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Regional waste materials as candidates for mineral carbonation-based CO_2 sequestration

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Abstract

This paper explores the application potential of regional waste materials for carbon dioxide (CO_2) sequestration through mineral carbonation. Seven waste materials of local origin were characterized using X-ray fluorescence (XRF) to assess their chemical suitability for carbonation. The results indicate that materials such as biomass ashes and concrete powder, due to their high CaO content, show promising potential for CO_2 uptake. Two complementary carbonation methods, dry carbonation in a climate chamber and wet carbonation via concurrent milling, are described as relevant reference approaches for future experimental validation.

Key words: mineral carbonation, CO_2 sequestration, waste materials, dry carbonation, wet carbonation

Regionalni otpadni materijali kao kandidati za vezanje CO_2 putem karbonatizacije

Sažetak

U ovom radu istražuje se mogućnost primjene regionalnih otpadnih materijala za vezanje ugljikova dioksida (CO_2) uz pomoć ubrzane karbonatizacije. Sedam otpadnih materijala lokalnog podrijetla analizirano je metodom rendgenske fluorescencije (XRF) kako bi se procijenila njihova kemijska pogodnost za ovaj proces. Rezultati pokazuju da materijali poput biopepela i betonskog praha, zbog visokog udjela kalcijeva oksida (CaO), imaju izražen potencijal za vezanje CO_2. Opisane su dvije metode karbonatizacije, suha karbonatizacija u klimatskoj komori i mokra karbonatizacija uz istodobno mljevenje, kao primjeri prikladnih pristupa za buduća laboratorijska ispitivanja.

Ključne riječi: karbonatizacija, vezanje CO_2, otpadni materijali, suha karbonatizacija, mokra karbonatizacija

1 Introduction

The urgent need to reduce carbon dioxide (CO_2) levels in the atmosphere, one of the main causes of global climate change, has led to extensive research into sustainable mitigation strategies, particularly in sectors with high emissions intensity, such as the construction industry. This sector remains a significant contributor to the climate crisis, accounting for around 32% of global energy consumption and 34% of CO_2 emissions [1]. The reliance on carbon-intensive materials such as cement and steel, which together account for around 18% of global emissions, further intensifies the environmental impact [1]. One of the biggest contributors is cement production, which is essential for concrete production and emits an estimated 600 kg of CO_2 per ton of cement produced [2]. In addition, the construction industry is a major generator of waste, producing over 10 billion tons of construction and demolition waste annually [3].

Various solutions and strategies are currently being developed to combat climate change and reduce CO_2 emissions. One important approach is the use of supplementary cementitious materials (SCMs), as evidenced by the steadily decreasing clinker factor worldwide. According to the Global Cement and Concrete Association [4], the ratio of clinker to cement was around 0.85 in 1990 and is estimated to be around 0.76 in 2022. Among the most recognized and effective long-term strategies for achieving climate neutrality are Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). These approaches aim to either permanently store captured CO_2 in geological formations or integrate it into useful products, thereby reducing the net amount of CO_2 released into the atmosphere [5, 6].

While many CCS and CCU methods require advanced technologies and significant energy input, mineral carbonation is a simpler process that converts CO_2 into stable carbonate minerals. In this process, CO_2 reacts with calcium- or magnesium-rich materials to form compounds such as calcite ($CaCO_3$), magnesite ($MgCO_3$) or dolomite ($CaMg(CO_3)_2$) [7]. Under atmospheric conditions, where the CO_2 concentration is only about 0.04%, the carbonation of reactive solids is extremely slow, so that natural mineral sequestration is largely ineffective [7, 8, 9]. Increased CO_2 quantities or pressures are often used to improve the reaction kinetics. One of the most reactive components of SCMs is calcium oxide (CaO), a highly alkaline compound (equation 1). However, the direct reaction between gaseous CO_2 and CaO is kinetically inhibited and proceeds only slowly [10]. The presence of moisture accelerates this process considerably. Under such conditions, CO_2 dissolves in water, forms carbonic acid and then reacts with calcium hydroxide ($Ca(OH)_2$), which is formed by the hydration of CaO (equation 2) [7]. This sequence leads to the precipitation of calcium carbonate ($CaCO_3$), a com-

pound with very low solubility in water (equation 3) [10]. This carbonation pathway changes both the chemical composition and the physical structure of the material.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \quad (1)$$

$$CaO(s) + H_2O(g) \rightarrow Ca(OH)_2(s) \quad (2)$$

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \quad (3)$$

In this paper, chemical composition of seven different regional waste streams is determined using X-ray fluorescence (XRF). In addition, two different methods for mineral carbonation, dry carbonation and wet carbonation, are described. Based on the chemical compositions obtained, the potential of these materials for CO_2 sequestration is discussed.

2 Materials

Seven waste materials were selected for this study based on their local availability and industrial origin, with the assumption that their composition, resulting from high temperature or chemically intensive processes, could be suitable for CO_2 mineral sequestration.

