



## Research article

# Mitigating CO<sub>2</sub> emissions through an industrial symbiosis approach: Leveraging cork ash carbonation

Giampiero Pasquale Sorrentino<sup>a</sup>, Renato Guimaraes<sup>b</sup>, Antonella Cornelio<sup>a</sup>,  
Alessandra Zanoletti<sup>a</sup>, Bruno Valentim<sup>b</sup>, Elza Bontempi<sup>a,\*</sup>

<sup>a</sup> *INSTM and Chemistry for Technologies Laboratory, Department of Mechanical and Industrial Engineering, University of Brescia, Via Branze, 38, Brescia, 25123, Italy*

<sup>b</sup> *Earth Science Institute–Porto Pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, Porto, 4169-007, Portugal*

## ARTICLE INFO

## Keywords:

Cork ash  
Municipal solid waste incineration  
Carbonation  
CO<sub>2</sub> capture  
Fly ash  
Bottom ash

## ABSTRACT

This study explores for the first time the potential use of carbonation as a method for managing cork ash, a byproduct of biomass waste incineration. Additionally, the cork ash was combined with fly ash from municipal solid waste incineration to leverage the carbonation reaction's ability to stabilize heavy metals. The findings suggest that subjecting biomass ash to carbonation can lead to the formation of mineral carbonates, effectively capturing CO<sub>2</sub> and reducing its release into the atmosphere. The combination of various alkaline wastes and the stabilization of leachable heavy metals through carbonation reactions also opens opportunities for synergies between different industrial sectors. Finally, the study proposes a route for the obtained materials valorisation via 'end of waste': the reuse of the resulting materials as substitutes for natural resources, particularly in applications like building materials and polymer composites, can further enhance carbon dioxide savings.

## 1. Introduction

Cork is a biomass, that can be found in some regions, such as the Iberian Peninsula, which is responsible for producing 147 kt/year (79 %) of the world's cork. Portugal alone produces approximately 85 kt/year (46 %) of the global cork supply [1]. During the cork process production, approximately 20–30 % of the cork is wasted, mainly as cork powder and other residues. Considering that Portugal generates about 5 Mt/year of greenhouse (GHG) gas emissions from waste management [2], the possibility of suitably managing cork waste may help to reduce the impact of GHG.

The cork powder is suitable for energy production since is mainly composed of suberin (45 %), lignin (27 %), polysaccharides (12 %), tannins (6 %), ceroids (5 %), and ash (5 %) [3,4]. The combustion byproduct, cork ash is typically disposed of in landfills rather than being valued by biomass processing companies [5]. Ash disposal in Europe is becoming increasingly difficult due to the scarcity and cost of landfill sites, in addition to being subject to increasingly stringent environmental regulations [6,7]. Hence, it is imperative to adopt solutions aligned with the principles of the circular economy. Although the available literature on the reuse of cork ash is relatively limited, there exist some possibilities for its reuse. One promising application involves utilizing cork ash as a substitute for

\* Corresponding author.

E-mail addresses: [g.sorrentino002@unibs.it](mailto:g.sorrentino002@unibs.it) (G.P. Sorrentino), [up200506169@fc.up.pt](mailto:up200506169@fc.up.pt) (R. Guimaraes), [antonella.cornelio@unibs.it](mailto:antonella.cornelio@unibs.it) (A. Cornelio), [alessandra.zanoletti@unibs.it](mailto:alessandra.zanoletti@unibs.it) (A. Zanoletti), [bvvalent@fc.up.pt](mailto:bvvalent@fc.up.pt) (B. Valentim), [elza.bontempi@unibs.it](mailto:elza.bontempi@unibs.it) (E. Bontempi).

<https://doi.org/10.1016/j.heliyon.2024.e32893>

Received 28 May 2024; Received in revised form 11 June 2024; Accepted 11 June 2024

Available online 13 June 2024

2405-8440/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

cement in construction materials. However, it has been found that cork waste ash cannot meet the necessary chemical requirements for use as a pozzolan or filler in cement-based materials [3]. Another potential use is as a fertilizer material, although it is not recommended for use in plant crops intended for human and animal consumption due to the presence of heavy metals [8]. Cork ash can also be pelletized for use as fuel in boiler systems, although its low bulk density can make storage and transportation challenging [9]. Finally, cork ash can be converted into biochar, which has been shown to have the potential for CO<sub>2</sub> capture [10], and it is an adsorbent for heavy metals [11].

Furthermore, given the limited recovery of this waste, it becomes evident that additional research and testing are necessary to thoroughly investigate the potential applications and constraints associated with reusing cork ash. In particular, the literature suggests that different ash typologies, such as biomass ash [12–14], coal combustion fly ash, waste incinerator fly and bottom ashes [15], industrial waste [16], and municipal waste combustion residues [17], can be used for carbonation [18].

CO<sub>2</sub> concentration in the atmosphere today ( $\approx 401$  ppm) is about 70 % higher than that observed during pre-industrial times (280 ppm) and is expected to rise to around 550 ppm by 2050 [19]. Among the options to reduce GHG emissions, CO<sub>2</sub> capture, directly obtained by carbonation of biomass ash during combustion and post-combustion of biomass, is a recent approach that has high potential [20,21], namely because biomass ashes present a considerable amount of alkaline and alkaline earth components [22] which theoretically confer a great potential to sequester CO<sub>2</sub> [23]. This technology also offers the advantage of being an exothermic process, thus reducing energy consumption and costs involved, in contrast to other technologies [24]. In addition, extra CO<sub>2</sub> capture potential was observed due to the additional fixation and immobilization of (1) CO<sub>2</sub> in flue gas during biomass combustion and biomass ash cooling [21]; and (2) atmospheric CO<sub>2</sub> during subsequent storage of biomass ash under natural conditions [25].

Then also cork ash may present a higher potential to capture CO<sub>2</sub> than other alkaline waste because, in addition to other factors, generally biomass ash presents a higher particle surface area [26]. However, the phenomenon of CO<sub>2</sub> capture by biomass ash is at an early stage of investigation, and more detailed studies are needed to investigate the different waste ash typologies, the CO<sub>2</sub> sequestration capacity, and the ash carbonation mechanisms (fresh and stored) from different types of biomasses [21]. The high theoretical potential of biomass ash to capture CO<sub>2</sub> is mainly attributed to the presence of minerals or specific phases of Ca, Mg, K, and Na, such as carbonates, bicarbonates, oxyhydroxides, phosphates, sulfates, chlorides, silicates, and amorphous [21,27].

Based on the literature data, it can be inferred that cork ash has the potential to be carbonated through CO<sub>2</sub> capture, due to its chemical composition. However, to the best of the authors' knowledge, no papers address the carbonation of cork ash by CO<sub>2</sub> capture.

This work aims to propose simple and sustainable technologies to produce new eco-materials, derived from waste, to be used as a substitute for natural resources. In particular, the novelties of the proposed research concern the demonstration for the first time of the ability of cork ash to capture CO<sub>2</sub>. Moreover, combining various waste typologies for recovery could play a pivotal role in promoting resource efficiency, ensuring environmental sustainability, and fostering economic growth. This strategic approach is essential for achieving a circular economy and mitigating the adverse effects of waste on our planet. For this aim, this work also assesses the behaviour of this ash, both in terms of CO<sub>2</sub> uptake and stabilization, when mixed with other waste, such as municipal solid waste incineration (MSWI) ashes, which are usually composed of bottom ash (BA) and fly ash (FA).

In particular, MSWI FA is considered a hazardous waste because of its volatile nature and its content of heavy metals, chlorides, and salts [28] and for this reason, it is necessary to treat it before landfilling or reusing it. MSWI BA is considered a byproduct, being a non-hazardous waste, which can generally be reintroduced into the market as a source of metals and aggregates for construction [12].

