

STUDY OF BELITE STRUCTURE CHANGES INFLUENCED BY POTASSIUM

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The production of clinker is carried out by burning process of raw material mixture modified by potassium ions in the form of potash (K_2CO_3). The potash carbonate is dosed in amounts ranging from 0 % to 3 mass %. Potassium ions are involved in clinker creation process and causing microstructure defects. These defects lead to increase of reactivity and thus increase of velocity of hydration process. Due to temperature instability of potassium ions at usual temperature of clinker burning process around 1250°C, temperature regimes of 950 and 1100°C were tested with isothermal times of 1, 3, 5 hours. Phase composition, physico-mechanical properties and hydration process were observed.

INTRODUCTION

Portland cement production is characterized by a series of drawbacks such as high fossil fuel-based energy consumption, a heavy environmental impact due to the use of natural prime materials and substantial part of GHG emissions [12]. The production of Portland cement on average emits about 0.83 tons of CO_2 per ton of cement, which is not particularly high for a chemical product. However, because of the enormous volumes of cement used worldwide to make concrete, such emissions amount to about 6 % of all anthropogenic CO_2 emissions. Cements based on belite have been proposed as environmentally friendly materials. Different papers [13-23] have been published on belite cement production involving the thermal treatment of raw mixes with industrial waste or by-products (such as fly ash, FBC ashes, etc.) as alternative prime materials. Our approach to this topic is utilization of recycled concrete, which is described in this paper. The possibility of exploitation of recycled concrete undersizes for the Portland clinker production is researched within the project on research of hydraulic binders based on non-traditional raw material sources. It was proved that recycled concrete undersizes are suitable partial raw material for production of alitic (C_3S) clinker, but production of belitic (C_2S) clinker would be more effective for larger exploitation of recycled concrete [1]. This solution is encountering on objectionable behaviour of belitic clinker in kinetics of hydration process, due to slow hydration of its main clinker mineral β - C_2S . Hence the modification of raw mill by potassium ions was suggested [6, 8, 10]. The

catalytic effect is expected from modification of raw mill influencing structure of C_2S leading to increased hydration velocity [6, 7]. Initial studies proved, that suggested modification is effective, but also proved that stability of potassium in the structure of nascent clinker is problematic and in case of rapid burning processes, thermodynamically impossible [9]. That is the reason why influence of burning process on velocity of belite structure creation in the presence of potassium was studied.

EXPERIMENTAL

The adjustment of raw meals adjustment starts by with the separate crushing and grinding of each raw material – undersizes of recycled concrete and high-percent limestone, followed by their mixing in the mass ratio 1 part recycled undersizes to 2.25 parts high-CaO limestone, and the addition of potassium carbonate at 1 and 3 mass %. Of course, a comparative set without potash addition was also prepared. The following symbols were used for the raw meals: “B0”, “B1” and “B3”, which denote additive contents of 0 %, 1 % and 3 %. For the experimental laboratory burning of belite clinkers the pellets were prepared by wet process and were burned in a “Kanthal Super[®]” furnace in three temperature re-gimes: 950 - 1100 - 1250°C. Three different isothermal times (1 - 3 - 5 hours) were used at each temperature.

All burned clinkers were milled in a vibration mill to the max particle size of 0.063 mm. Samples were

taken for chemical analysis, X-ray diffraction analysis and for the method of microscopic point counting phase - analysis [2]. The conversion of grinded clinkers to cement was effected by the addition and homogenization of 5 % grinded gypsum. Because of the character of the model and the quantities of cements for the testing of compressive strength, microbars 10 × 10 × 30 mm in size were prepared for testing. Test samples were produced with different water/cement ratios to obtain pastes of equivalent consistency. The de-molded microbar test samples were placed in a chamber under controlled conditions of 99 % R.H. at laboratory temperature (21°C) for 28 days, followed by compressive strength tests. The 56, 90 and 180-day prolongations of hydration dwelling will be studied in a further work. X-ray diffraction analysis and thermal analysis of hydration products as binding phases followed the testing of mechanical properties on the remains of micro-bars.

