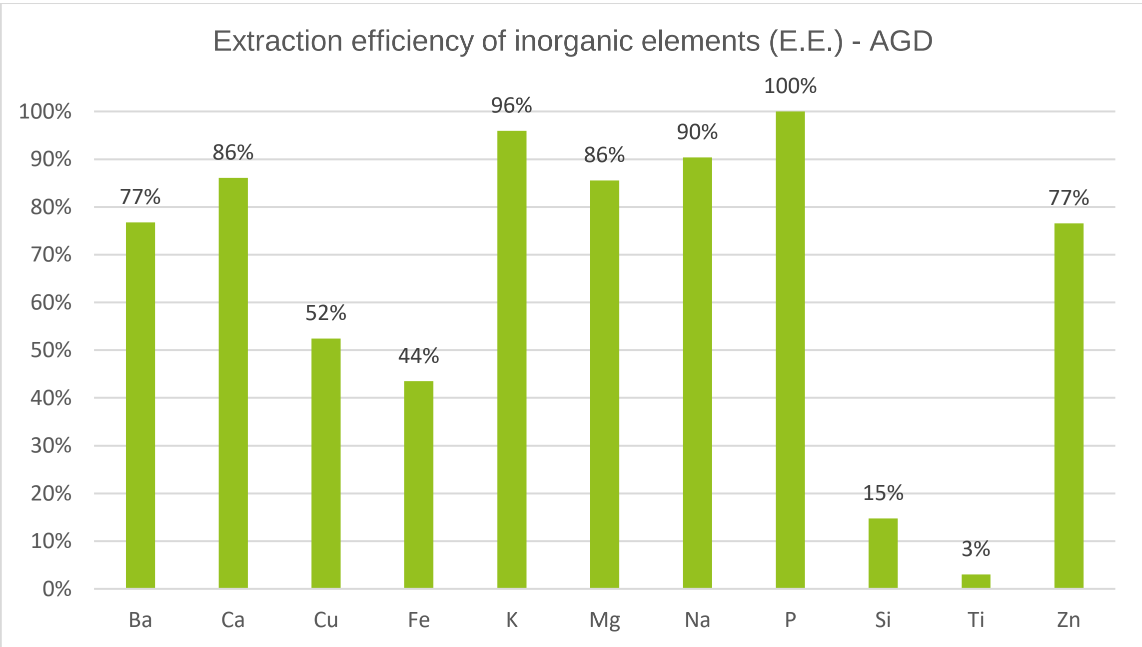
Most of P, K and Ca have been removed, while no effects was achieved for Si and Ti, as expected. As shown in Graph 3, the final biocoal contains much lower concentrations of Ca, and Mg in comparison with the raw char, and almost no more K, Na and P. The increase of Si and Al is due to the reduction of mass, and to that no extraction was achieved for such elements.

Graph 3. Concentration of inorganic elements in the char (CR-AGD) and in biocoal (CL-AGD)



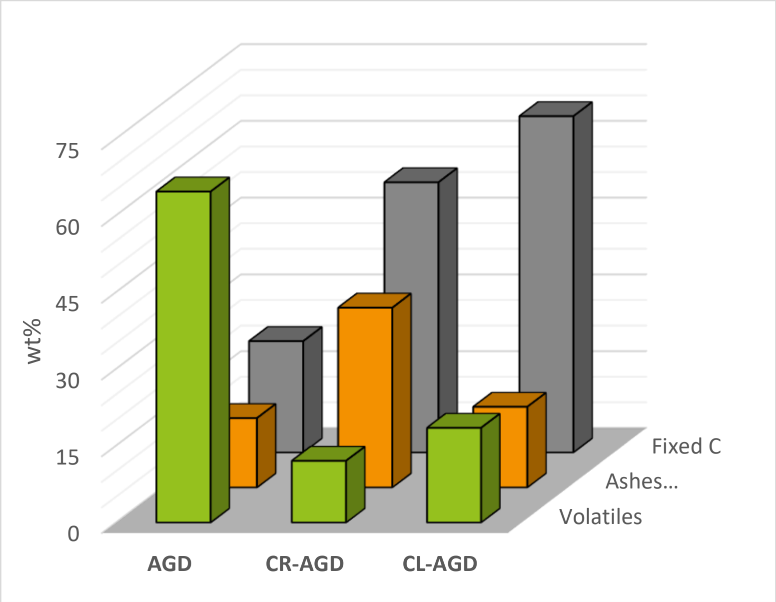
The extraction efficiency of main inorganic elements is reported in the chart below.

Graph 4. Extraction efficiency of main inorganic elements from CR-AGD after leaching



A further comparison between raw sludge, raw char and biocoal is reported in Graph 5.

Graph 5. Volatiles, ash and fixed C content in AGD, CR-AGD and CL-AGD



CL-AGD shows similar volatiles content than CR-AGD, slightly higher due to the reduction of the ash content. Fixed C increases while ash decrease, demonstrating the benefits oft he leaching process on the final biocoal quality.

3.4 Chemical leaching of char from AGW (CR-AGW)

3.4.1 Test conditions

Raw char from digestate was processed by chemical leaching adopting the following conditions

Table 14. Conditions selected for the leaching test on CR-AGW

TEST CONDITIONS	Unit	Value
acid:char ratio	$^{m}/_{m}$	0.3
liq:char ratio	$^{m}/_{m}$	10
Temperature	°C	75
Acid	-	HNO3
Time	h:min:sec	02:00:00
Washing water:char ratio	$^{m}/_{m}$	10
Stirrer velocity	Hz	55

The test was then performed with the below quantities

Table 15. Quantities dosed for the leaching test on CR-AGW

Material	Unit	Value
Char	kg	3.63
Process water	kg	34.65

Wash water	kg	36.3
Dosed acid	kg	1.677
Temperature dosage process water	°C	75
Liquid:char (eff., process)	$^{m}/_{m}$	10.0
Temperature dosage wash water	°C	80

3.4.2 Tests results

The acid leaching brought to extract 55% of the inorganics, obtaining a solid mass yield of 78 % wt db. In summary, 2.83 kg of biocoal were obtained from 3.63 kg of raw char. Below the picture of the solid and the liquid obtained from the test.

