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Low-emission wollastonite clinker and its effect on the properties of cementitious binders

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Abstract

The aim of the investigation was to synthesise clinker based on wollastonite and carbonate it afterwards to be used as a potential new supplementary cementitious material. The clinker was burned in a semi-industrial rotary kiln at 1240°C using secondary raw materials. The synthesised clinker was composed mainly of rankinite and pseudowollastonite, which are carbonatable. The burned clinker was treated by direct carbonation in a wet process. The carbonation products included calcium carbonate in various polymorphic forms, as well as an amorphous phase, mainly amorphous silica. The latter can react as a pozzolan in blends with Portland cements. The use of the carbonated clinker as supplementary cementitious material can lead to lower CO_2 emissions compared to plain Portland cement, due to the lower consumption of carbonate-containing raw material, the lower synthesis temperature and the possibility of CO_2 sequestration.

Keywords

Wollastonite-based clinker, CO_2 sequestration, mineral carbonation, carbon capture and utilization, supplementary cementitious material

1. Introduction

The cement industry is responsible for approximately 7% of anthropogenic carbon dioxide emissions. High-emission Portland clinker is a component of the vast majority of binders (1-3). Consequently, there is an urgent need to use alternative binding materials, such as alkali-activated binders, sulfoaluminate cements, carbonatable calcium silicate cements and magnesia binders (4). Additionally, it is essential to identify new non-clinker components and alternative supplementary cementitious materials (SCMs) for cement production due to the limited availability of currently utilized materials, such as granulated blast furnace slag and siliceous fly ash (5,6). Currently, one approach to minimize the carbon footprint of cement is through carbon sequestration technologies. These include carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies (7-12). A notable method for managing CO_2 emissions in the construction industry is mineral carbonation, which involves the conversion of carbon dioxide into poorly water-soluble, thermodynamically stable calcium and magnesium carbonates (12-15). Mineral carbonation can be categorized into direct and indirect carbonation processes, as illustrated in Fig. 1. Direct carbonation can occur via two primary mechanisms: direct gas-solid reactions or through aqueous solutions. The latter method has been extensively studied due to its superior reaction efficiencies compared to dry carbonation (15). This process can be executed through various pathways and under a wide range of conditions, including water-to-solid (w/s) ratio, CO_2 concentration, temperature, pressure, and the addition of catalysts or reactants (11,13,16,17).

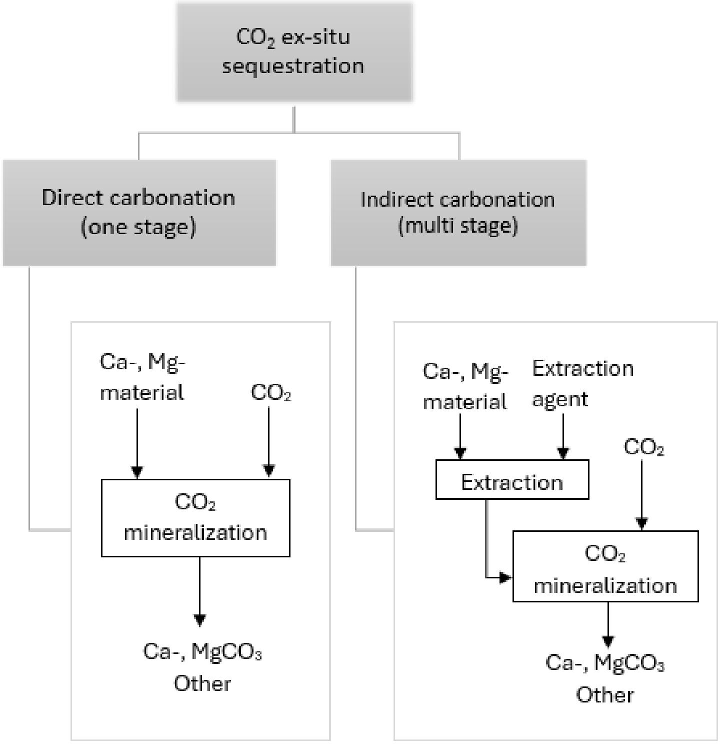


Fig.1. Types of mineral carbonation, based on (14)

