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Co-combustion of coal and sewage sludge: Chemical and ecotoxicological properties of ashes

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ABSTRACT

The co-combustion of sewage sludge (SS) and coal is widely used for the treatment and thermal valorization of SS produced in wastewater treatment plants. The chemical and ecotoxicological properties of the ashes produced in this thermal treatment have not been fully studied. Two combustion tests were performed in a fluidized bed combustor. Colombian coal was used as fuel in test A. A blend (1 + 1) of this coal and a stabilized SS (Biogran®) was used in a second test B. Samples of the bottom and fly ashes trapped in two sequential cyclones were collected. The characterization of the ashes was focused on two main aspects: (1) the bulk content of a set of metals and (2) the characterization of eluates produced according to the European Standard leaching test EN 12457-2. The eluates were submitted to an ecotoxicological characterization for two bio-indicators. In what concerns the bulk content of ashes, both combustion tests have produced ashes with different compositions. The ashes formed during the co-combustion test have shown higher concentrations of metals, namely Cr, Cu, Ni, Pb, Zn and Fe for all ashes. The leaching test has shown low mobility of these elements from the by-products produced during the combustion and co-combustion tests. Cr and Cr(VI) were mainly detected in the eluates of the 1st cyclone ashes produced in both combustion tests and in the 2nd cyclone ashes produced in the co-combustion test.

Considering the ecotoxicity assays, the eluates of bottom and fly ashes for both combustion and co-combustion tests have shown low ecotoxic levels. The micro-crustacean *Daphnia magna* was generally more sensitive than the bacterium *Vibrio fischeri*. CEMWE criterion has allowed to classify the bottom ashes for both combustion and co-combustion tests as non-toxic residues and the fly ashes collected in both cyclones as toxic.

1. Introduction

The high amounts of sewage sludge (SS) produced in wastewater treatment plants poses a problem related with its final destination. According to the European Commission [1], the production of SS (dm), in Europe, was of 5.5 million t in 1992. Muller et al. [2] referred a European production of SS of about 9 million t (dm), in 2005. This increase was due to the progressive implementation of the Urban Wastewater Treatment Directive (Directive 91/271/EC). Düring and Gäth [3] stated that the production of SS in USA was of 7.5 million t in 2005.

In the past, SS was mainly disposed off in landfills. This strategy is no longer possible, due to the limitation imposed by the European Landfill Directive. One of the possible routes for the treatment and valorization of SS is its use as a fuel for energy production through combustion or co-combustion. This contributes for the biological stabilization of SS, for its volume reduction and for the decrease on the need of fossil fuels for power production [4–6]. According to Leckner et al. [7], the high content of organic matter in SS has promoted its use in the co-combustion processes for the production of energy. Nevertheless, the SS is characterized by a high moisture content, which imposes the adoption of a pre-treatment prior to their use in thermal processes. The SS can therefore be converted in waste derived fuels (WDF), which is easier to be handled, due to its homogeneity and low moisture content.

The thermal valorization of any type of organic material leads to the production of different ashes, which are not chemically stable. The ashes produced during the co-combustion of coal with SS should be carefully studied, since the substitution of coal by SS can produce ashes with high content of heavy metal, as it was demonstrated by several authors [8–10]. Miller et al. [8] have studied the trace element emissions from the co-combustion of coal and waste secondary fuels in a bench scale fluidized bed combustor. Among the wastes used, SS was used too. The trace elements have been ranked based on their average retention in combustion ashes. Cd and Hg were reported to be potentially problematic trace elements

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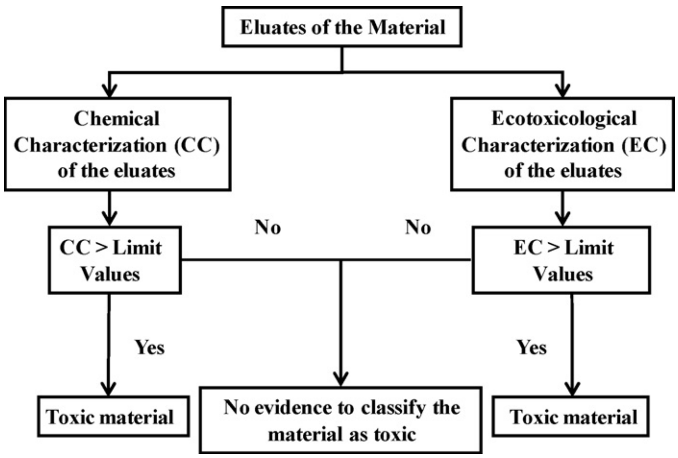

