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RESEARCH ARTICLE

Integrated management of ash from industrial and domestic combustion: a new sustainable approach for reducing greenhouse gas emissions from energy conversion

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Abstract This work supports, for the first time, the integrated management of waste materials arising from industrial processes (fly ash from municipal solid waste incineration and coal fly ash), agriculture (rice husk ash), and domestic activities (ash from wood biomass burning in domestic stoves). The main novelty of the paper is the reuse of wood pellet ash, an underestimated environmental problem, by the application of a new technology (COSMOS-RICE) that already involves the reuse of fly ashes from industrial and agricultural origins. The reaction mechanism involves carbonation: this occurs at room temperature and promotes permanent carbon dioxide sequestration. The obtained samples were characterized using XRD and TGA (coupled with mass spectroscopy). This allowed quantification of the mass loss attributed to different calcium carbonate phases. In particular, samples stabilized using wood pellet ash show a weight loss, attributed to the decomposition of carbonates greater than 20%. In view of these results, it is possible to conclude that there are several environmental benefits from wood pellet ash reuse in this way. In particular, using this technology, it is shown that for wood pellet biomass the carbon dioxide conversion can be considered negative.

To the memory of Serena Sganzerla

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Introduction

Today, waste incineration represents a necessity for the sustainable management of European solid wastes (Xin-gang et al. 2016). However, while modern waste incineration represents a consolidated technology for volume and waste mass reduction, combined with efficient energy recovery, an important amount of ash originates from combustion. Final solid residues are around 30% of the total mass input. Moreover, these residues can be divided into bottom and fly ash (Zacco et al. 2014). While bottom ash is already reused as, for example, additives for construction materials (Mehta and Siddique 2016), fly ash is generally disposed of in landfills because it represents a danger to the environment and human health (Guarienti et al. 2014). Municipal solid waste incineration (MSWI) fly ash comprises higher concentrations of heavy metals than bottom ash, and it therefore requires treatment to make it environmentally safe before disposal.

To safely handle and dispose of MSWI fly ash, several methods have been proposed. At present, separation processes, solidification/stabilization (S/S), and thermal treatments are the three main techniques used (Zacco et al. 2014). Separation methods are usually conducted to reduce the levels of chloride, other salts (such as sulfate, bromine, and iodine), alkalis, and heavy metals. For example, washing in water is a feasible method to remove chlorides and salts from ash. However, large amounts of heavy metals are released with the soluble salts (Colangelo et al. 2012), making this less a desirable process route.

S/S methods refer to technologies that use additives (or binders) to physically and/or chemically immobilize hazardous constituents in fly ash (Zacco et al. 2014). Addition of ordinary portland cement (OPC) for solidification is the most popular approach. Thermal treatments, which are energy intensive, are usually applied for fly ash reuse, and are mainly carried out by sintering, melting, or vitrification (Zacco et al. 2014).

In the last few years, a new technology for MSWI fly ash stabilization has been developed (Bontempi et al. 2010a) and optimized (Bosio et al. 2013, 2014). This technology is based on the use of a source of reactive amorphous silica and a source of calcium hydroxide. Amorphous silica reacts with leachable heavy metals allowing stable silicates phases ($PbSiO_3$ and Zn_2SiO_4) to be obtained, as confirmed by X-ray absorption spectroscopy (Struis et al. 2013). Calcium hydroxide contributes to fly ash carbonation, with the probable formation of immobile metal carbonates as an additional mechanism of metal entrapment (Bosio et al. 2014). Originally, the amorphous silica source was provided by commercial colloidal silica. Recently, the process was optimized to use silica by-products, such as silica fume (Rodella et al. 2014) and rice husk ash (RHA), an agricultural waste COSMOS-RICE, project (LIFE11 - ENV/IT/256). The calcium hydroxide source was always provided by flue-gas desulfurization (FGD) residues. The process is sustainable, because it is carried out at low temperatures and employs only water, by-products and wastes generated from industrial energy conversion processes. Although, also other recently proposed technologies use by-products and wastes for heavy metals stabilization in MSWI fly ash, they also use commercial chemicals and are therefore less sustainable and less economically viable (Ye et al. 2016). Another advantage of the proposed technology, in contrast to classical stabilization/solidification treatments, is that the final stabilized material is a powder, that could potentially be reused as a raw material in other applications, for example as a filler material.

The aim of this work was to build on the success of previous work (COSMOS-RICE) and to investigate the employment of a different ash typology in the stabilization procedure: biomass ash. In recent years, EU policy has supported increasing the demand for renewable energy sources. This is because it is widely accepted that the production and use of biofuels can contribute to the net reduction of greenhouse gas emissions due to their close-to-neutral carbon emission (Hansson and Hackl 2016). By switching from coal and natural gas to biomass, the net CO_2 emission per unit heating value can be reduced by 93 and 84%, respectively (Niu et al. 2016).

Among the different existing typologies of biomass, the use of pelletized fuels is one of the most widespread because pelletized fuels show advantages over other biomass products such as chips and briquettes due to their higher density and uniform dimensions. In particular, pellets of wood, such as beech or spruce, and straw, present lower ash contents and higher heat contents than most waste-derived pellets (Arranz et al. 2015).

To better define and describe the modification of the COSMOS-RICE technology, the pellet wood ash must first be properly characterized. Unfortunately, detailed and complete datasets from simultaneous chemical and phase-mineral analyses for wood pellet solid combustion products are scarce. Some studies have used data from the ash yield of biomass or the bulk chemical composition of ash to define mineral composition, but this is not ideal and can lead to confusion (Vassilev et al. 2013b).

A recent review article (Vassilev et al. 2013b) reports results from biomass ash compositional analysis. It shows that phases and minerals generally identified in biomass ash include approximately 291 species, in contrast to 188 species found in coal ash. Despite this, there is no specific data for only wood pellet ash, although the review reports that biomass ash from wood generally contains carbonates, glass, silicates, oxyhydroxides, and some sulfates and phosphates. Most of these phases are not normally identified in coal ashes, because of the enrichment of elements such as Ca, Cl, K, Mg, Mn, Na, and P in biomass ash compared to coal ash.

There is, in some literature, the inaccurate presumption that biomass combustion systems are nonpolluting or that biomass ash does not contain toxic metals (Ahmaruzzaman 2010). Indeed, literature shows that this ash can contain carcinogenic and mutagenic polycyclic aromatic hydrocarbons (Orecchio et al. 2016). Additionally, in biomass ash, heavy metals tend to occur in much more mobile and hazardous compounds than in coal ash (Niu et al. 2016). Unfortunately, systematic studies of the concentration, modes of occurrence, behavior and fate of hazardous phases, and trace elements in biomass fuels and their ashes are only at an initial stage of investigation (Vassilev et al. 2013a). In contrast, the stabilization technology proposed the work presented here can stabilize heavy metals, if present in the wood pellet ash.

