

DETERMINATION OF THE MAXIMUM CO₂ SEQUESTRATION CAPACITY OF SLOVENIAN WASTE ASHES USING THERMOGRAVIMETRY AND CALCIMETRY

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There are several ways to utilize as-received or pre-treated waste ash, one of the most promising is by accelerated mineral carbonation. Ashes with a high content of Ca and Mg compounds, such as ashes from wood biomass, are ideal candidates for sequestration. Due to the shift toward renewable fuels, ash from biomass as a by-product of solid fuel combustion is therefore available in huge quantities. As part of the EU AshCycle project, we have analyzed ashes from different incineration and thermal power plants to determine their carbon sequestration potential. These include various waste ashes from Slovenia, which were subjected to accelerated carbonation in a closed carbonation chamber with a CO₂ concentration of 4% (v/v), 80% relative humidity and a temperature of 40 °C until maximum CO₂ uptake was reached. CO₂ quantification was performed using calcimetry (pressure calcimeter) and thermogravimetry. We have shown that ash from wood biomass and the co-combustion of wood waste and paper sludge have a high CO₂ sequestration potential in comparison to others. The direct use of wood biomass ash for CO₂ sequestration in carbonated building products could significantly benefit the circular economy, especially since 70% of wood biomass ash is still landfilled.

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1 Introduction

Mineral sequestration is a carbonation approach, in which CO₂ is captured and stored using alkaline materials consisting of calcium (Ca) and magnesium (Mg) (hydr)oxides and silicates, resulting in the formation of solid, permanently stored carbonate products (Alturki 2022, Koch et al. 2021, Li and Wu 2022). Many different carbonate phases can be detected in waste materials; however, after carbonation, Ca-containing carbonates are the predominant products (Santos et al. 2013, Wang et al. 2021). Alkaline solid waste materials such as steel slag, cement waste and coal fly ash are well suited for mineral carbonation due to their high reaction rates, low energy requirements and superior carbonate conversion efficiency compared to natural minerals where carbonation is slow (Ahmed et al. 2024). Carbonation can be accelerated by increased CO₂ concentration, pressure, relative humidity, temperature or contact time (Ahmed et al. 2024, Capelo-Avilés et al. 2024, Li et al. 2022). To mitigate climate change fast enough, accelerated carbonation is very beneficial compared to natural carbonation. Therefore, a wide range of accelerated curing environments can be found in the literature (Koch et al. 2021, Zajac et al. 2022, Tominc and Ducman 2023, Winnefeld et al. 2022). In recent years, the direct wet carbonation process has been intensively investigated due to the highest carbonation efficiency, while studies on semi-dry carbonation are rare.

The use of CO₂ sequestration for the production of building materials is an economically sustainable industrial process with negative carbon emissions and therefore deserves attention for further development (Lippiatt et al. 2020). Possible sources from waste streams are ashes containing Ca and Mg compounds, as they enable the sequestration of CO₂ in the form of carbonate compounds, for example ash from wood biomass (WBA) (Koch et al. 2021, Tominc and Ducman 2023). This is not only a waste management option, but also has the benefit of reducing CO₂ emissions.

Various methods can be used to quantify the CO₂ sequestration capacity. In thermogravimetric analysis (TGA), the mass of the sample is recorded as a function of time during the decomposition of CaCO₃ into CaO and the release of CO₂ in a controlled (inert) atmosphere. This method accounts for possible hydration and dehydroxylation reactions that contribute to weight loss (Nielsen and Quaghebeur 2023). Using a pressure calcimeter, CaCO₃ reacts with 10% hydrochloric acid (HCl)

in a closed reaction cell to form CaCl₂, CO₂ and H₂O, measuring the pressure of the released CO₂ (Tominc and Ducman 2023). In this regard, comparing different methods for estimating the CO₂ or carbonate content in selected waste materials and determining the measurement uncertainty of each method can be challenging.

As part of the AshCycle project, we have proposed a methodology to assess the CO₂ sequestration potential of waste ashes, as not all ashes are equally suitable for CO₂ sequestration. Wood biomass ash has shown greater potential than coal ash because it contains higher content of Ca oxides and other minerals that react with CO₂ and convert it into stable carbonate minerals (Tominc and Ducman 2023). In this study, we shortened the duration of carbonation by optimizing the conditions, i.e. the temperature, and determined the maximum CO₂ sequestration capacity of selected ashes after 7 days of carbonation at 40 °C, 80% relative humidity and 4% CO₂ (v/v).