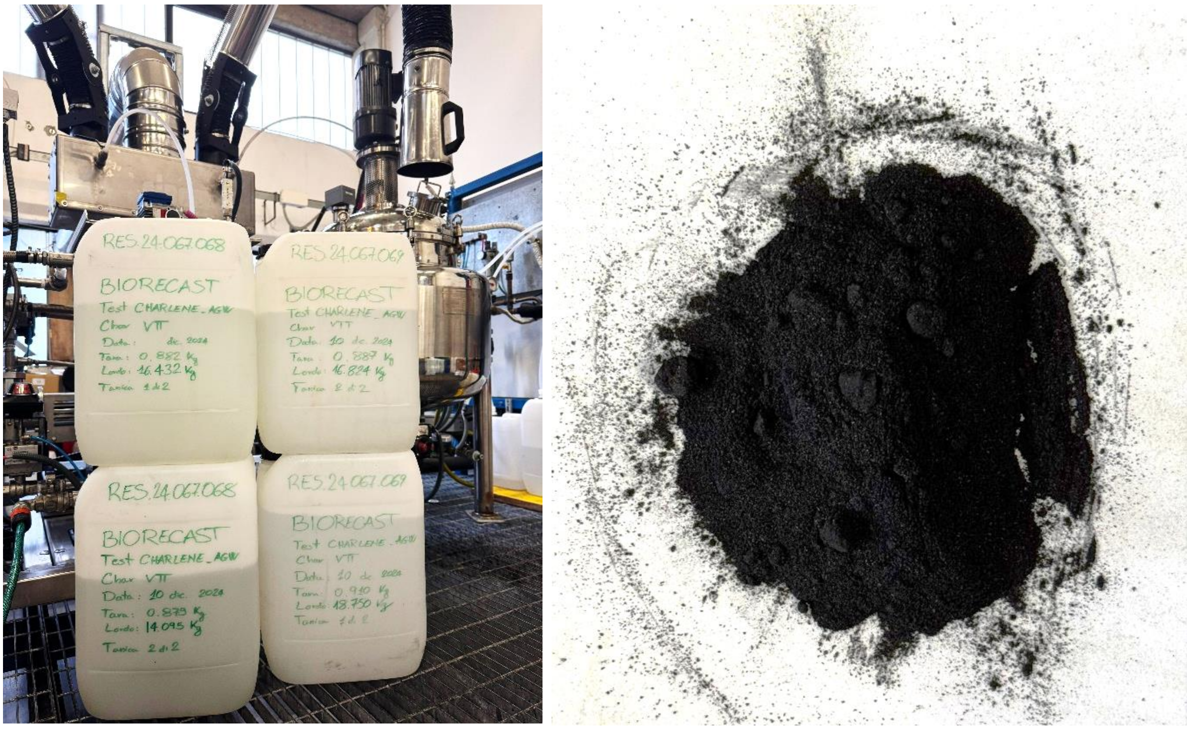


Figure 7. Liquids and solid obtained after the leaching test on AGW

The composition of the biocoal (CL-AGW) is reported below.

Table 16. Composition of the biocoal (CL-AGW)

Parameter	Unit	CL-AGW
Volatiles	%, db	16.9
Ashes (815)	%, db	16.9
Fixed C	%, db	66.2
C	%,db	69.3
H	%,db	2.0
N	%,db	2.0

S	%,db	0.1
Cl	%,db	0.02
O	%,db	9.7
O:C	mol/mol	0.105
H:C	mol/mol	0.346
HHV	MJ/kg, db	26.3
LHV	MJ/kg, db	25.9

Table shows a higher carbon content, which increased of 7%, from 64.4 %db to 69.3 % db, and a reduced ash content, decreased to 16.9 % db. Calorific value have also increased, from 24 to 26.3 MJ/kg.