The limited available literature data concerning biomass ash compositions (Niu et al. 2016) suggests that it could potentially be employed in the COSMOS-RICE stabilization technology. In particular, due to their composition, flue-gas desulfurization (FGD) residues, by-products generated by air pollution control equipment in coal-fired power plants to reduce atmospheric sulfur release, appear to be the best candidate that can be substituted by wood pellet ash. This provided the rationale for the present study.

The new stabilized material obtained from the COSMOS-RICE procedure has two advantages: it can sequestrate CO_2, and it can be employed as a partial or full substitute of some "critical raw materials" (Besco et al. 2013, 2014; Ponsot et al. 2015) for example in plastics and ceramics composites. Carbon capture and storage (CCS) is one approach that has been proposed for CO_2 mitigation from stationary sources (Siefert and Litster 2013). Moreover, CO_2 capture/separation is a critical step due to the low Technology Readiness Levels (TRL's) of the presently-available technologies, and their

relatively high costs. Indeed, previously-proposed technologies, for post-combustion CO_2 capture, require treatment at high temperatures and the employment of a material, i.e., calcium oxide (CaO), that generally must be regenerated. This oxy-combustion imposes an energy penalty (due to the consumption of fuel and oxygen) and generates additional CO_2 (Valverde et al. 2015; De et al. 2015). We have recently shown that the stabilized material obtained by means of COSMOS-RICE technology has a CO_2 sequestration capability of approximately 95 g/kg (Bosio et al. 2014).

In this work, for the first time, the opportunity of mixing several waste materials, with ash from biomass, without the addition of any commercial chemical, is presented. This article investigates the synergic effect due to the use of waste ash materials, but from different sources (industrial, agricultural, and domestic). In particular, industrial toxic fly ash (from MSWI), containing leachable heavy metals, is the major component (at 65%) used in the mixture, but the addition of biomass and agricultural ashes is necessary for the chemical stabilization of the leaching metals. The aim of this article is not only to shown that the obtained material, after the stabilization procedure, is safe and stable, but also that it can be reemployed as new material. In particular, it may be possible to reuse the materials generated by this treatment, for example as a filler material in a number of potential applications, reducing the requirement for virgin raw materials and helping to progress towards more sustainable societies. The concept of reusing valuable materials contained in toxic fly ash has already been discussed in the literature (Funari et al. 2015). However, the available articles on this subject are mainly devoted to the recovery of precious metals and earth elements that represent a limited content in these ashes. Here, for the first time, the present work shows that the opportune mixing of different fly ashes enables obtaining a valuable new material, with the complete recovery of all ashes. In particular, considering active MSWI plants in the European Union (EUROSTAT 2013), the annual total amount of resulting stabilized material from industrial fly ash may be approximately 2.9 million tons. This process can potentially improve the closure of symbiotic industrial cycles by reusing 100% of the produced ashes, for example in the plastic composites sector. Finally, this work also evaluates the contribution of the proposed technology to greenhouse gas emissions.

Materials and methods

Stabilized samples were prepared from MSWI fly ash (provided by an Italian grate firing incinerator and containing leachable metals) by adding other waste materials: coal fly ash, RHA, and wood pellet ash.

All samples were prepared following the same protocol, i.e., by wetting a mixture of 200 g of the three powders:

MSWI fly ash, wood pellet ash, coal fly ash (in the relative weight percent: 65, 20, and 15%) and 20 g of RHA with 300 g of water, and stirring for 30 min in a laboratory mixer at 100 °C (Bontempi et al. 2012). Five different wood pellet samples were purchased on the Italian market, combusted to completion in domestic wood stoves and used to obtain five different wood pellet-based ash samples via the stabilization process.

A reference sample was also prepared using the same powders, but replacing the wood pellet ash with FGD residues (Bosio et al. 2013, 2014). FGD residue is the main by-product of the desulfurization system used to remove SO_x from coal combustion products. This is not considered a waste; however, it is generally stored. The use of FGD residue represents a previously tested stabilization procedure that was established in the COSMOS-RICE project (COSMOS-RICE, PROJECT 2016). Afterwards, the residual water present in samples was evaporated at room temperature (approximately 21 °C). Thirty days later, all samples were completely dried.

After chemical stabilization of heavy metals, the solid inertized material can be washed to recover almost pure soluble salts (Bontempi et al. 2010a). In the present case, salt recovery was not realized. Leaching tests were performed according to the CEN normative (CEN 2002), in order to quantify the leachability of heavy metals from the products in water. The contact time of materials and aqueous solution was 2 h, a time sufficient to establish equilibrium in subsequent experiments with MSWI fly ash (Yang et al. 2009). Leaching tests were performed when samples were completely dried (i.e., 30 days after treatment, which corresponds to week 5 in Tables 3 and 4). The drying produce consisted in the samples storage in laboratory, at room temperature. The same test was repeated one, two, three and four weeks after the first test, to verify the materials stability. At all times, samples were stored in air in a laboratory at room temperature.

Wood pellets and corresponding ash samples were digested in acid solution for chemical composition analysis by means of a CEM Discover Microwave oven. Samples were prepared using 0.18 g of material in a solution of 4 ml HNO_3 (65 vol.%), 2 ml HF (47 vol.%), and 2 ml HCl (37 vol.%) (instrument parameters: temperature 210 °C, time 9 min, power 300 W, medium stirring).

Glass containers were covered with commercially available teflon cups, designed on purpose for HF involving procedures. After digestion, a small amount of solid particles, visible at the naked eye, was present at the bottom of the container. The suspension was carefully shaked and added with Ga, to be used as internal standard, in concentration 1 mg/l (Borgese et al. 2009). Elemental chemical analysis was carried out using total reflection X-ray fluorescence (TXRF) with a Bruker S2 Picofox (air cooled, Mo tube, Si-drift detector), with operating parameters of 50 kV and 750 µA. An aliquot of 10 µl of the suspension was directly pipetted on plexiglass

disks used as sample carriers. All work was performed under a fume hood. The life time of TXRF measurements was 600 s.

X-ray diffraction (XRD) measurements were performed with Panalytical X'Pert Pro diffractometer equipped with the X'Celerator detector and Cu anode. Operating values were 40 kV and 40 mA. Thermogravimetric analyses (TGAs) were performed using a TGA/DSC Star System manufactured by Mettler Toledo. Approximately 10 mg of each sample was heated in alumina crucible from 35 to 1000 °C at a heating rate of $10\ °C\ min^{-1}$ under an air flow of $40\ ml\ min^{-1}$. Thermogravimetric-mass spectrometry (TG-MS) measurements were carried out using a Netzsch Simultaneous Thermal Analyser 409 PG Luxx, which is coupled to an Aëolos mass spectrometer via a heated capillary transfer line. Transfer lines and adapter heads were heated to 180 °C. The heating rate was $10\ °C\ min^{-1}$, and the temperature range was 35–1100 °C. Air was used as flue gas with a flow rate of $40\ ml\ min^{-1}$. Alumina crucibles were used to contain about 20 mg of sample.