2 Materials and methods

We investigated the CO₂ sequestration capacity of seven waste ashes from different Slovenian plants (Figure 1). The first two ashes, fly ash (WA.FA.1) and bottom ash (WA.BA.1) came from a Slovenian combined heat and power plant and were produced during the combustion of wood biomass (wood chips). The next two ashes came from a paper mill industry, where the fuel source for fly ash (CC.FA.2) was coal, biomass and paper sludge, while the fuel source for mixed ash (CC.MA.2) was fibrous paper sludge, waste wood and bark. The next two ashes (CC.FA.3 and CC.BA.3) came from a Slovenian combined heat and power plant, where the fuel source was brown coal and wood biomass-wood chips (15%). The last bottom ash (CC.BA.4) came from a Slovenian heat and power station, where municipal waste (light fraction) and dehydrated sewage sludge were used as fuel. All obtained ashes were first homogenized by quartering (see Figure 1), packed in a PVC bag and stored in a plastic container.

For the chemical analysis, the samples were sieved below 125 µm and dried at 105 °C. The loss on ignition (LOI) was determined at 950 °C. A fused bead was then prepared with a mixture of sample and flux (50% lithium tetraborate/50% lithium metaborate) at a ratio of 1:10 (0.947 g: 9.47 g) and heated at 1100 °C. The chemical composition was determined using an ARL PERFORM'X wavelength dispersive X-ray fluorescence spectrometer (WDXRF; Thermo Fischer Scientific Inc., Ecublens,

Switzerland) with a Rh-target X-ray tube and UniQuant 5 software (Thermo Fisher Scientific Inc., Waltham, MA, USA). Two measurements were performed for each ash. For mineralogical analysis, the ashes were sieved below 63 μm and placed in 27 mm holders (in diameter). Analyzes were performed before and after CO_2 treatment with X-ray diffraction (XRD; Empyrean X-ray Diffractometer, Cu X-ray source; PANalytical, Almelo, The Netherlands) in 0.013° steps from angles of $4\text{--}70^\circ$ under clean room conditions using the external standard corundum NIST SRM 676a. The mineral phases were analyzed with the PANalytical X'Pert High Score Plus diffraction software v.4.8. Fourier transform infrared spectroscopy (FTIR) measurements were performed using an FTIR, PerkinElmer Spectrum Two, ATR mode. All infrared spectra were recorded in a wavenumber range of $4000\text{--}380\text{ cm}^{-1}$.

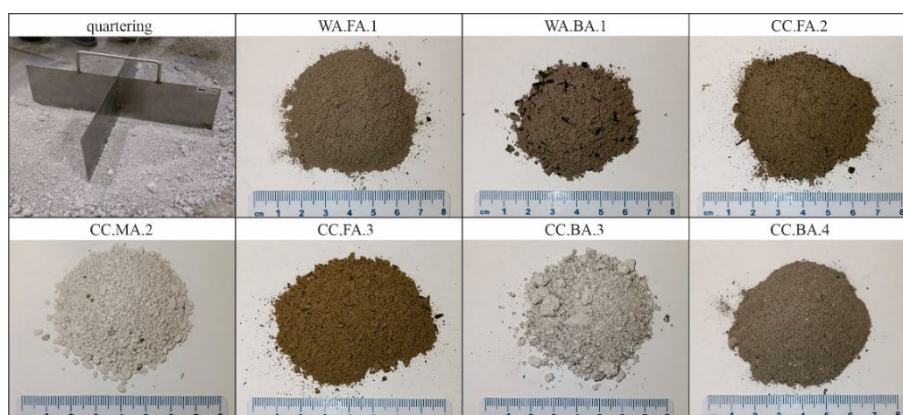


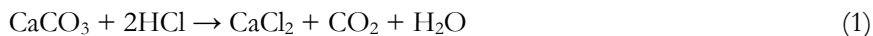
Figure 1: Waste ashes from different sources, homogenized by quartering, source: own.