RESULTS AND DISCUSSION

Chemical analysis

The content of characteristic oxides in the raw meals and corresponding clinkers burned for 3 hours at each used temperature and all three potassium carbonate addition variants are presented in Table 1.

The chemical analysis results demonstrate the ultimate content of free lime is the sign that the equilibrium state of burning was not attained in the main clinkers.

The highest free lime content was exhibited by clinker “B 0”, which was burned at the lowest temperature and the shortest isothermal dwelling (950°C / 1 hour). The prolongation of isothermal dwelling duration, and especially the rise in burning temperature, led the samples in this group to undergo a gradual decline in free lime content at temperatures up to 1250°C, at which

point to observed decline first became significant.

The difference between the “B 1” clinkers compared with the “B 0” clinkers in terms of free lime content was only just evident, but the first conspicuous difference was seen with the “B 3” clinkers modified through the addition of 3 mass % potassium carbonate. Using this criterion the highest potash addition positively modified the reaction rate of the burning process.

Another important criterion that was investigated was the behavior of potassium ions in the course of the burning process.

To obtain this it was necessary to search in order to make a unified base for K₂O content calculation e. g. the value after ignition loss correction; see Figure 1 for a graphical representation. The obtained results show very low or just non-volatile K₂O at low temperatures or short isothermal dwellings and low content of potassium alkali in the raw feed. As a rule, K₂O began to volatile when the potash content was raised in the raw meal, and in the middle burning regimes, but only to an extent not exceeding approx. 15 % of its initial content. The first

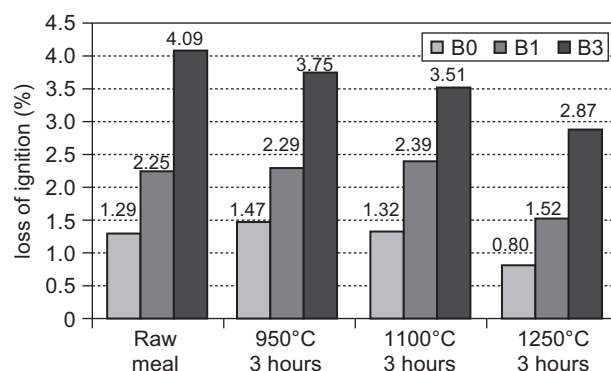


Figure 1. Influence of temperature at 3- hour isothermal dwelling on K₂O content.

Table 1. Partial chemical analysis of raw meals and clinkers.

Components selected (%)	raw meal	B 0			B 1			B 3		
		950°C	1100°C	1250°C	950°C	1100°C	1250°C	950°C	1100°C	1250°C
SiO ₂	20.5	27.2	28.4	29.5	25.2	27.0	26.7	27.5	25.9	27.8
CaO	40.5	50.8	55.8	59.9	52.0	55.3	60.8	55.0	56.9	58.3
Na ₂ O	0.52	0.81	0.78	0.80	0.79	0.85	0.77	0.87	0.78	0.66
K ₂ O	0.9/1.5/2.8	1.29	1.24	0.79	2.0	2.2	1.5	3.55	3.35	2.8
CaO _{free}	–	38.2	28.4	6.4	35.1	22.7	5.2	16.5	14.8	2.1

Table 2. The influence of the burning regime on K₂O content in clinkers.