Results and discussion

Results

Tables 1 and 2 respectively show the elemental compositions of wood pellet samples (A, B, C, D, and E) before and after combustion. It is evident that metal concentrations increase after pellet burning, due to combustion of the organic fraction of the material. In addition, some metals that were present at undetectable concentrations in the wood pellets can be detected in the respective ashes (Sr, Ba, and Pb) after combustion. The data in Table 2 is variable; this variability probably arising from compositional differences between different wood pellets. However, for all samples, the elements present in the highest quantities in the ashes obtained from combustion are K, Ca, Mn, and Fe.

XRD patterns collected from all pellet ashes are reported in Fig. 2. It is important to note that while XRD detects and identifies crystalline phases, it is more difficult to detect and identify amorphous phases, although these do exhibit broad peaks often described as "amorphous humps." Although some articles report compositions of wood pellet ash, these are only derived from elemental chemical analysis, and from which their corresponding oxides are attributed (for example Ca is expected to form CaO and so on) (Arranz et al. 2015). Therefore, it is not possible to directly compare data in the literature with that reported in Fig. 2, specifically concerning the phase composition of wood biomass ash. XRD therefore offers additional phase composition, which is essential to fully understand the chemical behavior of these ashes. The confirmed presence of CaO in all samples supports the decision to use wood biomass ash to substitute FGD residues, the source of calcium hydroxide in the process.

XRD measurements and composition analysis, made in previous works (Benassi et al. 2016; Rodella et al. 2014)

Table 1 Analyzed composition (mg/kg) of wood pellet samples (A, B, C, D, and E) and limits of detection (LODs) of determined elements

Element	A Mean	A SD	B Mean	B SD	C Mean	C SD	D Mean	D SD	E Mean	E SD	LOD (mg/kg)
P	–	–	–	–	130	10	80	10	140	40	45
S	270	30	280	30	1700	500	630	60	1200	200	70
Cl	760	80	540	50	1300	100	430	40	1300	300	40
K	170	20	270	30	330	30	200	20	340	50	25
Ca	540	50	820	80	880	90	820	80	1100	100	20
Ti	–	–	15	2	–	–	–	–	–	–	4
Cr	3	1	3.5	0.5	–	–	–	–	–	–	2
Mn	35	3	24	2	36	3	48	5	38	4	5
Fe	260	30	350	30	340	30	370	40	390	40	5
Ni	31	3	5.0	0.5	5	0.6	6	1	10	1	3
Cu	5.8	0.6	–	–	4	1	–	–	–	–	2
Zn	7	1	17	2	10	1	12	3	54	5	2
As	14	1	–	–	29	3	16	1	25	4	2
Br	–	–	–	–	–	–	–	–	–	–	1
Rb	–	–	–	–	–	–	–	–	–	–	6
Sr	–	–	–	–	–	–	–	–	–	–	10
Ba	–	–	–	–	–	–	–	–	–	–	75
Pb	–	–	–	–	–	–	–	–	–	–	6

SD standard deviation of three replicates

Table 2 Analyzed composition (mg/kg) of wood pellet ashes (A, B, C, D, and E), after combustion in domestic stoves

Element	A		B		C		D		E	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
P	4900	500	6500	600	4000	400	5500	500	6700	700
S	2800	300	4300	600	5000	500	2900	300	3400	300
Cl	650	70	400	100	510	60	900	100	1100	100
K	45,000	5000	57,000	6000	55,000	5000	46,000	5000	57,000	6000
Ca	81,000	8000	110,000	10,000	71,000	7000	150,000	20,000	110,000	10,000
Ti	900	100	570	60	4000	400	1000	100	300	30
Cr	100	10	200	20	60	6	100	10	40	4
Mn	13,000	1000	43,800	400	7700	700	12,000	1000	10,000	1000
Fe	10,000	1000	9600	100	10,000	1000	12,000	1000	4800	500
Ni	37	4	–	–	42	4	35	3	27	3
Cu	160	20	180	20	350	30	150	20	130	10
Zn	570	60	790	80	1300	100	550	50	1000	100
As	40	4	50	5	42	4	40	4	46	5
Br	72	10	12	2	–	–	–	–	–	–
Rb	140	10	300	30	160	20	130	10	200	20
Sr	460	50	600	100	440	40	650	60	350	30
Ba	710	70	1000	100	–	–	1200	100	1100	100
Pb	15	1	8	1	22	2	15	1	14	2

SD standard deviation of three replicates

showed that the MSWI fly ash is a mixture of amorphous and crystalline phases. The crystalline part is mainly composed of sulfates, chlorides, and calcite. FGD residues contains $CaSO_3 \cdot 0.5H_2O$ and $Ca(OH)_2$. Coal fly ash contains few crystalline phases (quartz and mullite).

Table 3 reports the results of the leaching tests made on MSWI fly ash and the samples treated using the COSMOS-RICE procedure (the stabilized wood pellet-based samples are named CR). The starting MSWI fly ash shows the important presence of leachable metals, mainly Pb and Zn. The leaching experiments performed during weeks 6, 7, and 8 verify that all samples are chemically stable.

Figure 4 presents the XRD patterns collected from the wood pellet ashes and FGD residues after treatment using the COSMOS-RICE procedure. The diffraction pattern for the reference sample shows the presence of a number of crystalline silicon oxides (SiO_2, as cristobalite and quartz), calcite ($CaCO_3$), sodium chloride (halite, NaCl), thaumasite ($Ca_3(SO_4)[Si(OH)_6](CO_3) \cdot 12(H_2O)$), and gypsum ($CaSO_4 \cdot 2(H_2O)$). Almost the same phases are found in the samples realized with wood pellet ashes presumably due to the same reactions that involve carbonation (Bosio et al. 2014).

Table 4 summarizes the findings from the XRD patterns in terms of phases detected in the reference and wood pellet ash samples created using the COSMOS-RICE procedure and at different times corresponding to the subsequent leaching experiments reported in Table 3 (i.e., weeks 6 to 8). The phases detected in XRD patterns collected 3 months after the stabilization procedure (corresponding to week 13) are also included to verify sample stability.