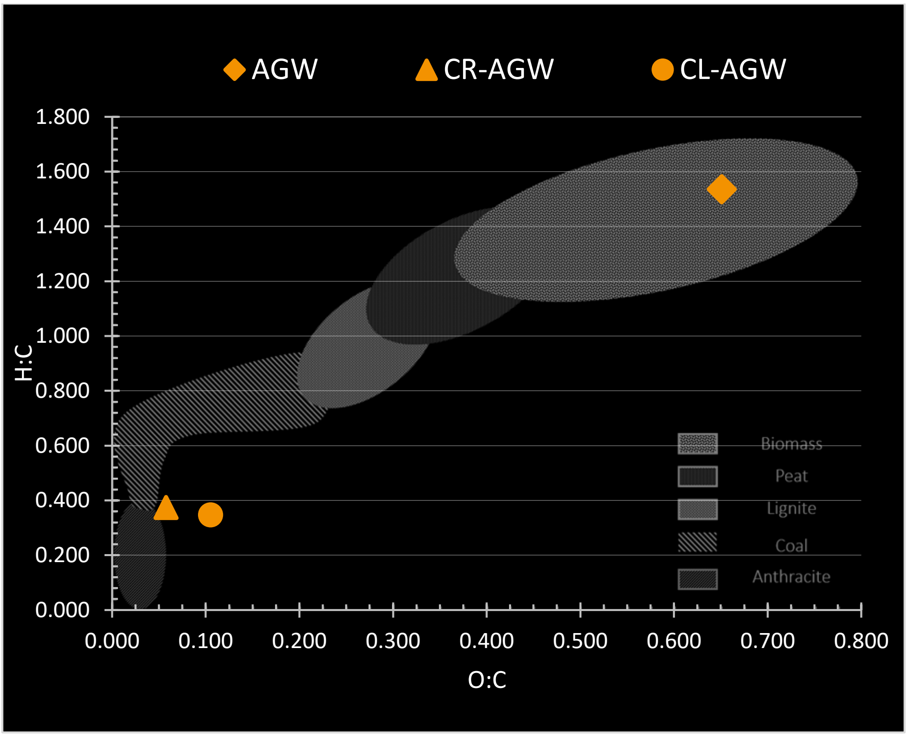


Figure 8. Classification of AGW, CR-AGW and CL-AGW by Van krevelen diagram

This achievement is due to the extraction of most of inorganic elements, excluding silicon, remaining inert to the process, as shown in the below table.

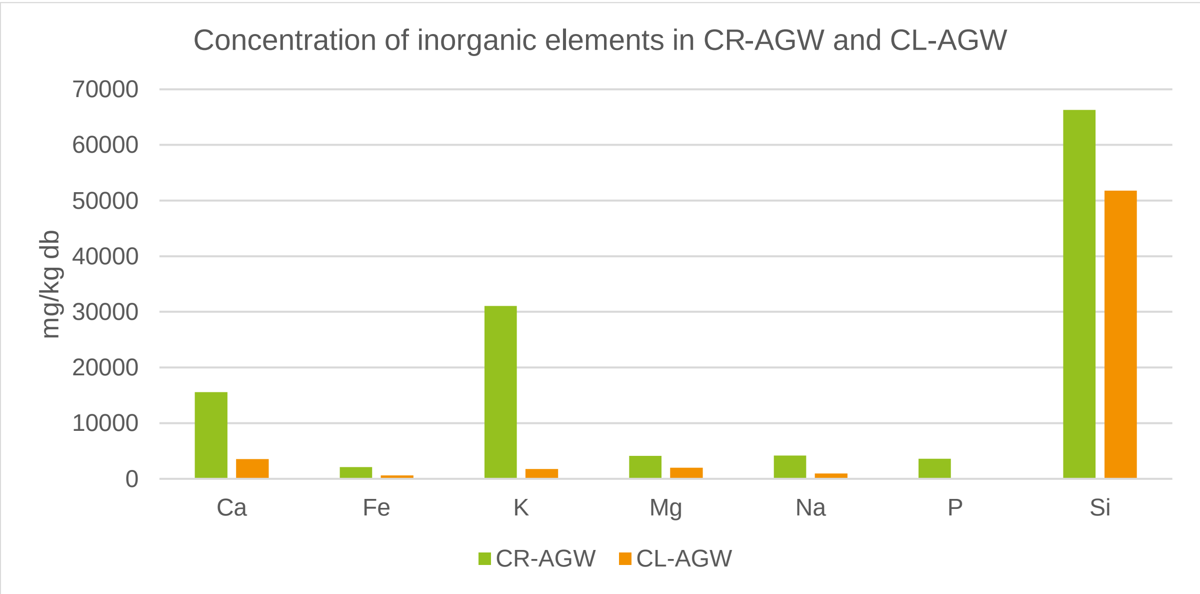
Table 17. Concentration of inorganic elements in CR-AGW and CL-AGW

Element	Unit	CR-AGW	CL-AGW
Al	ppm	4080	2342
Ba	ppm	121	37
Ca	ppm	15594	3547
Cr	ppm	12	8

Cu	ppm	9	b.d.l.
Fe	ppm	2131	639
K	ppm	31075	1743
Mg	ppm	4121	1997
Mn	ppm	210	71
Mo	ppm	b.d.l.	b.d.l.
Na	ppm	4203	963
P	ppm	3580	b.d.l.
Pb	ppm	b.d.l.	b.d.l.
Si	ppm	66311	51763
Ti	ppm	b.d.l.	191
V	ppm	4	b.d.l.
Zn	ppm	b.d.l.	b.d.l.

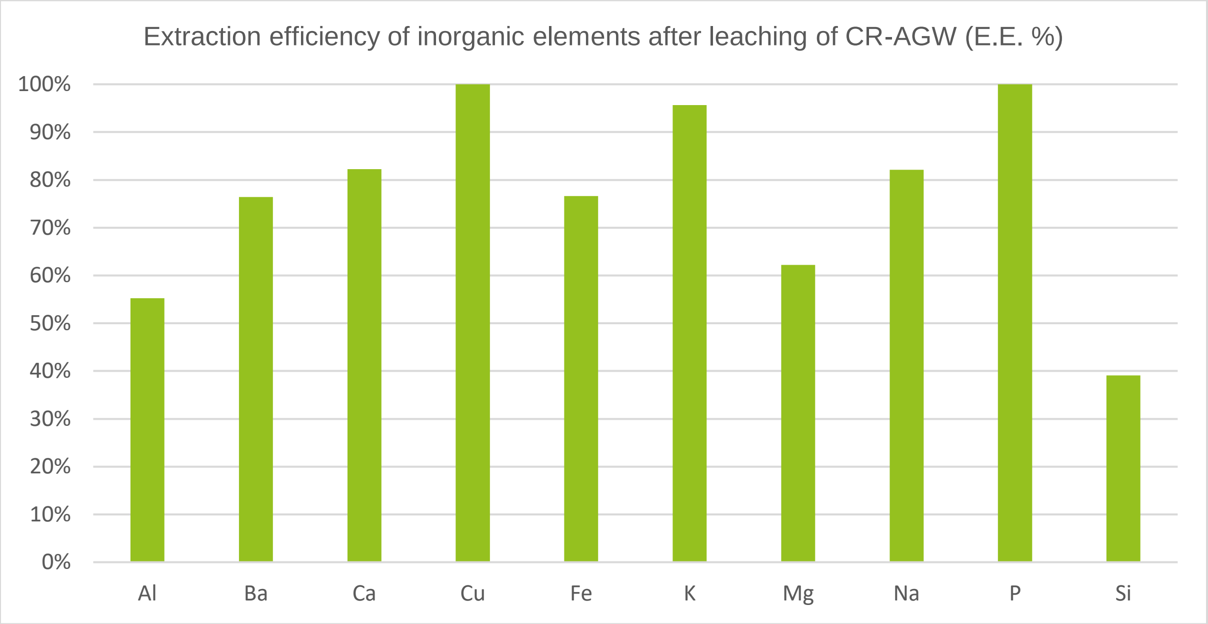
As shown in Graph 6, after leaching Ca is strongly reduce, as well as K and Mg, and P. However, given the low concentration of inorganics, a relevant impact is shown only on K and Ca.