Sample designation	Raw meal	K ₂ O content, net loss on ignition (%), Clinker 1100°C								
		950°C			1100°C			1250°C		
		1 hour	3 hour	5 hour	1 hour	3 hour	5 hour	1 hour	3 hour	5 hour
B 0	1,29	1,61	1,47	1,70	1,32	1,32	1,58	0,80	0	0
B 1 _s	2,25	2,27	2,29	2,20	2,38	2,39	2,13	1,52	0,074	0,076
B 3	4,09	3,91	3,75	3,95	3,64	3,51	3,62		2,87	

clearly volatile K_2O process occurred during burning at the highest temperature of $1250^\circ C$, when the initial K_2O content was lowered by 30 % and more. It is possible to say that modification with K_2O only has an effect up to the burning temperature of $1100^\circ C$. At the lowest temperature, $950^\circ C$, potassium modification is limited to 5 hours of isothermal dwelling, and most likely 3 hours at the middle burning temperature. All isothermal dwellings of clinkers at $1250^\circ C$ were unsuitable for modification by K_2O , as its application proved non-decisive or even had no effect at all.

Mineralogical composition

X-ray ($CuK\alpha$) diffraction analysis was used for the synthesized clinker samples. In the case of the samples without potassium at the burning temperature of $950^\circ C$, there was just time for the calcination process and the forming period to begin for low-calcium clinker minerals CA and C_2F ; however, it was not possible to identify the formation of calcium-silicate phase even at 5 hours of isothermal dwelling. On the other hand, the synthesis of modified potassium ions induced significantly higher SiO_2 reactivity in the used system even at the shortest

isothermal dwelling. For the “B 3” clinkers and 1 hour of isothermal dwelling a very low content of residual quartz was documented, along with the marginal formation of $\beta-C_2S$ together with the first presence of high-calcium clinker phase C_3A . After extension of the isothermal dwelling to 3 hours, the full binding of quartz occurred as semi crystalline $\beta-C_2S$, and brownmillerite was identified too. At the longest period of isothermal dwelling (5 hours) the formation of $\beta-C_2S$ had reached the full crystalline phase and the content of free lime in the system was significantly lower in correlation with the formation of new clinker minerals.

When the burning temperature rises to $1100^\circ C$, a higher synthesis level of clinker minerals is obtained. This partly took place just for the “B 0” clinkers at the shortest isothermal dwelling, where the presence of high-calcium clinker phase C_3A as well as brownmillerite was identified. It also partly occurred at longer isothermal dwellings of 3 and 5 hours, which caused the almost total passage of SiO_2 from quartz to $\beta-C_2S$ (see the X-ray pattern in Figure 2). As in the case of the afore-mentioned potassium-modified synthesis, the “B3” clinkers, for example, showed higher crystalline development of $\beta-C_2S$ at 3 hours of isothermal dwelling together with a very low content of free lime in the system (see the X-ray