TGA and TG-MS measurements were carried out to evaluate the amount of carbon dioxide sequestered in the CR samples and reference. DTG diagram obtained from CR samples and reference is illustrated in Fig. 5a. All samples exhibit similar profiles, indicating that the thermal events associated with weight loss in each sample have the similar origins. The reference sample shows a higher weight loss (TGA curves are not reported here), in comparison to all other CR samples, at temperature up to and including 120 °C, corresponding to the loss of physically bound water. Weight loss also continues above 120 °C in all samples. This combined low-temperature weight loss of approximately 10 to 15 wt% at temperatures up to 400 °C is consistent with the removal of physical water and evolution of chemically bound water from several hydrated phases in these samples (see Table 4). In particular, the reference sample exhibits a larger number of hydrate phases including hydrated calcium sulfates, as evidenced by XRD, and this explains the higher levels of weight loss from the reference sample than the CR samples at these lower temperatures.

A mass spectrometer was coupled with a thermogravimetric analyzer, to detect which gases (H_2O, CO_2, and SO_2) are emitted during the heating process, and over which temperature ranges. The reference and CR samples

Table 3　Results of leaching tests made on MSWI fly ash and samples treated with the COSMOS-RICE procedure

Element	Statistics	MSWI fly ash (mg/L)	Reference sample (mg/L)				CR sample A (mg/L)				CR sample B (mg/L)			
			Week 5	Week 6	Week 7	Week 8	Week 5	Week 6	Week 7	Week 8	Week 5	Week 6	Week 7	Week 8
S	Mean	–	190	130	90	170	9	–	–	12	–	–	–	–
	SD		20	20	5	20	5			2				
Cl	Mean	6700	1400	2600	3800	1300	3300	2800	3300	3800	3800	2700	3300	2800
	SD	100	100	100	500	200	400	300	300	400	400	400	300	300
K	Mean	1170	180	450	600	200	1000	800	1000	1000	1200	900	1100	900
	SD	40	20	40	100	30	100	100	100	100	100	200	100	100
Ca	Mean	5050	1400	2100	3300	1200	1700	1500	1700	1700	2100	1500	1700	1000
	SD	40	100	200	400	100	200	100	200	200	200	200	200	100
Fe	Mean	–	0.3	–	–	0.20	–	–	–	–	–	–	–	–
	SD		0.1			0.04								
Zn	Mean	9	0.38	0.32	0.51	0.19	0.44	0.22	0.01	0.35	0.67	0.25	0.12	0.24
	SD	1	0.04	0.07	0.05	0.02	0.05	0.02	0.01	0.04	0.19	0.03	0.02	0.02
As	Mean	–	–	–	–	–	–	0.13	–	–	0.11	0.12	0.10	0.10
	SD							0.01			0.02	0.01	0.01	0.01
Br	Mean	104	40	46	55	34	50	40	40	53	41	30	37	30
	SD	1	4	5	5	3	5	4	4	5	4	3	4	3
Sr	Mean	5.38	5.5	5.5	6.5	5.9	13	11	11	18	15	12	17	13
	SD	0.03	0.5	0.5	0.6	0.6	1	1	1.15	2	1	1	2	1
Ba	Mean	9.0	0.2	0.21	1.7	0.5	1.9	2.1	2.8	2.2	7.0	4.8	5.8	5.1
	SD	0.3	0.1	0.02	0.3	0.1	0.3	0.2	0.6	0.2	0.7	0.5	0.6	0.5
Pb	Mean	30	–	0.10	1.2	–	0.08	0.15				0.13	0.04	0.04
	SD	3		0.01	0.1		0.01	0.01				0.02	0.02	0.03

Element	Statistics	CR sample C (mg/L)				CR sample D (mg/L)				CR sample E (mg/L)			
		Week 5	Week 6	Week 7	Week 8	Week 5	Week 6	Week 7	Week 8	Week 5	Week 6	Week 7	Week 8
S	Mean	27	2.8	0.5	20	0.6	–	–	–	15	3.5	–	3.5
	SD	3	0.6	0.4	5	0.5				4	0.4		0.3
Cl	Mean	2500	2800	3500	1700	3800	3100	3800	2600	4000	2700	3700	2900
	SD	500	300	700	200	400	300	400	300	500	300	400	300
K	Mean	600	800	900	390	1300	1100	1400	860	1200	800	1100	800
	SD	100	100	200	50	100	100	100	90	200	80	100	100
Ca	Mean	1500	1600	1900	890	2200	1500	1900	1300	2500	1600	2100	1600
	SD	300	40	400	90	200	100	200	100	200	200	200	200
Mn	Mean	–	–	–	–	0.21	–	0.24	–	–	–	–	–
	SD					0.04		0.06					
Zn	Mean	0.8	0.04	0.30	0.20	0.33	0.03	0.05	0.20	0.35	0.03	0.12	0.18
	SD	0.4	0.01	0.03	0.04	0.03	0.01	0.01	0.02	0.04	0.00	0.02	0.02
As	Mean	–	–	–	–	0.14	–	0.030	0.09	0.14	–	0.08	0.09
	SD					0.02		0.001	0.01	0.02		0.01	0.01
Br	Mean	39	36	47	36	33	35	39	32	54	34	45	41
	SD	6	4	6	4	14	3	4	3	7	3	5	4
Sr	Mean	10	9	12	11	19	14	16	15	11	7.0	10	10
	SD	1	1	1	1	2	1	2	1	1	0.7	1	1
Ba	Mean	1.0	0.7	2.3	0.8	6.1	5.8	5.6	3.7	2.0	2.1	2.6	2.0
	SD	0.1	0.1	0.5	0.1	0.6	0.6	0.6	0.4	0.2	0.2	0.2	0.2
Pb	Mean	0.06	–	–	–	0.05	–	–	0.05	0.11	–	–	–
	SD	0.01				0.01			0.01	0.02			

A reference sample was also realized, following the standard procedure (Bosio et al. 2014), i.e. employing the FGD residues instead of wood pellet ash

SD standard deviation of three replicates

were measured with respect to the measured emitted gases (MW = 18 (H_2O), 44 (CO_2), and 64 (SO_2)), and all samples show similar behavior; thus, only the result for the reference sample is reported (Fig. 5b). The only difference among the emitted gases refers to MW = 64 (SO_2), which shows an undetectable contribution from CR samples obtained by using pellet ashes instead of FGD residues. This is because the reference sample contains gypsum and other calcium sulfate phases (Fig. 4 and Table 4).

Table 5 reports the weight loss from CR samples in selected temperatures ranges based on the type of calcium carbonate

(see below for further explanation). It shows that the amount of released CO_2 is consistently significant for all samples.

Discussion

To establish the reuse of wood pellet ashes by the application of COSMOS-RICE technology, the first important research step concerns their characterization.