Therefore, another fundamental novelty of this work is that all the materials involved in the technology are wastes or byproducts, then commercial chemicals or natural resources are not required for the process. Finally, it is also interesting to notice that the selected plant providing MSWI ashes is based on the co-combustion of municipal solid waste and sewage sludge, containing high concentrations of heavy metals (then it cannot be reused in agriculture). Then, this paper proposes a possible solution to manage the residues derived by the treatment of complex wastes, from different origins (biomass, sewage sludge, and municipal solid waste), with great attention to the Portugal situation, producing all these kinds of wastes.

## 2. Material and methods

### 2.1. Samples

3 different Cork fly ashes (CFA) from 2 combustion systems (grate combustor and fluidized bed combustor) from RELVAS II enterprise (Portugal), municipal solid waste incineration fly ash (MSWI FA), and bottom ash (MSWI BA) from A2A waste-to-energy plant (Brescia, Italy) were used for the procedures described thereafter and the characteristics of the sample are reported in Table 1. In the MSWI plant, sewage sludge is mixed with municipal solid waste to be incinerated [12].

**Table 1**

Description of fuel, type of ash, combustion system and capture system, and identification of sample code.

Fuel	Type	Combustion system	Capture system	Sample Code
Cork	Fly ash	Grate	Cyclone	CFA1
Cork	Fly ash	Grate	Electrostatic precipitator	CFA2
Cork	Fly ash	Fluidized bed combustor	Cyclone	CFA3
Waste	Fly ash	Grate	Bag filter	MSWI FA
Waste	Bottom ash	Grate	Hopper	MSWI BA

First, the MSWI BA was dried at 105 °C for approximately 2 h. It was then subjected to magnetic separation using a ferrite magnet to remove particles larger than 2 mm. Subsequently, the sample was successively ground and sieved to ensure a diameter of less than 106 µm, henceforth identified as MSWI BA. This particular diameter represents the smallest size attainable with the available sieves. The decision to utilize this particles dimension is twofold: it promotes pozzolanic reactions and acknowledges research indicating that even finer grain sizes of MSWI BA may harbor hazardous substances capable of leaching [29,30].

## 2.2. Blends preparation for carbonation trials

After, three blends were prepared containing 32 wt% of CFA1, CFA2 or CFA3 mixed with 59 wt% of MSWI FA, 9 wt% of MSWI BA. These are identified as “MIX”, followed by the cork ash identification, and the type of the process tested (natural carbonation (NC) and accelerated carbonation (AC)): for example, MIX CFA1 AC.

## 2.3. Carbonation

The maximum theoretical CO<sub>2</sub> sequestration capacity by carbonation reaction can be calculated as a function of parent material chemical composition using the *Stenoir* formula (Eq. (1)) [27,31,32]:

$$\text{CO}_2 (\%) = 0.785 \times (\text{CaO} - 0.7 \times \text{SO}_3) + 1.09 \times \text{Na}_2\text{O} + 0.93 \times \text{K}_2\text{O} \quad (1)$$

However, other studies claim that all carbonates present in biomass ash can react with CO<sub>2</sub> to form bicarbonates, thus, the maximum percentage of CO<sub>2</sub> sequestration by biomass ash can be calculated individually using Eq. (2) [23]:

$$\text{CO}_2 (\%) = \frac{m_{\text{carbonate}} \times M_{\text{CO}_2}}{M_{\text{carbonate}}} \quad (2)$$

Where CO<sub>2</sub> (%) is the theoretical percentage of CO<sub>2</sub> sequestration by each carbonate,  $m_{\text{carbonate}}$  is the carbonate content,  $M_{\text{carbonate}}$  is the molar mass of the carbonate, and  $M_{\text{CO}_2}$  is the molar mass of CO<sub>2</sub>.

In the general case of biomass ash, these normally contain a considerable amount of free CaO. Considering the aqueous carbonation reactions, the hydration of CaO (Eq. (3)) is an irreversible reaction, followed by the dissolution of Ca(OH)<sub>2</sub> (Eq. (4)). The reaction of carbon dioxide in water (Eq. (5)) makes available carbonate ions (Eq. (6)) for calcium carbonate precipitation (Eq. (7)) [33]:



Ca(OH)<sub>2</sub> may be available as a crystalline phase in the ashes (cork and MSWI FA) and may also contain CaClOH (MSWI FA), available for the carbonation reaction according to Eq. (8) [15].



It is important to point out that not all the Ca in the residues is contained in a reactive phase, such as CaSO<sub>4</sub> and CaCO<sub>3</sub> are not available for carbonation. It is very interesting to notice that all the samples also contain an amorphous phase which can be a provider of alumina-silica species necessary for the stabilization of the MSWI FA [17].

### 2.3.1. Natural carbonation

The samples, “MIX CFA1”, “MIX CFA2” and “MIX CFA3” were submitted to two trials of NC as already reported [18]. Each sample was mixed with ultrapure de-ionized water, with a 0.91 S/L ratio, obtained from a Milli-Q (MQ) purifier system (Millipore DirectQ-5 TM), and stirred for 10 min. From the obtained slurry, one portion (≈64 g) was cured for one month at room temperature (“NCA” trials) and another portion (≈64 g) was left in the oven at 120 °C for 4 h (“NCB” trials), all samples were ground and submitted to XRD analyses and TXRF analysis of the eluates after the leaching tests.

### 2.3.2. Accelerated carbonation

All the samples tested for carbonation corresponded to a mass of 33.6 g, and a water content of 30.2 mL. All the tests were realized in the same conditions. Several AC trials were carried out. For the “MIX CFA1” sample the tests were repeated several times, with a different duration of 5, 17, 24, 48, and 72 h, to make the samples characterization after the carbonation procedure. For “CFA1” sample the tests were repeated with a duration of 5 and 17 h. Each sample was prepared in the same way as described for the NC, and then placed into a reactor as described by Ref. [34]. The experimental equipment for the AC process is reported in supporting information

S1. To assess only the effect of CO<sub>2</sub> on the sample, all air inside the cylinder is removed with a vacuum pump. Then, CO<sub>2</sub> (99.99 %) is inserted into the cylinder at a maximum pressure of 15 bar, which corresponds to 1 g of CO<sub>2</sub>, and the pressure is recorded throughout the test, at room temperature. Finally, both the samples submitted to NC and AC tests were removed, dried at 105 °C, and ground before carrying out the characterization analysis reported in the next section. A summary of the NC and AC tests is presented in Table 2. The mineralogical identification and quantification of phases by XRD were performed on the samples before and after the carbonation tests.

#### 2.4. Leaching test

To assess the amounts of heavy metals in the samples, leaching tests were carried out following CEN guidelines [35,36]. 20 g of each dried sample was combined in a 1:10 ratio with 200 mL of Milli-Q water, which was then stirred at room temperature for 2 h [37]. After that, 0.45 µm pore membranes were used for filtering. An 827 pH Lab Metrohm was used to gauge the filtered fluids' pH levels.

#### 2.5. Chemical analysis (TXRF)

Using a Bruker S2 Picofox Total Reflection X-ray Fluorescence (TXRF) system (Bruker AXS Microanalysis GmbH, Berlin, Germany) outfitted with a Silicon Drift Detector and a Mo tube running at 50 kV and 750 A, the chemical analysis of the eluates was carried out. Ga was used as the internal standard for quantification (Ga-ICP Standard Solution, Fluka, Sigma Aldrich, Saint Louis, MO, USA). Weighing around 0.010 g of 100 mg/L Ga solution, 0.100 g of eluate, and 0.89 g of Milli-Q water produced 1 mL of solutions with a final concentration of 1 mg/L Ga. Prior to each TXRF measurement, the materials were homogenized in a vortex shaker for 1 min at 2500 rpm. A 10 µL drop of the sample was placed in the center of a plexiglas slide to create the sample for analysis. To dry the drops, a hot plate was used on a laminar hood at a temperature of 50 °C. By exposing the specimen to X-rays for 600 s, the residues were measured. Using routine deconvolution based on mono-element profiles, TXRF spectra were examined using the instrument PICOFOX version 2.3.14.0 to determine the peak areas. Chemical elements having atomic numbers below 19 cannot be studied by TXRF due to their poor fluorescence yield [38]. Examples of these are C, O, and Na.

