ABSTRACT: Short-term stored, long-term stored, and weathered biomass ashes (BAs) produced from eight biomass varieties were studied to define their composition, mineral carbonation, and CO₂ capture and storage (CCS) potential by a combination of methods. Most of these BAs are highly enriched in alkaline-earth and alkaline oxides, and the minerals responsible for CCS in them include carbonates such as calcite, kalicinite, and fairchildite, and to a lesser extent, butschliite and baylisite. These minerals are a result of reactions between alkaline-earth and alkaline oxyhydroxides in BA and flue CO₂ gas during biomass combustion and atmospheric CO₂ during BA storage and weathering. The mineral composition of the short-term stored, long-term stored, and weathered BAs is similar; however, there are increased proportions of carbonates and especially bicarbonates in the long-term stored BAs and particularly weathered BAs. The carbonation of BAs based on the measurement of CO₂ volatilization determined in fixed temperature ranges is approximately 1–27% (mean 11%) for short-term stored BAs, 2–33% (mean 18%) for long-term stored BAs, and 2–34% (mean 22%) for weathered BAs. Hence, biomass has some extra CCS potential because of sequestration of atmospheric CO₂ in BA, and the forthcoming industrial bioenergy production in a sustainable way can contribute for decreasing CO₂ emissions and can reduce the use of costly CCS technologies.

1. INTRODUCTION
Carbon dioxide in the Earth’s atmosphere is the major gas responsible for global warming and climate change as its share among the total anthropogenic greenhouse gases is about 72% at present. Globally, the fossil fuel use releases more than 38 Gt of CO₂ to the atmosphere annually, and extraordinary measures are under consideration to reduce these emissions. The most promising approaches toward decreasing CO₂ emissions nowadays include the application of low-carbon and renewable fuels and diverse methods for CO₂ capture and storage (CCS). The present research specifically addresses the topics related to biomass use as a fuel and CCS by mineral carbonation of biomass ash (BA).

The global growth of biomass is 112–220 Gt annually; however, only about 7 Gt of this huge amount is used for energy application at present (see ref 3 and references therein). The key environmental advantage of renewable biomass is to produce carbon-neutral energy when considering the green-house gas balance despite some limitations. It was emphasized that bioenergy is the most favorable renewable energy resource, however, only about 15% of the world energy supplies currently are based on biomass. The prognosis shows that biofuels would contribute up to 50% from the world’s primary energy consumption in 2050. The main conversion process for bioenergy production at present is the biomass combustion, and major products generated from this process are the neutral CO₂ emissions and BA. It is calculated that about 476 Mt of BA are produced annually worldwide as different biodiversity groups are used for that purpose. BAs have limited industrial application currently, and they are normally stored in depots and bunkers or transported using water to the disposal sites close to power plants. Diverse precombustion, combustion (especially oxy-combustion and chemical-looping combustion), and postcombustion technologies for CCS from fossil fuel power stations are nowadays under consideration; however, most of them use expensive resources, materials, sorbents, additives, and complex procedures and equipment. It was found that low-cost and effective alkaline-earth and alkaline industrial wastes are particularly prospective for permanent CCS by their carbonation. BA is the solid residue that results from the combustion of biomass. This waste is a complex inorganic–organic mixture with a multicomponent, heterogeneous, and variable composition and contains: (1) mostly inorganic matter (amorphous material and crystalline to semicrystalline minerals); (2) to a lesser extent, organic matter (char and organic minerals); and (3) some fluid matter (moisture, gas, and gas–liquid inclusions). BAs belong to the above-mentioned alkaline-earth and alkaline industrial wastes, and some investigations about their potential for CCS have been performed. These studies reveal that such combustion residues have high reactivity and favorable CO₂ fixation.
Table 1. Data for Eight BAs* Produced at 500 °C, Wt % (Unless Indicated Otherwise)

| characteristic                              | beechnock chips ash | corn cobs ash | marine macroalgae ash | sunflower shells ash | walnut shells ash | plum pits (weathered) ash | switchgrass ash | rice husks ash |
|---------------------------------------------|---------------------|--------------|-----------------------|---------------------|------------------|--------------------------|----------------|---------------|
| sample code                                 | BCA                 | CCA          | MMA                   | SSA                 | WSA              | PPA                      | SGA            | RHA           |
| biomass source                              | JRS Rosenberg, Germany | Debnevo, Bulgaria | Tsarevo, Bulgaria | Billa Sofia, Bulgaria | Debnuevo, Bulgaria | Debnuevo, Bulgaria | Mead, Nebraska, USA | Kovachevo, Bulgaria |
| A^b                                         | 1.3                 | 2.1          | 28.2                  | 3.0                 | 0.9              | 0.7                       | 5.1            | 18.5          |
| ash type (Figure 1)                         | C                   | K            | K                     | K                   | K                | K                         | K              | S             |
| ash subtype (Figure 1)                      | C-LA                | K-LA         | K-LA                  | K-LA               | K-LA             | K-LA                     | K-LA           | K-LA          |
| CaO                                         | 62.58               | 2.12         | 22.07                 | 15.57               | 38.11            | 43.95                     | 7.69           | 4.10          |
| MgO                                         | 7.49                | 1.97         | 7.69                  | 11.87               | 3.80             | 4.18                      | 4.20           | 0.49          |
| K2O                                         | 18.00               | 47.57        | 7.56                  | 49.84               | 49.33            | 16.29                     | 18.77          | 4.16          |
| Na2O                                        | 0.11                | 0.28         | 14.07                 | 0.22                | 0.12             | 0.07                      | 0.11           | 0.23          |
| SiO2                                        | 5.48                | 36.67        | 5.60                  | 1.45                | 2.84             | 12.01                     | 62.90          | 89.86         |
| Al2O3                                       | 0.49                | 0.81         | 0.98                  | 0.12                | 0.52             | 2.57                      | 0.89           | 1.04          |
| Fe2O3                                       | 0.36                | 1.50         | 0.69                  | 1.32                | 0.40             | 1.75                      | 0.42           | 0.41          |
| MnO                                         | 2.11                | 0.07         | 0.02                  | 0.07                | 0.05             | 0.14                      | 0.14           | 0.27          |
| TiO3                                        | 0.03                | 0.06         | 0.03                  | 0.01                | 0.05             | 0.16                      | 0.04           | 0.02          |
| P2O5                                        | 2.49                | 4.82         | 0.97                  | 6.54                | 2.37             | 10.17                     | 2.44           | 0.60          |
| SO3                                         | 0.77                | 3.44         | 28.49                 | 11.39               | 2.03             | 7.72                      | 2.17           | 1.31          |
| Cl2O                                        | 0.09                | 0.69         | 11.84                 | 1.60                | 0.38             | 0.27                      | 0.23           | 0.21          |
| Na2O + MgO + K2O + N2O for types           | 88.18               | 51.94        | 51.38                 | 77.50               | 91.36            | 65.21                     | 30.77          | 6.28          |
| CaO + MgO + K2O + Na2O for types           | 88.18               | 60.27        | 78.29                 | 60.27               | 80.23            | 18.53                     |
| (CaO + MgO)/(K2O + N2O) for types           | 3.87                | 0.09         | 1.38                  | 0.55                | 0.85             | 2.82                      | 0.63           | 0.43          |
| pH of leachate^c                          | 12.1                | 11.3         | 8.4                   | 12.9                | 10.5             | 8.9                       | 9.8            | 8.1           |
| pH of leachate for types                   | 12.1                | 10.9         | 10.9                  | 9.7                 | 9.0              | 9.0                       |
| DWR for types                              | 20.2                | 45.1         | 42.8                  | 29.8                | 41.1             | 9.4                       | 23.3           | 3.9           |
| DWR for types                              | 20.2                | 39.2         | 39.2                  | 39.2                | 39.2             | 25.3                      | 13.6           |