Fig. 1. Conceptual model for the classification of the bed material, fuels and ashes produced in the combustion and co-combustion tests (adapted from CEMWE [15]).

when the SS was used as a secondary fuel. The injection of SO_2 has increased the retention of Hg by ash, but caused a decrease of Cd retention. Later on, Miller et al. [9] have studied the co-combustion of SS with coal emphasizing the behavior of the most harmful metals in the raw fuels. In this study, the authors have concluded that the addition of SS to coal has conducted to increased losses of Cd and Hg from the system, due to their higher content in the raw sludge. Nevertheless, some benefits have been observed in the retention of As, Pb and Se, in the assays where the addition of SS was performed. Lopes et al. [10] have studied the combustion of granular dried SS on a fluidized bed pilot system, under mono-combustion and co-combustion conditions with coal. The authors found that the mineral matter of SS was essentially retained in the bottom ashes. During the mono-combustion of SS, the production of fine ashes was reduced, but it was high during the co-combustion with coal, due to the tendency of coal to produce fine ashes. The degree of volatilization of metals was slightly higher during the co-combustion trials. However, most of the metals were retained in the ashes and their emissions in the flue gases were low. In terms of the leachability, Lopes et al. [10] have found that the release of organic metals and heavy metals present in the sludge was very low from bed ashes, which were considered as non-ecotoxic materials. Cyclone ashes seemed to be more problematic due to the high pH values and contamination with steel corrosion products. Due to their properties, the reuse of these ashes needs a previous evaluation of their chemical and ecotoxic properties [11,12,10,13,14].

The evaluation of the toxic properties of the ashes can be based on the "Criterion and Evaluation Methods for Waste Ecotoxicity" (CEMWE) [15]. The CEMWE methodology shown in Fig. 1 was adapted according to the model shown in Lapa et al. [12,13] and Barbosa [16]. The CEMWE criterion is a French proposal to classify hazardous wastes under the H14 criterion according to the Council Directive 1991/689/EEC.

The main aim of this work is to understand the effect of the partial substitution of coal by sewage sludge in the quality of the by-products (bottom ashes and fly ashes) produced in a fluidized bed combustor. To achieve this aim, a comparative study on the chemical composition and the ecotoxic level of these by-products was performed.

2. Experimental

2.1. FBC, fuels and combustion conditions

The combustion and co-combustion tests were performed in a bubbling fluidized bed combustor (Fig. 2) of INETI/DEECA. The combustor has an internal square section of 0.3 m × 0.3 m and 5 m height. The internal chamber is made of refractory steel (AISI 310). Further details were shown in Lapa et al. [13].

Table 1
Proximate analysis of the fuels used in the combustion and co-combustion tests.

Parameter	Bituminous coal	Biogran®
Moisture content (wt% db)	1.6	6.6
Volatile content (wt% db)	37.8	49.8
Ashes (wt% db)	7.5	42.8
Fixed carbon (wt% db)	54.7	7.4
LHV (MJ/kg)	24.8	13.1

wt: weight; db: dry basis.

The bottom ashes are collected at the bottom of the combustor and the fly ashes are collected by two containers located at the bottom of each cyclone.

The bed material used was sand, which was collected on a river and submitted to a washing process with tap water.

The fossil fuel used was bituminous coal from the Colombian mine of El Cerrejón with a lower heat value (LHV) of about 24.8 MJ/kg.

The renewable co-fuel used as a WDF in the co-combustion test was the soil conditioner known as Biogran®. This material is produced through the anaerobic digestion and thermal treatment of SS coming from urban wastewater treatment plants. The digested sludge is submitted to a screening process and centrifuged up to a level of 30% total solids (wt db). The solid material produced is then submitted to a thermal drying process, at a temperature of 400 °C, for about 30 min. The final material has a dry mass of about 95% and is made up of particles of 2–4 mm. The LHV of Biogran® was of 13.1 MJ/kg.

Tables 1 and 2 show the results obtained in the proximate and ultimate analysis of the bituminous coal and Biogran®.

The combustion tests were performed according to Table 3. The mono-combustion test (test A) was performed with the bituminous coal and the co-combustion test (test B) was performed with a blend of the bituminous coal and Biogran® (1 + 1 w/w). The average temperatures in the 1st and 2nd cyclones were of 300 and 150 °C, respectively.

The fuel/sand ratio was similar in both combustion tests (2.7 and 2.5 in the tests A and B, respectively). The average fuel feeding rate was higher in test B, because of the low LHV of Biogran®.

2.2. Particle size distribution

The as-received ashes were sieved through DIN ISO sieves of 10, 40, 200 and 500 μm. The sieving process was performed in a Retsch vibrator. Each fraction retained in each sieve was weighed.