20 g of each ash with a particle size of less than 125 μm was then placed in a petri dish and exposed to 4% CO_2 (v/v) in a closed carbonation chamber at 80% relative humidity and a temperature of 40° C . Carbonation was completed when a constant mass was reached.

For the determination of carbonate content, as-received and carbonated ashes were analyzed using the pressure calcimeter (OFITE Calcimeter, OFI Testing Equipment Inc., Houston, TX, USA, according to ASTM D 4373) with an analytical error of $<5\%$. Each sample was ground and sieved below 125 μm and dried in an oven at 105° C for 24 hours. Then $1.0 \pm 0.01\text{ g}$ of the sample was weighed and added to the reaction cell. The acid cup was filled with 20 mL of 10% HCl and carefully placed

in the reaction cell. CaCO₃ reacts with 10% HCl in a closed reaction cell and the pressure of the released CO₂ is measured with a manometer. The calcimeter was calibrated before the actual measurements by reacting HCl with pure CaCO₃.

The calculations for the amount of CO₂ released were based on stoichiometry.



$$1\text{ mol} : 2\text{ mol} \text{ ----- } 1\text{ mol} : 1\text{ mol} : 1\text{ mol}$$

$$n(\text{CaCO}_3) = n(\text{CO}_2) = 1:1$$

$$M(\text{CaCO}_3) = 100.0869 \text{ g/mol}; M(\text{CO}_2) = 44.01 \text{ g/mol}$$

$$1 \text{ mol of CaCO}_3 \text{ releases } 44.01 \text{ g of CO}_2.$$

The thermal decomposition of each sample was analyzed before and after the carbonation process using a TGA Q5000IR thermal analyzer (TA Instruments, New Castle, Delaware, USA). Prior to the measurements, the ashes were dried at 105 °C and sieved to a particle size below 63 μm. The analysis included a controlled heating program with a ramp rate of 10 °C per minute, from 25 to 1000 °C. To prevent oxidation during the measurement, the sample chamber was filled with N₂ at a flow rate of 25 mL per minute. Samples were placed in 100 μL Al₂O₃ crucibles. We used TGA to measure the weight loss in the temperature range of decomposition of the carbonate mineral. The results were analyzed with TA Universal Analysis 2000 v.4.5A (TA Instruments, New Castle, Delaware, USA).

3 Results and discussion

First, the characterization of the different ashes before the carbonation reaction was assessed. Their CaO content is particularly important, as this is decisive for the extent of carbonation (Capelo-Avilés et al. 2024). X-ray fluorescence (XRF) analysis of the selected Slovenian ashes shows that they are mainly composed of CaO (20-55%), SiO₂ (6-31%), Al₂O₃ (3-18%), MgO (2-10%), Fe₂O₃ (1-10%) and K₂O (0.3-8%), with lower contents of Na₂O and SO₃. The average values of the primary oxides measured by XRF and LOI at 950 °C are shown in Table 1.

Table 1: Chemical composition of the analyzed Slovenian ashes in terms of primary oxides (wt%), measured by XRF and loss on ignition at 950 °C.

Sample ID	LOI _{950 °C}	Al ₂ O ₃	SiO ₂	CaO	MgO	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO ₃
WA.FA.1	29.91	5.62	19.04	29.27	3.78	1.70	5.65	0.56	1.00
WA.BA.1	26.09	3.35	5.64	44.95	5.88	0.68	8.14	0.48	0.32
CC.FA.2	11.71	11.28	22.90	34.01	5.99	8.53	0.99	0.74	1.70
CC.MA.2	14.55	11.08	14.45	55.40	2.12	0.56	0.25	0.41	0.20
CC.FA.3	16.98	10.87	27.78	19.77	8.21	10.44	2.16	0.28	1.69
CC.BA.3	12.79	7.43	31.17	28.98	10.25	3.56	3.21	0.57	0.07
CC.BA.4	7.21	17.77	27.14	30.59	3.89	3.09	0.48	2.12	0.99

The carbonation reaction of the waste ashes was then studied under the specified conditions (40 °C, 80% RH, 4% CO₂). The reaction was complete after 7 days, indicating a faster reaction rate at elevated temperature, as in our previous study (Tominc and Ducman 2023). With an increase in temperature from 20 to 40 °C, the kinetics of calcium species dissolution can be accelerated (Capelo-Avilés et al. 2024). However, at higher temperatures, the nucleation and growth of CaCO₃ can be hindered due to lower CO₂ solubility, which has a detrimental effect on the carbonation reaction (Capelo-Avilés et al. 2024).