#### 2.6. Mineralogy (XRD)

X-ray diffraction (XRD) was made to structurally characterize the raw ash (starting raw materials), the mix of the raw ashes ("MIX" sample) and "AC", "NCA" and "NCB" samples, in terms of crystalline and amorphous composition. An X'Pert PRO diffractometer (PANalytical, Malvern, UK) equipped with a Cu K $\alpha$  anode (40 kV, 40 mA) was used for the XRD measurements on the powder samples. The collection range was 15–60° in 2theta. The phase compositions were determined using the PANalytical X'Pert HighScore Plus version 2.1.0 software (associated with the ICDD PDF2 database, 1998); moreover, the quantification of the crystalline and amorphous phases in the samples was done using the Rietveld method and corundum (Al<sub>2</sub>O<sub>3</sub>) as internal standard (25 % in weight). The quantification of the phases was based on the calculations performed using the PROFEX software packages connected with the Crystallography Open Database (COD) and the BGMN Database provided by the software itself [39].

### 3. Results and discussions

#### 3.1. Ash composition

The composition of the MSWI ash used in the mixtures was characterized by Ref. [18] MSWI BA has a large amount of Ca (79 g/kg)

**Table 2**

Samples description, based on the carbonation tests. Three blends were prepared containing 32 wt% of CFA1, CFA2, or CFA3 mixed with 59 wt% of MSWI FA, 9 wt% of MSWI BA. These are identified as "MIX", followed by the cork ash identification, and the type of the process tested (natural carbonation (NC) and accelerated carbonation (AC)). The number defines the time (h) of the carbonation. NCA stands for samples cured for one month at room temperature. NCB stands for samples left in the oven at 120 °C for 4 h.

Samples	Time	Carbonation Type	Oven treatment (4 h at 120 °C)
CFA1 AC5	5 h	Accelerated	No
CFA1 AC17	17 h	Accelerated	No
MIX CFA1 AC5	5 h	Accelerated	No
MIX CFA1 AC17	17 h	Accelerated	No
MIX CFA1 AC24	24 h	Accelerated	No
MIX CFA1 AC48	48 h	Accelerated	No
MIX CFA1 AC72	72 h	Accelerated	No
MIX CFA 1 NCA	1 month	Natural	No
MIX CFA 1 NCB	4 h	Natural	Yes
MIX CFA 2 NCA	1 month	Natural	No
MIX CFA 2 NCB	4 h	Natural	Yes
MIX CFA 3 NCA	1 month	Natural	No
MIX CFA 3 NCB	4 h	Natural	Yes

and Fe (29 g/kg) and the presence of S (2 g/kg), K (8 g/kg), Cl (4 g/kg); in addition, it also contains heavy metals such as Zn (4 g/kg), Pb (3 g/kg), and Cu (2 g/kg). Compared to MSWI BA, MSWI FA contains a higher amount of S (13 g/kg), and K (25 g/kg), while Fe has a lower amount (4 g/kg). The Ca is about the same order of magnitude (69 g/kg), and regarding heavy metals, Zn is higher (9 g/kg) and Pb lower (1 g/kg). According to Assi et al. the heavy metals present in the MSWI FA are in a leachable form (Pb 42.17 mg/L and Zn 9.72 mg/L) which justifies the need for its stabilization, which can be achieved through natural carbonation [15].

The complete characterization of the CFA samples used in the mixtures is reported in the supporting information (S1). Compared to MSWI ash samples, they have a higher amount of Ca (184–245 g/kg), a similar amount of Fe (11–12 g/kg), and much smaller amounts of Pb (0.030–0.055 g/kg) and Zn (0.071–0.187 g/kg). The solubility of Pb and Zn, evaluated by the leaching tests, is quite low (Zn < 0.3 mg/L, Pb < 0.1 mg/L).

According to XRF analyses (supporting information S2), the cork ashes have a composition made mainly by CaO (30.4–40.87 %) and SiO<sub>2</sub> (32.69–45.45 %), followed by Al<sub>2</sub>O<sub>3</sub> (6.34–7.64 %), K<sub>2</sub>O (5.85–8.41 %), MgO (1.63–5.84 %), Fe<sub>2</sub>O<sub>3</sub> (2.1–2.44 %), P<sub>2</sub>O<sub>5</sub> (1.5–3%) and TiO<sub>2</sub> (0.51–1.7 %).

Through XRD analysis and quantification of phases by the Rietveld method (reported in Fig. 1), it is possible to observe a high presence of calcium-based species in all CFA samples, such as calcite, lime, portlandite, anhydrite, and perovskite, in accord with XRF data. These samples have also a consistent amount of quartz and an amorphous phase (see Supporting S3). In CFA1 and CFA2 the presence of sylvite was found.

MSWI ashes also contain Ca-bearing species, such as calcium chloride hydroxide, and calcite for both MSWI BA and FA, only the last one contains portlandite and anhydrite (with its hydrated and semi-hydrated forms). Both MSWI ashes contain tripotassium phosphate because of the co-incineration of municipal solid waste and sewage sludge. Finally, there is the presence of halite and sylvite in MSWI FA. The presence of CaClOH could be due to the scrubbing treatment located before the capturing system of the MSWI FA, which consists of the addition of CaO/Ca(OH)<sub>2</sub> to remove acid gases such as SO<sub>2</sub> and HCl produced by the combustion of waste [18].

### 3.2. Carbonation tests

Based on the X-ray Fluorescence (XRF) data reported in the supporting information S2, the maximum CO<sub>2</sub> uptake capacity of the cork fly ash has been calculated and results to be in the range of 30–37 %.

The AC test was realized for the three cork ash samples, to verify their carbonation capability, due to the lack of information in the literature. Supporting information S4 reports the results of the test performed on CFA1. It appears that the pressure drops from 15 bar to less than 2 bar, after 17 h, demonstrating the capability of this waste to sequester CO<sub>2</sub>. A similar trend was observed for the CFA2 and CFA3 samples (not reported here). Then these ashes were mixed with MSWI fly ash, as described in the experimental section, to verify their capability in CO<sub>2</sub> sequestration, in combination with the heavy metals' stabilization properties. The Rietveld analysis was realized for all the mixtures, to evaluate the amount of CO<sub>2</sub> theoretically sequesterable, calculated stoichiometrically (Table 3), based on the quantity of the crystalline reactive compounds such as CaO, Ca(OH)<sub>2</sub>, and CaClOH. It results 1.8, 2.6, and 2.4 g respectively for MIX CFA1, MIX CFA2, and MIX CFA3, considering the starting mixture amount of 33.6 g. Fig. 2 reports the trend of the pressure during the AC test for sample MIX CFA1, with the indication of the test repetition, at different times, to follow the kinetics of the CO<sub>2</sub> sequestering process.

For the AC tests, the quantification of sequestered CO<sub>2</sub> was determined using three methods: (i) system pressure difference during the test by using the ideal gas law; (ii) mass variation before and after the test; and (iii) phase quantification by Rietveld refinement, before and after the AC trials. Instead, for the NC tests, only the Rietveld refinement method was utilized.