Table 2
Ultimate analysis of the fuels used in the combustion and co-combustion tests.

Element (wt% db)	Bituminous coal	Biogran®
C	79.1	30.9
H	5.0	3.8
N	1.8	3.7
Cl	0.06	0.07
F	<0.01	<0.01
S	2.15	0.96
P	0.51	3.11
Ca	0.20	5.3
K	0.04	0.6
Na	0.03	0.2
Mg	0.02	0.5
Si	1.8	7.1

wt: weight; db: dry basis.

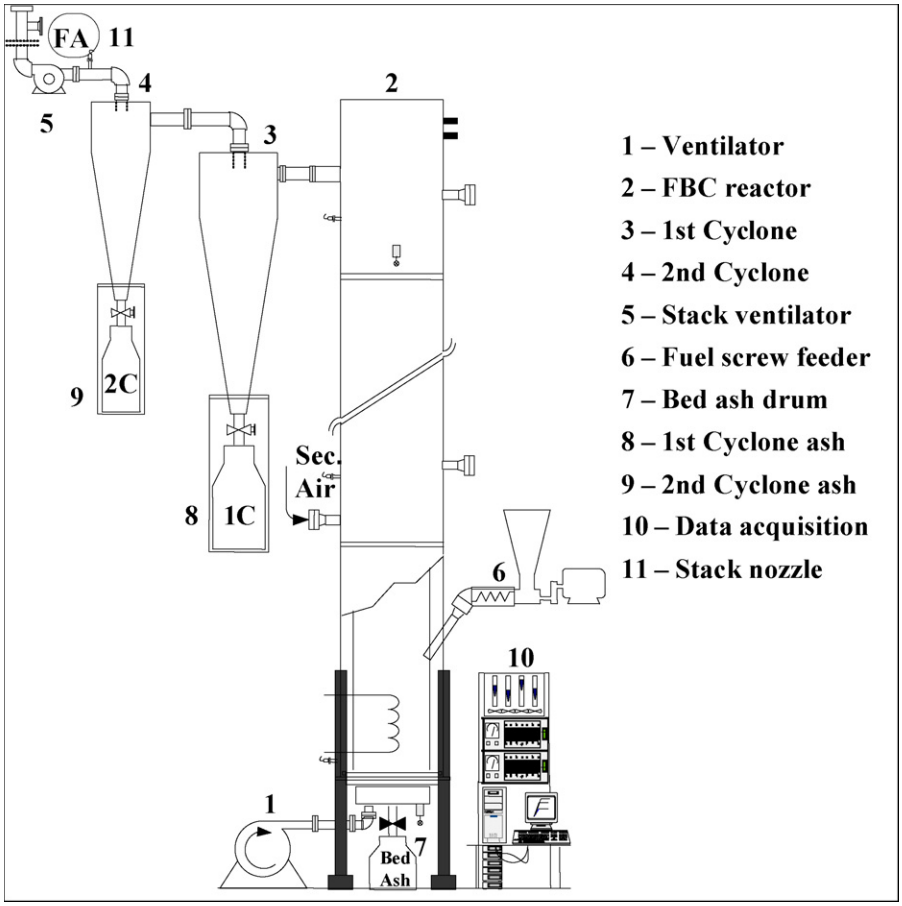

Fig. 2. Diagram of the bubbling fluidized bed combustor of INETI/DEECA.

2.3. *Bulk characterization of fuels, sand and ashes*

All samples were submitted to an acidic digestion with 10 mL of HNO_3 65% (v/v) for 0.25 g sample. The digestion was performed in closed vessels in a microwave digester (Milestone, Ethos 1600) for 20 min: 250 W – 5 min; 350 W – 5 min; 400 W – 5 min; 250 W – 5 min (USEPA 3051A method). The acidic eluates were filtered through fiber glass filters (Schleicher & Schuell) and the following chemical elements were analyzed: As (EN ISO 11969, 1996), Hg (ISO 5666/1, 1983), Cd, Cu, Ni, Pb and Zn (ISO 8288, 1996), Al (AAS flame quantification after reaction with 8-hydroxyquinoline and extraction with MIBK – APHA et al., 1996), Fe (AAS flame quantification – APHA et al., 1996) and Cr (AAS flame quantification/Method A – ISO 9174, 1990). These elements were selected because: (a) they are present in the fuels used in the combustion and co-combustion tests; (b) they contribute for the contamination of the by-products of the combustion processes; (c) they represent a risk to the environment; and (d) they are highlighted in the European Union (EU) legislation and in several regulations of EU member states.