Biomass ashes (Figure 1. a, b, c) were obtained from bioenergy facilities in Strizivojna, Spačva, and Ljubešćica (Croatia). These ashes are byproducts of bioenergy production processes, rich in calcium, and thus highly reactive with CO_2.

Concrete powder (Figure 1. d) was provided by a company from Pula (Croatia), specializing in concrete products. This powder originates from waste generated during the manufacturing process, making it a material potentially suitable for CO_2 sequestration.

Red mud (Figure 1. e), a byproduct of alumina production, was sourced from Dobro Selo (Bosnia and Herzegovina). This highly alkaline material presents significant potential for CO_2 sequestration due to its chemical composition.

Raw olive pomace (Figure 1. f) was sourced from an oil mill in Vodnjan (Croatia). This material was first dried and subsequently calcined in an electric furnace at 800 °C, with a temperature increase of 10 °C per minute, resulting in olive pomace ash (Figure 1. h). Similarly, raw paper sludge (Figure 1. g), obtained from a packaging and paper manufacturing company in Belišće (Croatia), was dried and calcined under the same conditions to produce paper sludge ash (Figure 1. i).

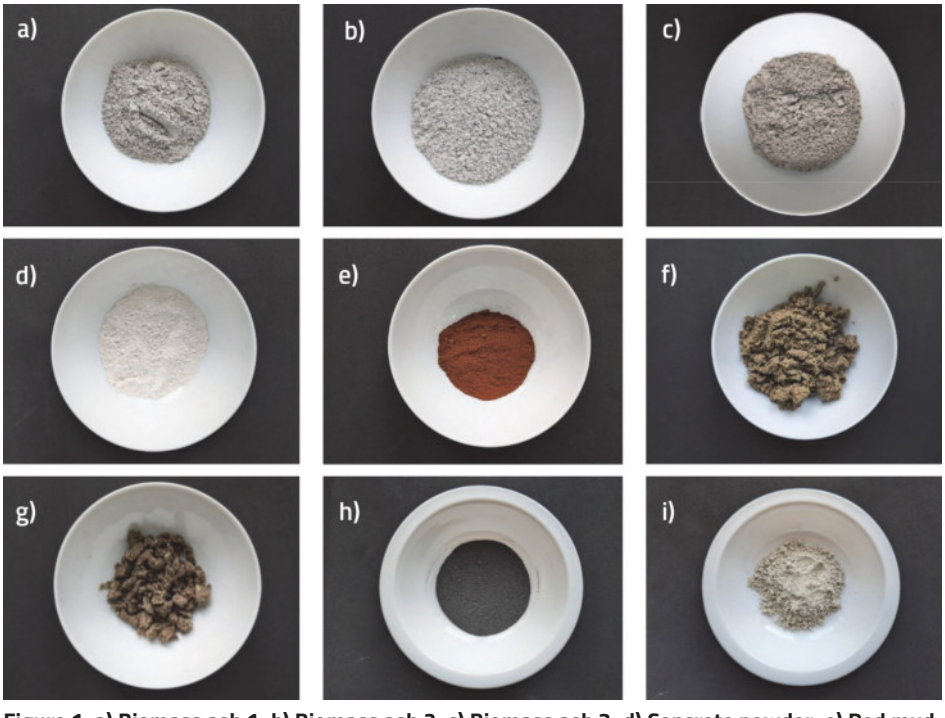

Figure 1. a) Biomass ash 1; b) Biomass ash 2; c) Biomass ash 3; d) Concrete powder; e) Red mud; f) Raw olive pomace; g) Raw paper sludge; h) Olive pomace ash; i) Paper sludge ash

2.1 X-ray fluorescence

Following initial sample preparation, the chemical composition of all seven materials was determined using XRF. The results, expressed as weight percentages of major oxides, are shown in Table 1. These values provide insight into the potential reactivity of each material towards CO_2, particularly in terms of calcium and magnesium content, which are key for mineral carbonation.

Based solely on XRF results, it can be estimated that concrete powder (CP) and biomass ashes, particularly BA2, exhibit the highest potential for CO_2 sequestration via mineral carbonation. This is primarily due to their elevated CaO content - above 68% for all biomass ashes and over 85% for CP, which indicates a strong presence of reactive calcium phases. In contrast, red mud (RM), while rich in Fe_2O_3 and Al_2O_3, contains relatively low levels of CaO (approx. 10%), suggesting limited reactivity with CO_2 through conventional carbonation pathways.