#### 3.2.1. Pressure system difference

During the AC trials ("MIX" sample), the pressure shows a sudden drop in the first 5 h, reaching a drop of about 9 bar. After, the

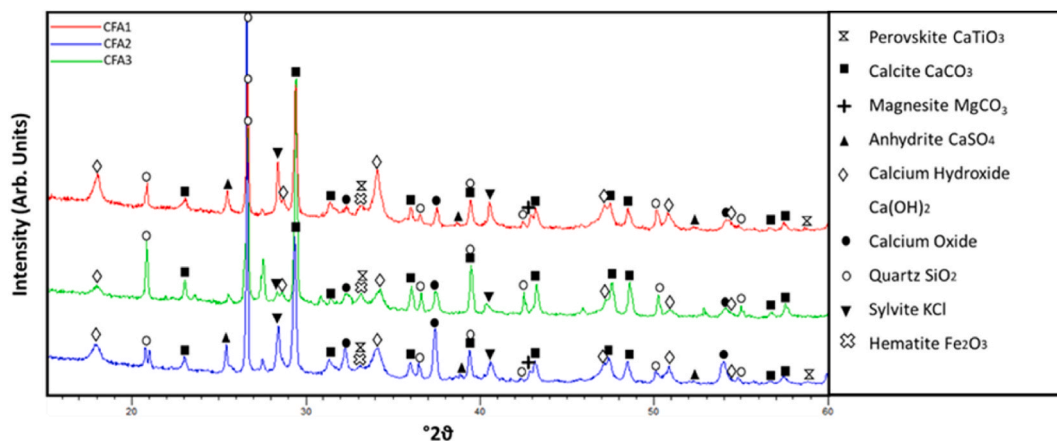
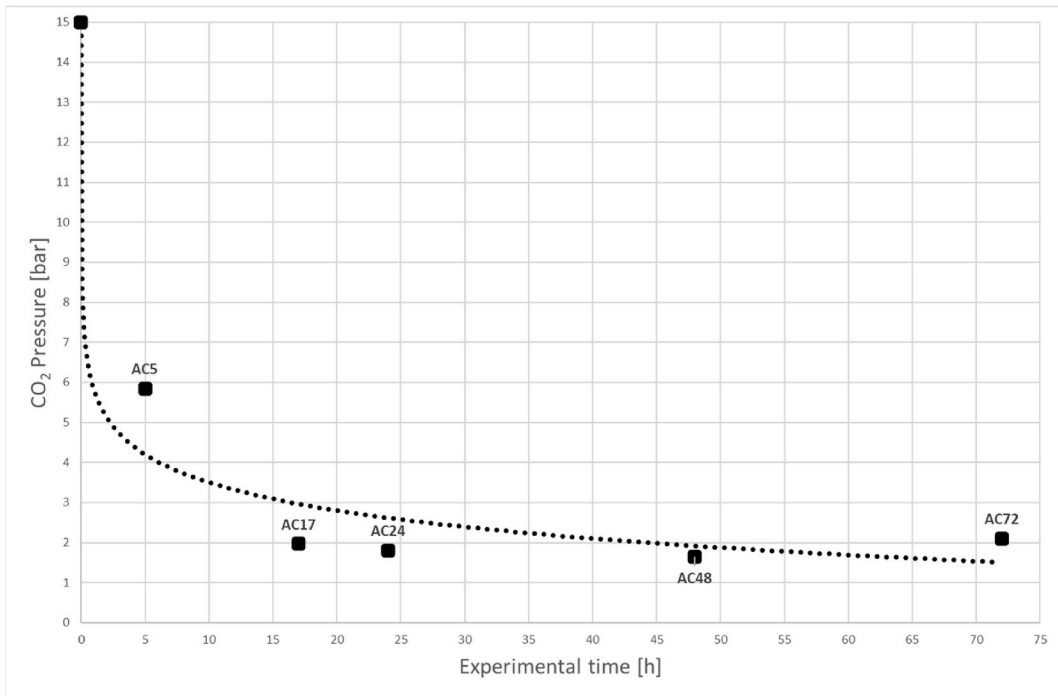


Fig. 1. XRD Spectrum results of cork ashes.

**Table 3**  
XRD-Rietveld results of ashes (cork and MSWI) and ash mixtures, before and after carbonation tests, expressed in %.

Sample	CFA1		MIX CFA1							MIX CFA2			MIX CFA3			
	AC5	AC17	Bulk	AC5	AC17	AC24	AC48	AC72	NCA	NCB	Bulk	NCA	NCB	Bulk	NCA	NCB
Portlandite (Ca(OH) <sub>2</sub> )	10	8	2		3					4	4		2	4		1
Calcium hydroxy chloride (CaClOH)			13	9	10	7	9	7	3	10	16	3	10	16	4	10
Calcite (CaCO <sub>3</sub> )	20	23	16	18	18	19	20	21	29	13	16	22	16	15	19	16
Vaterite (CaCO <sub>3</sub> )									1			7			6	
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	1	1	2	2	2	2	2	3		2	1		2	1		2
Perovskite (CaTiO <sub>3</sub> )	3	2	2	2	2	2	2	2	2	2	2	1	2	2	1	2
Magnesite (MgCO <sub>3</sub> )	3	2	3	3	2	3	2	3	1	2	3	1	3	3	2	3
Anhydrite (CaSO <sub>4</sub> )	1	1	3	5	4	4	4	3	2	6	3	3	6	2	2	4
Gypsum (CaSO <sub>4</sub> ·2 H <sub>2</sub> O)	2	2	1	1	3	1	1	2	2	1	1			2	1	
Bassanite (CaSO <sub>4</sub> ·0.5 H <sub>2</sub> O)		1	4	3	2	4	4	3	4	3	3	4	3	3	3	3
Quartz (SiO <sub>2</sub> )	10	10	4	3	4	7	4	4	5	3	5	5	4	5	4	8
Sylvite (KCl)	2	2	3	3	2	2	3	3	2	3	3	2	3	3	2	2
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	1	1	1		1	1				1	1					
Halite (NaCl)	1	2	4	4	3	3	3	3	2	3	4	3	3	4	3	3
Tripotassium phosphate (K <sub>3</sub> PO <sub>4</sub> )	3	2	3	4	3	5	4	4	2	3	2	1	3	2	1	2
Amorphous	45	44	39	44	40	40	45	45	45	45	37	46	44	40	51	45

<sup>a</sup> The mineral composition of the materials refers to the dry samples.

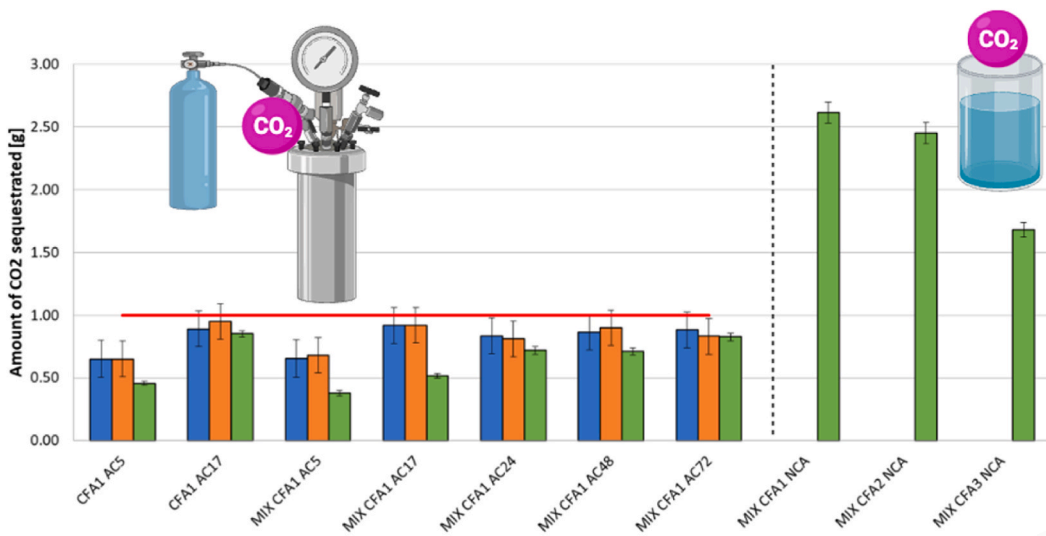


**Fig. 2.** Results of pressure trend (bar) during the accelerated carbonation (AC) tests conducted on MIX CFA1. The dotted line is the log. curve interpolating the experimental data.

pressure trend slowly decreases towards a plateau, stabilizing already between 17 and 24 h (Fig. 2). The pressure drop behavior suggests the possible conclusion of the carbonation reaction in one day, due to the sequestration of almost all the available CO<sub>2</sub>. Similar behavior was obtained for the AC tests realized by using just the CFA1 (supporting information S4). By the variation of the pressure, it was possible to evaluate the CO<sub>2</sub> mass variation.