The CO₂ content of each ash (in wt%) was compared using TGA and measured with a pressure calcimeter, as shown in Table 2. The weight loss in the temperature range of CaCO₃ decomposition was between 550-950 °C, based on dry matter at 105 °C (or between 620-950 °C for some samples). The main problem in determining CO₂ content using TGA is that thermal decomposition of carbon species sometimes overlaps with other thermal events (Protić et al. 2021). However, the results obtained with the calcimeter and TGA are very comparable in our case, as they differ by less than 3% (the difference is within the measurement error of the calcimeter, which is up to 5%).

Of the analyzed Slovenian ashes, the ash from wood biomass and the mixed ash from co-combustion showed the highest sequestration potential, as the amount of sequestered CO₂ in 1 kg of sample was 298 g for WA.BA.1 and 274 g for CC.MA.2 (according to the calcimetric measurements).

Table 2: TGA and calcimetric measurements for Slovenian wood and co-combustion ashes.

Sample ID	TGA (weight losses-%)		Calculations (TGA)		Calculations (calcimeter)
	0-150 °C	550-950 °C	% dry matter	%CO ₂ /dry matter	% CO ₂
WA.FA.1	2.0	16.3*	98.0	16.6	13.7
WA.BA.1	2.8	27.9	97.2	28.7	29.8
CC.FA.2	1.3	7.5*	98.7	7.6	8.6
CC.MA.2	2.3	26.2	97.7	26.9	27.4
CC.FA.3	2.2	8.8*	97.8	8.9	8.3
CC.BA.3	1.0	12.2	99.0	12.3	14.8
CC.BA.4	1.9	10.8	98.1	11.0	11.7

*T:620-950 °C

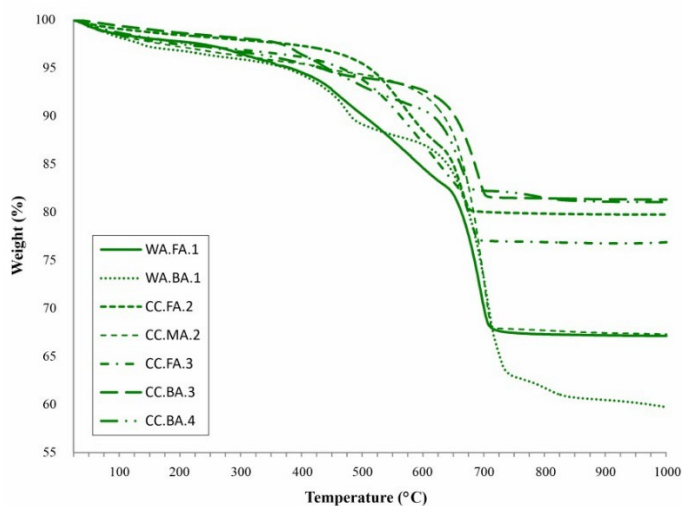


Figure 2: TGA of selected samples after 7 days of carbonation

Source: own.

The presence of carbonates was also observed by FTIR spectra of as-received and carbonated ashes, recorded in the range between 4000 cm⁻¹ and 380 cm⁻¹ (Figure 3). The intense band centered at around 1400 cm⁻¹ corresponds to the ν₃ vibrations of CO₃²⁻ (asymmetric C-O stretching), while the peaks at 872 cm⁻¹ and at 712 cm⁻¹ are associated with out-plane and in-plane bending (ν₂) vibrations of CO₃²⁻, respectively (Capelo-Avilés et al. 2024). The peak at 1795 cm⁻¹ can also be attributed to CaCO₃ (Capelo-Avilés et al. 2024). The increase in intensity of these bands in the carbonated sample indicates that the carbonation of the sample occurred during the CO₂ mineralization process, which was also confirmed by the X-ray diffraction (XRD).