2.4. *Leaching test*

Sand, coal, Biogran®, bottom and fly ashes were submitted to the leaching test described in the European Standard number EN 12457-2. The samples were mixed with de-ionised water in a single-stage batch test performed at a liquid-to-solid (L/S) ratio of 10 L/kg (20 ± 2 °C).

The glass bottles (Schott) were shaken in a roller-rotating device at 10 rpm (24 ± 0.5 h). The eluates were filtered in a nitrate-cellulose membrane with a porosity of 0.45 μm. The filtered eluates were divided into sub-samples and each one was preserved according to the chemical species to be analyzed (ISO 5667-3, 1985). One of the sub-samples was preserved at a temperature below 4 °C, in gas tight vessel, for a period no longer than 48 h up to the biological assays.

The eluates were characterized for: pH (ISO 10523, 1994), conductivity (ISO 7888, 1985), chemical oxygen demand (COD) (ISO 15705, 2002), phenol index (ISO 6439, 1990), free cyanides (ISO 6703/2, 1984), total dissolved solids (TDS) (gravimetric method – APHA et al., 1996), Cr(VI) (NF T90-043, 1988), As (EN ISO 11969, 1996), Hg (ISO 5666/1, 1983), Cd, Cu, Ni, Pb and Zn (ISO 8288, 1996), Al (AAS flame quantification after reaction with 8-hydroxyquinoline and extraction with MIBK – APHA et al., 1996), Fe (AAS flame quantification – APHA et al., 1996) and Cr (ISO 9174, 1990).

The eluates were also characterized for the following ecotoxic parameters: (a) luminescence inhibition of the bacteria *Vibrio fischeri* (Microtox® system, Azur Environmental) (ISO 11348-3, 2003)

Table 3
Experimental conditions of the combustion and co-combustion tests.

Test	Fuel	Mass of fuel (kg)	Mass of sand (kg)	Combustion temperature (°C)	Combustion duration (min)	Fuel feeding rate (g/min)
A	Bituminous coal	46.3	17.0	850	306	151.3
B	Bituminous coal + Biogran®	25.1 + 25.1	19.9	850	270	185.9

Table 4
Bulk characterization of the sand and fuels used in the combustion and co-combustion tests (mg/kg db).

Material	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Al
Sand	3.0	<2.7	<12.1	<9.9	0.03	<15.2	<24.2	9.2	15.5	185
Bituminous coal	4.6	<18.1	<28.2	<23.1	6.8	<35.5	<56.4	74.4	11,183	9,982
Biogran®	3.1	<17.2	78.9	417	4.2	<33.8	277	1,471	10,108	13,817

db: dry basis.

and (b) mobility inhibition of the crustacean *Daphnia magna* (Daphtoxkit F magna™ of Microbiotests Company).

3. Results and discussion

3.1. Particle size distribution

The ashes collected in both combustion tests were similar in what concerns the particle size distribution:

(a) Fly ashes:
 (i) 1st cyclone – 70 wt% of the ashes retained in the 1st cyclone had a dimension ≤40 μm (wt) and 30 wt% had a dimension of 40–200 μm;
 (ii) 2nd cyclone – 82 wt% of the ashes trapped in the 2nd cyclone had a dimension ≤10 μm and 18 wt% had a dimension of 10–40 μm.
(b) Bottom ashes: 55 wt% had a dimension ≤200 μm and 35 wt% had a dimension of 200–500 μm.

3.2. Bulk characterization of fuels, sand and ashes

Table 4 shows the results obtained in the bulk characterization of the sand and fuels. It is possible to observe that the concentration of metals in the sand was much lower than in both fuels, and it was generally higher in the Biogran® than in the coal. The highest concentrations of Hg and As were observed in the coal.

Table 5 shows the results of the bulk characterization of the bottom and fly ashes. The ash samples are identified by an alphanumeric code: the letter identifies the combustion test and the number identifies the origin of the ash (#1 – bottom ashes; #2 and #3 – fly ashes collected in the 1st and 2nd cyclones, respectively).

Fe and Al have shown the highest concentrations in the ashes. These two metals can be classified as major elements [17]. The other metals were classified as minor or trace elements in the ashes. The results also indicate that there is a tendency for the accumulation of metals in the fly ashes, namely in the ashes collected in the 2nd cyclone, which can be attributed to the lower particle size of ashes retained in this cyclone, as stated by Miller et al. [18] and Van de Velden et al. [19].

Both combustion tests have produced ashes with different compositions. The ashes formed during the co-combustion test have shown higher concentrations of metals. Comparing with the fly ashes, the bottom ashes collected in both combustion tests have shown the lowest concentrations of Cr, Cu, Ni, Pb, Zn and Fe.