Wollastonite ($CaSiO_3$, CS) is a naturally occurring calcium silicate that is also found in waste slags produced during ferrosilicon manufacturing. It is utilized in various industries, including ceramics, metallurgy, and the production of plastics and paints (18,19). Wollastonite, along with γ-dicalcium silicate (γ-Ca_2SiO_3, γ-C_2S) and rankinite ($Ca_3Si_2O_7$, C_3S_2), belongs to a group of non-binding silicates in alkaline environments. However, it exhibits binding properties in acidic conditions or after carbonation (17,20-22). Current global reserves of wollastonite are insufficient to support its widespread use in the cement industry (18), making synthesis the one viable option. Research has demonstrated the potential for utilizing materials containing CS and C_3S_2 in cement systems (17,20,23-25). This material has been referred to as wollastonite-based clinker or CS-clinker. Compared to conventional Portland clinker (OPC), the amount of carbonate raw material required for the production of CS clinker is significantly lower. Additionally, the synthesis temperature for CS clinker is approximately 1250°C, which is about 200°C lower than for OPC. Furthermore, CS clinker has the ability to take up carbon dioxide (23-27). The reactions of the calcium silicates present in CS clinker with carbon dioxide are shown using wollastonite and rankinite as examples (Eq. 1,2).The application of CS clinker represents a promising strategy for reducing the carbon footprint of produced cements.

$$CaSiO_{3(s)} + CO_{2(g)} \xrightarrow{H_2O} CaCO_{3(s)} + SiO_{2(s)} \qquad (1)$$

$$Ca_3Si_2O_{7(s)} + 3C0_{2(g)} \xrightarrow{H_2O} 3CaCO_{2(s)} + 2SiO_{2(s)} \qquad (2)$$

This article focuses on the synthesis and characterization of a low-emission clinker with a low Ca/Si ratio, from secondary raw materials, which has the ability to sequester CO_2. The synthesis method for the produced clinker is described, along with its properties before and after the carbonation process. Additionally, the carbon footprint of the investigated clinker is calculated in comparison to that of conventional Portland clinker.

2. Experimental part

2.1. Raw materials

In order to reduce the carbon footprint of the wollastonite clinker produced, 3 waste raw materials, named 1,2,3 and one natural raw material, 4, were used. Raw material 1 contains CaO in non-carbonate form. The chemical compositions of the raw materials used are shown in Tab. 1.

Table 1. Chemical composition of raw materials

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Other	LOI*
	wt%									
1	4,18	2,23	0,60	61,41	0,60	0,72	0,00	0,02	3,03	27,20

2	6,94	1,46	55,84	5,39	1,64	0,60	0,25	0,12	4,57	23,19
3	89,06	2,15	2,42	0,25	0,75	0,00	0,09	0,44	3,62	1,22
4	60,22	27,10	0,81	0,14	0,30	0,01	0,04	1,40	0,74	9,24

*LOI = loss on ignition

Each raw material was dry ground in a ball mill to a grain size of less than 90 µm before further use. After grinding, batches of raw meal were prepared at a SiO_2:CaO molar ratio of 1:1, at raw materials: 1:2:3:4 weight ratio of 100:1:58:7. These batches were homogenized in a powder mixer over a period of 1 hour and granulated.

The synthesis of wollastonite clinker was carried out in a semi-technical scale rotary kiln of Φ 0.38 m x 7 m fired with diesel fuel, located at Łukasiewicz - Institute of Ceramics and Building Materials in Krakow (Fig.2). The fusion temperature varied between 1240-1250°C at a furnace speed of 1.5 rpm. Approximately 200 kg of finished product was obtained. After cooling, the clinker was ground in a ball mill to a specific surface area of 4750 cm^2/g.

Fig.2. Semi-technical scale rotary kiln (dimensions: Φ 0.38 m x 7 m; temperature range 800 - 1450°C; capacity 50 kg/h; kiln speed: 0.5-4.0 rpm, fuel: diesel).