Graph 6. Concentration of inorganic elements in raw char and biocoal from AGW



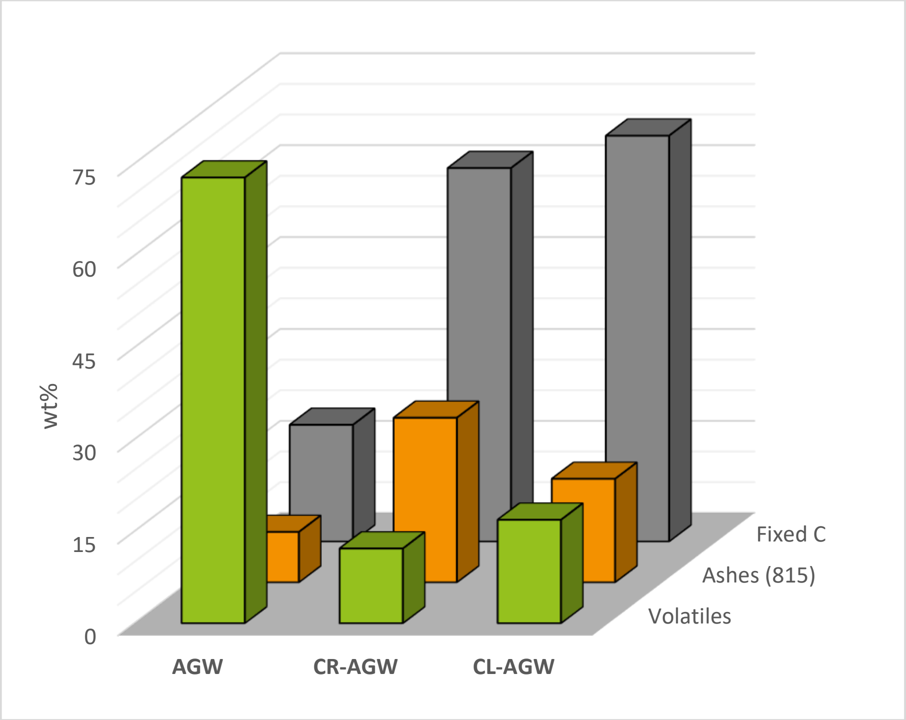
The extraction efficiency of main inorganic elements is reported in the chart below.

Graph 7. Extraction efficiency of inorganic elements after leaching of CR-AGW (E.E. %)



A further comparison between raw sludge, raw char and biocoal is reported in Graph 8

Graph 8. Volatiles, ash and fixed C content in AGW, CR-AGW and CL-AGW



The impact of the leaching process on the final char quality is reduced compared to AGD and SS. In fact, the final Fixed C content in the CL-AGW is only few points higher than in the CR-AGW. However, the extraction of potassium can enable to valorise the element in other sectors (such as agriculture), obtaining economic benefits.

3.5 Chemical leaching of OFMSW-Char

3.5.1 Test conditions

Raw char from digestate was processed by chemical leaching adopting the following conditions

Table 18. Conditions of the leaching test on CR-OFMSW

TEST CONDITIONS	Unit	Value
acid:char ratio	**$^m/_m$**	0.4
liq:char ratio	**$^m/_m$**	10
Acid	-	HNO3
Temperature	**°C**	75
time	**h:min:sec**	02:00:00
Washing water:char ratio	**$^m/_m$**	10
Stirrer velocity	**Hz**	55

The test was then performed with the below quantities.

Table 19. Quantities dosed in the reactor

Material	Unit	Value
Char	kg	2.0
Process water	kg	18.78
Wash water	kg	20.0
Dosed acid	kg	1.231
Temperature dosage process water	°C	80
Liquid:char (eff., process)	$^m/_m$	10.0
Temperature dosage wash water	°C	80

3.5.2 Tests results

The acid leaching brought to extract 77% of the inorganics, obtaining a solid mass yield of 57 % wt db. In summary, 1.147 kg of biocoal were obtained from 2 kg of raw char. A picture of the products after the leaching test is reported below.

Figure 9. Solid and liquid samples of chemical leaching tests

The composition of the biocoal (CL-OFMSW) is reported below.

Table 20. Composition of the CL-OFMSW

Parameter	Unit	CL-OFMSW
Volatiles	%, db	18.7
Ashes (815)	%, db	18.4
Fixed C	%, db	62.9
C	%,db	65.8
H	%,db	2.0
N	%,db	4.4
S	%,db	0.21
Cl	%,db	0.18
O	%,db	9.2
O:C	mol/mol	0.105
H:C	mol/mol	0.36
HHV	MJ/kg, db	24.5

Table shows a higher carbon content, which increased of 43.4%, from 45.9 %db to 65.8 %db, and a reduced ash content, decreased to 18.3 % db. Calorific value also increased of 47 %, passing from 16.4 to 24.5 MJ/kg.