Concerning the ashes collected in the 1st cyclone, the differences between the concentrations were more significant for the parameters Cu, Hg, Pb and Zn. The ashes collected in the combustion test A have shown lower concentrations of these metals. In what concerns the ashes from the 2nd cyclone, the same pattern in their composition was observed.

These differences can be attributed to the composition of the fuels. The metals present in higher concentrations in the treated sewage sludge have generally promoted higher concentrations in the ashes formed during the co-combustion test.

3.3. Chemical characterization of eluates

Table 6 shows the results of the chemical characterization of the eluates of the sand, coal, Biogran®, bottom and fly ashes.

The Biogran® has shown the highest concentrations of TDS, COD, phenol index and free cyanides.

The bottom ashes (A1 and B1) were characterized by the high pH values of the eluates, which can be explained by the presence of oxides that produce hydroxides during the leaching test. The eluates produced by the ashes collected in the 2nd cyclone (A3 and B3) have shown lower pH values than the eluates of the ashes collected in the 1st cyclone. According to Lopes [20], this fact can be explained by the presence of acidic condensates in the 2nd cyclone of the FBC.

In the eluates of the ashes resulting from the co-combustion test, higher values of COD were observed than in the eluates of the ashes resulting from the combustion of coal. This fact can be related with the higher COD values of the Biogran® when compared with the bituminous coal. A higher combustion temperature and a higher time of residence of the fly ashes in the combustion chamber could be necessary to promote a more complete conversion of the organic matter present in the Biogran® to CO_2.

Regarding the free cyanides and phenol index, it was observed a significant reduction in the release of these compounds from the bottom and fly ashes when compared to the Biogran®. This fact can be related with the complete thermo-chemical conversion of these compounds during co-combustion test.

Table 5
Bulk characterization of the bottom and fly ashes collected during the combustion and co-combustion tests (mg/kg db).

Element	Combustion test A			Combustion test B		
	Bottom ash (A1)	1st cyclone ash (A2)	2nd cyclone ash (A3)	Bottom ash (B1)	1st cyclone ash (B2)	2nd cyclone ash (B3)
As	<0.78	6.2	2.9	3.1	5.0	5.3
Cd	<7.8	<15	<7.2	<7.9	<12	<11
Cr	21	409	151	159	466	336
Cu	<10	71	72	123	329	473
Hg	7.4	0.84	2.4	5.0	7.4	4.8
Ni	<15	179	131	97	282	305
Pb	<24	<47	<23	64.0	251	360
Zn	73	338	362	413	1,211	1,583
Fe	2,462	23,952	21,405	4,871	26,125	31,754
Al	6,333	34,434	38,088	6,067	33,607	47,784

db: dry basis.

Table 6
Chemical characterization of the eluates of the sand, coal, Biogran®, bottom and fly ashes produced in the combustion and co-combustion tests.

Combustion test	Sample	Parameter						
		Moisture content (wt% db)	pH	Conductivity (μS/cm)	TDS (mg/kg db)	COD (mg/kg db)	Phenol index (mg/kg db)	Free cyanides (mg/kg db)
n.a.	Sand	0.03	8.9	3.8	11,542	<97	0.70	<0.10
n.a.	Coal	7.6	3.6	878	8,985	321	<0.54	<0.14
n.a.	Biogran®	8.1	7.5	1,288	50,847	56,514	12	1.2
A	A1	0.04	11	177	1,781	99	<0.50	<0.13
	A2	4.5	7.6	1,660	20,619	97	<0.52	<0.14
	A3	5.1	6.8	1,472	23,511	97	<0.53	<0.14
B	B1	0.09	10	375	3,765	165	<0.50	<0.13
	B2	2.4	8.3	1,310	17,298	102	1.4	<0.13
	B3	2.9	7.3	1,348	16,623	102	<0.52	<0.13

wt: weight; db: dry basis; n.a.: not applicable.

It was also observed a higher content of TDS in the eluates of the fly ashes when compared with the bottom ashes. As a consequence, higher conductivity values were observed in the eluates of these ashes. This can be attributed to the retention of particles containing higher levels of salts (chlorides and sulfates) in the fly ashes.

Table 7 shows the concentration of metals in the eluates of the sand, coal, Biogran® and ashes.

In the eluate produced by the sand it was possible to quantify As, with a relatively high content. This value might indicate that a significant part of this element is not strongly bounded to the matrix of this material. In the eluate produced by the coal it was possible to detect Ni, Zn and Fe. The solubility of Zn and Ni was particularly high. Based on the data reported by Chandler et al. [17] and Dijkstra et al. [21], the high solubility rate of these elements might be due to the reduced pH level of the eluate. Ni shows increasing solubility with decreasing pH, reaching a maximum solubility at a pH less than 7. In the pH range below 6, the leachability of Zn reflects the amount available for leaching with a maximum level between pH 4 and 5.