*aBased on ref 26. ^bAsh yield of biomass at 500 °C/2 h. *Acid–base value of ash (solid–liquid mass ratio = 1:50). **Dry water-soluble residue.

capacity, and they can be used as sorbents even without preliminary and costly treatments. CCS by mineral carbonation is based on reactions mainly between inorganic matter of BA and both flue CO2 gas and atmospheric CO2. The process of enhanced capture and immobilization of CO2 and other air pollutants in combustion products was described in the literature as the concept of "self-cleaning fuels." It was identified that specific minerals or phases of alkaline and alkaline-earth elements, as well as amorphous matter and char in solid fuel ashes, exhibit sorbent properties, which are favorable for CCS.

The direct CCS by mineral carbonation of BA during biomass combustion and particularly postcombustion (BA storage and weathering) is a prospective approach and has been described earlier. It was emphasized therein that BA is normally highly enriched in alkaline-earth and alkaline compounds as their abundance can reach very high concentrations, namely, 84% of CaO, 64% of K2O, 29% of Na2O, and 22% of MgO for certain BA varieties. These elements in BA are represented by carbonates, oxhydroxides, sulfates, chlorides, phosphates, inorganic amorphous materials, and char, and such minerals and phases, particularly carbonates, play a crucial role in CCS of BA. The carbonates are newly formed minerals in BA because of reactions between alkaline-earth and alkaline oxhydroxides and flue CO2 gas formed during biomass combustion. Consequently, supplementary postcombustion carbonates and bicarbonates are formed by reactions between the unreacted oxhydroxides and carbonates in BA and atmospheric CO2 and moisture in air during BA storage. For example, it was found that different short-term stored BAs have the capacity to capture between 1 and 27% (mean 11%) of CO2 based on the decomposition temperature of carbonates at 600–900 °C and the mass loss measured in this temperature range. However, the investigations on the application of BA as a sorbent for CCS are limited in contrast to those for other sorbents.

The direct CCS by mineral carbonation of BA during biomass combustion and especially BA storage is a new approach with huge potential considering the expected amount of BA that will be generated in the future large-scale biomass combustion and gasification instead of fossil fuels. Finally, our former results show that the bioenergy has both carbon-neutral behavior and extra CCS potential because the BA carbonation fixes permanently flue CO2 gas during biomass combustion, as well as atmospheric CO2 during BA storage. Therefore, comprehensive studies are required to evaluate the CCS potential for different BA types.

The major aim of the present work is to investigate the mineral carbonation of diverse short-term stored, long-term stored, and weathered BAs and their potential for CCS. For that purpose, an original systematic approach and a combination of methods are used to elucidate the: (1) chemical and phase-mineral composition, (2) mineral carbonation/decarbonation behavior, and (3) CCS capacity of different BAs and their chemical types.

2. MATERIALS AND METHODS

2.1. Material Preparation. Eight laboratory produced BAs such as beechnock chips ash (BCA), corn cobs ash (CCA), marine macroalgae ash (MMA), sunflower shells ash (SSA), walnut shells ash (WSA), plum pits ash (PPA), switchgrass ash (SGA), and rice husks ash (RHA) were investigated. These
high-temperature ashes were produced in an electric oven under static air at 500 °C for 2 h as the heating and cooling rate used was about 5 °C min⁻¹. The above temperature is the minimum one for nearly complete biomass combustion.⁴⁵ The BA samples studied are especially appropriate for comparative studies because they belong to various biodiversity groups among woody, herbaceous, agricultural, and algal biomasses, as well as different inorganic chemical types ("C", "K", "CK", and "S" ash types) and subtypes with high, medium, and low acid tendencies (Table 1 and Figure 1). Three categories of ash

**Figure 1.** Positions of eight BA samples and area of 141 BA varieties in the chemical classification system of inorganic matter in biomass and BA (based on ref 30 and present data), wt %.

**Table 2.** Inorganic Phases and Minerals Identified by XRD in Eight BAs Produced at 500 °C According to Figures 2 and 3

| ash type | formula | C type | K type | CK type | S type |
|----------|---------|--------|--------|---------|--------|
| IAM      | +       | +      | +      | +       | +      |
| carbonates and bicarbonates | + | + | + | + | + |
| calcite (Cc) | CaCO₃ | + | + | + | + | + |
| kalcinite (K) | KHCO₃ | + | + | + | + | + |
| fairchildite (F) | K₂Ca(CO₃)₂ | + | + | + | + | + |
| butschliite (Bu) | K₂Ca(CO₃)₂ | + | + | + | + | + |
| baylissite (B) | K₂Mg(CO₃)₂·4H₂O | + | + | + | + | + |
| oxides and hydroxides | + | + | + | + | + |
| portlandite (Port) | Ca(OH)₂ | + | + | + | + | + |
| chlorides | + | + | + | + | + | + |
| halite (Ha) | NaCl | + | + | + | + | + |
| carbonates | + | + | + | + | + | + |
| gypsum (Gp) | CaSO₄·2H₂O | + | + | + | + | + |
| arcanite (Arc) | K₂SO₄ | + | + | + | + | + |
| picromerite (P) | K₂Mg(SO₄)₂·6H₂O | + | + | + | + | + |
| phosphates | + | + | + | + | + | + |
| apatite (Ap) | Ca₃(PO₄)₂(Cl,F,OH,CO₃) | + | + | + | + | + | + |
| struvite (S) | KMg(PO₄)₂·6H₂O | + | + | + | + | + | + |
| archerite (Ar) | K(H₂PO₄)₂ | + | + | + | + | + | + |
| silica | + | + | + | + | + | + | + |
| quartz (Q) | SiO₂ | + | + | + | + | + | + |
| plagioclase (Pl) | NaAlSi₃O₈, CaAl₂Si₂O₈ | + | + | + | + | + | + |
| leucite (Le) | KAlSiO₄ | + | + | + | + | + | + |
| kalsilite (Ks) | KAlSi₂O₆ | + | + | + | + | + | + |

Abbreviations: BCA, beech wood chips ash; CCA, corn cobs ash; MMA, marine macroalgae ash; PPA, plum pits ash; RHA, rice husks ash; SGA, switchgrass ash; SSA, sunflower shells ash; WSA, walnut shells ash.
samples were generated from the initial BAs and subsequently studied, namely, (1) short-term stored BAs (denoted as S) kept in open plastic envelopes under ambient conditions, namely, room temperature of 20–25 °C and relative humidity of 50–75%, for a couple of months before their characterization; (2) long-term stored BAs (denoted as L) kept under the above conditions for 10 years before their characterization; and (3) weathered BAs (denoted as W) subjected to induced weathering and produced from the long-term stored BAs following 30 hydration (1:20 ash-distilled water mass ratio) and dehydration cycles under ambient conditions for 4 months before their characterization.