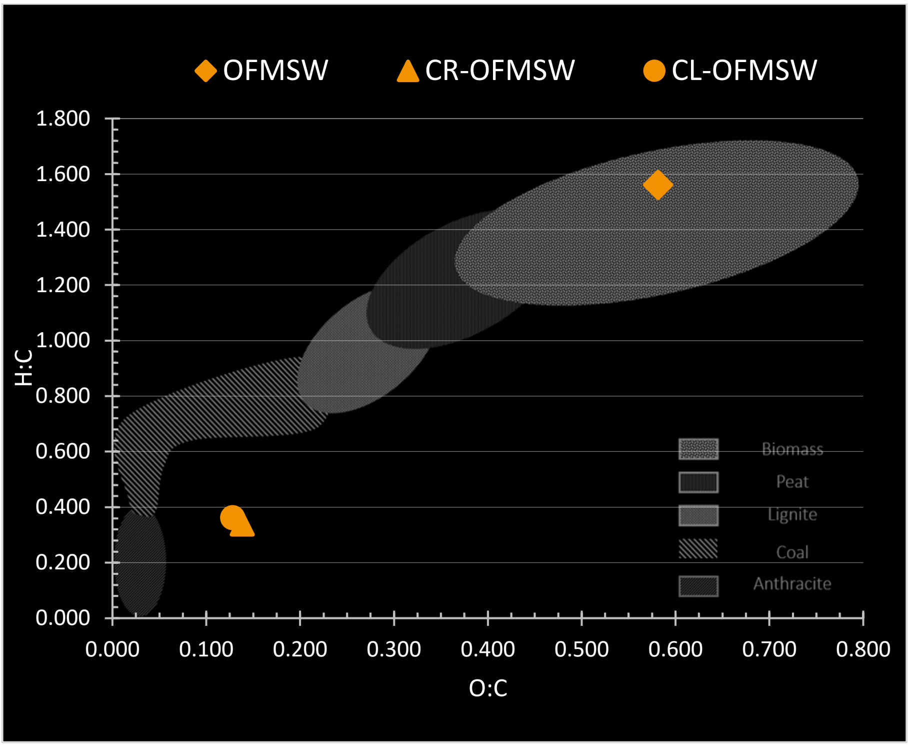


Figure 10. Classification of OFMSW, CR-OFMSW and CL-OFMSW by Van Krevelen diagram

This achievement is due to the extraction of most of inorganic elements, excluding silicon, remaining inert to the process, as shown in the below table.

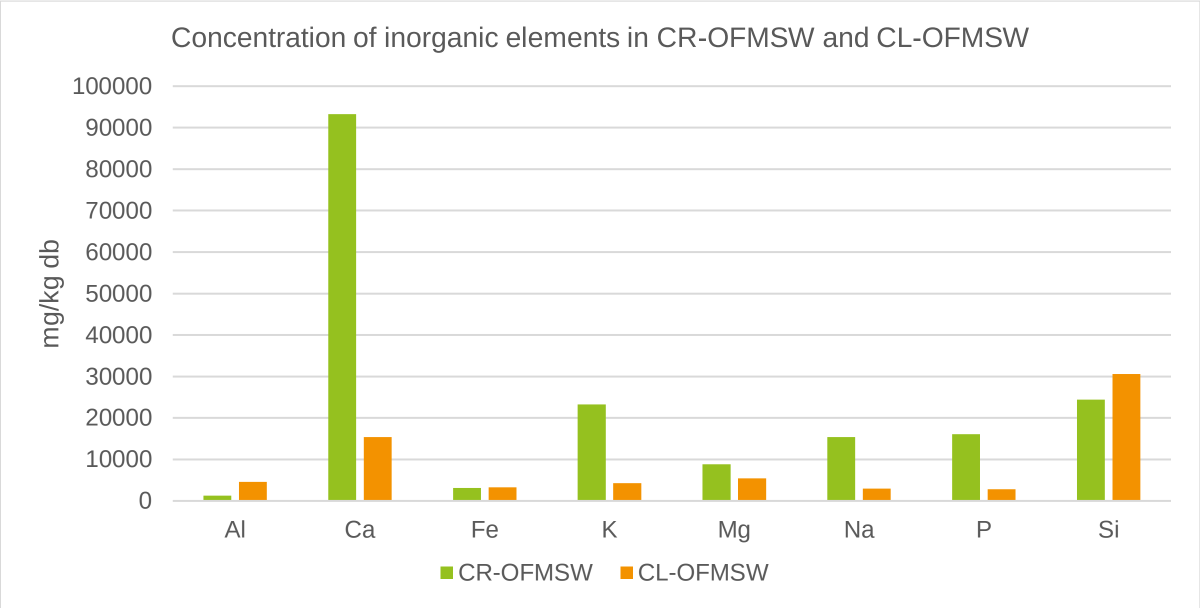
Table 21. Inorganic elements in CL-OFMSW and CR-OFMSW

Element	Unit	CR-OFMSW	CL-OFMSW
Al	ppm	1284	4611
Ba	ppm	138	226
Ca	ppm	93247	15391
Cr	ppm	48	49
Cu	ppm	96	154
Fe	ppm	3135	3309
K	ppm	23275	4259
Mg	ppm	8808	5467
Mn	ppm	375	158
Na	ppm	15427	2973
Ni	ppm	b.d.l.	b.d.l.
P	ppm	16123	2798