The eluate of Biogran® has shown high concentrations of metals. Cr, Cr(VI), Cu, Ni, Zn and Fe were detected in the eluate of this co-fuel. Since the eluate of Biogran® was characterized by high concentrations of COD and TDS (Table 4), the release of Ni and Cu might be due to the presence of dissolved organic matter (DOC) [17,22]. Leachable Cu is fractioned in labile DOC, like low molecular weight organic acids and more stable DOC complex [22] and Ni form strong complexes with DOC [17].

Cr and Cr(VI) were detected in the eluates of the 1st cyclone ashes produced in both combustion tests and in the 2nd cyclone ashes produced in the co-combustion test. The high concentration of Cr in the ashes produced in the co-combustion test might be explained by two main reasons: (i) the higher concentration of Cr in Biogran®, when compared to coal; and (ii) the slightly acidic pH values of the eluates of fly ashes. Materials with Cr in their matrices that produce acidic eluates are characterized by high release rates of Cr. The solubility of this metal decreases as the pH increases up to the point of neutrality and is independent of the pH for alkaline values, as stated by Chandler et al. [17] and van der Sloot [22].

Zn leaching did not seem to be related with its concentration in the matrices of fly ashes. This behavior might indicate that the Zn is associated to different compounds, which are characterized by different solubility rates [17]. The high concentrations of Zn in the eluates of the ashes collected in the 2nd cyclone may be attributed to the pH values of the eluates which were close to the neutrality or slightly acidic [21]. The pH value could be also an inducer of the high solubility of Ni in the eluates of the ashes of the 2nd cyclone.

3.4. Chemical Index

All materials were ranked according to a Chemical Index based on the composition of the eluates and the limit values defined in CEMWE. This Chemical Index was established in accordance with the following steps:

(a) Toxicity Equivalent (TE) – TE values were calculated through the conversion of each limit value indicated in the CEMWE from mg/L to μmol/L, as follows:
   [μmol chemical species/L] = $A/M \times 1000$, in which "A" indicates the concentration limit value of the chemical species, defined in CEMWE, expressed in mg/L and M is the atomic weight of the chemical species, expressed in g/mol.
   Example for As: [μmol As/L] = 0.05 (mg As/L)/M(As) × 1000 = 0.67, in which "0.05 mg As/L" is the limit of As defined in the CEMWE and "M" is the atomic weight of As, expressed

Table 7
Concentration of a set of metals on the eluates produced by the sand, coal, Biogran® sludge and by the ashes produced in the combustion tests.

Combustion test	Sample	Parameter (mg/kg db)										
		As	Cd	Cr	Cr(VI)	Cu	Hg	Ni	Pb	Zn	Fe	Al
n.a.	Sand	0.44	<0.32	<0.50	<0.50	<0.41	<0.01	<0.63	<1.0	<0.13	<0.60	<3.4
n.a.	Coal	<0.04	<0.35	<0.54	<0.54	<0.44	<0.01	2.3	<1.1	8.9	6.1	<3.7
n.a.	Biogran®	<0.04	<0.35	1.5	1.0	4.1	<0.01	2.9	<1.1	2.4	3.9	<3.7
A	A1	<0.03	<0.32	<0.50	<0.50	<0.41	<0.01	<0.63	<1.0	<0.13	<0.60	11
	A2	<0.03	<0.34	1.7	1.3	0.89	<0.01	<0.66	<1.0	0.73	<0.63	<3.6
	A3	<0.03	<0.34	<0.53	<0.53	<0.43	<0.01	5.3	<1.1	7.8	<0.63	<3.6
B	B1	<0.03	<0.32	1.3	0.83	<0.41	<0.01	<0.63	<1.0	<0.13	3.3	14
	B2	<0.03	<0.33	15	11	<0.42	<0.01	<0.64	<1.0	<0.13	<0.60	10
	B3	<0.03	<0.32	20	12	<0.42	<0.01	2.7	<1.0	0.38	<0.60	<3.5

db: dry basis; n.a.: not applicable.

Table 8
Ecotoxicological characterization of the eluates of sand, coal, Biogran® and ashes produced in the combustion and co-combustion tests by using the indicators *Vibrio fischeri* and *Daphnia magna*.

