Stabilisation of belite prepared from modified limestone waste sludge

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Abstract. Presenting work deals with the use of waste materials - waste sludge from mining and washing of limestone and waste material from acetylene gas cylinders containing mainly tobermorite and xonotlite. Both materials were characterized by X-ray powder diffraction, laser granulometry and chemical analysis. After drying and milling of raw materials, they were mixed together and homogenised resulting in 3 sample series with different ratios of these materials. The mixtures were then burned at 1150°C and 1350°C and the main products formed were lime, dicalcium silicate, wollastonite, pseudowollastonite and gehlenite. To preserve hydraulically active belite, K₂O as stabilizing agent was added in amount of 1 and 3 wt. %. Burned products were studied by means of X-ray diffraction and optical microscopy. Also hydration was observed.

1. Introduction

Since cement manufacturing is responsible for 5% of global CO₂ emission [1], many researches have been done in order to find less energy consuming binders. The main sources of CO₂ during cement manufacturing are limestone which decomposes to CaO and CO₂ and also fuels used during burning. Very effective way to reduce CO₂ emission is to reduce clinker content in cements by using of supplementary cementitious materials (SCMs), to reduce energy demand by lowering the final temperature of burning or to prepare clinker with different ratio of clinker phases. Lower burning temperature can be achieved by preparing clinker, which main component is belite instead of alite. Many authors [2–5] prepared reactive belite clinkers with properties comparable to ordinary Portland clinker (OPC). Belite (β-C₂S, β-Ca₂SiO₄), that usually forms 15–30% of OPC, can be synthetized by burning at temperature around 1200°C while alite (C₃S, Ca₃SiO₆), that is the main component of OPC – content of 50–70%, requires high burning temperatures – around 1450°C [6, 7].

The main interest required on burning process is the stabilization of C₂S which has 5 polymorphic modifications – α, α’H, α’L, β and γ. All of them except γ are metastable at room temperature and could be preserved only by burning at high temperatures or by addition of stabilizing ions. Unfortunately, the thermodynamically stable modification – γ-C₂S usually formed from β-C₂S transformation at 630°C has not any hydraulic properties. This transformation is accompanied by volume increase which causes phenomenon called “dusting” [8, 9]. Polymorphic modifications α, α’ and β are considered hydraulic, but reactivity of β-C₂S depends on many factors such as crystal imperfections, crystal size etc. [7]. To maintain hydraulic modification of belite, the burning process requires fast cooling and/or addition of dopants (e.g. Ba, Na, K, Fe, Mg, S in various compounds as BaCl₂, Na₂SO₄, NaF, K₂CO₃, Na₂CO₃, FeSO₄) [2, 10, 11]. However even hydraulically active belite
modification has a disadvantage in very low early strength due to its high thermodynamic stability and dense structure that slows down reaction with water [12].

Apart from belite based clinkers, some alternative ideas have been published – cements based on completely different materials, secondary materials, binary or ternary binders made of SCMs and activators. Calcium sulfoaluminate binders or binders based on highly reactive C₂S are studied to greater extent nowadays [1]. These are made of conventional raw materials but could be based also on some industrial by-products, such as fly ash, blast furnace slag, metallurgical slags. Potential alternative raw materials for production of cementitious binders that have been studied are for example rice hush ash, sewage sludge, municipal solid waste incineration fly ash and metakaolin. [3]

The aim of the present work is to prepare belite-based binders with use of waste materials. In this paper, waste sludge from mining and washing of limestone was used for preparation of clinkers. Waste from acetylene storage cylinders was chosen as an additional raw material. Both these materials are stored in landfill and their amount is still increasing. Use of these products is possible, by burning of their mixtures to form potentially hydraulic binder, mainly based on belite. As a dopant for maintaining hydraulic modification K₂O in form of K₂CO₃ was used.

2. Experimental

2.1. Materials and methods

For the purpose of this project, two waste materials were chosen as they are stored uselessly in landfills and their composition could be suitable for preparing of hydraulic binders. The first material A is a waste sludge from mining and washing of limestone, the second one B is a waste from acetylene storage cylinders. Both materials were dried at 60°C, milled and characterized by XRD (X-ray diffraction) analysis (table 1), TG/DTA (thermogravimetry and differential thermal analysis) and also their chemical composition was determined (table 2). Specific surface before milling was evaluated according to British Standard B.S.12:1958 as follow – 262 m²/kg for sample A and 1848 m²/kg for sample B.

| Calcite/Quartz/Albite/Illite/muscovite/Xonotlite/Tobermorite/amorphous phase |
|---|
| A  | 81.0 | 14.0 | 2.0 | 3.0 | - | - | - |
| B  | 18.0 | 26.0 | -  | -  | 17.5 | 19.5 | 19.0 |

Table 1. Approximate phase composition of raw materials (wt. %).

| SiO₂ | Al₂O₃ | CaO | Na₂O | K₂O | Fe₂O₃ | SO₃ | LOI |
|------|-------|-----|------|-----|-------|-----|-----|
| A    | 19.40 | 3.09 | 41.79 | 0.03 | 0.44  | 1.47 | 0.02 | 33.27 |
| B    | 51.32 | 0.17 | 33.68 | 0.56 | 0.10  | 0.06 | 0.11 | 13.36 |

Table 2. Chemical composition of raw materials (wt. %).