Pb	ppm	b.d.l.	b.d.l.
Si	ppm	24396	30574
Ti	ppm	293	374
Zn	ppm	109	52

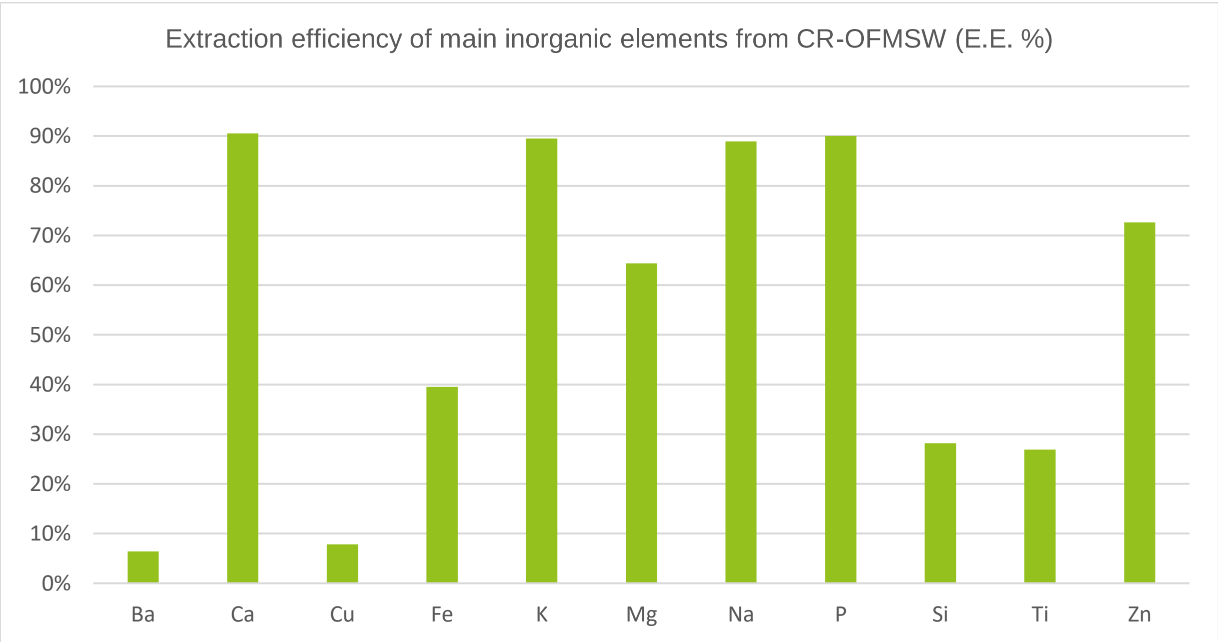
As shown in Graph 9, a strong reduction was achieved for most of the inorganic elements, such as Ca, K, Mg, Na and P. Silicon is increased in relation of the decrease of all other elements.

Graph 9. Concentration of inorganic elements in raw char and biocoal from OFMSW



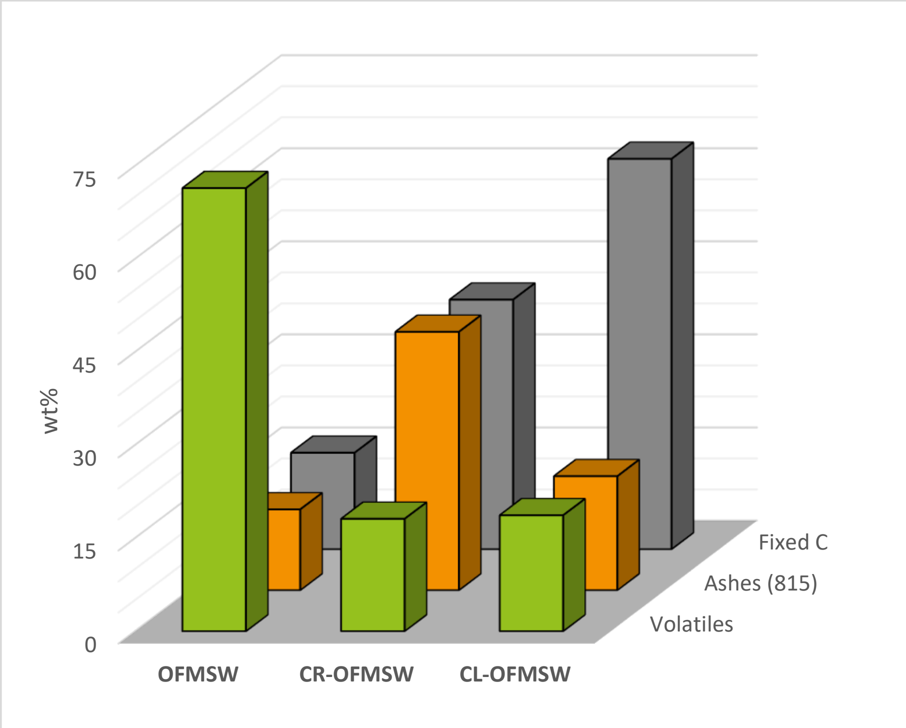
The extraction efficiency of main inorganic elements is reported in the chart below.

Graph 10. Extraction efficiency of main inorganic elements from CR-OFMSW (E.E. %)



As reported in Graph 10, an extraction efficiency of > 90 % was achieved for Ca, K, Mg, Na and P, enabling the high demineralization degree. As for other tests, low extraction is obtained for Si and Ti. A further comparison between raw material, raw char and biocoal from OFMSW is reported in Graph 11.

Graph 11. Volatiles, ash and fixed C content in OFMSW, CR-OFMSW and CL-OFMSW



The leaching process demonstrated to have a strong impact on the biocoal quality. As shown in the char, Fixed C content increased from less than 40%, to more than 60% on dry basis, whil ashes decreasede from 45 to 18 % db.