3.2.2. Mass variation

The assessment of CO<sub>2</sub> sequestration yield occurs at the process’s conclusion by leveraging Lavoisier’s law. This involves measuring the difference in mass of a closed system (a cylinder containing the sample and CO<sub>2</sub>) before and after introducing CO<sub>2</sub> during the trials.



**Fig. 3.** Amount of CO<sub>2</sub> sequestered (g) in the NCA trials (samples cured for one month at room temperature) through Rietveld refinement and in the accelerated carbonation (AC) tests, through 3 different methods: i) System pressure difference; ii) mass variation; iii) Rietveld refinement. The amount of the inserted CO<sub>2</sub> in the accelerated carbonation experiments is also reported.

By applying this method, we observe that both cork ashes and the ash mixture exhibit similar behavior. In both cases, approximately 67 % of the  $\text{CO}_2$  is sequestered within the first 5 h, eventually reaching around 90 % of the initially inserted  $\text{CO}_2$  after 17 h (Fig. 2). Comparing the cork ash with the ash mixture trials, in the 5 and 17-h trials the cork ash seems to sequester more  $\text{CO}_2$  (Fig. 3).

### 3.2.3. Rietveld refinement

Although the XRD analysis does not allow the evaluation of the composition of the amorphous phase, it can allow the evaluation of the proceeding of the carbonation, considering the evolution of the amount of crystalline phases. The results of the Rietveld analysis (Table 3, Fig. 3) allow quantifying the decrease in the main reactive species with carbon dioxide, which are calcium chloride hydroxide ( $\text{CaClOH}$ ), calcium oxide ( $\text{CaO}$ ), and portlandite ( $\text{Ca(OH)}_2$ ), and the increase in calcium carbonate ( $\text{CaCO}_3$ ). This can allow to confirm the hypothesis of the occurrence of the carbonation reaction. The results of the Rietveld refinements performed after all the carbonation tests are reported in Fig. 3. The results, particularly those related to the equilibrium condition, are very similar to those obtained through the evaluation of the mass difference of the circuit before and after the carbonation reaction, especially for the ash mixtures, and to the results obtained through the pressure variation. These observations allow us to conclude that these 3 methods are efficient in determining the amount of  $\text{CO}_2$  sequestered in AC trials, confirming previous results [34] for similar processes.

Thus, it is possible to observe that the amount of the sequestered  $\text{CO}_2$  increased in AC for both ashes (cork or ash mixture) with increasing test time. Particularly, the Rietveld refinement shows that the decrease in the percentage of the  $\text{Ca(OH)}_2$  and  $\text{CaClOH}$  phases corresponds to an expected amount of resulting calcite.

However, it was lower than the theoretical amount of  $\text{CO}_2$  sequestration calculated based on the stoichiometry of the reactions which indicates that the carbonation reaction is not completed after 17 h and 72 h for the cork ashes and the ash mixture (cork and MSWI), respectively. Indeed, the Rietveld refinement procedure allows us to highlight the residual presence of  $\text{Ca(OH)}_2$  (8 %) in the trials with cork ash and  $\text{CaClOH}$  (7 %) in the trials with a mixture of ashes, showing that after 17 and 72 h, respectively. The data show that the amount of the sequestered  $\text{CO}_2$  is always lower than 1 g, for the accelerated carbonation experiments. The initial amounts of  $\text{CaClOH}$  and  $\text{Ca(OH)}_2$  in the ash mixture show a reduction after 5 h, the amount of  $\text{Ca(OH)}_2$  reduces to zero and the amount of  $\text{CaClOH}$  reduces by 31 %. In contrast, a calcite increase of 13 % was observed in the first 5 h and 31 % after 72 h, compared to the ash mixture sample before the trial. In the cork ashes,  $\text{Ca(OH)}_2$  initially increases in an amount equivalent to the  $\text{CaO}$  decrease, due to the  $\text{CaO}$  hydration reaction (Eq. (3)). After the 17 h trial, a decrease (11 %) of  $\text{Ca(OH)}_2$  and an increase (35 %) of calcite can be observed, in comparison to the initial sample, which indicates that despite the occurring of the carbonation reaction, the reaction is not complete since the presence of  $\text{Ca(OH)}_2$  is still observed in the sample. On the contrary, NC samples show the amount of sequestered  $\text{CO}_2$  was greater than the stoichiometric expected values. This suggests that the amorphous phase is also involved in NC reactions, in accordance with similar experiments realized with MSWI FA by Ref. [34]. In particular, the formation of vaterite, observed for all the NCA-MIX samples, was often attributed to the crystallization of the amorphous phase [15,18]. Indeed, calcium carbonate exhibits both amorphous and crystalline forms. The amorphous variant usually manifests as monohydrated  $\text{CaCO}_3$ , while the crystalline variations are generally anhydrous and classified as rhombic calcite, needle-like aragonite, or spherical vaterite. In ambient conditions, calcite is the most stable phase, followed by aragonite and then vaterite [40]. Then, over longer periods, a slower carbonation mechanism may occur for the amorphous phases, as suggested by Ref. [15]. After a month, the NC of the ash mixture with cork ash allows the capture of about 132, 124, and 85  $\text{gCO}_2/\text{Kg MSWI FA}$  respectively, which is in accordance with values observed for a mixture of MSWI FA with coal fly ash and flue gas desulphurization residues (165  $\text{gCO}_2/\text{Kg MSWI FA}$ ) [34]. This conclusion is also corroborated by the XRD results of the samples submitted to the NC trials since the presence of vaterite and a significant increase in the amount of calcite can be observed (Table 3) in comparison to the AC trials. To better understand the difference between the AC and NC process, the behavior of the cork ash sample submitted to both processes can be discussed. In both cases, there is an increase in calcite, much higher in the case of the NCA tests, where the formation of vaterite is observed, despite the AC where it is not detected. In particular, the total amount of  $\text{CaCO}_3$  phases (30 %, 29 % and 25 % respectively) after the NCA test cannot be justified taking into account the carbonation of only the crystalline phases  $\text{Ca(OH)}_2$  and  $\text{CaClOH}$  present in the original ash mixture. Accordingly, similar results were obtained by Ref. [34]. The presence of an amorphous phase in biomass ash is considered favorable for carbonation [41].

Therefore, the AC technology used on CFA or MIX CFA may have the potential to sequester more  $\text{CO}_2$  if the carbonation conditions are optimized, such as different pressure conditions or L/S ratio as shown in a recent publication [17]. Moreover, the aim of this work is to show the potentialities in  $\text{CO}_2$  sequestration of CFA combined with other ash, containing leachable metals. The optimization conditions are dependent on the different ashes' composition, origin and mixture, so dedicated studies are mandatory.