Data in Table 1 can be compared with the values reported by Chandrasekaran et al. (2012), corresponding to wood pellet

Table 4 Phase analyses from XRD patterns collected at different times (corresponding to the leaching experiments reported in Table 3)

Sample	Weeks	SiO_2	KCl	NaCl	$CaCO_3$	μ-$CaCO_3$	$Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot12(H_2O)$	$CaSO_4\cdot2(H_2O)$	$CaSO_4$	$Ca(SO)_3\cdot0.5(H_2O)$
Reference	5	✓		✓	✓			✓	✓	✓
	6	✓			✓		✓	✓	✓	✓
	7	✓	✓	✓	✓		✓	✓	✓	✓
	8	✓			✓		✓	✓	✓	✓
	13	✓		✓	✓			✓	✓	✓
CR sample A	5	✓	✓	✓	✓		✓			
	6	✓	✓	✓	✓		✓			
	7	✓	✓	✓	✓		✓			
	8	✓	✓		✓		✓		✓	
	13	✓			✓	✓		✓		
CR sample B	5	✓	✓		✓		✓			
	6	✓	✓	✓	✓		✓			
	7	✓	✓	✓	✓		✓			
	8	✓	✓	✓	✓		✓			
	13	✓			✓	✓		✓		
CR sample C	5	✓		✓	✓		✓			
	6	✓	✓		✓		✓			
	7	✓	✓	✓	✓		✓			
	8	✓		✓	✓	✓	✓	✓		
	13	✓			✓	✓		✓		
CR sample D	5	✓	✓		✓		✓			
	6	✓	✓		✓		✓			
	7	✓	✓	✓	✓		✓			
	8	✓	✓	✓	✓		✓			
	13	✓	✓		✓	✓		✓		
CR sample E	5	✓	✓		✓		✓			
	6	✓	✓	✓	✓		✓			
	7	✓	✓	✓	✓		✓			
	8	✓	✓	✓	✓		✓			
	13	✓	✓		✓	✓				

Phase analysis from XRD patterns collected on the week 8 sample is also reported. SiO_2 quartz and cristobalite, $CaCO_3$ calcite, μ-$CaCO_3$ vaterite, $Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot12(H_2O)$ thaumasite, $Ca(SO)_3\cdot0.5(H_2O)$ hannebachite, NaCl halite, KCl sylvite, $CaSO_4$ anhydrite, $CaSO_4\cdot2(H_2O)$ gypsum

compositions of 132 American samples. This is the first article reporting many analyzed wood pellet samples and highlights the problem of heavy metals contained in biomass for domestic combustion. It is interesting to note that pellet samples analyzed in this work show high concentrations of As and Cl. Also, the concentrations of Mn, Ba, and Pb found in the present work are generally higher than in data obtained by (Chandrasekaran et al. 2012). Finally, Zn and Ni are also found in samples analyzed in this work, but they were not reported in the analyses of the American wood pellets.

Table 5 TGA-analyzed weight loss (%) of all CR samples in three selected temperature ranges

Temperature range (°C)	Reference	CR sample A	CR sample B	CR sample C	CR sample D	CR sample E
550–680	10.2	11.6	9.5	10.7	11.4	11.4
680–780	1.3	1.5	1.2	1.3	1.4	2.2
780–990	7.4	8.6	10.5	9.7	8.7	11.8
Total	18.9	21.7	21.2	21.7	21.5	25.5

Fig. 1 Graphical representation of the data reported in Tables 1 and 2, for easier comparison and for easier identification of the enrichment due to combustion. A1, B1, C1, D1, and E1 refers to data of corresponding samples reported in Table 1. A2, B2, C2, D2, and E2 refers to data of corresponding samples reported in Table 2
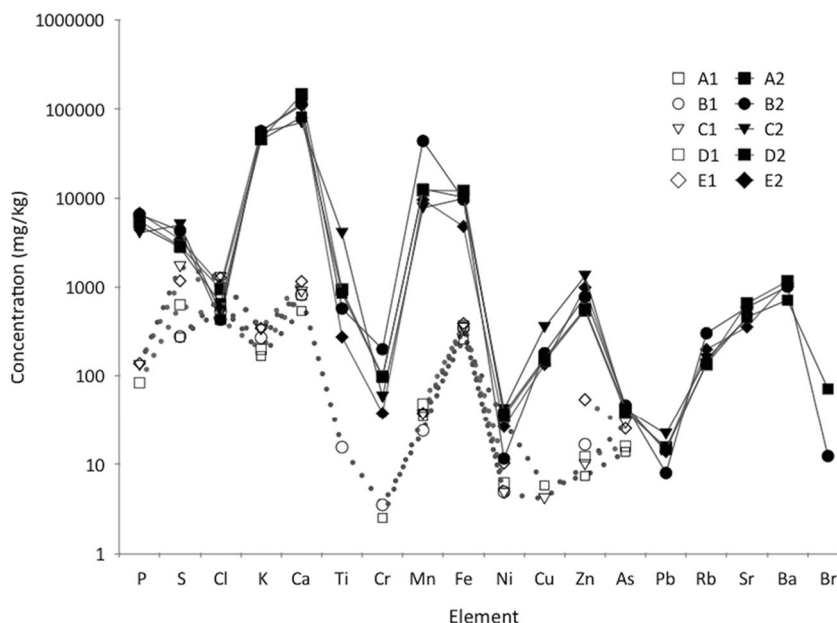

Figure 1 graphically displays the results reported in Tables 1 and 2, for ready comparison and identification of the enrichment due to combustion. It appears that the metal content is not uniform across the different selected wood pellet ashes (for example, Ti can be found only in sample B, Cr in samples A and B), which may have been due to the properties of the original biomasses and the conditions of their cultivation. However, general trends can be highlighted in the heavy metals enrichment in the ashes. Using a logarithmic scale to display the data it is shown that the detected elements exhibit similar enrichment behavior. Moreover, the metals that display the most significant enrichment are Ca, K, and Mn. This result is consistent with the literature, which reports that biomass ashes are commonly enriched in Mn and K in comparison with coal ashes (Vassilev et al. 2013b). Also, Zn shows generally high enrichment in ashes, except for sample E. Pb, Ru, Sr, and Ba, which generally cannot be detected in wood pellets, are present in relatively high quantities in the corresponding ashes (up to around 1000 mg/kg).

In Fig. 2, which reports XRD patterns collected on all wood pellet ashes, some halos are present in the range 28°–36° (2θ), which are consistent with the presence of amorphous phases. It is interesting to note that all diffraction patterns show the presence of calcium oxide, calcite and magnesium oxide, in agreement with (Vassilev et al. 2013b). The ash composition is variable for some other phases: samples A and C contain also quartz; samples B, C, D, and E contain also potassium calcium carbonate [$K_2Ca(CO_3)_2$]; samples B, D, and E contains also calcium phosphate hydroxide [$Ca_5(PO_4)_3(OH)$]; sample A contains also potassium chloride (sylvite, KCl); and samples C and E contain also potassium sulfate ($K_2S_2O_7$). These phases are known to occur in biomass ash (Vassilev et al. 2013b). Finally, all samples show the presence

of an unexpected phase: calcium manganese oxide ($Ca_2Mn_2O_5$). This phase, which is consistent with elemental data reported in Table 2, was not previously reported in biomass ashes. Previously, the presence of Mn has been generally attributed to the formation of manganese containing phases in ash from biomass (Mellbo et al. 2008) or more generally to Mn enrichment (Vassilev et al. 2013b). Unfortunately, the lack of data for wood pellet biomass ash compositions does not allow a more detailed consideration of this phase.