2.2. Material Characterization. Methods such as powder X-ray diffraction (XRD), light microscopy, scanning electron microscopy (SEM), and chemical analyses as well as differential scanning calorimetry (DSC), thermogravimetry (TG), differential thermogravimetry (DTG), and mass spectrometry (MS) of evolved gases were used to study the BA samples. The light microscopy investigations were carried out using a stereomicroscope under reflected and transmitted light. The XRD patterns of finely ground short-term, long-term, and weathered BA samples were recorded using a D2 Phaser Bruker AXS diffractometer and collected at 5–70° 2θ using Cu Kα radiation to identify the minerals in BAs. The SEM studies were conducted on a JEOL JSM 6390 microscope equipped with an Oxford INCA energy dispersive X-ray spectroscopy (EDX) analyzer. The DSC, TG, and DTG analyses were carried out for long-term stored BAs and weathered BAs on a SETSYS2400, SETARAM analyzer in the temperature range from 20 to 900 °C. BA samples with a mass of 10–15 mg were gradually heated in corundum crucibles under a dynamic Ar atmosphere with a flow rate of 30 mL min⁻¹ and a heating rate of 10 °C min⁻¹. Simultaneous analyses of the evolved gases were performed via MS using an OmniStar equipment connected to the TG apparatus. The intensities related to the main m/z value of H₂O (18) and CO₂ (44) were examined. The concentrations of 12 elements in short-term stored BAs were measured by inductively coupled plasma-mass spectrometry (ICP-MS) for Mn, laser ablation ICP-MS for Al, Ca, Fe, K, Mg, Na, P, Si, and Ti, and SEM–EDX for Cl and S. The water-soluble solutions leached from the short-term stored BAs were subjected to evaporation and precipitation to obtain dry water-soluble residues (DWRs). For that purpose, 10 g of BA were soaked in a glass container with 500 mL distilled water for 24 h at room temperature. The generated suspension was periodically stirred and then decanted and filtered to produce the water leachate. A pH-mV-conductivity meter was used to measure the pH value in the water solution. Finally, the water leachate was subjected to evaporation and crystallization in a drying oven at 80 °C to produce DWRs.
3. RESULTS AND DISCUSSION

3.1. Composition and Some Properties of BAs. The chemical and phase-mineral composition of the BAs studied is given in Tables 1 and 2, and Figures 2 and 3. The data reveal that the key sum of alkaline-earth and alkaline oxides for BAs is highly variable (6–91%, mean 58%). This sum for ash types decreases in the following order "C" > "CK" > "K" > "S", and it is much lower for the "S" ash type in comparison with other types (Table 1). The ratio between alkaline-earth and alkaline oxides for ash types has the same order as the above sum (Table 1). Hence, the influence of alkaline-earth oxides is more characteristic for "C" and "CK" ash types, while the alkaline oxides are more typical for "K" and "S" ash types.

The value of pH for ash types follows the order "C" > "K" > "CK" > "S", while the order for the DWR value is "K" > "CK" > "C" > "S" (Table 1). The above pH and DWR orders show that the "C" ash type has a decreased amount of water-soluble fraction probably because of the abundance of less soluble calcite (Table 2 and Figure 2a) and a more alkaline environment (Table 1). The phase-mineral composition of BAs includes inorganic amorphous materials, mineral species among carbonates, sulfates, silicates, and phosphates, and to a lesser extent, chlorides and oxyhydroxides (Table 2), and some char. These results show that the composition and properties of BAs are highly variable and depend on the biomass source and ash type (Tables 1 and 2 and Figures 1–3).

The thermal behavior of the eight biomasses studied during combustion at 500–1500 °C was described in detail earlier. It was identified that the formation of carbonates and their consecutive transformations with increasing temperature include: (1) intensive crystallization of alkaline-earth and alkaline carbonates at 500 °C during burning of organic matter and (2) partial and complete decomposition of carbonates and their transformation to more stable phases in the temperature range of 500–900 °C. Additionally, postcombustion carbonation (including bicarbonation or hydrocarboxation) occurs during BA storage and weathering (see Section 3.2). Hence, the carbonates in BA can be original precombustion minerals in biomass (primary), newly formed minerals during biomass combustion (secondary), and newly formed postcombustion minerals during BA storage and weathering (tertiary).

3.2. General Carbonation Behavior of BA. The modes of occurrence of the most important alkaline-earth and alkaline elements in biomass and BA have been described in detail earlier. The reference and our own data reveal that carbonates are dominantly secondary and tertiary minerals in BA because only traces of carbonates were identified as original detrital and authigenic minerals in biomass. In contrast, 26 carbonates and bicarbonates were identified in different BAs worldwide (Table 3).

The common carbonation reactions in BA according to Tables 2 and 3 can be simplified as follows:

(1)
The general carbonation mechanisms involving the origin of newly formed carbonates in BA have been described. Shortly, the formation of secondary carbonates in BA is mostly due to solid–gas reactions between flue CO$_2$ gas released during biomass combustion and Ca, Mg, K, and Na oxyhydroxides generated from the decomposition and oxidation of organic matter, oxalates, original carbonates, chlorides, sulfates, and phosphates in biomass during combustion. Then, tertiary carbonates and bicarbonates are formed by both solid–gas and solid–liquid reactions between the unreacted alkaline-earth and alkaline oxyhydroxides and carbonates in BA, and CO$_2$ and moisture in air during the BA storage. Finally, additional tertiary carbonate formation also takes place as a result of hydration, hydroxylation, and supplementary carbonation (Tables 2 and 3) of other less stable carbonates and unreacted oxyhydroxides by CO$_2$ and moisture in air, as well as water during BA weathering. For instance, the hydrocarbonation of alkaline carbonates by CO$_2$ and moisture occurs up to 110 °C as these bicarbonates have very high CO$_2$ capture capacity. It was also found that the mass of DWRs for the eight BAs studied increases significantly (1−22%, mean 13%) after one-month room storage, and these data correspond to the determined CCS by the same short-term stored BAs (1−27%, mean 11%). This finding is also in agreement with the tertiary carbonation of BA during storage even for a relatively short period of time.

The mineral composition of the BAs studied reveals the occurrence of Ca, K, K–Mg, and K–Ca carbonates and bicarbonates (Table 2 and Figures 2 and 3). The identified carbonate and bicarbonate species include mainly calcite (CaCO$_3$), kalicinite (KHCO$_3$), and fairchildite (K$_2$Ca(CO$_3$)$_2$), and to a lesser extent, butschliite (K$_2$Ca(CO$_3$)$_2$), and baylissite (K$_2$Mg(CO$_3$)$_2$.4H$_2$O). It can be seen that the role of Mg- and Na-bearing carbonates for CCS of the BAs studied is relatively limited in comparison with Ca- and K-bearing carbonates. It was found that the qualitative mineral composition of the short-term stored and long-term stored BAs is identical and includes calcite, kalicinite, fairchildite, and butschliite (Figures 2 and 3). However, there is some difference in their quantitative composition for both sets of samples. This