According to XRD, the major component of sample A is calcite (CaCO₃) following by quartz (SiO₂). Also illite/muscovite (KAl₂(AlSi₃O₁₀)(OH)₂) and albite (NaAlSi₃O₈) are present in small amounts - under 5 wt.%. For sample B, all components are presented in comparable amounts. Sample contains quartz, calcite, tobermorite (5CaO·6SiO₂·5H₂O), xonotlite (6CaO·6SiO₂·H₂O) and amorphous phase.

TG/DTA results confirmed results of XRD – for sample A clay mineral dehydroxylation and calcite decarbonation (amount of calcite around 80%) are depicted. For sample B, insignificant dehydration can be seen. Calcite decarbonation showed amount of calcite around 20%.

The raw materials were mixed in weight proportions A:B – 75:25, 50:50 and 25:75 and resulting raw meals were denoted AB1, AB2, AB3. With and without addition of K₂CO₃ they were homogenized for
2 hours. \( \text{K}_2\text{CO}_3 \) addition was calculated so that resulting amount of \( \text{K}_2\text{O} \) in raw meals was 1% and 3% respectively. These raw meals were then pressed into pellets 4 cm in diameter and burned in a super-kanthal furnace at 1150°C and 1350°C for 2 hours following by rapid cooling. Burned samples were milled in laboratory vibrating mill to fineness under 0.09 mm. All range of samples was analysed by XRD.

X-ray powder diffraction analysis was carried out on Bruker D8 Advance apparatus with Cu anode \((\lambda K\alpha = 1.54184 \, \text{Å})\) and variable divergence slits at Θ-Θ Bragg-Brentano reflective geometry. Quantitative phase analysis was done using Rietveld method. The amorphous phase content was calculated using internal standard method, as a standard 20 wt. % of fluorite \((\text{CaF}_2)\) was used.

Monitoring of hydration of samples was done also by XRD analysis. Milled sample was mixed with water (water to binder ratio was 0.5), inserted into XRD sample carrier, covered with kapton foil and measured immediately. After the measurement that lasted 1 hour, sample carrier was uncovered and placed into high humidity environment and measured again after 1, 2, 3 and 7 days.

The structure of burned samples was studied by petrographic polarizing microscopy using Eclipse LV100ND by Nikon. Parts of burned pellets (before milling for XRD analysis) were crushed and mixed with epoxy resin. A polished section was prepared from samples with resin and was etched by vapour of acetic acid to get different interference colours of phases that are not resistant to the acid. For this test only samples AB1 and AB3 with 0% and 3% addition of \( \text{K}_2\text{O} \) were chosen.

Thermogravimetry and differential thermal analysis of hydrated samples was done on Perseus STA 449 (Netzsch) in dynamic atmosphere in temperature range 35–1150°C with temperature rise 10°C/min. Before testing, samples were milled under 0.09 mm and dried at 50°C for 24 hours.

3. Results and discussion

3.1. Burning of samples and phase composition

As the first stage, samples were burned with and without addition of \( \text{K}_2\text{O} \) at 1150°C and 1350°C. After milling, phase composition was evaluated by XRD.

Sample series AB1

In sample series AB1 dominating phase was β-belite \((\beta-\text{Ca}_2\text{SiO}_4)\). The addition of 1% \( \text{K}_2\text{O} \) did not have significant effect on β-belite content. All samples in this series contained around 40% of β-belite, except AB1 3% \( \text{K}_2\text{O} \) 1350°C. This sample contained 97% of β-belite. Higher burning temperature and \( \text{K}_2\text{O} \) additions led to stabilization of β-C\(_2\)S, as proved in literature [2, 13, 14].

