Preparation, manufacture and properties of new β-belite cement

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Abstract. The objective of this work is the optimization of the synthesis of β-belite cement. Belite cement (dicalcium silicate) is a promising material due to a lower CO₂ emission and lower energy consumption during its production. Cement with a high content of β-belite was prepared from ground limestone, amorphous silica and alkaline silicate solution. The raw materials were mixed, the mixtures were compacted and then burnt in an electric furnace. Different CaO/SiO₂ ratios, firing temperatures, raw materials and firing time were tested. The samples were characterized by XRD, SEM and free lime content. Differences between the cements with high content of β-belite prepared on a laboratory scale (tens of grams) and on a larger scale (tens of kilograms) were studied. Belite cement prepared on a larger scale had better properties compared to a laboratory scale. Optimal synthesis of β-belite cement consisted of mixing ground limestone, silica fume and liquid potassium silicate and burning at temperature 1100°C for more than 2 hours.

1. Introduction
Belite is dicalcium silicate, Ca₂SiO₄. It occurs in multiple forms (α, β and γ). The occurrence of α, β or γ form of belite is determined by the temperature of the firing during its manufacture. Belite in the forms α and β is an important component of Roman cement. A small amount of belite, in the γ form is also found in Portland cement, but the main component of Portland cement is tricalcium silicate, alit, Ca₃SiO₅. CO₂ emissions in belite production are stoichiometrically a third lower than the CO₂ emissions found with the formation of alite, as they arise according to the equations (1) and (2):

\[2\ \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\ CO_2\ ] \quad (1)
\[3\ \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5 + 3\ CO_2\ ] \quad (2)

The production of belite cement is also much less energy-intensive than the production of Portland cement, as belite cement is produced at temperatures of 800 to 1100°C, while Portland cement at temperatures above 1400°C. This will result in further reductions in CO₂ emissions at a significant fuel savings rate. Production is therefore also more economically advantageous.

Methods of the preparation of belite cement or pure belite in laboratory scale have been studied more intensely in the recent decades. The most widespread process involves the mixing of powdered raw materials, agglomeration and final burning of the mixture [1, 2]. Dispergation of the raw materials in the water or ethanol provides a better homogeneity of the mixture [3, 4]. Another common methods of the preparation of belite cement or pure belite are a hydrothermal method [5, 6] or sol-gel process [7, 8].

In a previous study, a simple procedure was developed to prepare cement based on β-belite [9]. The procedure was based on solid-state reaction, using pure raw materials (powdered limestone, amorphous silica and liquid alkali silicate) produced industrially in large quantities, which ensures the constant quality of the materials. The alkali silicate was used as a source of reactive SiO₂ and of alkali ion and for his ability to bind effectively powdered raw materials. The procedure was aimed at...
preparing β-belite at a fixed stage at high temperatures. Since the preparation of units of grams of belite cement in laboratory conditions, tens of kilograms have been prepared. The new procedure of preparation of β-belite cement is protected by a patent CZ 306912 B6 [10]. The aim of this work was therefore to verify the possibility of producing belite cement on a larger scale and to compare its properties with the properties of cement produced from the same raw materials by analogue process on a scale of several orders smaller.

2. Experiment

2.1. Raw materials and methods

2.1.1. Raw materials. For the preparation of β-belite in small quantities, the following basic raw materials were used. Silica fume (České lupkové závody, a.s., Czech Republic), limestone (Omyacarb 5VA; Omya) and potassium silicate (Water Glass, a.s., Czech Republic). All raw materials were described and analysed in detail. Bulk materials using XRF, XRD, BET, SEM, particle size distribution, bulk volume mass, humidity and annealing loss were determined. For water glass, the total water content, density, silica content and the aggregate content of alkaline metal oxides were determined by titration. The ICP-OES method determined the oxide content of other elements and the ratio of potassium oxides to sodium.

The chemical composition and physical properties of solid materials and potassium water glass are presented in table 1 below.