### Table 3. Carbonate and Bicarbonate Minerals Identified in BAs Worldwide (Based on Ref 4 and Present Data)

| carbonate, bicarbonate                      | formula                |
|---------------------------------------------|------------------------|
| calcite                                     | CaCO$_3$               |
| hydrocalcite                                | CaCO$_3$.H$_2$O        |
| paraalumohydrokalcit                        | CaAl$_2$(CO$_3$)$_2$(OH)$_4$.6H$_2$O |
| Ca-K or K-Ca carbonate                      | Ca$_2$K$_2$(CO$_3$)$_3$ or K$_2$Ca$_2$(CO$_3$)$_3$ |
| Ca-K carbonate                              | CaMg(CO$_3$)$_2$       |
| dolomite                                    | CaMg$_2$(CO$_3$)$_4$   |
| huitite                                     | Ca(MgFe)(CO$_3$)$_2$   |
| Cr-bearing carbonates                        |                        |
| K carbonate (potash)                        | FeCO$_3$               |
| kalicinite (K hydrocarbonate, bicarbonate)   | K$_2$CO$_3$            |
| butschliite (dimorphous with fairchildite)  | KHCO$_3$               |
| fairchildite (more stable at higher temperature) | K$_2$Ca(CO$_3$)$_2$   |
| baylissite                                   | K$_2$Ca(CO$_3$)$_2$.4H$_2$O |
| K-Na-Ca-Mg carbonates                       | MgCO$_3$               |
| magnesite                                    | MgCO$_3$.3H$_2$O       |
| nesquehonite                                 | MgCO$_3$.4(OH).3H$_2$O |
| artele                                        | MgAl$_2$CO$_3$.4(OH).4H$_2$O |
| natrite                                      | Na$_2$CO$_3$           |
| natrofairchildite                            | Na$_2$Ca(CO$_3$)$_2$   |
| pirsonite                                    | Na$_2$Ca(CO$_3$)$_2$.2H$_2$O |
| njerereite                                   | Na$_2$Mg(CO$_3$)$_2$.5H$_2$O |
| eteliate                                     | Na$_2$Na$_2$(CO$_3$)$_2$.5H$_2$O |
| hydrozincite                                 | Na$_2$Zn$_5$(CO$_3$)$_2$.6H$_2$O |

CaO or MgO + CO$_2$ → CaCO$_3$ or MgCO$_3$

(2)

CaO or MgO + H$_2$O → Ca(OH)$_2$ or Mg(OH)$_2$

(3)

Ca(OH)$_2$ or Mg(OH)$_2$ + CO$_2$
→ CaCO$_3$ or MgCO$_3$ + H$_2$O

(4)

K$_2$O or Na$_2$O + CO$_2$ → K$_2$CO$_3$ or Na$_2$CO$_3$

(5)

K$_2$CO$_3$, Na$_2$CO$_3$, H$_2$O + CO$_2$
↔ 2KHCO$_3$ or 2NaHCO$_3$

(6)

R$_2$O + MO + 2CO$_2$ → R$_2$M(CO$_3$)$_2$  
(M = Ca or Mg and R = K or Na)
difference is related to the increased proportions of carbonates and especially bicarbonate (kalicinite) in the long-term stored BAs according to the major XRD peak intensities. The qualitative mineral composition of the weathered BAs also includes the above listed four minerals plus baylissite, which results from the hydration of the long-term stored BAs. A trend for an additional increase of carbonation and especially bicarbonation can also be seen for the weathered BAs (Figures 2 and 3).

Figure 4. TG, DSC, and evolved CO₂ profiles of long-term stored (denoted as L) and weathered (denoted as W) BAs: (a) BCAs; (b) CCAs; (c) MMAs; and (d) SSAs.
The above mineral data show that the carbonation of BAs depends on the biomass source and ash type. For instance, “C” and “CK” ash types, and to a lesser extent “K” ash type, are enriched in carbonates, while the “S” ash type is poor in such minerals and abundant in silicates and amorphous inorganic matter (Table 2 and Figures 2 and 3). It is interesting to note that the weathered and air-dried BAs increase their mass significantly in comparison with the long-stored BAs, namely, SSA (13.5%) > MMA (12.2%) > BCA (11.0%) > WSA (10.3%) > PPA (6.3%) > CCA (2.3%) > SGA (1.6%) > RHA (0.9%). It is clear that the weathering processes (carbonation and hydration) are typical for “K” and “C” ash types (excluding CCA), to a lesser extent for the “CK” ash type, and they have limited influence for the “S” ash type because of their specific mineral composition. The BA hydration with the formation of minerals containing water molecules (baylissite, gypsum, picromerite, and struvite) or hydroxyl groups (portlandite and apatite) is more characteristic of the “K” ash type (Table 2 and Figures 2 and 3).

It was found in our previous investigation that the decomposition of carbonates in the eight short-term stored BAs studied is consistent with endothermic effects mostly at 600–900 °C, and the mass loss measured in this temperature range approximately determines the CO2 volatilization from the carbonates. Therefore, some quantitative determinations and comparisons about the carbonation of the short-term stored, long-term stored, and weathered BAs from different ash types are described below based on their decomposition behavior up to 900 °C. For that purpose, our previous differential thermal and TG data for the eight short-term stored BAs were compared with the present TG, DTG, DSC, CO2, and H2O results for the eight long-term stored BAs and the eight weathered BAs.

### 3.3. Carbonation Behavior of the “C” Ash Type

**BCA:** belongs to the “C” ash type, and characteristic features of this type are the high values of Ca, Mg, and Mn oxides, CaO + MgO + K2O + Na2O, (CaO + MgO)/(K2O + Na2O), and pH in comparison with other ash types (Table 1 and Figure 1). BCA shows very high concentrations of carbonates, namely, calcite, and to a lesser extent, butschliite, fairchildite, and kalicinite (Table 2 and Figure 2a). BCA is the most abundant in calcite among other BAs (Table 2 and Figures 2 and 3). The formation of calcite, butschliite, and fairchildite is due to the carbonation reactions between CaO, K2O, and CO2 released from the organic matter and Ca oxalates during biomass combustion, as well as CO2 occurring in air and moisture during the prolonged storage and weathering of BA. Kalicinite was detected only in the weathered BCA (Figure 2a), and its formation is a result of carbonation of K2O and subsequent hydrocarbonation of K2CO3 by CO2 and moisture in air and water during weathering. Hence, this mineral is mostly a product of K2CO3 weathering. It should be stated that the above-mentioned formation mechanisms for these carbonates and kalicinite are valid to other BAs studied in the present investigation.

The data for long-term stored BCA (Figure 4a and Figure S1a in the Supporting Information) reveal that the decomposition of calcite and K–Ca carbonates occurs at 595–897 °C with a mass loss of 33%. On the other hand, the results for weathered BCA (Figure 4a and Figure S1b in the Supporting Information) show that the partial decarbonation of kalicinite to K2CO3 accompanied by some water liberation takes place at 104–218 °C with a mass loss of 4%, while the decarbonation of calcite and K–Ca carbonates occurs at 623–895 °C with a mass loss of 30%.

The partial decarbonation of alkaline bicarbonates follows the reaction: 2KHCO3 or 2NaHCO3 → K2CO3 or Na2CO3 + H2O + CO2. It is well known that the heat treatment of alkaline bicarbonates at 100–200 °C regenerates alkaline carbonates and liberates CO2. Hence, the total released CO2 from carbonates and bicarbonates is 33% and 34% for long-term stored and weathered BCA, respectively (Table 4).

The data (Table 4) indicate that the carbonation and bicarbonation of ash from the “C” type increase slightly in time and under weathering conditions in comparison with the respective short-term stored ash. It can be seen that the great abundance of stable calcite suppresses the supplementary carbonation and bicarbonation in BCA. Despite that, the ash from “C” type has the highest CCS potential compared to other ash types (Table 4).