Samples burned at 1150°C contained also unreacted lime \((\text{CaO})\) formed from calcite \((\text{CaCO}_3)\). Its amount decreased with increasing addition of \( \text{K}_2\text{O} \). Samples burned at 1350°C contained significant amount of rankinite \((\text{Ca}_2\text{Si}_3\text{O}_9)\), which usually forms as accompanying phase of belite [8] and also \( \gamma \) modification of belite. \( \gamma \)-belite content also decreased with increasing \( \text{K}_2\text{O} \) content. Minor phases in samples were wollastonite \((\beta-\text{CaSi}_2\text{O}_3)\), pseudowollastonite \((\alpha-\text{CaSi}_2\text{O}_3)\), quartz \((\text{SiO}_2)\), gehlenite \((\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_12)\), \( \alpha' \)-belite \((\alpha'-\text{Ca}_2\text{Si}_3\text{O}_7)\) and cristobalite \((\text{SiO}_2)\).
Sample series AB2

In these samples, dominating phase became pseudowollastonite. Its amount is increasing with higher temperature and also with higher addition of K$_2$O. Pseudowollastonite (α-CaSiO$_3$) is high temperature modification of wollastonite (β-CaSiO$_3$). Transformation temperature is 1125°C [8] but it is also affected by SiO$_2$ content. Higher SiO$_2$ content accelerates β to α transformation [15], which was proved also by our samples.

Samples burned at 1150°C contained also β-belite in amounts around 43%, for 3% K$_2$O it is 26% – it seems that K$_2$O supports SiO$_2$ reaction towards more pseudowollastonite formation. Accompanying phases in samples burned at 1150°C were wollastonite, rankinite, quartz, gehlenite, α´-belite and in small quantities also lime, cristobalite and γ-belite.

Burning at 1350°C led to the formation of around 70% of pseudowollastonite and 25% of rankinite. The rest was formed by α´ and γ modifications of belite.

Samples series AB3

Here, the major phase in all samples was pseudowollastonite. It formed more than 96% in samples burned at 1350°C. The rest was wollastonite. In samples burned at 1150°C pseudowollastonite also dominated, but its amount increased with amount of K$_2$O, as in previous sample series. High temperature and also high content of SiO$_2$ (for this series it was 43%, for series AB1 it was only 27%) stabilized pseudowollastonite. The same findings were reported by [8, 15]. However, pseudowollastonite is obviously stabilized also by K$_2$O addition, or at least transformation from wollastonite is faster if K$_2$O...
is presented in system. Since no record about this phenomenon was found in literature, the process and its dynamics should be studied furthermore.

For samples burned at 1150°C similar dynamics were observed as in previous samples. β-belite and wollastonite content decreased with increasing K$_2$O. Additional phases were rankinite, quartz, gehlenite, cristobalite and γ-belite.

**Figure 3.** Content of β-belite, wollastonite and pseudowollastonite in samples AB3 with different ratio of K$_2$O burned at 1150°C (left) and 1350°C (right).

### 3.2. Microstructure

Microstructure of burned samples was studied by optical microscopy. Only samples AB1 and AB3 with 0% and 3% of K$_2$O were chosen, as other samples represent only the transition between these ones. For samples burned at 1150°C, details were not very well recognisable, as the structure was too fine for distinction, however, there were areas with distinguishable phases. In the sample AB1 0% K$_2$O 1150°C free lime and β-belite was observed that corresponds to XRD analysis results. In the sample AB3 0% K$_2$O 1150°C, areas of β-belite and probably wollastonite and pseudowollastonite were recognisable as well as a minor amount of free lime. Sample AB3 3% K$_2$O 1150°C contained areas of free lime and β-belite, although by XRD analysis free lime was not found. This is caused probably by very small overall amount of lime in the sample, that is under detection limit of XRD, especially when β-belite’s peaks are present (they overlap with lime’s peaks). The structure of AB1 3% K$_2$O 1150°C was not possible to distinguish.

The structure of samples burned at 1350°C is shown in figures 4–8. Grains of crystallised phases are visible. The areas between grains is solid amorphous melt formed during cooling. Solid melt with high SiO$_2$ content is amorphous probably due to inadequate chemical composition and cooling conditions for crystallization of other phases. Therefore, it is not possible to use XRD analysis for melt composition identification. During cooling, secondary overgrowth of lamellae occurs on the edge of the belite grain. In belite grains, cracks were formed that are probably connected with partial substitution of γ-C$_2$S modification (AB1 3% K$_2$O 1350°C) which occurs during cooling [16]. AB1 3% K$_2$O 1350°C contains only β-C$_2$S according to XRD. By optical microscope it can be seen that β-C$_2$S is bigger and more rounded than in the previous case. The melt is present as well. Microscope image of the sample AB3 0% K$_2$O 1350°C corresponds to XRD – grains of pseudowollastonite are present, the melt occurs in a smaller amount. On the section of the sample AB3 3% K$_2$O 1350°C, pseudowollastonite and a small amount of wollastonite are shown. Grains of wollastonite are needle-like, grains of pseudowollastonite are more angular. Both of them, wollastonite and pseudowollastonite, are resistant to vapour of acetic acid, they have no specific colour.
Figure 4. AB1 0% K₂O 1350°C, brown rounded grains - belite, light areas between grains - melt, dark diffused areas - open pores.