Test	Material	*V. fischeri*		*D. magna*	
		EC_{50} 30 min (% v/v)	Toxicity Units (TU)	EC_{50} 48 h (% v/v)	Toxicity Units (TU)
n.a.	Sand	>99.0	<1.0	>95.0	<1.1
n.a.	Coal	47.8	2.1	16.2	6.2
n.a.	Biogran®	88.1	1.1	15.9	6.3
A	A1	47.3	2.1	>95.0	<1.1
	A2	>99.0	<1.0	42.5	2.4
	A3	>99.0	<1.0	>95.0	<1.1
B	B1	>99.0	<1.0	44.9	2.2
	B2	>99.0	<1.0	57.6	1.7
	B3	>99.0	<1.0	66.5	1.5

n.a.: not applicable.

in g/mol. The limit value of As in μmol/L is therefore 0.67.
It was calculated the ratio between the limit value of the most hazardous parameter, i.e., the parameter with the lowest limit value, and the limit value for each parameter, as follows: *C*(ht)/*C*(chemical species), in which *C*(ht) represents the limit concentration of the parameter with the highest toxicity, i.e., the lowest limit value expressed in μmol/L, and *C*(chemical species) the limit concentration of the chemical species, expressed in μmol/L.
The most hazardous parameter is Hg, since it is the element with the lowest limit expressed in μmol/L (0.25 μmol/L).
Example for As: TE of As is (0.25 μmol/L)/(0.67 μmol/L) = 0.373.
The following parameters were considered for the calculation of the Chemical Index: As, Cd, Cr, Cr(VI), Cu, Hg, Ni, Pb, Zn, free CN– and phenol compounds.

(b) Relative Toxicity (RT) – RT values of each chemical parameter were calculated through the multiplication of TE values by the concentration of each chemical parameter, as follows:
TE(chemical species) × *C*(chemical species), in which TE(chemical species) is the Toxicity Equivalent of the chemical species and *C*(chemical species) is the concentration of this chemical species in the eluate, expressed in mg/L.
Example for As in what concerns bottom ash A1: TE(As) × *C*(As) = 0.373 × 0.0032 mg/L = 0.0012 mg As/L.

(c) Toxicity Level (TL) – TL values of each sample were calculated through the sum of the RT values.
TL(Mat) = RT(As) + RT(Cd) +···+ RT(Phenolic compounds).
Example for As in what concerns bottom ash A1: TL values for bottom ash A1: "RT(As)" + "RT(Cd)" +···+ "RT of Phenol compounds" = 0.0012 + 0.0045 + ··· + 0.0117. The TL of A1 is 0.04.

Fig. 3 shows the TL values of the sand, fuels and ashes. From the chemical point of view, the Biogran® had shown the highest TL value among the materials analyzed. TL values of the coal and sand were similar. TL value of the sand was mainly due to the concentration of As in its eluate, while for coal, the TL value was due to the presence of Zn and Ni in its eluate.

The fly ashes produced in the combustion test had shown lower TL values than the fly ashes produced in the co-combustion test, which have presented higher concentrations of Cr and Cr(VI) in the ashes of both cyclones, and Ni in the ash trapped in the 2nd cyclone.

The bottom ashes produced in both combustion tests have not shown significantly different TL values.

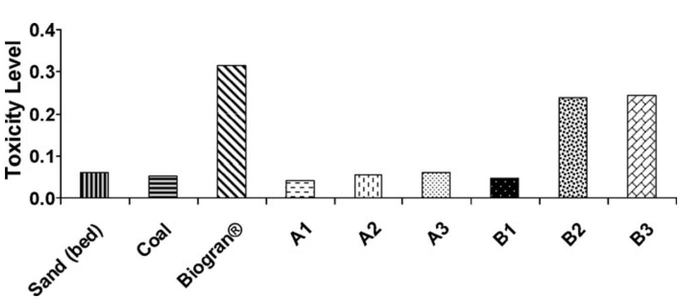

Fig. 3. TL values of the sand, fuels and ashes collected in combustion and co-combustion tests.

3.5. Ecotoxic levels

The ecotoxic levels of the eluates of sand, fuels and ashes are shown in Table 8. The values of the Toxicity Units (TU) were calculated as follows: $TU = 100/EC_{50}$.

The micro-crustacean *D. magna* was generally more sensitive than the bacterium *V. fischeri*. The higher sensitivity of the *D. magna* may be explained by its higher sensitivity to pH. The study of the effect of the pH to bio-indicators and its relation with metals present in the eluates has been discussed by different authors [13,16,23,24]. These authors have referred that, apart from the direct effect of pH, this parameter affects the concentration in solution due to precipitation and the speciation of metals. More studies are, therefore, needed.