Since biomass contains significant amounts of flame-volatile alkali metal salts, it can contribute more strongly to the corrosion of the boilers than fossil fuels (Niu et al. 2016). In particular, it was reported that heavy metal compounds can significantly decrease the melting point of a deposit, and thus,
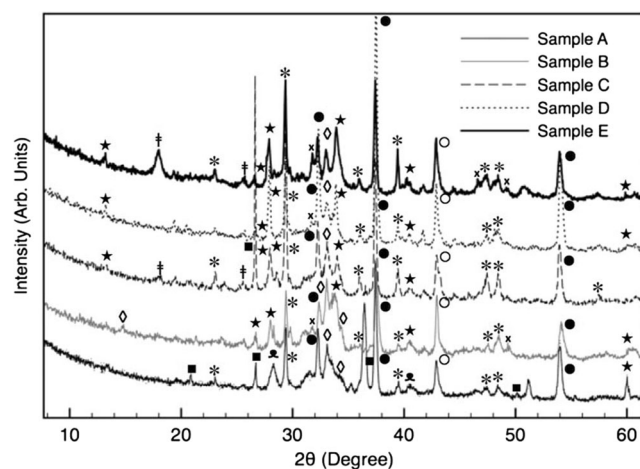
Fig. 2 XRD patterns collected on all wood pellet ashes. Calcite ($CaCO_3$) (✳), calcium oxide (CaO) (●), magnesium oxide (MgO) (○), potassium calcium carbonate [$K_2Ca(CO_3)_2$] (★), quartz (SiO_2) (■), calcium phosphate hydroxide [$Ca_5(PO_4)_3(OH)$] (◇), calcium manganese oxide ($Ca_2Mn_2O_5$) (◉), sylvite (KCl) (⸷), potassium sulfate ($K_2S_2O_7$)

the corrosion caused by molten salts (as for example chlorides) can be of great importance (Bankiewicz et al. 2009). The presence of such a high content of Mn in ash should be investigated in more detail, also considering possible corrosion mechanisms of domestic stoves.

Despite the presence of high levels of heavy metals, which may pose concerns for the re-use of ash from wood pellet combustion, XRD patterns highlight the presence of some potentially useful phases, such as CaO and MgO, that may be recovered for reuse in certain applications. This is very interesting and is a challenging research topic, and it correlates well with the European "raw material" initiative. CaO and MgO can be found in high quantities in biomass ashes: up to 63% for CaO and 12% for MgO (Vassilev et al. 2013b). Furthermore, carbonates can be formed by reaction of these phases with water and carbon dioxide. Since there are high levels of heterogeneity in wood pellet materials, whose physical and chemical properties depend on several factors such as the part that is used (e.g., bark, wood, or branches) and typology (e.g., forest or herbaceous). The resulting ash composition will not only relate to the origin and composition of the waste pellets, but also to the stoves in which the pellets are burned. One aim in this work has been to show that different ashes, produced from pellets with different compositions and burned in different stoves, can be utilized in the context of compensating raw materials scarcity. Indeed, despite their differences in composition, all ashes contain useful phases that can potentially be employed to produce new materials and products. Suggested future work may therefore consider the effects of different combustion systems.

In this work, wood pellet ashes were employed as a stabilizing agent, with the addition of RHA and coal fly ash, to treat MSWI fly ash. We have recently shown (Bosio et al. 2014) that the stabilization of heavy metals can be obtained by a sustainable process, based on the use of all wastes and by-products since the employment of amorphous silica and calcium oxide (or hydroxide) sources allows the occurrence of two reactions, silica stabilization, and carbonation. RHA contains amorphous silica that can be used in chemical stabilization of Pb and Zn (Bosio et al. 2014). X-ray absorption spectroscopy identified Pb and Zn silicates ($PbSiO_3$ and Zn_2SiO_4) as main phases obtained after stabilization of MSWI fly ash with colloidal silica (Struis et al. 2013). Moreover, the evidence of carbonation supports the hypothesis of formation of immobile metal carbonates as an additional mechanism of metal entrapment.

Data reported in Table 3 show that the leachability of Pb and Zn is highly decreased in the stabilized samples. This is evident considering the first leaching test, made 1 month after the stabilization procedure (week 5). This is verified for both the reference sample and all samples prepared using all the wood pellet ashes employed. The leaching experiments made during weeks 6, 7, and 8 show that all samples remain stable

during this time. In addition, as already found (Bosio et al. 2014), the concentration of Pb and Zn in the leaching solutions decreased with time, in respect to the data obtained after week 5 supporting further stabilization with time. Stabilization of residual Pb and Zn with time is a consequence of carbonation (Rodella et al. 2016). In particular, Pb concentrations were often lower than the detection limit. To better highlight the change of Pb and Zn concentrations during the time, these values (reported in Table 3) are displayed in Fig. 3.

The attention of this work was devoted to the reduction of Pb and Zn, mainly because generally they are the most problematic elements. However, some considerations about other metals can be done. In particular, the technology seems to be effective in the Ba stabilization, with the exception of CR samples B and D, that contain large amounts of this metal in the starting wood pellet ashes.

Considering the starting concentrations of about 5.38 mg/L for Sr in MSWI fly ash solution, and its final values ranging about from 5.9 to 18 mg/L in the leaching solutions of stabilized samples (due to the amount of Sr already present in pellet wood ash), it is possible to conclude that the stabilization treatment seems not produce evident effects in the reduction of Sb leachability.

Finally, K + Ca and Cl + Br + S concentrations evaluated in all leaching tests result highly correlated, strongly suggesting that these elements are contained in the soluble salts fraction.