2.2. Carbonation process

The burnt and milled CS clinker was carbonated directly in aqueous solution in a laboratory scale reactor, shown schematically in Fig. 3. 100% CO_2 was fed into the reactor with an aqueous suspension of clinker with a solid/liquid ratio of 0.21by mass at a pressure of 2 bar. The reactor was open to laboratory conditions during the carbonation process. During the experiment, the suspension was stirred at a constant speed of 350 rpm, so that the gas bubbles were homogeneously distributed in the clinker suspension. The process was controlled by measuring the change in system mass, temperature and pH. When the system mass and pH showed a constant level, the process was considered complete. The pH changes occurring during carbonation are shown in Fig. 4. Once the process was complete, the system was left to complete sedimentation. The process water was decanted from the sediment, which was then put in an oven at 105°C until a constant mass was obtained. The dry material was used directly for testing and was not subjected to further grinding.

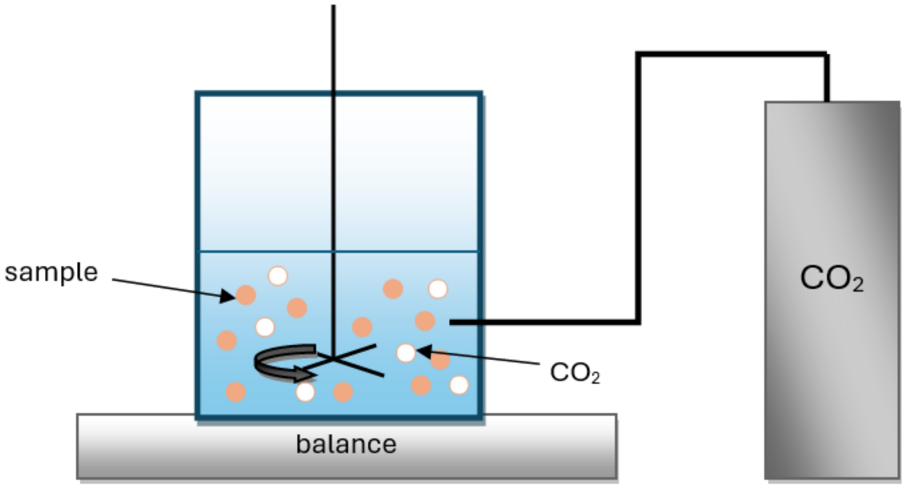


Fig.3. Schematic diagram of the carbonatation station

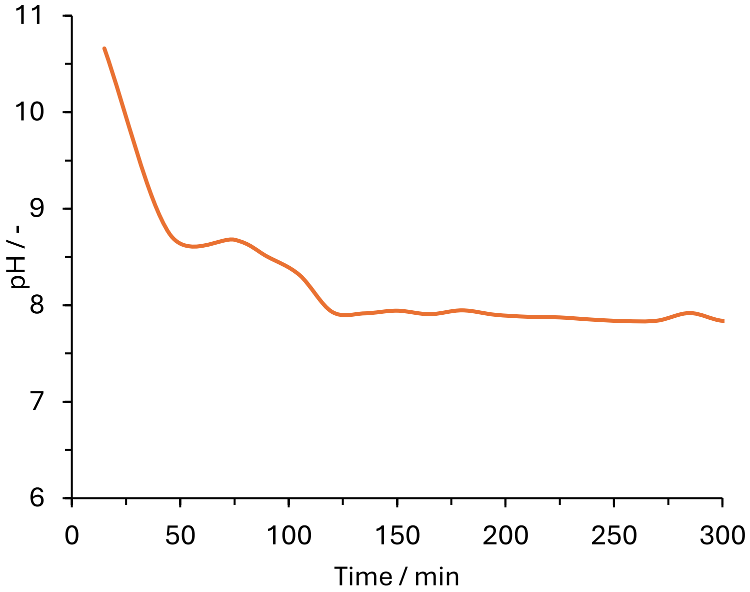


Fig. 4 Change in pH with time of carbonation;
from approx. 120 min from the start of the process pH remains constant

2.3. Materials

The synthesized CS clinker before and after carbonation was used in the study. Industrial Portland cement CEM I 52.5 R (PC) according to the PN EN 197-1:2011 (28) and siliceous fly ash (FA) were used for the binders. The chemical composition of the materials used is shown in Tab. 2.