### 3.3. Leaching tests

The leaching of MSWI FA sample shows high Pb and Zn values (42 and 10 mg/L, respectively) [15], Therefore, either for landfilling or for reutilizing, their stabilization is required. Conversely, the cork ash samples show Pb and Zn values below 0.3 mg/L. The first samples analyzed are the NCB trials, where after drying the mixtures (MIX CFA1, MIX CFA2 and MIX CFA3) for 4 h at 120 °C (NCB trial), their leaching showed that the concentration of heavy metals in the solutions was markedly reduced (supporting information S5): the Pb concentration decreased by 344, 1580 and 1577 % and the Zn concentration by 352, 1396 and 2870 % in the MIX CFA1, MIX CFA2 and MIX CFA3 samples, respectively. This could be justified by the effect of the temperature, which accelerates the stabilization reaction [42]. Regarding the AC tests, in particularly the 72 h trial, if compared with the NCB trial (sample was left in the oven at 120 °C for 4 h), it is possible to note a decrease in terms of Pb, 6.19 mg/L against 9.50 mg/L, and a slight decrease of Zn, 1.44 mg/L against 2.15 mg/L. The observed behavior indicates that carbonation reactions may play a role in enhancing the drying effect, which, in turn, aids in the stabilization of heavy metals, as previously proposed [34]. The best results are obtained by the NCA (samples



cured for one month at room temperature) experiments. Indeed, both for the MIX CFA1 and MIX CFA3 there is a high decrease, of an order of magnitude, of the Pb and Zn concentration. Respectively, for the MIX CFA1, it was observed 0.28 mg/L and 0.18 mg/L while for the MIX CFA3, 0.78 mg/L and 0.83 mg/L. On the other hand, MIX CFA2 did not exhibit significant improvement when compared to the corresponding NCB trial. The enhanced efficiency in stabilizing heavy metals observed in the NCA tests may result from a combination of both carbonation and pozzolanic mechanisms, which are more comprehensive in this specific test compared to the others [15].

#### 4. Additional potential CO<sub>2</sub> sequestration: material substitution

Given the gradual development of carbon capture and storage (CCS) in the geosphere, exploring carbon capture and utilization (CCU) becomes crucial as an alternative approach to address point source CO<sub>2</sub> emissions. The emergence of CCU technologies offers significant potential for effectively managing biomass waste, creating value, and concurrently reducing CO<sub>2</sub> emissions, leading to the acronym CCUS [43].

Biomass incineration is often considered to have zero net CO<sub>2</sub> contribution due to the assumption that the CO<sub>2</sub> emissions from combustion are balanced by the CO<sub>2</sub> removed from the atmosphere during the growth of the biomass [44]. Moreover, biomass ash is a waste, then it is generally disposed of in landfills.

Given that biomass incineration can result in significant quantities of ash and carbon dioxide emissions (even if with no net contribution to greenhouse gas, GHG), there is a pressing need for innovative management approaches capable of addressing both. While the ideal scenario involves returning biomass ash to the land for enrichment, the substantial ash volumes generated by energy-from-waste processes often fall under waste management regulations, leading to practices like landfilling [43]. However, these landfill “deposits” represent a relatively consistent and potential resource to produce manufactured goods. The potential sequestration capacity of CFA has been calculated and results to be in the range of 30–37 %.

In this frame, biomass ash carbonation has the potential to contribute to negative GHG emissions. Indeed, the carbonation process involves the reaction of CO<sub>2</sub> with the ash, resulting in the formation of stable carbonates, which can effectively sequester additional CO<sub>2</sub> and mitigate its impact on the environment [18]. This was shown in the present case, by carbonation of the mixtures containing cork ash. Considering the cork production in Portugal, the capability to sequester CO<sub>2</sub> by its ash carbonation may reach about 7 kt/year, for this country.

In the present case also the stabilization capacity of this waste must be considered, with the idea of reusing toxic waste and reducing its landfilling. It is already reported that also this practice contributes to reducing the carbon impact on the environment, even if this is complicated to evaluate.

Additionally, the use of biomass ash as a substitute for natural resources, as a low-carbon construction material, further increases its potential for negative GHG contribution.

The global use of hydraulic cement is second only to water. In 2022 the world producers reached a consumption higher than of 4 Gt [45]. To lessen the impact of cement production and address associated emissions, effective management strategies such as the implementation of mineral carbonation technologies, along with the utilization of lower-temperature (less carbon-intensive) alternative clinkers, can be employed. The use of biomass ash may potentially contribute to these efforts.

Table 4 shows the potential CO<sub>2</sub> saved emissions in the USA considering the potential substitution of cement and plastic fillers. In 2022, according to ([45,46]), the USA sand production and hydraulic cement importation were 97000 and 24000 (1000 metric tons), respectively. Considering that the stabilized material can be carbonated and then may partially sequester CO<sub>2</sub>, its 20 % substitution in the hydraulic cement may reduce, the global CO<sub>2</sub> emission by about 4315 (1000 metric tons). Considering the substitution of sand and gravel, cement production may save about 3972 (1000 metric tons) of CO<sub>2</sub> emissions.

Moreover, also other sectors, such as plastic may be suitable to accept this kind of material, for example, to substitute commercial fillers. Indeed, filler masterbatches are composed of significant levels of inorganic fillers like calcium carbonate, talc, and kaolin, along with pigments and other additives. These fillers are introduced into plastic resins during processing to lower the production cost of final products and enhance their mechanical properties, including stiffness, impact resistance, and dimensional stability. The 2030 projection for the filler market [47] reveals that the filler masterbatch market, valued at USD 346.54 million in 2022, is poised for growth with an expected compound annual growth rate of 7.3 % from 2023 to 2030. The total substitution of the stabilized material to kaoline, talc and pyrophyllite, and feldspar may reduce the CO<sub>2</sub> emissions of about 125, 354 and 395 (1000 metric tons), respectively.

The current findings indicate that the reuse of ash derived from the incineration of cork residues ensures the permanent sequestration of additional CO<sub>2</sub> as carbonate. This contributes to further carbon savings beyond those achieved by biomass power generation,

**Table 4**

Total CO<sub>2</sub> saved emissions in polymers and cement production. The materials production is referred to USA in 2022, except for kaoline, referred to 2021. The carbon footprint (CF) values, expressed as mean values, of the different materials, were provided by Granta Selector 2023 R2.

Matrix	Polymer			Cement	
	Kaoline	Talc and pyrophyllite	Feldspar	Sand	Hydraulic Cement
Material Production (1000 metric tons)	4100	580	420	97000	24000
Mean CF (kgCO <sub>2</sub> /kgmaterial)	0.03	0.61	0.94	0.04	0.90
Material substitution (%)	100	100	100	100	20
Total Carbon dioxide emission avoided (1000 metric tons)	125	354	395	3972	4315

ultimately enhancing the overall carbon balance of the entire process. Moreover, apart from the saving of additional waste to be combined in the stabilization process, the possibility to substitute natural resources as building materials and fillers for polymer composites allows to an increase in the total carbon dioxide sequestration.

## 5. Conclusions

Cork Fly Ash (CFA) demonstrates the potential for CO<sub>2</sub> sequestration through natural and accelerated carbonation (AC) tests. Additionally, it exhibits a high potential for stabilizing metals in fly ash from urban waste via natural carbonation (NC). The maximum CO<sub>2</sub> uptake capacity of cork fly ash falls within the range of 30–37 %.

When mixed with MSWI Fly Ash (MSWI FA), in AC tests, 0.82 g of CO<sub>2</sub> is sequestered from a starting mass mixture of 33.6 g. In NC trials, due to greater CO<sub>2</sub> availability and a longer test duration, the amount of CO<sub>2</sub> sequestered increases to 2.6 g.

Stabilization of metals using CFA in MSWI ash shows promising results, particularly in reducing Pb and Zn content across all samples. Moreover, the resulting eco-material can potentially substitute natural resources, contributing to GHG emissions.

Implementing the mixture of ashes (cork powder and MSWI) on a larger scale can be achieved through industrial symbiosis. Geographically close plants producing these wastes can avoid greenhouse gas emissions during transport.