These results support the conclusion that wood pellet ash, independently from the origin and the burning system, represents an effective substitute for FGD residue, to promote heavy metals stabilization. Additionally, the use of this ash allows a valuable material to be obtained by employing all waste starting materials, that can have application as a filler for example in polymer composites (Benassi et al. 2015).
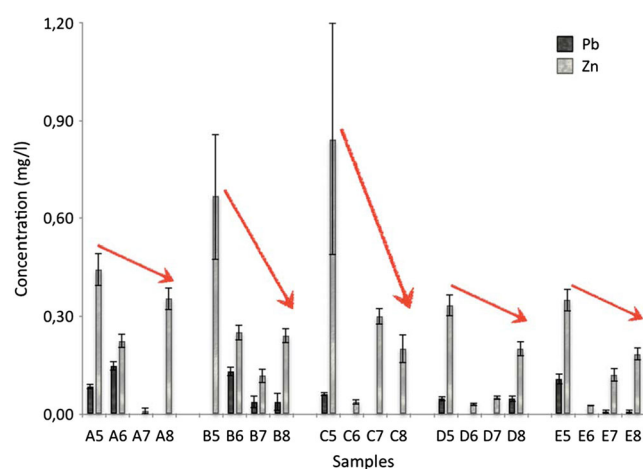

Fig. 3 Results of leaching tests for Pb and Zn, made on samples treated with the COSMOS-RICE procedure and stabilized by using wood pellet ashes (A, B, C, D, and E). The data, which are obtained at different weeks after the stabilization (week 5, 6, 7, and 8), are reported in Table 3

The leaching test results, considered holistically, highlight some final considerations. Sulfur is highly leachable in the reference sample prepared using the FGD residue in the stabilization process whereas for the CR samples it is always very low (often near to the detection limit). Samples A and C show, 8 weeks after the stabilization process, leachate concentrations of sulfur higher than 10 mg/L. This is probably due to the formation of some soluble phases containing sulfur (in accord with XRD data, see Table 4).

XRD patterns collected on all stabilized samples after 10 weeks (except for the reference sample (see Fig. 4) show the presence of the same phases. The biggest difference in the reference sample is the soluble salt KCl, in accordance with the data obtained from the leaching tests (see Table 3). Another difference from the standard sample is the absence of gypsum in the stabilized samples made using wood pellet ashes. Indeed, the FGD residues have a high content of S (Struis et al. 2013). After the stabilization process, it is notable that the reference sample shows in addition to the presence of gypsum, other calcium sulfate phases (anhydrite ($CaSO_4$) and hannebachite ($Ca(SO)_3 \cdot 0.5(H_2O)$)) (see Table 4). This generally does not occur for the other CR samples. Only several weeks after stabilization some sulfate phases appear (generally gypsum, see Table 4) for samples stabilized with wood biomass ash. It is clear that the employment of this ash, instead of FGD residues, can provide several advantages in view of the possible reuse of this material in building applications, due to the absence of sulfate phases in the first weeks after the stabilization.

XRD patterns collected 3 months after the stabilization process show the presence of vaterite (μ-$CaCO_3$) for all samples realized with the wood pellet ashes (see Table 4).
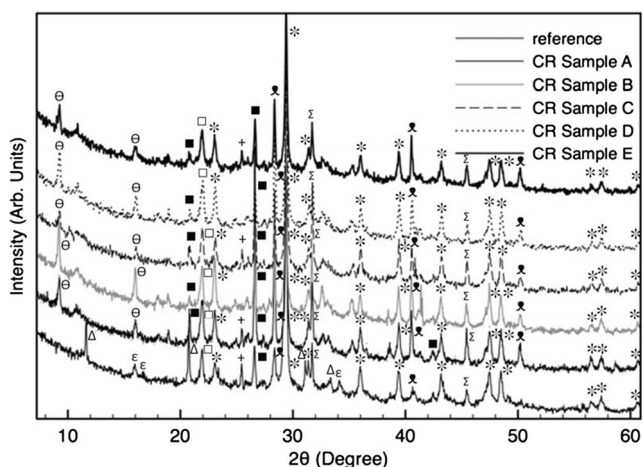

Fig. 4 XRD patterns collected on all samples obtained by treating MSWI fly ash with different wood pellet ashes by COSMOS-RICE procedure. (✳) Calcite ($CaCO_3$), (+) anhydrite ($CaSO_4$), (■) quartz (SiO_2), (Δ) gypsum ($CaSO_4 \cdot 2H_2O$), (ε) hannebachite [$2CaSO_3 \cdot (H_2O)$], (Θ)thaumasite $Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot12(H_2O)$,(☽) sylvite (KCl) ,(Σ) halite (NaCl) ,(☐) xristobalite SiO_2

Thaumasite ($Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot12(H_2O)$) has disappeared and, generally, gypsum can be found in the patterns. Thaumasite phase is generally formed at low temperatures (below 15 °C), with an abundance of moisture and the availability of calcium silicate, sulfate and carbonate ions (Bensted 1999). However, thaumasite formation has been reported in cementitious systems at higher temperatures (Bassuoni and Nehdi 2009). Thaumasite was demonstrated to be formed with pH > 10.5 (Gaze and Crammond 2000) and decomposes with pH < 10.5 to form calcite in the deteriorated matrix (Rahman and Bassuoni 2014). When sulfate is present and the pH is lower than 10.5 gypsum can be formed (Rahman and Bassuoni 2014). These findings are in accordance with the results shown in a recent publication (Bosio et al. 2014) were XRD patterns of all stabilized samples collected 3 months after the stabilization showed an increase in calcite contribution. This is attributed to a slow rate of carbonation in the stabilized samples. The MSWI fly ash had pH 12.5, and this value remained unaltered for all samples in the first weeks. Because of the carbonation, the pH of all stabilized samples (3 months after the stabilization) was observed to be in the pH range 7.5–8.5. This is consistent with the disappearance of thaumasite.

Concerning vaterite, this phase is the thermodynamically least stable phase among three polymorphic forms of calcium carbonate, but it is frequently formed under specific conditions. It was previously found in carbonation experiments involving MWSI fly ash (Bosio et al. 2014). Furthermore, it has been shown that the direct aqueous carbonation of FGD residue produces a mixture of vaterite and calcite phases (Song et al. 2012). Therefore, due to the carbonation reaction occurring for all samples, the final phases present in aged samples are calcite, gypsum, vaterite, and some crystalline silica and soluble salts. The increase of calcite contribution allows us to conclude that carbon dioxide sequestration is occurring and can thus be considered as an additional advantage of the proposed technology. It shows that biomass combustion can not only be considered to not contribute to the greenhouse effect, but also, it has been shown to be a potential means to promote the CO_2 sequestration.