Tab.2. Chemical composition of Portland cement (PC) and fly ash (FA)

Material	SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	MnO	TiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O	SO_3	LOI*	Total	TC*
	wt%														
PC	19,72	4,22	3,69	0,01	0,06	0,24	0,25	61,42	0,57	0,42	0,20	2,84	3,06	98,85	0,40
FA	52,96	26,17	6,13	0,02	0,08	1,08	0,43	2,9	2,53	3,29	0,87	0,09	3,06	99,60	2,77

* LOI = loss on ignition, TC = total carbon

Binders with the compositions given in Tab.3. were prepared and used for compressive strength tests.

Tab. 3. Composition of binders used for compressive strength tests (w/c = water/cement ratio, w/b = water/binder ratio)

Mixture	CEM I [g]	CS [g]	CSc [g]	FA [g]	w/c	w/b
PC	100	-	-	-	0,50	0,50
PC-CS	70	30	-	-	0,71	0,50
PC-CSc	70	-	30	-	0,71	0,50
PC-FA	70	-	-	30	0,71	0,50

2.4. Methods

The loss on ignition (LOI) and chemical composition tests by X-ray fluorescence spectrometry (XRF) were carried out according to EN 196-2 (29). Total carbon content was tested according to ISO 10694 (30). Density and Blaine specific surface area were determined according to EN 196-6 (31).

Particle size distribution was analyzed using a Malvern Mastersizer X laser particle size analyzer. Samples were dispersed in isopropanol using ultrasound.

The phase composition of the clinker samples was determined by X-ray diffraction analyses (XRD). The XRD pattern was recorded using a PANalytical X'PERT PRO diffractometer with

CoKα radiation, a divergence slit 0,5°, the X-Celerator detector and a rotating sample stage. The X-ray tube was operated at 45 kV and 40 mA. Samples were ground for 20 min in an isopropanol suspension in a McCrone mill. The powdered sample was scanned between 5° and 90° for 45 min. The step size was 0.0167°. The quantification was done by Rietveld refinement, using X'Pert HighScore software v.4.9. The amorphous phase was calculated using the G-factor method with CaF_2 as the external standard (32).

FTIR data was collected using a Bruker Tensor 27 device. The spectra were collected by averaging 32 scans from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

TG/DTA thermal analysis was performed on 50 mg samples heated under nitrogen conditions from 30°C to 980°C with a temperature increment of 20 K/min on a Mettler-Toledo TGA 2 apparatus.

The compressive strength of the mortars was measured according to EN 196-1 (33) after 2, 7 and 28 days.

3. Results

The results of the chemical composition tests of the obtained wollastonite clinkers: before carbonation (CS) and after carbonation (CSc) are presented in Tab.4.

Tab. 4. Chemical composition of CS-clinkers

Material	SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	MnO	TiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O	SO_3	LOI*	Total	TC*
	wt%														
CS	44,44	3,75	2,95	0,404	0,08	0,12	0,06	46,86	0,77	0,27	<0,06	0,05	0,11	98,85	<0,06
CSc	34,06	2,88	2,25	0,283	0,06	0,10	0,05	36,27	0,60	0,20	0,07	0,05	23,06	99,91	5,28

* LOI = loss on ignition, TC = total carbon

Non-carbonated wollastonite-based clinker has a Blaine surface area of 4750 cm^2/g and a density of 2.96 g/cm^3. The specific surface area of the clinker after carbonation is similar (4650 cm^2/g) to that of the CS clinker, while the density is lower (2.55 g/cm^3). The mean particle size D50 for carbonated clinker shows a higher value (22 µm compared to 13 µm for CS) (Tab.5.). The maximum of the particle size distribution curve in the clinker after carbonation is shifted towards larger particle diameters (Fig. 5).