In conclusion, the mineral carbonation of cork ash presents an innovative approach with substantial potential for reducing GHG emissions and promoting environmental sustainability and new eco-materials diffusion. This is particularly significant considering the expected rise in biomass production from future large-scale biomass combustion and gasification, serving as an alternative to fossil fuels.

## Data availability

The data are available in the manuscript and Supporting information.

## CRediT authorship contribution statement

**Giampiero Pasquale Sorrentino:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Renato Guimaraes:** Writing – original draft, Investigation, Formal analysis, Data curation. **Antonella Cornelio:** Writing – review & editing, Formal analysis, Data curation. **Alessandra Zanoletti:** Methodology, Formal analysis, Data curation. **Bruno Valentim:** Writing – review & editing, Validation, Supervision, Conceptualization. **Elza Bontempi:** Writing – review & editing, Supervision, Project administration, Methodology, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Elza Bontempi is on the Advisory Board of the Heliyon Environment section.

## Acknowledgment

All authors thank Paolo Iora, Costante Mario Invernizzi, Gioele Di Marcoberardino, and Modestino Savoia for their support in the accelerated carbonation test.

Authors acknowledge financial support from the Next-GenerationEU (Italian PNRR – M4 C2, Invest 1.3 – D.D. 1551.11-10-2022, PE00000004) within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership for her research fellowship.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e32893>.

## References

- [1] APCOR, Cortiça, Cork 2020, Assoc. Port. Da Cortiça, 2020, pp. 1–108. <https://www.apcor.pt/portfolio-posts/boletim-estatistico-2020/>.
- [2] European Union, EUROSTAT. <https://ec.europa.eu/eurostat>, 2020.
- [3] T. Ramos, A.M. Matos, J. Sousa-Coutinho, Strength and durability of mortar using cork waste ash as cement replacement, *Mater. Res.* 17 (2014) 893–907, <https://doi.org/10.1590/S1516-14392014005000092>.
- [4] A.M. Matos, S. Nunes, J. Sousa-Coutinho, Cork waste in cement based materials, *Mater. Des.* 85 (2015) 230–239, <https://doi.org/10.1016/j.matdes.2015.06.082>.
- [5] B.A. Knapp, H. Insam, Recycling of biomass ashes, *Recycl. Biomass Ashes*. (2011) 1–16, <https://doi.org/10.1007/978-3-642-19354-5>.
- [6] I. Obernberger, F. Biedermann, W. Widmann, R. Riedl, Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions, *Biomass Bioenergy* 12 (1997) 211–224, [https://doi.org/10.1016/S0961-9534\(96\)00051-7](https://doi.org/10.1016/S0961-9534(96)00051-7).
- [7] P. Ohecova, P. Tlustos, J. Szakova, Wheat and soil response to wood fly ash application in contaminated soils, *Agron. J.* 106 (2014) 995–1002, <https://doi.org/10.2134/agronj13.0363>.