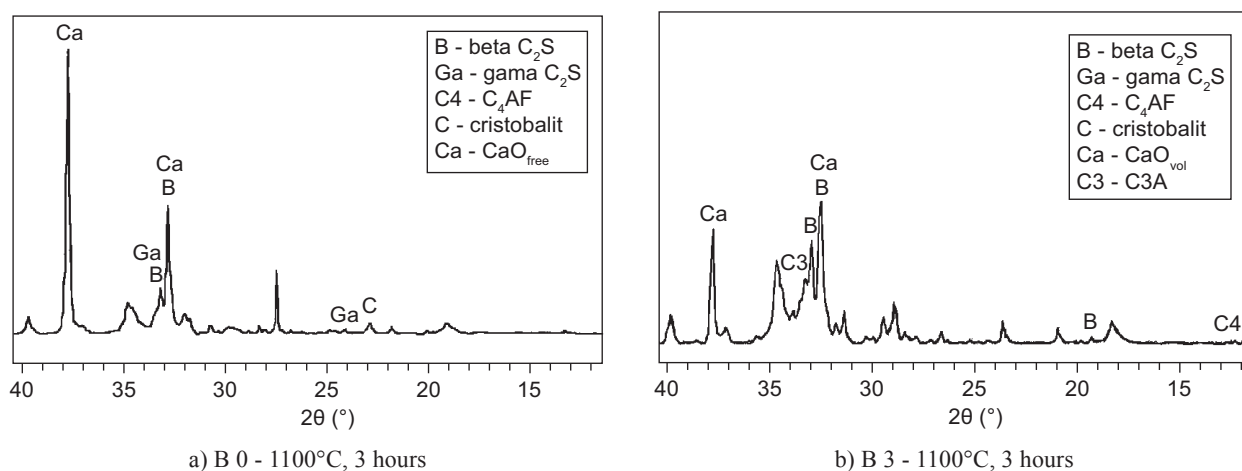


Figure 2. X-ray diffraction analysis of clinkers B 0 (a) and B 3 (b).

Table 3. Mineralogical analysis of clinkers B 0 and B 3.

Quantified phase	B 0			B 3		
	950°C	1100°C	1250°C	950°C	1100°C	1250°C
$\beta-C_2S$	20	38.2	24.1	32.7	53.3	46.6
$\gamma-C_2S$	0	3.8	54.6	0	0	19
C_3A	0	0	9.5	1	5.2	9.4
C_4AF	6.6	7.6	7	8.2	8.7	7.6
free lime	11	22.6	0.6	10.7	4.8	0
Quartz	8.5	4.1	0.7	11.5	0	0
Cristobalite	0	2.9	0	0	0	0

pattern in Figure 2).

At the highest burning temperature of 1250°C in all of the synthetic clinker samples the main identified phase was dicalcium silicate, but in variable ratio of modifications β and γ , which provides the possibility of evaluating the parameters that influenced the synthesis. First of all, longer isothermal dwellings of 3 and 5 hours cause the growth of C_2S content, which as the next parameter, i.e. the ratio between β and γ C_2S , is intensified by potassium oxide for the precedential formation of the necessary β - C_2S clinker mineral modification.

As a result, it seems the potassium ions intensify and stabilize the β - C_2S synthesis. The microscopic point counting method was not usable for the mineralogical analysis of synthesized clinkers because of their highly dispersed structure and so was substituted with the method by Rietveld [3, 4, 5] of the refinement of X-ray diffraction analysis (RIBM Laboratory). For the evaluation of objectivity this quantification was done by back calculation of the chemical composition from the RIBM's results and correlation with the chemical analysis of synthesized clinkers; see Table 3. The correlation of the results shows a relatively low difference between what are in principle different methods of defining clinker oxide (CaO, SiO₂, Al₂O₃ and mostly Fe₂O₃) reactivity. On this basis it is possible to apply Rietveld's method to quantify the main clinker minerals in real systems. It is then possible to follow-up with summarization.

The catalytic effect of potash in the raw feed starts to influence the process as the burning temperature of 950°C is reached. For example, at the isothermal dwelling of 3 hours with modification by potassium carbonate at 3 mass%, clinker "B 3" has a β - C_2S content of 33 % while, in contrast, clinker "B 0", without modification by potassium but at the same dwelling of 3 hours, only has a β - C_2S content of 20 %. The raising of the burning temperature to 1100°C was followed by an almost twofold higher β - C_2S content in clinker "B 3" with potash modification of 53 % of the total value. On the other hand, the unmodified raw feed for clinker "B 0" has a content of dicalcium silicate which approaches the same level but it presented a total β - C_2S content of only 38 % together with a 4 % γ - C_2S content in the final product.

At the highest burning temperature of 1250°C and an isothermal dwelling of 3 hours then the content of β - C_2S in clinker "B 3" decreased only imperceptibly in comparison with 1100°C. At first, γ - C_2S phase was only identified but in the minority content, while unmodified clinker "B 0" showed a one third lower content of β - C_2S (24 %) through its change to γ - C_2S phase and its formation in parallel to the major approx. 55 % content.

The presented quantification of synthesized phases in the investigated clinkers shows how the stabilization effect on the β -modification of formed dicalcium silicate occurs in parallel with the catalytic influence of potassium, in the manner evident in previous section on phase analysis.