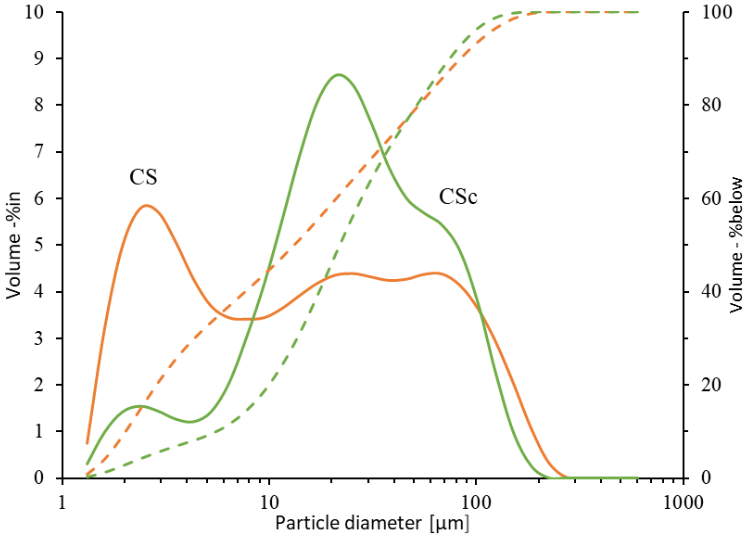


Fig. 5. Particle size distribution of CS and CSc clinkers

Tab.5. Particle size distribution of CS and CSc clinkers; µm

	CS clinker	CSc clinker
D10	2,0	5,5
D50	13,2	21,9
D90	83,7	74,4

The phase composition of the investigated clinkers is shown in Tab. 6. The non-carbonated wollastonite clinker consists mainly of rankinite and pseudowollastonite - the main phases that can be carbonated. In addition to these phases, belite, γ-dicalcium silicate and wollastonite present in this sample have the potential to react with carbon dioxide. Melilite is another main crystalline phase present in the CS clinker, which cannot be carbonated under the conditions used in the reactor (17). In addition, quartz and cristobalite are present in the clinker before the carbonation process, as well as some amorphous phase. In contrast, the main phases after carbonation are calcium carbonate (mainly calcite, but also vaterite) and an amorphous phase, rich in amorphous silica, which is consistent with other studies (17,20,24-27). In addition, the carbonated clinker consists of melilite, quartz, cristobalite and gypsum. Some amounts of rankinite and pseudowollastonite are also present, which means that the carbonation process has not been fully completed.

Tab. 6. Phases composition of CS clinkers

Phase	Mineralogical composition Mass%	
	CS clinker	carbonated CS clinker
Quartz	6,1	4,4
Melilite	17,5	11,4
Pseudowollastonite	23,2	2,6
Wollastonite	0,9	-
Rankinite	38,6	2,1
$\beta - C_2S$	7,4	-
$\gamma - C_2S$	1,4	0,5
Cristobalite	1,4	1,2
Gypsum	-	0,7
Vaterite	-	0,8
Calcite	-	40,1
Amorphous	3,6	33,2

On the basis of the FT-IR data, changes in the structure and intermolecular interactions of the clinkers: wollastonite-based clinker (CS) and carbonated wollastonite-based clinker (CSc) were observed (Fig.6.). The main banks for the CS clinker occur in areas: 987, 941, 849 cm^{-1}, which is related to the presence of asymmetric tensile vibrations of Si-O bonds in this material, and which show high absorption between 800 and 1200 cm^{-1} (26,27). The bands at about 420 and 535 cm^{-1} are associated with bending vibrations of the O-Si-O bonds, while those at 655 and 710 cm^{-1} are due to the presence of combined silicon tetrahedra/ring silicates, i.e. pseudowollastonite (34,35). In the case of CSc clinker, the main absorption band occurs at higher wavenumbers - 1073 cm^{-1}, which is related to the decomposition of silicates and the formation of silica gel (26), consistent with the high content of the amorphous phase (Tab.6). The band located at 1405 cm^{-1} is due to asymmetric stretching vibrations of the C-O bonds present in $CaCO_3$, and the band at 871 cm^{-1} is due to out-of-plane bending vibrations of the same C-O bonds (27,36). The band at 710 cm^{-1} also originates from the bonds present in $CaCO_3$ (36).