The sand did not show significant ecotoxic levels for both bio-indicators, and the higher ecotoxic levels were detected in the eluates of coal and Biogran®. The eluates of bottom and fly ashes for both combustion and co-combustion tests have shown low ecotoxic levels.

3.6. Toxic classification of sand, fuels and ashes

The concentrations of the chemical parameters shown in Tables 6 and 7 were compared with the limit values defined in CEMWE (Table 9). The toxic classification of the sand, fuels and ashes was performed according to the methodology shown in Fig. 1.

The eluates of the sand and coal did not show any concentration above the limit values defined in CEMWE. The eluate of the Biogran® has shown levels of free cyanides and phenol compounds above the limit values defined by the French Regulation. Therefore, from the chemical point of view, the sand and coal were classified as non-toxic materials, while the Biogran® was classified as a toxic material.

The bottom ashes produced in both combustion tests have shown concentrations of all chemical parameters below the limit values indicated in CEMWE. Therefore, from the chemical point of view, the bottom ashes were classified as non-toxic materials.

Table 9
Limit values defined in the CEMWE for chemical and ecotoxicological parameters.

Chemical parameters (mg/L)										
As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Cr(VI)	CN^-	Phenol. comp.
0.05	0.2	0.5	0.5	0.05	0.5	0.5	2.0	0.1	0.1	0.1
Ecotoxicological parameters (% v/v)										
Vibrio fischeri			10							
Daphnia magna			10							

From the chemical point of view, the combustion test in which only bituminous coal was used has produced fly ashes with toxic properties, since the eluates produced by the ashes collected in the 1st and 2nd cyclones have shown concentrations of Cr(VI) and Ni, respectively, above the limit values defined in CEMWE.

The co-combustion of coal and Biogran® has also produced toxic fly ashes, due to the concentrations of Cr, Cr(VI) and phenol compounds in the ashes of the 1st cyclone and the concentrations of Cr and Cr(VI) in the ashes of the 2nd cyclone.

Based on the ecotoxic levels of the eluates, determined for the organisms *V. fischeri* and *D. magna* (Table 8), and taking into account the limit values defined in CEMWE (Table 9), for these bio-indicators, none of the materials have shown toxic properties.

Taking into account, both the chemical and the ecotoxicological characterization, the ashes must be classified as follows:

(a) Bottom ashes: non-toxic residues for both combustion tests.
(b) Fly ashes from the 1st cyclone: toxic residues for both combustion tests.
(c) Fly ashes from the 2nd cyclone: toxic residues for both combustion tests.

4. Conclusions

The use of the thermal treated sewage sludge (Biogran®) as a co-fuel has promoted differences in the composition of the ashes when compared with those produced during the combustion of coal. Bottom and fly ashes formed during the co-combustion test have shown higher concentrations of metals, namely Cr, Cu, Ni, Pb, Zn and Fe.

For combustion and co-combustion tests, it was observed higher concentrations of metals in the fly ashes, especially in those collected in the 2nd cyclone, than in the bottom ashes present in the bed material.

The leaching test has shown low mobility of metals from the by-products produced during the combustion and co-combustion tests. Mainly, Cr and Cr(VI) were detected in the eluates of the ashes of the 1st cyclone produced in both combustion tests and in the ashes of the 2nd cyclone produced in the co-combustion test.

According to the Chemical Index proposed, Biogran® was the material that has reached the highest value for this index (0.31), meaning this was the material with the highest toxicity level concerning the chemical composition of the eluates produced. The use of this thermal treated sewage sludge has caused higher Chemical Index values of the fly ashes collected in both cyclones, produced during the co-combustion test. The Chemical Index of the fly ashes produced in the combustion test was very similar, like the Chemical Index of the fly ashes produced in the co-combustion test. The Chemical Index has increased from 0.06 (average value of the Chemical Index of the fly ashes produced in the combustion test) to 0.24 (average value of the Chemical Index of the fly ashes produced in the co-combustion test).

Considering the ecotoxicity assays the eluates of bottom and fly ashes for both combustion and co-combustion tests have shown low ecotoxic levels. The micro-crustacean *D. magna* was generally more sensitive than the bacterium *V. fischeri*. The French Regulation CEMWE has allowed achieving similar conclusions when compared with the Chemical Index proposed. According to CEMWE, the Biogran® and fly ashes were classified as toxic materials and the bottom ashes for both combustion and co-combustion tests as non-toxic residues.

Finally, it is important to stress that the results obtained in this work were limited by the combustion conditions observed in the pilot scale fluidized bed combustor. Extrapolations of the results to large scale fluidized bed combustors must be assessed case by case, since the combustion conditions can vary widely.

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