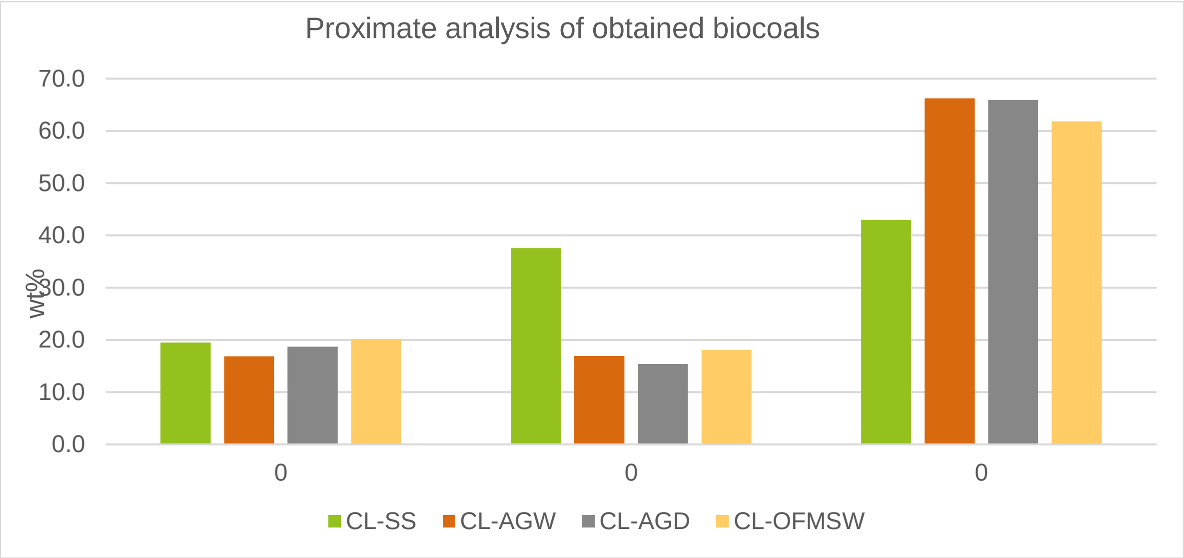
4 Discussion on tests results

The results oft he four tests showed that, when ash-rich feedstock are processed, the chemical leaching process can have a strong impact on the obtained biocoal quality. In particular, valuable biocoals, with volatile content below 20% and high stability have been obtained from all the chars processed. Moreover, the fixed carbon content increased for all products after the leaching tests.

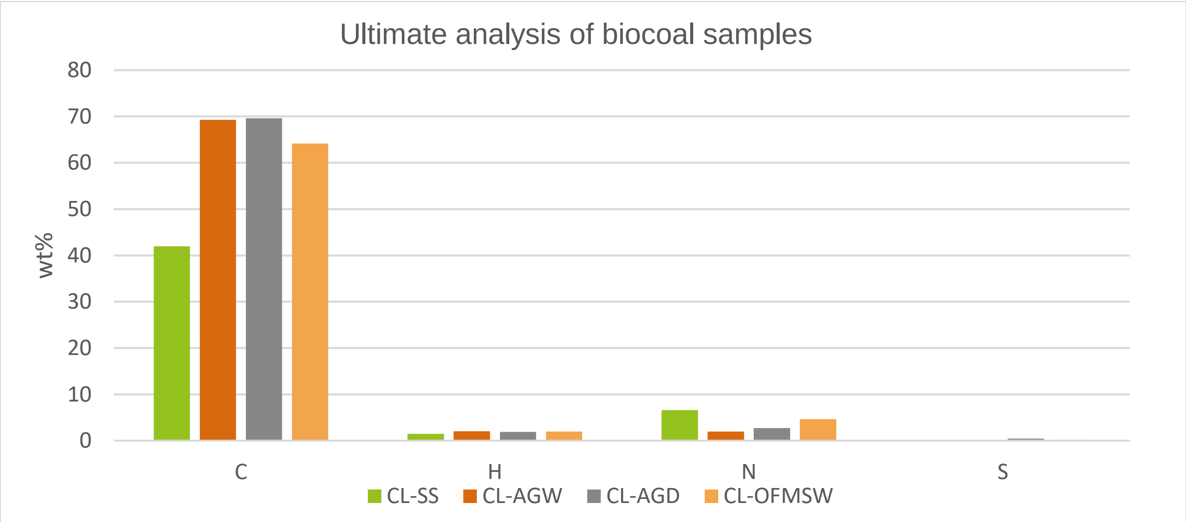
The biocoal from sewage sludge presents the higher ash content, and by consequence, the lowe Carbon and fixed carbon content. As shown in Graph 12 and Graph 13, Biocoals from AGD, AGW and OFMSW all achieved a high Fix C, above 60 %, and a low ash content (below 20% db). The total carbon content also increased to around 64-69 % for all the three feedstock, but remained low when sludge was processed.

The reason stay in the high SiO_2 content of the sludge, and on the low extraction efficiency obtained on SiO_2 with the acid leaching.

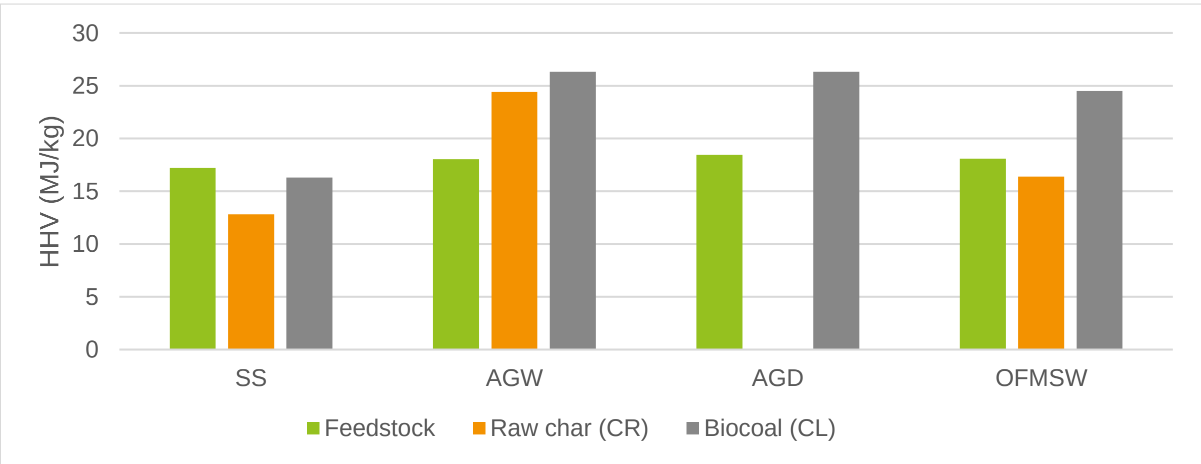
Graph 12: Proximate analysis of biocoals