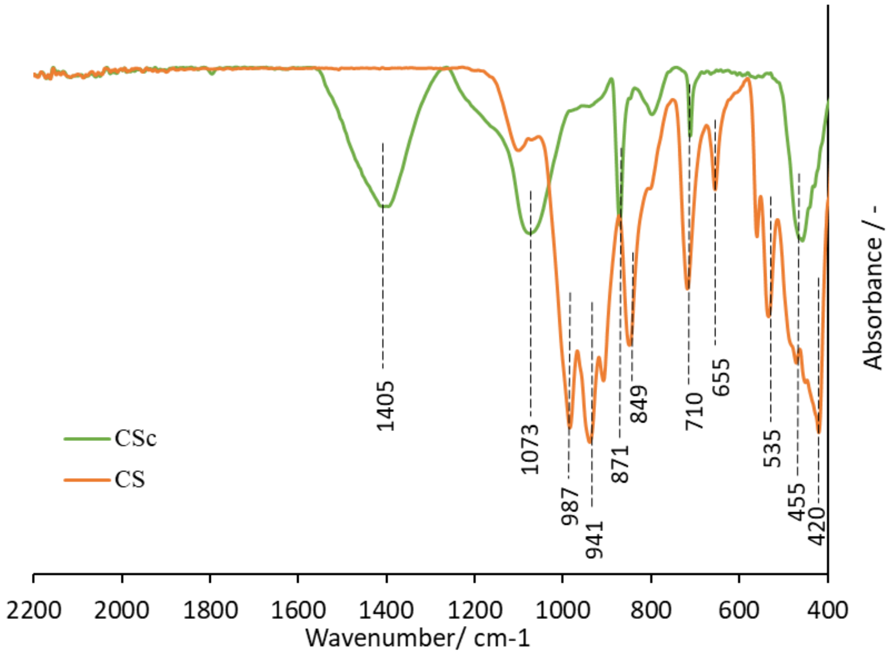
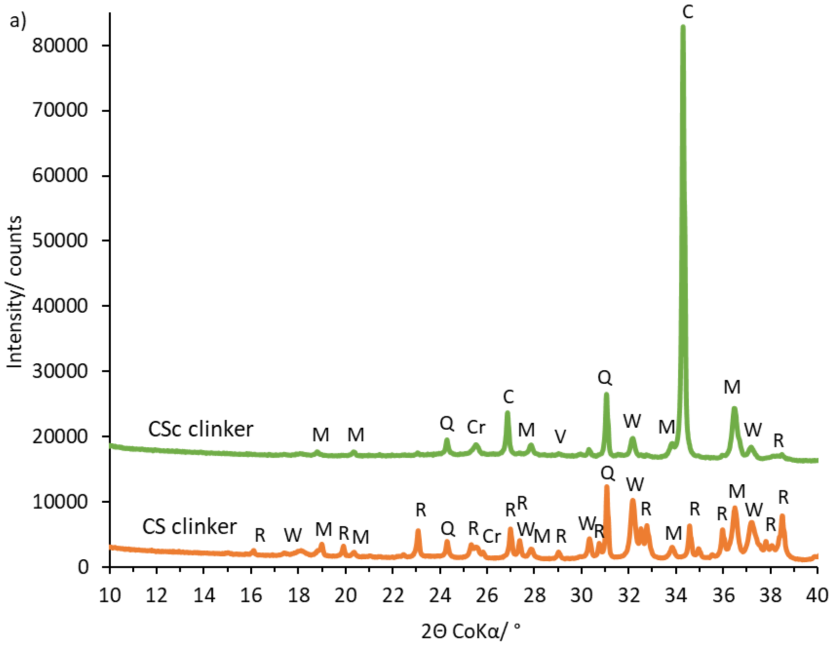


Fig. 6. FTIR data of the clinkers before and after carbonation

The differences in phase composition (XRD) and thermal analysis (TGA) of the clinkers before and after carbonation are shown in Fig.7. XRD confirms the presence of the phases described in Tab.6. On the basis of the TGA and total carbon content (Tab.4), the amount of carbon dioxide absorbed was calculated. The calculated values from both methods were very close and compatible with each other. 1 t of wollastonite clinker stored 191 kg of carbon dioxide in the carbonated clinker.