### 3.4. Carbonation Behavior of the “K” Ash Type

CCA, MMA, and SSA belong to the “K” ash type, and specific features of this type are the high values of K, S, Mg, Na, Cl, P, and Fe oxides, CaO + MgO + K2O + Na2O, pH and DWRs in comparison with other ash types (Table 1 and Figure 1). These ashes show high concentrations of carbonates, namely, calcite and kalicinite, and to a lesser extent, fairchildite and baylissite (Table 2 and Figure 2b–d). The formation of these carbonates and bicarbonates is similar to that of the “C” ash type and includes the carbonation and hydrocarbonation.

---

**Table 4. Mass Loss of BAs Determined in Fixed Temperature (T) Ranges, wt %**

| Ash Type | Short-term Stored (600–900 °C) | Long-term Stored (600–900 °C) | Weathered (600–900 °C) |
|----------|-------------------------------|-----------------------------|------------------------|
| **C** (BCA) | TSCC (65%): 65 | 27 | 32 | 33 (595–897) | 32 | 34 (104–218 & 623–895) |
| **K** (mean) | 30 | 8 | 14 | 20 | 16 | 23 |
| CCA | 24 | 6 | 9 | 23 (127–243 & 654–898) | 8 | 24 (128–256 & 545–895) |
| MMA | 24 | 11 | 21 | 22 (187–291 & 571–899) | 27 | 30 (124–206 & 600–893) |
| SSA | 42 | 8 | 11 | 15 (150–257 & 516–894) | 12 | 16 (169–277 & 563–897) |
| **CK** (mean) | 50 | 14 | 20 | 23 | 22 | 30 |
| WSA | 56 | 18 | 16 | 21 (142–239 & 575–895) | 18 | 31 (126–234 & 564–896) |
| PPA | 43 | 10 | 24 | 24 (598–891) | 26 | 28 (516–898) |
| **S** (mean) | 11 | 2 | 4 | 4 | 3 | 5 |
| SGA | 18 | 3 | 6 | 6 (568–885) | 4 | 7 (150–263 & 582–894) |
| RHA | 3 | 1 | 2 | 2 (542–890) | 2 | 2 (561–892) |

“TSCC on mortars and concrete using the modified Steinour equation.” Based on ref 4.
reactions between CaO, K2O, MgO, CO2, and H2O in the system. The formation of baylissite is a result of hydration of K-Mg carbonate during weathering of SSA (Table 2 and Figure 2d). It can be seen that the occurrence of bicarbonate (kalccinite) is typical for this ash type, especially for CCA and long-term stored and weathered SSA and MMA samples (Figure 2b–d).

CCA is the most abundant in kalccinite among other BAs (Table 2 and Figures 2 and 3), and this is the only carbonate mineral found in CCA (Figure 2b). The results for long-term stored CCA (Figure 4b and Figure S2a in the Supporting Figure 5. TG, DSC, and evolved CO2 profiles of long-term stored (denoted as L) and weathered (denoted as W) BAs: (a) WSAs; (b) PPAs; (c) SGA; and (d) RHAs.

https://doi.org/10.1021/acsomega.1c01730
ACS Omega 2021, 6, 14598−14611
Information) show that the partial decarbonation of kalicinite occurs at 127−243 °C with a mass loss of 15%, while the K₂CO₃ decomposition takes place at 654−898 °C with a mass loss of 8%. On the other hand, the data for weathered CCA (Figure 4b and Figure S2b in the Supporting Information) reveal that the partial decarbonation of kalicinite is detected at 128−256 °C with a mass loss of 16%, while the K₂CO₃ decomposition is observed at 545−895 °C with a mass loss of 8%. Therefore, the total released CO₂ from bicarbonates and carbonates in the above temperature ranges is approximately 23 and 24% for long-term stored and weathered CCA, respectively (Table 4).

The carbonate minerals in MMA include calcite and kalicinite (Table 2 and Figure 2c). The results for long-term stored MMA (Figure 4c and Figure S3a in the Supporting Information) show that the partial kalicinite decarbonation takes place at 187−291 °C with a mass loss of 1%, while the decarbonation of calcite and K₂CO₃ plus some decomposition of chlorides and sulfates (Table 2) occurs at 571−899 °C with a mass loss of 21%. On the other hand, the data for weathered MMA (Figure 4c and Figure S3b in the Supporting Information) reveal that the partial kalicinite decarbonation is detected at 124−206 °C with a mass loss of 3%, while the decarbonation of calcite and K₂CO₃ plus some decomposition of chlorides and sulfates (Table 2) is observed at 600−893 °C with a mass loss of 27%. Hence, the total released CO₂ from carbonates and bicarbonates in the above temperature ranges is overestimated, and it is up to 22 and 30% for long-term stored and weathered MMA, respectively (Table 4). The CO₂ release at 291−412 and 412−571 °C for long-term stored MMA, as well as at 289−436 and 436−600 °C for weathered MMA, is related to the decomposition of residual char observed by light microscopy.

The carbonate minerals in SSA include kalicinite, fairchildite, calcite, and baylissite (Table 2 and Figure 2d). The data for long-term stored SSA (Figure 4d and Figure S4a in the Supporting Information) reveal that the partial decarbonation of kalicinite occurs at 150−257 °C with a mass loss of 3%, while the decarbonation of K, Ca, and K−Ca carbonates plus some decomposition of sulfates (Table 2) takes place at 516−894 °C with a mass loss of 12%. On the other hand, the results for weathered SSA (Figure 4d and Figure S4b in the Supporting Information) show that the partial decarbonation of kalicinite is detected at 169−277 °C with a mass loss of 3%, while the decarbonation of K, Ca, K−Ca, and K−Mg carbonates plus some decomposition of sulfates (Table 2) is observed at 563−897 °C with a mass loss of 13%. Therefore, the total released CO₂ from bicarbonates and carbonates in the above temperature ranges is approximately 15 and 16% for long-term stored and weathered SSA, respectively (Table 4). The CO₂ release at 257−516 °C for long-term stored SSA and at 277−563 °C for weathered SSA is related to the decomposition of some residual char observed by light microscopy.

The above results for the “K” ash type show that the carbonation and bicarbonation of these long-term stored and weathered ashes increase greatly (CCA) or significantly (MMA and SSA) in time and under weathering conditions in comparison with the respective short-term stored ashes (Table 4). The reason for the additional carbonation and bicarbonation is the great abundance of kalicinite, and to a lesser extent, fairchildite and baylissite in “K” type ashes. It can be seen that the “K” ash type has moderate CCS potential compared to other ash types (Table 4).

3.5. Carbonation Behavior of the “CK” Ash Type. WSA and PPA belong to the “CK” ash type, and characteristic features of this type are the high values of Ca, K, P, S, Al, Na, Cl, and Ti oxides, CaO + MgO + K₂O + Na₂O, (CaO + MgO)/(K₂O + Na₂O), and DWRs in comparison with other ash types (Table 1 and Figure 1). It was found that the “CK” ash type shows an intermediate composition, properties, and thermal behavior between “C” and “K” ash types. WSA and PPA show high concentrations of carbonates, namely, calcite and kalicinite, and to a lesser extent, fairchildite and butschliite (Table 2 and Figure 3a,b). The formation of these carbonates and bicarbonates is similar to those of “C” and “K” ash types and includes the carbonation and hydrocarbonation reactions between CaO, K₂O, MgO, CO₂, and H₂O in the system. It can be seen that the occurrence of bicarbonate (kalicinite) is typical for this ash type, especially for long-term stored and weathered WSA (Figure 3a).