Physico-mechanical properties of prepared cements

Because the experiments were only of an investigative character, and only a very small sample of synthesized clinkers was tested, it was not possible to arrange ordinary testing of technological properties. Only a mechanical strength test was carried out on selected prepared 10 × 10 × 30 mm cement paste microbar samples after 28 days of hardening, which was after the content of β - C_2S as the main hydraulic phase had become ready to form a binding system during the hydration process.

The best results from the compressive strengths after 28 days of hardening show that the potash-modified cement "B 3" after burning at a temperature of 950°C and at an isothermal dwelling of 3 hours, had a compressive strength of 31 MPa. When the isothermal dwelling was prolonged to 5 hours of burning, the result was identical. Both of the higher burning temperatures (1100 and 1250°C) caused the lowering of the compressive strength of modified cement "B 3" to 18 MPa for both samples under identical test conditions. This "lowering" may be caused on the one hand through the dicalcium silicate modification of hydraulic active β - C_2S , which was changed to non active γ - C_2S for the 1250°C clinker, and on the other hand by the lowering of free lime content and the formation of hydraulic active β - C_2S for the 1100°C clinker, which seems to be an optimum product.

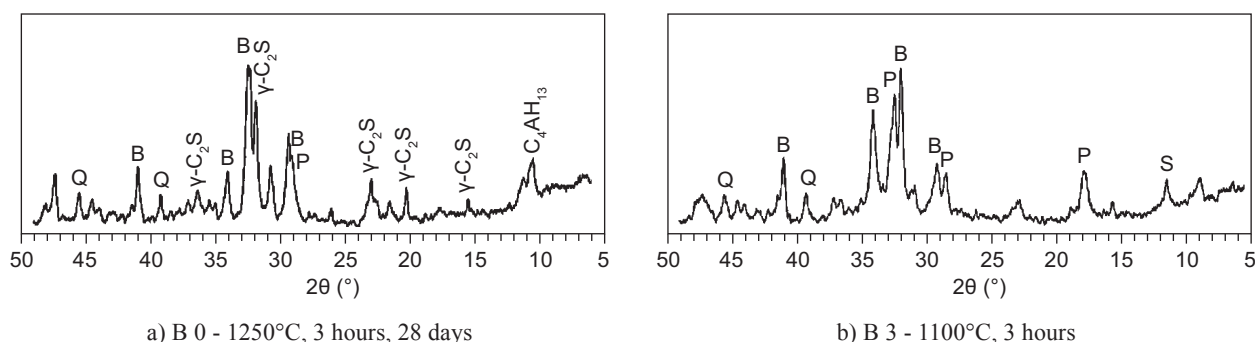


Figure 3. X-ray diffraction analysis of clinkers B 0 (a) and B 3 (b) after 14 days of hydration.

Study of the hydration process in the prepared cements

Representative samples were examined with the aid of X-ray diffraction analysis to obtain the mineralogical compositions of samples after 28 days hydration. In the group of cement pastes related to clinkers burned at 950°C there was just a difference in the content of quartz and portlandite in samples “B 0” and “B 1”, which is typical for hydraulic limes. This contrasted with sample “B 3”, which exhibited the typical behavior of belitic cement. The next typical difference in the content of portlandite in a hydrated system of cements burned at the temperature 1100°C was shown by sample “B 3” (Figure 4). In this case it occurred because of the limited portlandite content as the product of the hydration of β -C₂S, which was opposite to the case of “B 0”, where a higher portlandite content was created by the remainder of the free lime after imperfect clinker synthesis without modification by potassium carbonate (Figure 3). The last group of cement pastes related to clinkers burned at a temperature of 1250°C merely showed the absence of portlandite in the hydration products of samples “B 0” and “B 1”, while γ -C₂S as the main clinker phase is not hydraulically active and only one hydrated aluminate, C₄AH₁₃, is present in the products of both samples.