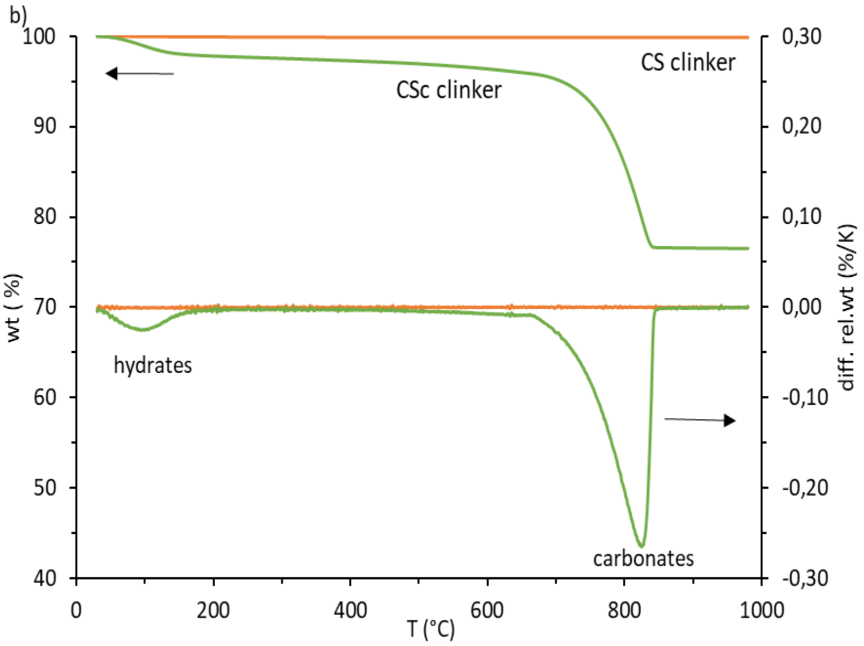


Fig. 7 XRD phase composition (a) and TGA thermal analysis (b) of CS and CSc clinkers (W-wollastonite, R-rankinite, Q-quartz, C-calcite, V- vaterite, Cr- cristobalite, M-melilite)

Tab.7 shows approximate calculations of the CO_2 emissions of the tested wollastonite clinkers before (CS) and after (CSc) the carbonation process, compared to Portland clinker. The CaO content of Portland clinker is approximately 65-70% by weight, resulting in approximately 550 kg of CO_2 being emitted for each ton of clinker produced (37,38). Wollastonite clinker (CS) contains approx. 47% CaO by weight (Tab.4), thus emitting approx. 370 kg CO_2/t clinker. This represents a reduction in CO_2 emissions of about 33% at the raw material decarbonation stage. It should be noted that one of the secondary raw materials used in the production of wollastonite clinker (CS) contains CaO in a form other than $CaCO_3$. The addition of 1% CaO by weight in non-carbonated form to the raw material mix is assumed to reduce its emissions by approximately 8 kg CO_2/t clinker (38). This means that the use of raw material 1 resulted in an additional reduction in CO_2 emissions of approximately 295 kg/t clinker to 75 kg/t clinker. In addition, carbon dioxide sequestration by CS clinker occurred during the carbonation process. However, the drying stage of the material after the carbonation process must be taken into account, which makes the emissions of carbonated CS clinker similar to non-carbonated CS clinker, but still lower than CS clinker from natural raw materials or Portland clinker. The production of calcined clay, currently one of the most forward-looking SCM, emits, depending on the production method, approximately 250-300 kg CO_2/t material (39). This is higher than wollastonite-based clinker, both before and after the carbonation process.