To evaluate the amount of carbon dioxide that can be sequestered when using wood pellet biomass ashes instead of FGD residues, TGA and TG-MS measurements were performed (see Table 5 and Fig. 5). According to literature, three modes of decomposition of calcium carbonate can be distinguished (Thiery et al. 2007) and progressively appear when the level of carbonation increases: first, mode I (780 °C < T < 990 °C), then, mode II (680 °C < T < 780 °C), and finally, mode III (550 °C < T < 680 °C). Mode I is attributed to the decomposition of highly crystalline $CaCO_3$, namely calcite. Mode II decomposition is attributed to less perfect crystalline calcium carbonate, as for example vaterite (Šauman 1971). Finally, mode III decomposition is attributed to the presence of amorphous calcium
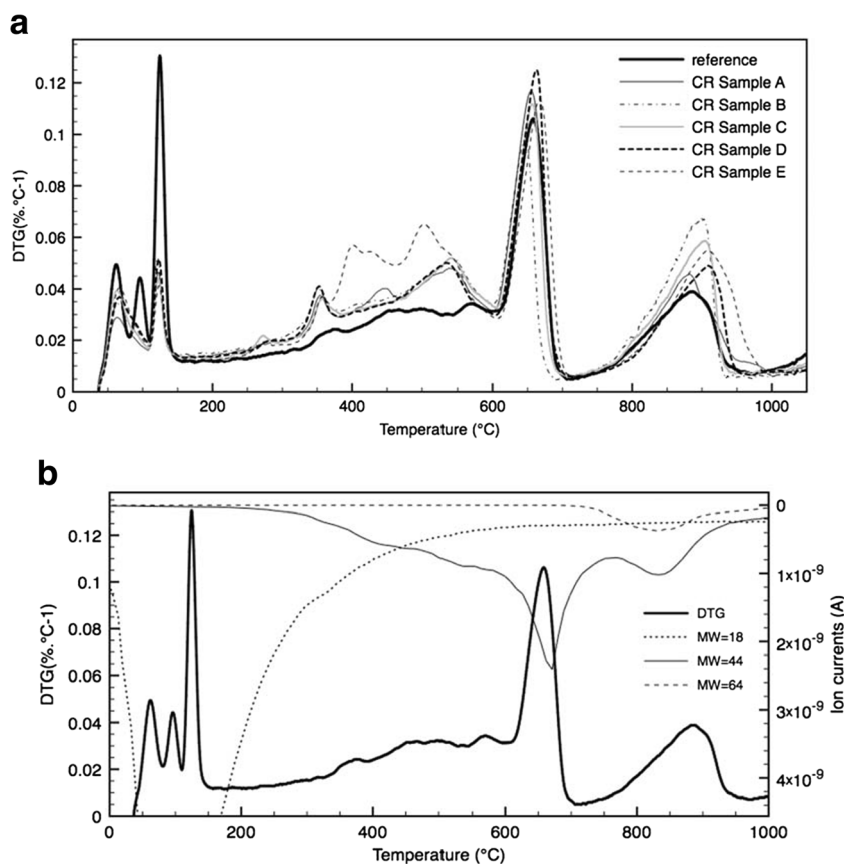
carbonate (Thiery et al. 2007). These three decomposition modes appear in the TGA and TG-MS data for all CR samples. TGA analyses (Table 5) show significant mass loss over the temperature range indicated by Thiery et al. (2007). Moreover, mass spectrometry data referring to MW = 44 (CO_2) shows a trend that is consistent with the TGA behavior in these temperature ranges. Therefore, from the data obtained from TGA and TG-MS, and summarized in Table 5, it is clearly shown that the amount of released CO_2 is extremely significant for all samples. The total weight loss of all CR samples attributed to CO_2 release is in the range of 19–25% for all samples, corresponding to a total calcium carbonate content ranging from 36 to 48%.

Although it is not the most prominent phase, calcium carbonate in the form of calcite was also found in the wood pellet ash (see Fig. 2). In particular, in the XRD patterns shown in Fig. 2, it is possible to identify several phases containing Ca in these samples. Moreover, it is also evident that wood pellet ash contains several other crystalline phases. In addition, an amorphous phase is also present. As a consequence, TGA diagrams of these samples (not shown) are very complicated and the quantification of the original, preexisting calcite is extremely difficult. However, from the data reported in Table 2, it is possible to conservatively estimate the theoretical total amount of calcite originally present in the wood ash samples, which would be added to the CR samples, by attributing all the Ca present in the wood pellet

ash, to calcite. On this basis, i.e., supposing that all Ca in wood pellet ash is contained in the calcite (this allows to make a very conservative estimation), the theoretical maximum amount of calcite added to CR samples, by using wood pellet ash, is less than 6%.

Considering MSWI fly ash, it is possible to evaluate the amount of calcium carbonate (crystalline and amorphous), present in original ash. It corresponds to about 45.8%. Taking into account this quantity and the theoretical maximum amount of calcium carbonate that may be present in biomass ashes (less than 6%), the theoretical conservative maximum amount of carbonates found in stabilized samples, that may be attributed to the raw materials, corresponds to a 27%. As a consequence, the minimum amount of calcium carbonate that can be attributed to carbonation reactions occurring during the stabilization processes, range from 9 to 21% in the stabilized materials.

The obtained quantities of calcite for the reference sample are consistent with previous analysis realized by means of XRD, that allowed quantification of the amounts of only calcite and vaterite (crystallized phases), which were found to be greater than 20% (in the present case it results in about 22%) (Bontempi et al. 2010b). In particular, the contributions due to amorphous calcium carbonate and vaterite (very low) of all samples obtained here by means of wood pellet ash

stabilization are comparable with values obtained for the reference CR sample. The main difference with the reference sample can be attributed to the first mode of calcium carbonate decomposition (calcite), with higher results for samples realized with wood pellet ashes in respect to the reference sample. From the data obtained by means of TGA it can be shown that mode III decomposition corresponds to approximately one half of the weight loss. This indicates that a substantial amount of amorphous calcium carbonate is present in the samples.

It is important to highlight that in the range of 780–990 °C, SO_2 decomposition also takes place (see Fig. 5b). However, this contribution is undetectable for samples realized using wood pellet ashes. On the contrary, this contribution is appreciable in the reference sample. This means that the values of mass loss attributed to calcium carbonate decomposition are lower for the CR reference sample (in respect to the values reported in Table 5). As a consequence, the carbonation capability of other COSMOS-RICE samples obtained using wood pellet ash, are much higher than that of the reference CR sample.

Conclusions

In the coming years, waste management strategy must address improved sustainability by closing production cycles, wherein a waste material will become the raw material input for production in another plant or process, improving both environmental and economic benefits through efficient reuse of resources. Moreover, the technologies used for the valorization of wastes must, as much as possible, mitigate any additions to the environmental footprint to the existing waste-derived processes. The work presented here shows that wood biomass ash, which can represent an unexpected environmental problem, can be reused, with the addition of industrial ashes, to stabilize MSWI fly ash and to produce a new material that could be employed to partially solve the European problem of "raw materials." In particular, our results demonstrate that ash produced by domestic and industrial combustion can potentially be recovered, to provide decreased waste generation from these sectors and to improve the sustainability of some industrial processes (as for example thermal valorization of waste and the coal combustion), by producing added value compounds. The final obtained product has been shown to provide carbon dioxide permanent sequestration, with a carbonate content higher in samples realized by using wood pellet ash, in respect to sample realized by using FGD residues. In particular, TGA analysis showed that the TGA-mass spectroscopy determined weight loss of CR samples attributed to the carbonates decomposition is always higher than 20% for samples realized using wood pellet ash, making it possible to conclude that for this process wood pellet biomass CO_2 conversion can be negative.

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