The carbonate minerals in WSA include calcite, fairchildite, kalicinite, and butschliite (Table 2 and Figure 3a). The data for long-term stored WSA (Figure 5a and Figure S5a in the Supporting Information) reveal that the partial decarbonation of kalicinite occurs at 142−239 °C with a mass loss of 4%, while the decarbonation of Ca, K−Ca, and K carbonates plus very limited decomposition of sulfates (Table 2) takes place at 575−895 °C with a mass loss of 17%. On the other hand, the results for weathered WSA (Figure 5a and Figure S5b in the Supporting Information) show that the partial decarbonation of kalicinite is detected at 126−234 °C with a mass loss of 12%, while the decarbonation of Ca, K−Ca, and K carbonates plus very limited decomposition of sulfates (Table 2) is observed at 564−896 °C with a mass loss of 19%. Hence, the total released CO₂ from bicarbonates and carbonates in the above temperature ranges is about 21 and 31% for long-term stored and weathered WSA, respectively (Table 4). The CO₂ release at 239−575 °C for long-term stored WSA and at 234−564 °C for weathered WSA is related to the decomposition of some residual organic matter observed by light microscopy.

The carbonate minerals in PPA include calcite, fairchildite, and kalicinite (Table 2 and Figure 3b). The data for long-term stored PPA (Figure 5b and Figure S6a in the Supporting Information) reveal that the decarbonation of kalicinite cannot be identified, while the decarbonation of Ca and K−Ca carbonates accompanied by limited decomposition of sulfates (Table 2) occurs at 598−891 °C with a mass loss of 24%. On the other hand, the results for weathered PPA (Figure 5b and Figure S6b in the Supporting Information) show that the decarbonation of Ca and K−Ca carbonates plus limited decomposition of sulfates (Table 2) is observed at 516−898 °C with a mass loss of 28%. Therefore, the total released CO₂ from carbonates and bicarbonates in the above temperature ranges is approximately 24 and 28% for long-term stored and weathered PPA, respectively.

The above data for the “CK” ash type indicate that the bicarbonation and carbonation of these long-term stored and weathered ashes increase greatly in time and under weathering conditions in comparison with the respective short-term stored ashes (Table 4). The reason for the additional carbonation and bicarbonation is the great abundance of kalicinite, and to a lesser extent, fairchildite and baylissite in “CK” type ashes. It can be seen that the “CK” ash type has high CCS potential compared to other ash types (Table 4).
3.6. Carbonation Behavior of the “S” Ash Type. SGA and RHA belong to the “S” ash type, and specific features of this type are the high values of Si and Al oxides in comparison with other ash types (Table 1 and Figure 1). These ashes are abundant in silicates and inorganic amorphous matter, and they show low concentrations (especially RHA) of carbonates, namely, calcite and kalicinite (Table 2, Figure 3c,d). The formation of these carbonates and bicarbonates is similar to that of other ash types and includes the carbonation and hydrocarbonation reactions between CaO, K2O, CO2, and H2O in the system. It can be seen that the occurrence of bicarbonate (kalicinite) is typical only for SGA (Figure 3c). It was also found that the “S” ash type shows a diverse composition, properties, and thermal behavior in comparison with other ash types.

The carbonate minerals in SGA include calcite and kalicinite (Table 2 and Figure 3c). The data for long-term stored SGA (Figure 5c and Figure S7a in the Supporting Information) reveal that the partial decarbonation of kalicinite cannot be identified, while the decarbonation of Ca and K carbonates plus very limited decomposition of anhydrite (Table 2) is detected at 568–885 °C with a mass loss of 6%. On the other hand, the results for weathered SGA (Figure 5c and Figure S7b in the Supporting Information) show that the partial decarbonation of kalicinite occurs at 150–263 °C with a mass loss of 3%, while the decarbonation of Ca and K carbonates plus very limited decomposition of anhydrite (Table 2) takes place at 582–894 °C with a mass loss of 4%. Hence, the total released CO2 from carbonates and bicarbonates in the above temperature ranges is about 6 and 7% for long-term stored and weathered SGA, respectively. The CO2 release at 265–568 °C for long-term stored SGA and 263–582 °C for weathered SGA is related to the decomposition of some residual char observed by light microscopy.

Calcite is the only carbonate mineral in RHA (Table 2 and Figure 3d). The data for long-term stored RHA (Figure 5d and Figure S8a in the Supporting Information) reveal that the decarbonation of calcite plus very limited decomposition of sulfates and chlorides (Table 2) occurs at 542–890 °C with a mass loss of 2%. On the other hand, the results for weathered RHA (Figure 5d and Figure S8b in the Supporting Information) show that the decarbonation of calcite plus very limited decomposition of sulfates and chlorides (Table 2) takes place at 561–892 °C with a mass loss of 2%. Therefore, the total released CO2 from carbonates and bicarbonates in the above temperature ranges is about 2% for both long-term stored and weathered RHA. The CO2 release at 300–540 °C for long-term stored RHA at 246–561 °C for weathered RHA is related to the decomposition of some residual organic matter observed by light microscopy.

The above results for the “S” ash type reveal that the bicarbonation and carbonation of these long-term stored and weathered ashes increase significantly (SGA) or slightly (RHA) in time and under weathering conditions in comparison with the respective short-term stored ashes (Table 4). The reason for the limited supplementary carbonation and bicarbonation is the low content of calcite and kalicinite and the abundance of silicates and inorganic amorphous matter in “S” type ashes. It can be seen that the “S” ash type has limited CCS potential compared to other ash types (Table 4).

The summarized data reveal that each BA has individual CCS behavior, which is strongly dependent on its mineral composition; however, there are substantial CCS similarities among BAs belonging to a specific chemical type. It was found that there are some typical BA examples for each ash type such as BCA from the “C” type (Figure 4a), CCA from the “K” type (Figure 4b), WSA from the “CK” type (Figure 5a), and SGA from the “S” type (Figure 5c), which clearly show the major carbonation and bicarbonation trends during weathering.

3.7. Significance of Carbon Capture and Storage by Carbonation of BAs. Our former 4 and present results show the intensive formation of carbonates in BAs at 500 °C, excluding ashes from the “S” type where silicates and inorganic amorphous matter have dominant occurrence (Table 2 and Figures 2 and 3). Most carbonates have secondary origin in BAs; however, significant tertiary origin of carbonates and especially bicarbonates is also typical for long-term stored and particularly weathered BAs. Hence, the long-term storage and weathering of BAs have the possibility to capture additional atmospheric CO2. The theoretically and experimentally determined carbonation of the short-term stored, long-term stored, and weathered BAs (Table 4) is as follows.

First, the theoretical CO2 sequestration capacity (TCSC) known also as maximum theoretical CO2 uptake capacity (or theoretical CO2 binding capacity) was calculated for the short-term stored BAs according to the modified Steinour equation for mortars and concrete (see ref 21 and Table 4). Their TCSC values are 3–65% (mean 34%) and decrease in the following order: BCA (65%) > WSA (56%) > PPA (43%) > SSA (42%) > CCA (24%) = MMA (24%) > SGA (18%) > RHA (3%) and “C” > “CK” > “K” > “S” for ash types.