| description         | limestone  | silica fume | potassium silicate |
|---------------------|------------|-------------|--------------------|
| SiO₂ [%]            | 0.50       | 95.6        | 21.29              |
| Al₂O₃ [%]           | 0.27       | 0.23        | 0.03               |
| Fe₂O₃ [%]           | < 0.01     | 0.30        | < 0.01             |
| CaO [%]             | 55.1       | 1.34        | < 0.01             |
| MgO [%]             | 0.41       | < 0.01      | < 0.01             |
| K₂O [%]             | < 0.01     | < 0.01      | 8.18               |
| Na₂O [%]            | < 0.01     | < 0.01      | 0.70               |
| P₂O₅ [%]            | < 0.01     | 0.44        | < 0.01             |
| ZrO₂ [%]            | < 0.01     | 1.14        | < 0.01             |
| SO₃ [%]             | < 0.01     | 0.11        | < 0.01             |
| humidity [% r.h.]   | 0.07       | 0.55        | not specified      |
| loss on ignition [%] | 43.69     | 0.68        | not specified      |
| D₅₀ [µm]            | 6.27       | 3.80        | not specified      |
| D₉₀ [µm]            | 17.67      | 13.61       | not specified      |
| BET [cm²/g]         | 6.77       | 15.32       | not specified      |
| bulk density [kg/m³]| 787        | 303         | not specified      |
| total water content [%] | not specified | not specified | 69.02 |
| specific gravity [g/cm³] | 2658 | 2204 | 1.327 |
2.1.2. Analytical and testing methods. The chemical compositions of powdered raw materials were determined by X-ray fluorescence (BRUKER S8 Tiger).

A BRUKER D8 Advanced X-Ray diffraction system (XRD) equipped with a BRUKER SSD 160 detector and operating with Cu-Kα radiation at 40 kV and 25 mA was used for analysis of raw materials and prepared dicalcium silicates. XRD scanning was taken at the 20 = 0.02 step over an angular range from 5° to 70° with 1 s counting time. The crystalline phases were identified using the powder diffraction files from database ICDD - International Centre for Diffraction Data PCPDFWIN v.2.2. (2001).

A Mastersizer 2000 laser diffraction particle size analyser (MALVERN Instruments) was used to determine size distribution of powdered raw materials. Agglomerates were disrupted by ultrasound treatment.

A gas sorption analyser Autosorb iQ from Quantachrome was used for the determination of specific surface area by the Brunauer-Emmett-Teller method (BET).

Free lime content in dicalcium silicate samples was determined by a glycerine-alcohol test.

The morphology of belite cement at a laboratory scale was studied by a scanning electron microscope Mira 3 from TESCAN. For SEM analysis of belite cement on a larger scale, the sample was coated with about 5 nm of gold to make it conductive under the microscope JEOL JSM-IT500HR. Representative secondary electron images of the microstructure were taken at 7000x magnifications in high vacuum mode using an accelerating voltage of 10 keV and a working distance of 10.3 mm.

An inductively coupled plasma optical emission spectrometer OPTIMA 8000 (Perkin Elmer) was used to determine the content of micro-elements and K/Na ratio in liquid alkali silicates. Total content of alkali metals (Na, K) and content of SiO₂ in alkali silicates were determined by conventional acid-base titration methods; the reason for their application being higher accuracy at higher concentrations compared with other methods.

Specific gravity was determined by the pycnometric method.

2.2. Procedure

2.2.1. Laboratory preparation procedure. Raw materials were used in a weight ratio of silica : limestone : water glass 100 : 454 : 175. The CaO/SiO₂ molar ratio was 2 mol/mol. Actual preparation consisted of homogenizing bulk components by hand in a beaker. The bulk components were thermal silica and ground limestone. Then potassium water glass was poured into the beaker and the mixture was further mixed by hand, homogenized. Finally, 20 g of the mixture was compressed into tablets with a diameter of 40 mm and with a pressure of approx. 20 MPa for 2 minutes using a hand hydraulic press. The resulting tablets (agglomerates) were calcined in an electric laboratory furnace at 1100°C for 8 hours. Cooling was spontaneous in the furnace. In the end, the calcinates were crushed in a friction bowl and ground in a planetary mill. The above conditions of preparation were selected as optimal on the basis of previous work [1].

2.2.2. Preparation procedure in larger quantities. The preparation of larger quantities was based on optimised preparation of belite cement in small quantities. Thus, such raw materials were used and procedures were chosen that allowed β-belite to be produced in the best quality. The same raw materials were used to produce cement in larger quantities as in small quantities. Cement was therefore made of ground limestone, thermal silica and potassium water glass. Raw materials were used in a weight ratio of silica : limestone : water glass 100 : 454 : 175. The CaO/SiO₂ molar ratio was 2 mol/mol.

Dry ingredients were homogenized in a mixer type nautamix (Nauta-mixer). This homogenized mixture was sprinkled into a planetary mixer on potassium water glass. The mixture of all raw materials was homogenized in the mixer for 10 minutes. The prepared mixture was compacted by hand into a ball shape with a diameter of approx. 60 mm. These compacts were calcined in an electric furnace at 1100°C for 8 hours. After firing, the calcinates spontaneously cooled in the closed furnace. After cooling,
the balls were crushed with the help of a jaw crusher and further ground in a ball mill. In the end, all cement was homogenized. A total of 25 kg of belite cement was produced.