Tab.7. Approximate CO_2 emissions of CS and CSc clinkers compared to Portland clinker

Material	Process emission [kg/t clinker]	Reduction of CO_2 emissions due to use of non-carbonate CaO [kg/t clinker]	CO_2 sequestration in carbonation [kg/t clinker]	CO_2 emissions from drying** [kg/t clinker]	CO_2 emissions from fuel combustion [kg/t clinker]	Final emission [kg/t clinker]
Portland clinker*	550	-	-	-	350	900
CS clinker from natural raw materials	370	-	-	-	200	570
CS clinker from secondary raw materials	370	295	-	-	200	275
CSc clinker from secondary raw materials	370	295	191	123	200	282

* assumed that Portland clinker is obtained from natural raw materials
**based on (40) and the data from Łukasiewicz – Institute of Ceramics and Building Materials

In the next stage of the study, the wollastonite clinkers were used as SCMs to partial replace Portland cement. A replacement by siliceous fly ash was tested for comparison. The results are shown in Fig.8. The addition of wollastonite-based clinker both after (CSc) and before (CS) the carbonation process reduces the compressive strength at each time comparted to plain Portland cement. Already after 7 days, a slight increase in the strength of the PC-CSc sample compared to the PC-CS can be observed. After 28 days, the PC-CSc sample shows higher strengths than the PC-CS sample, similar to the strengths obtained for the PC-FA sample.

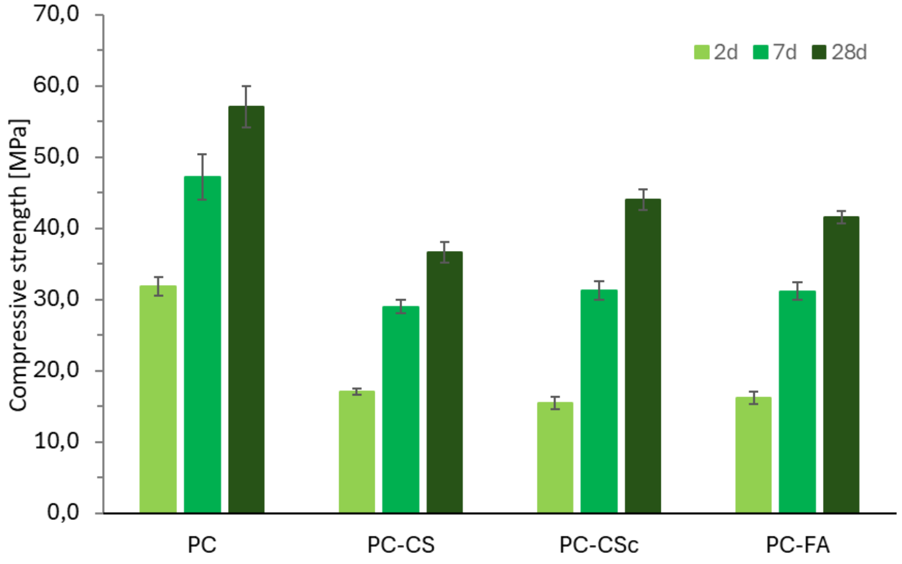


Fig.8. Compressive strength after 2, 7 and 28d.

4. Summary

1) Wollastonite-based clinker, whose main phases were pseudowollastonite ($CaSiO_3$, CS) and rankinite ($Ca_3Si_2O_7$, C_3S_2), was designed and burned in a rotary kiln at a semi-technical scale at 1240-1250°C. The material was obtained from secondary raw materials.
2) The resulting wollastonite-based clinker was treated by direct carbonation in aqueous suspension. The product of this process was an amorphous phase, which consisted mainly of amorphous SiO_2. In addition, calcium carbonate was obtained, both in the form of calcite and vaterite.
3) Both wollastonite-based clinker before and after the carbonation process shows a reduction in CO_2 emissions compared to Portland clinker. 1 t of wollastonite clinker stored 191 kg of carbon dioxide in the carbonated clinker. The carbon footprint of carbonated and non-carbonated CS clinker is lower than calcined clay, which indicates its high potential as an SCM.
4) The presence of amorphous SiO_2 suggests pozzolanic properties of carbonated wollastonite-based clinker, so further studies focusing on verifying its reactivity are needed. The addition of 30 wt% carbonated wollastonite-based clinker as cement replacement shows a similar performance of compressive strength than a cement with 30 wt% siliceous fly ash addition. The non-carbonated clinker shows less contribution to strength than the carbonated one due to the lack of amorphous silica.
5) Carbonated wollastonite clinker is a potential, novel SCM. The production of the clinker in the 100 kg scale and its carbonation could be successfully demonstrated. In blends with Portland cement it provides a strength contribution at least in the same order as fly ash.

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