Figure 5. AB1 3% K₂O 1350°C, brown rounded grains - belite, light areas between grains - melt, dark diffused areas - open pores.

Figure 6. Detail of AB1 3% K₂O 1350°C, brown rounded grains - belite, light areas between grains - melt.

Figure 7. AB3 0% K₂O 1350°C, grey grains - pseudowollastonite, areas between grains - melt, dark diffused areas - open pores, large grey area - epoxide.

Figure 8. AB3 3% K₂O 1350°C, needle-like grains - wollastonite, other grains - pseudowollastonite, areas between grains - melt, dark diffused areas - open pores.
3.3. Hydration
Since results of XRD, confirmed by microscopy observations, showed that samples AB1 and AB3 with 3% K$_2$O burned to 1350°C contained around 97% of β-belite and pseudowollastonite respectively, the ability to hydrate was studied by means of XRD analysis.

In sample AB1 3% K$_2$O 1350°C, β-belite as a major phase did not hydrate, but carbonated. After 1 day of hydration significant amount of calcite occurred. Calcite peaks increase in time while β-belite peaks decrease (see figure 9). Belite is not probably hydraulically active, as stabilized β modification should be. The reason may be in its structure, as is reported in [7] or probably in its formation process, which needs further observations.

On the other hand, calcium silicates’ carbonation is very well known in literature. They react with CO$_2$ in aqueous conditions to generate calcium silicate hydrate (C-S-H) and calcite instead of portlandite (Ca(OH)$_2$). In adequate conditions, carbonation of alite (C$_3$S) and belite (C$_2$S) occurs immediately within a few minutes or hours [17, 18], as this was probably the case of our samples. Even hydraulically not active belite carbonates quite fast. During short-term carbonation all C$_2$S/C$_3$S grains do not fully react, therefore continued exposure to moist or humid environments post-carbonation allows for the subsequent hydration of residual unreacted portion [19]. For our samples, different environments of hydration will be studied. Also similar condition for long-term hydration/carbonation will be studied, since according to [20, 21] extensive carbonation leads to formation of silica gel and calcite.

![Figure 9. Hydration of sample AB1 3% K$_2$O 1350°C (C – calcite, B – β-belite).](image)

![Figure 10. Hydration of sample AB3 3% K$_2$O 1350°C (C – calcite, P – pseudowollastonite).](image)

The same experiment was done for sample AB3 3% K$_2$O 1350°C. It was confirmed that also pseudowollastonite carbonates, though not that intensively as β-belite. Calcite peak could be seen after 1 day of hydration and its intensity is slightly increasing (see figure 10).

Similar phenomenon is the base of non-hydraulic concrete system, calcium-silicate binder (SCS), known as Solidia Cement [22, 24], patented in 2015. Low-lime calcium silicate minerals such as wollastonite/pseudowollastonite and rankinite reacts with CO$_2$ to form a binder with low carbon footprint. SCS paste can store up to 17% of CO$_2$ by mass into a form of stable carbonates [23].
Considering lower production temperature and lower limestone use, the overall CO$_2$ footprint of carbonated concrete made of SCS has been reported [24] to be about 70% less than that of OPC concrete. Also, according to [22], concrete elements made of SCS have satisfactory freeze-thaw resistance and resistance to high temperature environment.

As we prepared pseudowollastonite from waste materials, the carbon footprint of potential product would be even smaller than that of the Solidia. The carbonation in humid environment will be studied furthermore, as well as mechanical and durability properties of these and previous samples.

4. Conclusions
Mixtures of two different waste materials (waste sludge from mining and washing of limestone and waste from acetylene storage cylinders) with and without addition of K$_2$O were burned at 1150°C and 1350°C. XRD analysis results showed that lower content of SiO$_2$ in mixture led to formation of β-C$_2$S while higher SiO$_2$ content supported the formation of wollastonite and pseudowollastonite. Higher temperature and higher K$_2$O addition stabilised β-belite in samples with higher CaO and lower SiO$_2$ content while for samples with lower CaO and higher SiO$_2$ content pseudowollastonite was stabilized.

Hydration of sample with β-C$_2$S showed no common hydration products. Only calcite peaks were detected after 1 day. Fast carbonation was observed at this sample. Similar trend could be seen also for sample containing pseudowollastonite. Calcite peaks were present after 1 day of hydration.

Both prepared materials require further research. However according to presented results tested waste materials could be conveniently used together for preparation of low-energy alternative binder.

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