Graph 13. Ultimate analysis of obtained biocoals



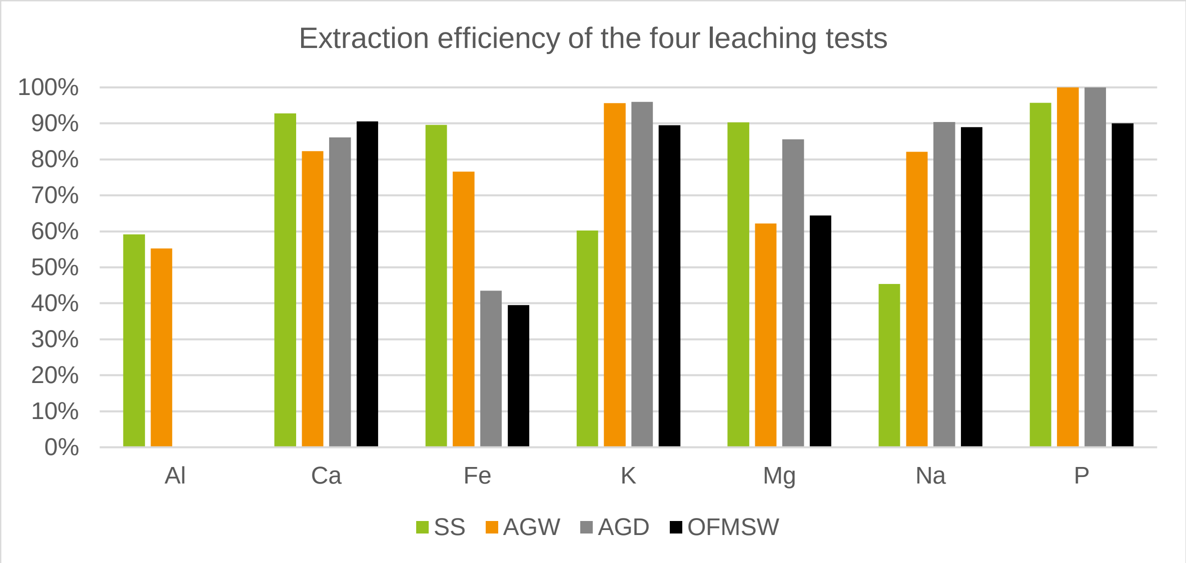
Graph 14. Calorific value oft he obtained products from the four feedstocks processed



Graph 14 shows that, in line with the carbon content, the calorific value of the biocoals increases after leaching for all the raw chars processed. In the case of sludge, due to the high ash content, the HHV is 16.2 MJ/kg, while about 25 MJ/kg are achieved for all the other samples.

Graph 15. shows that, apart when elements have found in low concentrations, such as Fe for AGD and OFMSW, similar extraction efficiency have been achieved after all tests for Ca, K, P, Fe an Na. Enabling to predict the performances of further larger scale trials.

Graph 15. Extraction efficiency of the four leaching tests



5 Conclusions

The tests showed that the chemical leaching process has relevant impact on the achievable biocoal quality, particularly for those chars obtained from high-ash materials. In the case of sludge, despite the highest ash extraction efficiency is achieved, the high SiO_2 content avoided to obtain a biocoal with high carbon content. Differently, biocoals from AGW, AGD and OFMSW present good calorific values and a carbon content in line with a coal usable in EAFs.

Starting from the mass yield of pyrolysis, the cumulative mass balance of the integrated process is similar for all the feedstock, and it starts from 21% of the OFMSW, to 28 % of the sewage sludge, with AGD and AGW showing 27% and 24% respectively.

Thanks to the leaching process, even in the case of low C biocoal obtained from sludge, many harmful inorganics are removed from the char, leaving mainly silicates. Therefore, the applicability as coal substitute could be feasible for all, by adapting the required quantity.

Small scale tests are ongoing in small furnaces to assess the usability of all the produced biocoals, so that to select the two feedstocks, or a mixture to be processed at large scale in the rotary kiln.

6 References

[1] S. Behera, U. Kumari, and B. Meikap, “A review of chemical leaching of coal by acid and alkali solution,” *Journal of Mining and Metallurgy A: Mining*, vol. 54, no. 1, pp. 1–24, 2018, doi: 10.5937/JMMA1801001B.

[2] H. Dhawan and D. K. Sharma, “Advances in the chemical leaching (inorgano-leaching), bio-leaching and desulphurisation of coals,” *Int J Coal Sci Technol*, vol. 6, no. 2, pp. 169–183, 2019, doi: 10.1007/s40789-019-0253-6.

[3] S. Behera, U. Kumari, and B. Meikap, “A review of chemical leaching of coal by acid and alkali solution,” *Journal of Mining and Metallurgy A: Mining*, vol. 54, no. 1, pp. 1–24, 2018, doi: 10.5937/jmma1801001b.