Second, the carbonation or CCS potential of short-term stored BAs based on the measurement of CO2 volatilization from carbonates in BAs at 600–900 °C is approximately 1–27% (mean 11%), namely, BCA (27%) > WSA (18%) > MMA (11%) > PPA (10%) > SSA (8%) > CCA (6%) > SGA (3%) > RHA (1%) and “C” > “CK” > “K” > “S” for ash types (see ref 4, and Table 4).

Third, the carbonation or CCS potential of long-term stored BAs based on the measurement of CO2 volatilization from carbonates and bicarbonates in fixed temperature ranges is about 2–33% (mean 18%) and decreases in the following order: BCA (33%) > PPA (24%) > CCA (23%) > MMA (22%) > WSA (21%) > SSA (15%) > SGA (6%) > RHA (2%) and “C” > “CK” > “K” > “S” for ash types.

Fourth, the carbonation or CCS potential of weathered BAs based on the same measurement as the long-term stored BAs is approximately 2–34% (mean 22%) and decreases in the following order: BCA (34%) > WSA (31%) > MMA (30%) > PPA (28%) > CCA (24%) > SSA (16%) > SGA (7%) > RHA (2%) and “C” > “CK” > “K” > “S” for ash types (Table 4).

These data show that the determined carbonation values for short-term stored BAs are 2–6 times (mean 3) less than the calculated TCSC, while the long-term stored and weathered BAs are 1–3 times (mean 2) less than the TCSC. It was expected that the calculated maximum theoretical CO2 uptake capacity for mortars and concrete is hard to be achieved for BAs because of occurrence of other noncarbonate minerals containing alkaline-earth and alkaline elements, which do not capture CO2 (Table 2). However, the above carbonation orders for short-term stored, long-term stored, and weathered BAs are similar to those for TCSC, sum of alkaline-earth and alkaline oxides, and ratio between alkaline-earth and alkaline.
oxides, while the carbonation orders for their ash types are always identical, namely, “C” > “CK” > “K” > “S” (see also Section 3.1). Hence, the carbonation for “C”, “CK”, and “K” ash types is much higher compared to the “S” ash type because of the diverse composition (Tables 1 and 2). The fluctuation of the carbonation orders among the specific BAs is related to the different phase-mineral composition and phase transformations of these BAs (Table 2 and see ref 25).

The determined carbonation based on the mass loss measurements in fixed temperature ranges was slightly overestimated for specific BAs because of some water volatilization and partial decomposition of certain non-carbonate minerals. For example, the CO$_2$ volatilization determined at 600−900 °C for MMA was overestimated because of some partial decomposition of sulfates and chlorides at 800−900 °C (Table 2 and see ref 4). On the other hand, the CO$_2$ volatilization determined at 600−900 °C for some short-term stored BAs (CCA, SSA, and PPA) was underestimated because of partial kalicinite decarbonation to K$_2$CO$_3$ at 104−291 °C (Table 4). Hence, the actual CCS values for the short-term stored BAs containing bicarbonates are slightly higher because their partial decomposition in the above low-temperature range was not measured. It is well known that the mass factor of CO$_2$ capture is normally doubled if bicarbonates form instead of carbonates, as the former minerals are more typical for the long-stored and weathered BAs (Figures 2 and 3). Our results also show that more advanced and precise methods for experimental measurements of carbonates, bicarbonates, and CO$_2$ sequestration are required. On the other hand, the theoretical calculations used at present should be improved based on comprehensive chemical and mineralogical data for numerous BAs as they can be a subsidiary procedure to the experimental determinations.

The reference data for different BAs worldwide show that their CCS capacity is 1−17% (mean 5%), and such values are comparable or greater to those of many commercial adsorbents. The above values are also similar to those determined for the short-term stored BAs, while the long-term stored and weathered BAs mostly reveal significantly higher CCS potential in comparison with the reference data. The present results and literature data demonstrate that BA is particularly prospective for CCS because the concentrations of key alkaline-earth and alkaline oxides can reach very high values. For instance, one ton of lime has the theoretical capacity to capture up to 799 kg of CO$_2$ as calcite. Other phases among alkaline-earth and alkaline oxhydroxides, chlorides, sulfates, phosphates, silicates, amorphous matter, and char occur in BA, and some of them or their decomposition products may also have the ability to capture and store CO$_2$ during biomass combustion and BA storage and weathering. For example, the decomposition of Ca, K, Mg, and Na chlorides, sulfates, and phosphates to their active oxides above 800−900 °C may have significant importance in CCS of BA. Our data also show that the role of Mg- and Na-bearing carbonates for the CO$_2$ sequestration of BAs is relatively limited in comparison with Ca- and K-bearing carbonates (Tables 1 and 2). Furthermore, about 178 mineral species and mineral groups containing alkaline-earth and alkaline elements were found in BAs, and such species could have more or less CCS behavior. Unfortunately, the CCS mechanisms of BA are at an initial stage of investigations, and future comprehensive studies are required.

The mineral carbonation of BA is an effective method for CCS because this natural weathering process stores CO$_2$ permanently in the form of stable carbonates in depots and landfills. Such a carbonation process serves not only as a CO$_2$ sink, but can also increase the ash utilization because of the stabilization of this waste. BAs have highly variable composition and properties, and their potential industrial applications are numerous, namely, production of building materials, soil amendments and fertilizers, and sorbents; synthesis of minerals and ceramics; and recovery of valuable fractions, components, and elements. The classifications of BAs (Figure 1) can assist in finding the appropriate BA utilization.

The present results and reference data show that the biomass and BA can be used as a prospective resource for CCS. For instance, it was assumed that about 13 Gt of the current fossil fuel CO$_2$ emissions could be reduced by 35% increasing of bioenergy application. On the other hand, the produced alkaline-earth and alkaline industrial wastes globally each year are about 7 Gt, and their role in CCS has been assessed recently. It was calculated therein that these products have a CCS potential of 2.9−8.5 Gt of CO$_2$ per year by 2100, which is about 18−37% of the negative emission requirements to limit global temperature change to <2 °C. Finally, the future increase of industrial combustion and gasification of sustainable second (nonedible) and third (algae) biofuel generations is particularly prospective to decrease CO$_2$ emissions in the atmosphere and to reduce the use of expensive CCS technologies.

4. CONCLUSIONS

The carbonation behavior of eight BAs that belong to different biomass groups and diverse chemical ash types was studied to evaluate the CCS potential of these waste products during their short-term and long-term storage and weathering. The following conclusions could be made:

(1) BAs are normally highly enriched in alkaline-earth and alkaline elements, and the minerals responsible for CCS include Ca, K, and K−Mg and K−Ca carbonates and bicarbonates, namely, calcite, kalicinite, and fairchildite, and to a lesser extent, butschliite and baylissite.

(2) Each BA has individual CCS behavior, which is strongly dependent on its chemical and mineral composition; however, there are substantial CCS similarities among BAs belonging to a specific ash type. Carbonates and bicarbonates are abundant in “C” and “CK” ash types, to a lesser extent in the “K” ash type, and they have limited occurrence in the “S” ash type.