Table 4. Quantification of CaO content in B 3 sample after hydration for 28 days.

Quantified parameter	Burning temperature (°C), isothermal dwelling 3 hours	
	950	1250
CaO _{p/c.p.}	9,05	1,6
CaO _{k/c.p.}	4,41	4,9
CaO _{h/c.p.}	13,5	6,5

Next, a better definition of the portlandite ratio was calculated with the aid of thermogravimetry. The content of CaO in the cement paste was established in the equation, 1st for portlandite (CaO_{p/c.p.}), 2nd for carbonate (CaO_{k/c.p.}), and 3rd for the sum of both (CaO_{h/c.p.}), for the “B 3” samples burned at temperatures of 950 and 1250°C and at an isothermal dwelling of 3 hours after their hydration for 28 days, see Table 4 Lower burning temperature gives belite higher hydraulic reactivity than when the burning temperature reaches 1250°C.

CONCLUSION

The aim of the work was the study of potassium-modified belite cement prepared on the basis of recycled concrete rejects by using the low temperature method of burning. The optimum addition of 3 mass % of potassium carbonate with 3 hours isothermal dwelling at a temperature of 1100°C forms belite clinker with hydraulically active β -C₂S as the main phase and very low free lime content. As belite cement, this clinker gives compressive strengths of 18 MPa after 28 days, a value which will probably grow as the hardening process continues. Of course, it is necessary to verify the results of this study on selected samples in larger scale technological tests.

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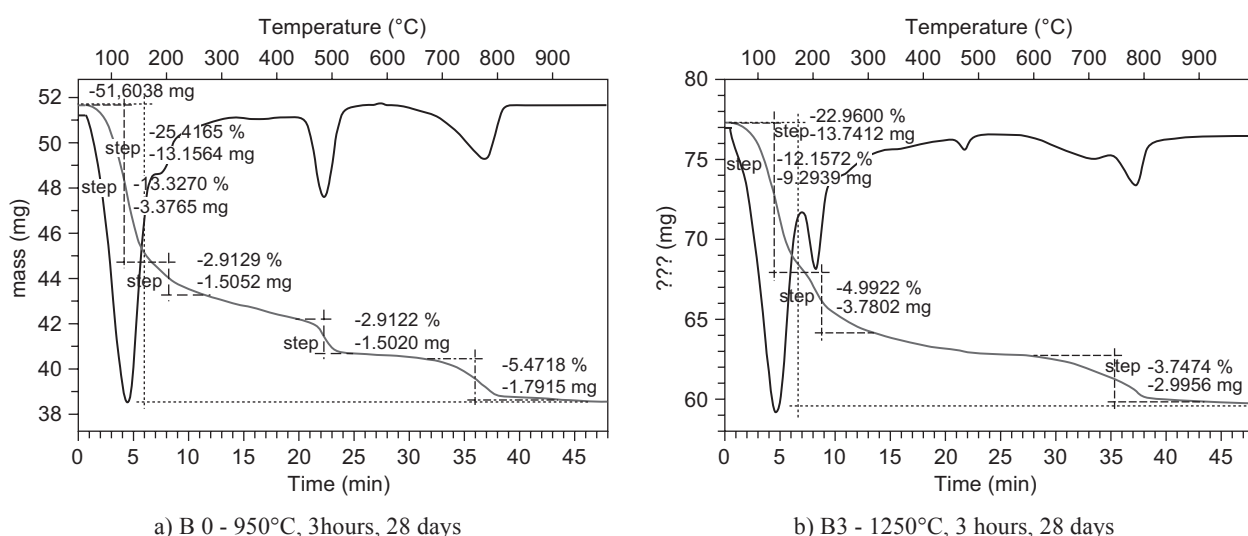


Figure 4. Thermogravimetry of clinkers B 0 (a) and B 3 (b) after 28 days of hydration.

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