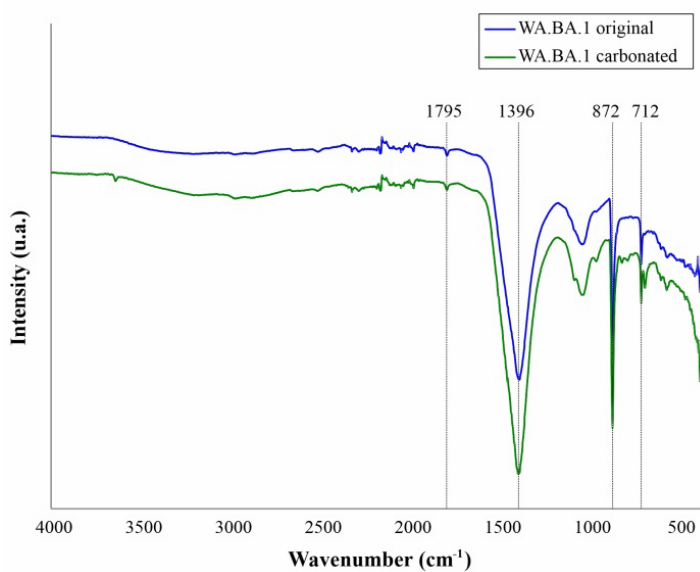


Figure 3: FTIR spectra of original and carbonated WA.BA.1

Source: own.

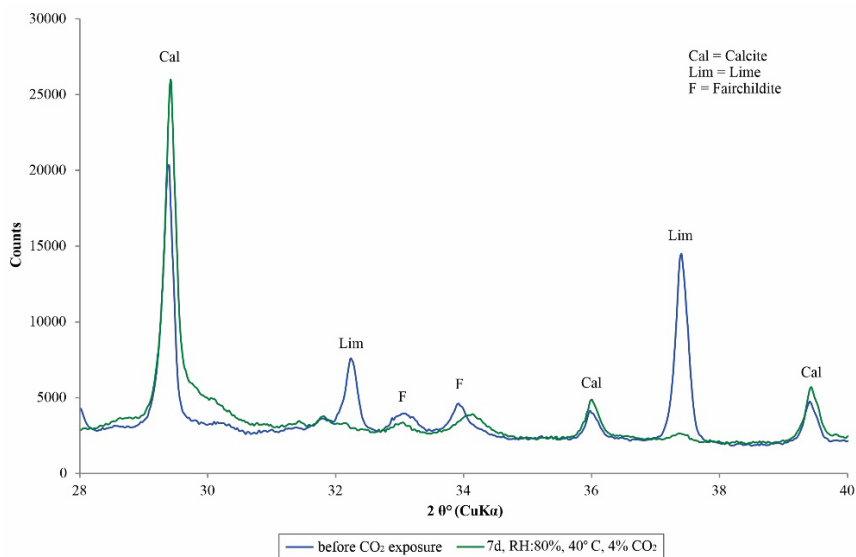


Figure 4: X-ray diffractograms of wood biomass ash (WA.BA.1) before and after 7 days of carbonation.

Source: own.

The XRD analysis enabled us to determine the composition of the crystalline minerals. For example, the main phases detected in sample WA.BA.1 (Figure 4) were calcite (CaCO₃), fairchildite (K₂Ca(CO₃)₂) and lime (CaO). After CO₂ treatment, a clear change in the intensity of the calcite peak can be observed, while the lime peak almost disappeared, indicating that CaO is the main reactant in the mineralization process. In the case of fairchildite, only a slight change in the intensity of the peak can be observed.

4 Conclusions

In this study, seven different waste ashes from Slovenia were subjected to accelerated carbonation to determine their sequestration potential. Depending on their chemical and mineralogical composition, the ashes showed different sequestration capacities. The highest CO₂ sequestration capacity, i.e. 298 g_{CO₂}/kg_{ash}, was measured for ash from wood biomass (WA.BA.1). A high sequestration potential was also found for ash from the co-incineration of wood waste and paper sludge (CC.MA.2), while other waste ashes showed a lower potential. As most waste ashes are still landfilled, the use of these ashes for CO₂ sequestration for carbonated building products would be very beneficial in terms of a circular economy.

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Funding & Data availability

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The data presented in this study are openly available from the repository DiRRROS at link: <http://hdl.handle.net/20.500.12556/DiRRROS-20544>.

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