(3) The qualitative mineral composition of the short-term stored, long-term stored, and weathered BAs is similar; however, there are some differences related to the increased proportions of carbonates and especially bicarbonate (kalicinite) in the long-term stored BAs and particularly weathered BAs.

(4) The CCS capacity of BAs based on the measurement of CO$_2$ volatilization from carbonates and bicarbonates in fixed temperature ranges follows the order: short-term stored BAs (mean 11%) < long-term stored BAs (mean 18%) < weathered BAs (22%); hence, the CCS potential of BAs increases in time and under weathering conditions.
(5) The mineral carbonation of BA fixes permanently both flue CO2 gas during biomass combustion and atmospheric CO2 during BA storage and weathering because of the intensive crystallization of newly formed carbonates and bicarbonates in this waste product.

## ASSOCIATED CONTENT

* Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01730.

**Abbreviations**

| Abbreviation | Description |
|--------------|-------------|
| BA           | biomass ash |
| BCA         | beech wood chips ash |
| CCA         | corn cobs ash |
| CCS         | CO2 capture and storage |
| DSC         | differential scanning calorimetry |
| DTG         | differential thermogravimetry |
| DWR         | dry water-soluble residue |
| EDX         | energy dispersive X-ray analyzer |
| IAM         | inorganic amorphous matter |
| ICP         | inductively coupled plasma |
| MMA         | marine macroalgae ash |
| MS          | mass spectrometry |
| PPA         | plum pits ash |
| RHA         | rice husks ash |
| SEM         | scanning electron microscopy |
| SGA         | switchgrass ash |
| SSA         | sunflower shells ash |

**REFERENCES**

(1) Oke, D.; Olatilu, A. Carbon storage in agroecosystems: A case study of the cocoa based agroforestry in Ogbese forest reserve, Ekiti state, Nigeria. *Environ Prot* 2011, 02, 1069−1075.
(2) Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-combustion CO2 capture using solid sorbents: A review. *Ind. Eng. Chem. Res.* 2012, *S1*, 1438−1463.
(3) Vassilev, S.; Baxter, D.; Andersen, L.; Vassileva, C. An overview of the composition and application of biomass ash. Part 1. Phosphate and chemical composition and classification. *Fuel* 2013, *105*, 40−76.
(4) Vassilev, S.; Vassileva, C. Extra CO2 capture and storage by carbonation of biomass ashes. *Energ. Convers. Manage.* 2020, *204*, No. 112331.
(5) Demirbas, A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energ. Convers. Manage.* 2008, *49*, 2106−2116.
(6) Saidur, R.; Abdelaziz, E. A.; Demirbas, A.; Hossain, M. S.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* 2011, *15*, 2262−2289.
(7) McEndry, P. Energy production from biomass (part 1): overview of biomass. *Bioresour. Technol.* 2002, *83*, 37−46.
(8) Vassilev, S.; Baxter, D.; Andersen, L.; Vassileva, C. An overview of the composition and application of biomass ash. Part 2. Potential utilization, technological and ecological advantages and challenges. *Fuel* 2013, *105*, 19−39.
(9) Nie, L.; Mu, Y.; Jin, J.; Chen, J.; Mi, J. Recent developments and consideration issues in solid absorbents for CO2 capture from flue gas. *Chin. J. Chem. Eng.* 2018, *26*, 2303−2317.
(10) Li, B.; Duan, Y.; Luebbe, D.; Morreale, B. Advances in CO2 capture technology: A patent review. *Appl. Energy* 2013, *102*, 1439−1447.
(11) Lee, S.-Y.; Park, S.-J. A review on solid absorbents for carbon dioxide capture. *J. Ind. Eng. Chem.* 2015, *23*, 11−11.
(12) Modak, A.; Jana, S. Advancement in porous absorbents for post-combustion CO2 capture. *Micropor Mesopor Mat* 2019, *276*, 107−132.
(13) Renforth, P. The negative emission potential of alkaline materials. *Nat. Commun.* 2019, *10*, 1401.
(14) Wang, W.; Zheng, Y.; Liu, X.; Wang, P. Characterization of typical biomass ashes and study on their potential of CO2 fixation. *Energy Fuel* 2012, *26*, 6047−6052.
(15) Sanna, A.; Dri, M.; Hall, M. R.; Maroto-Valer, M. Waste materials for carbon capture and storage by mineralisation (CCSM) − A UK perspective. *Appl. Energy* 2012, *99*, 545−554.
(16) Guo, Y.; Zhao, C.; Chen, X.; Li, C. CO2 capture and sorbent regeneration performances of some wood ash materials. *Appl. Energy* 2015, *137*, 26−36.
(17) Mohamed, M.; Yusup, S.; Bustam, M. A. Synthesis of CaO-based sorbent from biomass for CO2 capture in series of calcination-carbonation cycle. *Procedia Eng* 2016, *148*, 78−85.
(18) Lira-Zuniga, S.; Saez-Navarrete, C.; Rodriguez-Cordova, L.; Herrera-Zepelin, L.; Herrera-Urbeina, R. CO2 adsorption on agricultural biomass combustion ashes. *Maderas Cienc Tecnol* 2016, *18*, 607−616.
(19) Yan, S.; He, Q.; Wang, W.; Li, S. CO2 absorption using biogas slurry: CO2 absorption enhancement induced by biomass ash. *Energy Procedia* 2017, *114*, 890−897.
(20) Wang, P.; Guo, Y.; Zhao, C.; Yan, J.; Lu, P. Biomass derived wood ash with amine modification for post-combustion CO2 capture. *Appl. Energy* 2017, *201*, 34−44.
(21) López, R.; Díaz, M. J.; González-Pérez, J. A. Extra CO₂ sequestration following reutilization of biomass ash. Sci. Total Environ. 2018, 625, 1013–1020.
(22) Juárez, M. F.-D.; Mostbauer, P.; Knapp, A.; Müller, W.; Tertsch, S.; Bockreis, A.; Insam, H. Biogas purification with biomass ash. Waste Manag. 2018, 71, 224–232.
(23) Vassilev, S.; Vassileva, C.; Baxter, D.; Andersen, L. A new approach for the combined chemical and mineral classification of the inorganic matter in coal. 2. Potential applications of the classification systems. Fuel 2009, 88, 246–254.
(24) Vassilev, S.; Baxter, D.; Andersen, L.; Vassileva, C.; Morgan, T. An overview of the organic and inorganic phase composition of biomass. Fuel 2012, 94, 1–33.
(25) Vassilev, S.; Baxter, D.; Vassileva, C. An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. Fuel 2013, 112, 391–449.
(26) Vassilev, S.; Vassileva, C.; Baxter, D. Trace element concentrations and associations in some biomass ashes. Fuel 2014, 129, 292–313.
(27) Vassilev, S.; Vassileva, C. Water-soluble fractions of biomass and biomass ash and their significance for biofuel application. Energy Fuel 2019, 33, 2763–2777.
(28) Vassilev, S.; Baxter, D.; Vassileva, C. An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. Fuel 2014, 117, 152–183.
(29) Uliasz-Bochenczyk, A.; Pawluk, A.; Pyzalski, M. The mineral sequestration of CO₂ with the use of fly ash from the co-combustion of coal and biomass. Gospod Surowcami Min 2018, 33, 143–155.
(30) Vassilev, S.; Vassileva, C.; Song, Y.-C.; Li, W.-Y.; Feng, J. Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. Fuel 2017, 208, 377–409.