Table 1. Chemical composition of materials determined by XRF analysis

Material	Sample ID	Chemical composition [%]										
		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	P_2O_5	Na_2O	K_2O	TiO_2	MnO	SO_3
Biomass ash 1	BA1	68.62	10.46	3.08	1.95	4.02	4.33	0.420	4.87	0.260	0.463	1.06
Biomass ash 2	BA2	79.72	7.74	1.63	0.97	2.67	1.60	0.00	3.31	0.138	0.307	1.57
Biomass ash 3	BA3	67.95	11.15	2.81	1.62	3.14	2.31	0.78	6.42	0.198	0.97	1.42
Concrete powder	CP	85.70	7.56	1.67	1.10	1.95	0.07	0.10	0.29	0.12	0.01	1.56
Red mud	RM	9.96	21.95	16.94	37.88	0.61	0.47	7.23	0.18	4.13	0.43	0.24
Olive pomace ash	OPA	10.35	0.10	0.48	1.41	3.87	6.66	5.32	69.55	0.05	0.01	2.34
Paper sludge ash	PSA	48.50	24.40	14.40	2.19	3.47	0.50	0.10	0.58	1.21	0.01	4.80

Olive pomace ash (OPA) and paper sludge ash (PSA) display more complex compositions. OPA is characterized by a high potassium content (K_2O > 69%), indicating potential for alternative reaction mechanisms, while PSA contains a moderately high CaO content (48.5%) and significant amounts of SiO_2 and Al_2O_3, which may influence both its carbonation behavior and reactivity.

It is important to note that while XRF provides insight into the total elemental composition, it does not distinguish between chemically bound and reactive (free) phases. For example, the high CaO content observed in the concrete powder (CP) may largely originate from limestone aggregates, where calcium is present in a stable mineral form ($CaCO_3$) and not readily available for carbonation. Therefore, to better assess the actual carbonation potential, complementary analysis such as X-ray diffraction (XRD) is needed to quantify the amount of free CaO and other reactive phases. This distinction is crucial, as only the unbound CaO and $Ca(OH)_2$ fractions can effectively participate in the mineral carbonation process.

3 Methods for mineral carbonation

In order to assess the CO_2 sequestration potential of SCMs, various mineral carbonation techniques have been developed. Among them, two approaches stand out due to their simplicity, scalability, and relevance for construction materials: dry (gas–solid) carbonation and wet (liquid–solid) carbonation coupled with mechanical activation.

This section presents two representative methodologies from the literature that can be used to evaluate the carbonation behavior of solid waste streams. Although these methods were not applied to the materials in this study, they are presented as useful examples for designing future experiments to evaluate and compare the CO_2 reactivity of waste-based SCMs.

3.1 Dry carbonation

Dry carbonation, also known as gas-solid carbonation, solid materials are exposed to elevated concentrations of CO_2 in a controlled environment. The method developed by Tominc and Ducman [11] provides a robust framework for assessing the sequestration capacity of combustion ashes under mild, accelerated conditions.

In this method, the ashes are first dried, homogenised and sieved (usually below 125 μm). The samples are then placed in trays inside a sealed carbonation chamber where they are exposed to a continuous stream of CO_2 flow with a concentration of 4 ± 0.1 vol% at a constant temperature (20 ± 1 °C) and varying relative humidity (typically 50–55% or 80–85%). The exposure lasts up to 28 days, with intermediate sampling at predefined intervals (e.g. 1, 7, 14, 21 and 28 days).

The extent of carbonation is quantified by thermogravimetric analysis (TGA), measuring the mass loss due to carbonate decomposition in the 550–950 °C range. The theoretical maximum CO_2 uptake is calculated using the Steinour equation [12], which estimates the stoichiometric CO_2 binding potential based on the oxide composition (in particular CaO, MgO, K_2O, Na_2O). The carbonation efficiency (CE) is then derived by comparing the experimental uptake with the theoretical maximum.

This method is particularly suitable for the evaluation of materials under realistic and low-energy conditions and has already been successfully applied to a variety of biomass and industrial ashes.

3.2 Wet carbonation

Wet carbonation, also known as liquid–solid carbonation, can be significantly accelerated by mechanical activation, i.e. simultaneous wet milling of the material under CO_2 pressure. The method, developed by De Schutter et al [13], shows how planetary ball milling can intensify the carbonation process, especially for hard-to-react residues such as steel slags.

In this technique, small amounts of the dry sample (1 g) are mixed with ultrapure water (typically 20 mL) and placed in a high-strength grinding jar with a gassing lid. The jar is filled with zirconia grinding media and placed in a planetary ball mill, which subjects the sample to rapid rotations. The jar is pressurized to 5 bar with

CO_2 and periodically re-pressurized during the experiment to ensure a consistent environment. The duration of the grinding ranges from seconds to several minutes, depending on the desired extent of the reaction.
Carbonation is driven by several simultaneous effects: reduction of particle size, break-up of crystalline structures, increase in surface area and improved CO_2 dissolution in the aqueous phase. The method enables rapid carbonation, in some cases achieving more than 50% of the theoretical CO_2 uptake in less than 10 minutes.
The extent of carbonation is determined by TGA and quantitative XRD. The method is particularly important for screening carbonation kinetics and can serve as a precursor for larger scale testing or product development.

4 Conclusion

This study underlines the potential of waste materials from the region for CO_2 sequestration through mineral carbonation. XRF analyses revealed that several materials, in particular biomass ashes and concrete powder, have a high CaO content and are therefore suitable candidates for carbonation processes. Two representative methods, dry and wet carbonation, were presented as useful reference frameworks for future testing. Although the experimental application of these methods to the selected materials is still pending, the chemical data and methodological overview provide a solid basis for further research focusing on the integration of carbon capture with the circular use of waste in construction materials.

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