- [8] B.R.V. Guimarães, Renato; guedes, alexandra; valentim, characterization, concentration of biochar and titanspheres and heavy metals assessment of quercus suber cork powder fly ash fractions, *J. Solid Waste Technol. Manag.* 47 (2021) 605–618.
- [9] I. Montero, T. Miranda, F.J. Sepúlveda, J.I. Arranz, S. Nogales, Analysis of pelletizing of granulometric separation powder from cork industries, *Materials* 6 (2014) 6686–6700, <https://doi.org/10.3390/ma7096686>.
- [10] J.W. Lee, B. Hawkins, D.M. Day, D.C. Reicosky, Sustainability: the capacity of smokeless biomass pyrolysis for energy production, global carbon capture and sequestration, *Energy Environ. Sci.* 3 (2010) 1695–1705, <https://doi.org/10.1039/c004561f>.
- [11] Q. Wang, Z. Lai, J. Mu, D. Chu, X. Zang, Converting industrial waste cork to biochar as Cu (II) adsorbent via slow pyrolysis, *Waste Manag.* 105 (2020) 102–109, <https://doi.org/10.1016/j.wasman.2020.01.041>.
- [12] A. Assi, F. Bilo, S. Federici, A. Zacco, L.E. Depero, E. Bontempi, Bottom ash derived from municipal solid waste and sewage sludge co-incineration: first results about characterization and reuse, *Waste Manag.* 116 (2020) 147–156, <https://doi.org/10.1016/j.wasman.2020.07.031>.
- [13] M. Pasquali, A. Zanoletti, L. Benassi, S. Federici, L.E. Depero, E. Bontempi, Stabilized biomass ash as a sustainable substitute for commercial P-fertilizers, *Land Degrad. Dev.* 29 (2018) 2199–2207, <https://doi.org/10.1002/ldr.2915>.
- [14] A. Fahimi, F. Bilo, A. Assi, R. Dalipi, S. Federici, A. Guedes, B. Valentim, H. Olgun, G. Ye, B. Bialecka, L. Fiameni, L. Borgese, M. Cathelineau, M.C. Boiron, G. Predeanu, E. Bontempi, Poultry litter ash characterisation and recovery, *Waste Manag.* 111 (2020) 10–21, <https://doi.org/10.1016/j.wasman.2020.05.010>.
- [15] A. Assi, S. Federici, F. Bilo, A. Zacco, L.E. Depero, E. Bontempi, Increased sustainability of carbon dioxide mineral sequestration by a technology involving fly ash stabilization, *Materials* 12 (2019), <https://doi.org/10.3390/ma12172714>.
- [16] G. Biava, A. Zacco, A. Zanoletti, G.P. Sorrentino, C. Capone, A. Princiçallo, L.E. Depero, E. Bontempi, Accelerated direct carbonation of steel slag and cement kiln dust: an industrial symbiosis strategy applied in the bergamo–brescia area, *Materials* 16 (2023), <https://doi.org/10.3390/ma16114055>.
- [17] G.P. Sorrentino, R. Guimarães, B. Valentim, E. Bontempi, The influence of liquid/solid ratio and pressure on the natural and accelerated carbonation of alkaline wastes, *Minerals* 13 (2023) 1–16, <https://doi.org/10.3390/min13081060>.
- [18] A. Assi, F. Bilo, A. Zanoletti, J. Ponti, R. La Spina, A. Zacco, E. Bontempi, Zero-waste approach in municipal solid waste incineration: reuse of bottom ash to stabilize fly ash, *J. Clean. Prod.* 245 (2020) 118779, <https://doi.org/10.1016/j.jclepro.2019.118779>.
- [19] A. Modak, S. Jana, Advancement in porous adsorbents for post-combustion CO<sub>2</sub> capture, *Microporous Mesoporous Mater.* 276 (2019) 107–132, <https://doi.org/10.1016/j.micromeso.2018.09.018>.
- [20] F. Dong, D.W. Kirk, H. Tran, Biomass ash alkalinity reduction for land application via CO<sub>2</sub> from treated boiler flue gas, *Fuel* 136 (2014) 208–218, <https://doi.org/10.1016/j.fuel.2014.07.059>.
- [21] S.V. Vassilev, C.G. Vassileva, Extra CO<sub>2</sub> capture and storage by carbonation of biomass ashes, *Energy Convers. Manag.* 204 (2020) 112331, <https://doi.org/10.1016/j.enconman.2019.112331>.
- [22] N.S. Trivedi, S.A. Mandavgane, S. Mehetre, B.D. Kulkarni, Characterization and valorization of biomass ashes, *Environ. Sci. Pollut. Res.* 23 (2016) 20243–20256, <https://doi.org/10.1007/s11356-016-7227-7>.
- [23] W. Wang, Y. Zheng, X. Liu, P. Wang, Characterization of typical biomass ashes and study on their potential of CO<sub>2</sub> fixation, *Energy Fuel.* 26 (2012) 6047–6052, <https://doi.org/10.1021/ef300781e>.
- [24] L. Benassi, R. Dalipi, V. Consigli, M. Pasquali, L. Borgese, L.E. Depero, F. Clegg, P.A. Bingham, E. Bontempi, Integrated management of ash from industrial and domestic combustion: a new sustainable approach for reducing greenhouse gas emissions from energy conversion, *Environ. Sci. Pollut. Res.* 24 (2017) 14834–14846, <https://doi.org/10.1007/s11356-017-9037-y>.
- [25] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, *Fuel* 94 (2012) 1–33, <https://doi.org/10.1016/j.fuel.2011.09.030>.
- [26] J. Yan, C. Zhao, P. Wang, P. Lu, Studies on several fly ashes and their modified materials for CO<sub>2</sub> capture, *Am. Soc. Mech. Eng. Power Div. POWER.* 1 (2017), <https://doi.org/10.1115/POWER-ICOPE2017-3420>.
- [27] L. Ji, X. Zheng, L. Zhang, L. Feng, K. Li, H. Yu, S. Yan, Feasibility and mechanism of an amine-looping process for efficient CO<sub>2</sub> mineralization using alkaline ashes, *Chem. Eng. J.* 430 (2022) 133118, <https://doi.org/10.1016/j.cej.2021.133118>.
- [28] Y. Niu, L. Wen, X. Guo, S. Hui, Co-disposal and reutilization of municipal solid waste and its hazardous incineration fly ash, *Environ. Int.* 166 (2022) 107346, <https://doi.org/10.1016/j.envint.2022.107346>.
- [29] E. Loginova, D.S. Volkov, P.M.F. van de Wouw, M.V.A. Florea, H.J.H. Brouwers, Detailed characterization of particle size fractions of municipal solid waste incineration bottom ash, *J. Clean. Prod.* 207 (2019) 866–874, <https://doi.org/10.1016/j.jclepro.2018.10.022>.
- [30] L. Black, Low clinker cement as a sustainable construction material, in: *Sustain. Constr. Mater.*, Elsevier, 2016, pp. 415–457, <https://doi.org/10.1016/B978-0-08-100370-1.00017-2>.
- [31] M. Fernández Bertos, X. Li, S.J.R. Simons, C.D. Hills, P.J. Carey, Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO<sub>2</sub>, *Green Chem.* 6 (2004) 428–436, <https://doi.org/10.1039/b401872a>.
- [32] M.G. Nyambura, G.W. Mugeru, P.L. Felicia, N.P. Gathura, Carbonation of brine impacted fractionated coal fly ash: implications for CO<sub>2</sub> sequestration, *J. Environ. Manag.* 92 (2011) 655–664, <https://doi.org/10.1016/j.jenvman.2010.10.008>.
- [33] A. Sanna, M. Uibu, G. Caramanna, R. Kuusik, M.M. Maroto-Valer, A review of mineral carbonation technologies to sequester CO<sub>2</sub>, *Chem. Soc. Rev.* 43 (2014) 8049–8080, <https://doi.org/10.1039/c4cs00035h>.
- [34] G.P. Sorrentino, A. Zanoletti, S. Ducoli, A. Zacco, P. Iora, C.M. Invernizzi, G. Di Marcoberardino, L.E. Depero, E. Bontempi, Accelerated and natural carbonation of a municipal solid waste incineration (MSWI) fly ash mixture: basic strategies for higher carbon dioxide sequestration and reliable mass quantification, *Environ. Res.* 217 (2023) 114805, <https://doi.org/10.1016/j.envres.2022.114805>.
- [35] E. Bontempi, A. Zacco, L. Borgese, A. Gianoncelli, R. Ardesi, L.E. Depero, A new method for municipal solid waste incinerator (MSWI) fly ash inertization, based on colloidal silica, *J. Environ. Monit.* 12 (2010) 2093, <https://doi.org/10.1039/c0em00168f>.
- [36] N. Rodella, M. Pasquali, A. Zacco, F. Bilo, L. Borgese, N. Bontempi, G. Tomasoni, L.E. Depero, E. Bontempi, Beyond waste: new sustainable fillers from fly ashes stabilization, obtained by low cost raw materials, *Heliyon* 2 (2016) e00163, <https://doi.org/10.1016/j.heliyon.2016.e00163>.
- [37] A. Bosio, A. Gianoncelli, A. Zacco, L. Borgese, N. Rodella, D. Zanotti, L.E. Depero, G. Siviero, A. Cinosi, P.A. Bingham, E. Bontempi, A new nanotechnology of fly ash inertization based on the use of silica gel extracted from rice husk ash and microwave treatment, *Proc. Inst. Mech. Eng. - Part N J. Nanoeng. Nanosyst.* 228 (2014) 27–32, <https://doi.org/10.1177/1740349913490683>.
- [38] P. Colombi, D.K. Agnihotri, V.E. Asadchikov, E. Bontempi, D.K. Bowen, C.H. Chang, L.E. Depero, M. Farnworth, T. Fujimoto, A. Gibaud, M. Jergel, M. Krumrey, T.A. Lafford, A. Lamperti, T. Ma, R.J. Matyi, M. Meduna, S. Milita, K. Sakurai, L. Shabel'Nikov, A. Ulyanenkov, A. Van Der Lee, C. Wiemer, Reproducibility in X-ray reflectometry: results from the first world-wide round-robin experiment, *J. Appl. Crystallogr.* 41 (2008) 143–152, <https://doi.org/10.1107/S0021889807051904>.
- [39] N. Doebelin, R. Kleeberg, Profex: a graphical user interface for the Rietveld refinement program BGMN, *J. Appl. Crystallogr.* 48 (2015) 1573–1580, <https://doi.org/10.1107/S1600576715014685>.
- [40] J.Y. Lin, E.A. Garcia, F.C. Ballesteros, S. Garcia-Segura, M.C. Lu, A review on chemical precipitation in carbon capture, utilization and storage, *Sustain. Environ. Res.* 32 (2022), <https://doi.org/10.1186/s42834-022-00155-6>.
- [41] S.V. Vassilev, C.G. Vassileva, N.L. Petrova, Mineral carbonation of biomass ashes in relation to their CO<sub>2</sub> capture and storage potential, *ACS Omega* 6 (2021) 14598–14611, <https://doi.org/10.1021/acsomega.1c01730>.
- [42] L. Benassi, A. Zanoletti, L.E. Depero, E. Bontempi, Sewage sludge ash recovery as valuable raw material for chemical stabilization of leachable heavy metals, *J. Environ. Manag.* 245 (2019) 464–470, <https://doi.org/10.1016/j.jenvman.2019.05.104>.
- [43] C.D. Hills, N. Tripathi, R.S. Singh, P.J. Carey, F. Lowry, Valorisation of agricultural biomass-ash with CO<sub>2</sub>, *Sci. Rep.* 10 (2020) 1–14, <https://doi.org/10.1038/s41598-020-70504-1>.
- [44] T. Pulles, M. Gillenwater, K. Radunsky, CO<sub>2</sub> emissions from biomass combustion Accounting of CO<sub>2</sub> emissions from biomass under the UNFCCC, *Carbon Manag.* 13 (2022) 181–189, <https://doi.org/10.1080/17583004.2022.2067456>.

- [45] U.S. Geological Survey, MINERAL COMMODITY SUMMARIES 2023, 2023. <http://pubs.er.usgs.gov/publication/mcs2023>.
- [46] Statista, Statista, 2022. <https://www.statista.com/getting-started/publishing-statista-content-terms-of-use-and-publication-rights>.
- [47] G. view Research, Filler masterbatch market size & trends. <https://www.grandviewresearch.com/industry-analysis/filler-masterbatch-market-report>, 2021. #.