3. Result and discussion
Comparing the resulting properties of belite cements on a scale of tens of grams and on a scale of tens of kilograms was the basic goal of this work. The results of XRD, SEM and free lime concentrations were compared. Physical properties were evaluated only for cement produced in larger quantities. Cement produced on a laboratory scale was too little for physical analysis.

3.1. XRD
From the diffractogram shown in figure 1 below, it is clear that the belite cement contained dicalcium silicate mainly in the form of β-belite (larnite, ICDD 33-0302). A small amount of another form of dicalcium silicate (C₂S, ICCD 31-0297) was also present. No other phases (α-belite, γ-belite, wollastonite, etc.) were identified in the prepared belite cement compared to other studies [4, 5, 11–14]. The resulting diffractograms show that samples of belite cement produced in small and larger quantities have almost the same phase composition.

![Diffractogram of belite cements](image)

**Figure 1.** Comparison of diffractograms of belite cements produced on a laboratory scale and on a larger scale.

3.2. Free lime
The mass concentrations of free lime are given in table 2. The mass concentration of free lime in the belite cement sample produced in larger quantities is much less than the free lime concentration in the belite cement sample produced in small quantities. This difference was probably caused by different homogenization of dry components (ground limestone and thermal silica) during production. Machine homogenization during production of higher volumes of belite cement was better than manual homogenization in the production of belite cement in small quantities. Similar results of free lime in the belite cement were observed by El-Didamony et al. [12] (approx. 2%) and Mazouzi et al. [13] (approx. 2%).
Table 2. Mass concentration of free lime in samples of belite cements.

| belite cement         | free lime [% wt.] |
|-----------------------|-------------------|
| laboratory scale      | 4.19              |
| larger scale          | 1.63              |

3.3. Physical properties

The results of physical analyses are presented in Table 3. Due to the very small amount of belite cement sample produced on a laboratory scale, physical properties were determined only for belite cement produced in larger quantities. Belite cement produced in larger quantities was very sintered as it had a specific surface of only 3.8 m²/g and its specific gravity was 3.3 g/cm³. After grinding, the vast majority of particles were below 100 μm in size. Maheswaran et al. [14] had a comparable result of specific gravity (3.16 g/cm³) of belite cement prepared from calcined lime sludge and silica fume. The result of specific surface area of belite cement was lower compared to other study [5]. The difference was probably caused by the presence of potassium ions (in the liquid alkali silicate) that support the sintering.

Table 3. Physical properties of belite cement produced in larger quantities.

| description             | belite cement |
|-------------------------|---------------|
| D50 [μm]                | 5.20          |
| D90 [μm]                | 70.5          |
| BET [m²/g]              | 3.8           |
| bulk density [kg/m³]    | 886           |
| specific gravity [g/cm³]| 3.303         |
| total pore volume [mm³/g]| 435          |
| average pore size [nm]  | 607           |

3.4. Surface morphology

The particles of belite cement and their surface were examined in detail using a scanning electron microscope (SEM) and are shown in figure 2 (laboratory scale) and figure 3 (larger quantities). The morphology of the particles of the belite cement sample produced under laboratory conditions and the sample of cement produced in larger quantities were compared. There are no differences between belite cement on a laboratory scale and belite cement on a larger scale. The particles of both cement samples had a smooth sintered surface. The particles were individual without impurities.
Figure 2. Micrograph of belite cement on a laboratory scale.

Figure 3. Micrograph of belite cement on a larger scale.
4. Conclusions
A new process was developed to produce cement with a high content of β-belite. Production was very simple and consisted of mixing industrial raw materials normally available on the market. The amount of cement produced was gradually increased up to tens of kilograms. The resulting belite cement produced in larger quantities showed better properties than cement produced in laboratory quantities. Analyses showed high β-belite content and low free lime content. Cement produced in larger quantities contained more than 2.5 times less free lime than cement made on a laboratory scale. The resulting cement was of a very bright color and with a high content of β-belite, therefore it is a very promising material for the production of building materials, especially for the restoration of monuments.

In the following works, the application of belite cement, i.e. its hydration properties and the properties of mortars based on it, will be verified.

Acknowledgement
The author wishes to thank Karol Bayer (Faculty of Restoration, University of Pardubice) for providing SEM pictures using an electron microscope from TESCAN. This publication is a result of the project Development of the UniCRE Centre (LO1606) which has been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic (MEYS) under the National Sustainability Programme I. The result was achieved using the infrastructure of the project Efficient Use of Energy Resources Using Catalytic Processes (LM2015039) which has been financially supported by MEYS within the targeted support of large infrastructures.

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