Thermodynamic Modelling Of Belite Clinker Mineralogy during Manufacture

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Abstract - The production of belite-rich clinkers is an alternative to reduce the environmental impacts of using fossil fuels, as it decreases the clinkering temperature in cement manufacturing. The sustainability of this approach can be improved by combining it with the co-processing of industrial by-products as raw materials in clinker production. However, using alternative materials can add impurities that change the stability of the clinker phases. Na_2O and K_2O are widely available in co-processed materials in the cement industry. However, their effects on all manufacturing steps still need to be clarified, and running extensive experimental programs can be costly and time-consuming. In this context, this study aimed to evaluate the effect of alkali metals Na and K on the phase evolution of belite clinker during manufacturing. The influence of Na and K was evaluated by thermodynamic modelling based on the Gibbs energy minimization parameters and developed in the FactSage software. The discussion focused on the phase assemblage during heating and cooling in manufacturing, melt phase viscosity, and compatibility with findings from experimental investigations of reference studies. Thermodynamic calculations allowed the accurate modelling of the belitic clinker composition. The modelling results agreed with the findings of previous experimental studies, which reported an increased melt viscosity and the decrease of C_2S by about 6 and 12 wt.% in the presence of 2.0 wt.% K_2O and 1.5 wt.% Na_2O. The alkali metals enhanced the Ca_3SiO_5 (C_3S) content and extended the temperature range of additional Ca_2SiO_4 α' (C_2S) formation on cooling. $Ca_3(Al,Fe)O_6$ ($C_3(A,F)$) was destabilized in doped clinkers. With K_2O, the decrease was associated with increased $Ca_2(Al,Fe)O_5$ ($C_2(A,F)$) and potassium-doped calcium silicates as minor phases ($K_2Ca_6Si_4O_{15}$, K_2CaSiO_4, K_2MgSiO_4, and $K_2Ca_2Si_2O_7$). For Na_2O, the decrease resulted in the formation of orthorhombic tricalcium aluminate (C_3A-o) and minor phases, including $Na_2Ca_3Al_{16}O_{28}$, Na_2CaSiO_4, $NaAlSiO_4$, Na_2MgSiO_4, $NaFeO_2$, and Na_2SiO_3. The alkali metals notably altered the highest melt content from 26.17 wt.% (B) to 40.38 wt.% (2.0% K_2O) and 36.95 wt.% (1.5% Na_2O). It may cause implications during manufacturing on an industrial scale. However, besides the content, the viscosity of the melt phase also plays a crucial role in the stability of clinker nodules during manufacturing. It can indicate the necessary conditions for the formation of clinker compounds. The highest C_3S amount was obtained when the melt viscosity of the systems reached 0.15 ± 0.02 Pa.s.

Keywords: Clinker, Cement, Thermodynamic modelling, Belite cement, Alkali metals.

1. Introduction

The clinkering process in ordinary Portland cement (OPC) production occurs at high temperatures of around 1450 °C [1]. This thermal treatment and clinker grinding are the main steps responsible for the consumption of fossil fuels and consequent CO_2 emissions during cement manufacture [2]. It is estimated that up to 130 kg of fuels from non-renewable sources are consumed for every ton of OPC produced [3]. In this sense, several studies have investigated alternatives for reducing emissions and environmental impacts associated with the consumption of fossil fuels in cement manufacture. Alternatives include lowering the clinkering temperature, using alternative fuels, developing new cements, and manufacturing alternative binders without heat treatment [4].

A decrease in the clinkering temperature of up to 150 °C can be obtained through the production of belite Portland cement [5]. It has compounds similar to OPC but with higher levels of Ca_2SiO_4 (C_2S) instead of Ca_3SiO_5 (C_3S) [6]. The predominance of dicalcium silicate comes from the clinkering temperature, which generally does not reach the point of

maximum reaction of C_2S and CaO to form C_3S (>1400 °C) [1]. Belite cement has delayed hydration kinetics, producing the same hydrated products as OPC but with a lower hydration heat in the early ages [7]. This characteristic is fundamental for applications in concrete with large volumes or where high compressive strength is not required in the early ages. The similarity with the chemical composition of anhydrous and hydrated OPC and the feasibility of using the same raw materials and manufacturing processes classify belite cement as easily adaptable to the existing infrastructure in the OPC industry. Therefore, it is a possible alternative to mitigate the emissions associated with cement manufacture by reducing the clinkering temperature.

The sustainability of belite cement can be improved by co-processing alternative materials and industrial by-products as a replacement for natural raw materials or fuels. This approach reduces the environmental impacts related to the extraction of natural resources and the depletion of non-renewable sources [4]. However, the oxides added beyond those essential for the clinker composition (CaO, SiO_2, Al_2O_3, Fe_2O_3) are considered impurities and can alter the stability of the clinker phases [1]. Alkali metals are widely found in these alternative materials [2]. Previous investigations reported altering the crystalline structure of $Ca_3Al_2O_6$ and Ca_2SiO_4 in OPC produced with clinker raw meals doped with sodium or potassium [8], [9].

For belite cement, Na and K alkalis were used as activators to improve C_2S reactivity [3], [10]. However, understanding their effects on clinker mineralogy at all manufacturing stages is essential for improving operational requirements. Furthermore, it is important to understand how these elements promote the formation of new compounds in cement. In this sense, using computational tools simulating the thermodynamic processes of clinkering can increase the understanding of limited experimental data sets.

Thermodynamic modelling processes the chemical composition of the raw materials to predict the clinker mineralogical composition. Among the main advantages of the method are the reduction of time and costs of experimental programs, the modelling of systems containing minor elements, the analysis of the melt phase viscosity, and the enhanced precision of the predictive calculations compared to the method of the potential composition of Bogue. Thus, thermodynamic modelling can broaden the understanding of the effects of alkalis on the phase stability of belite clinker during manufacturing.

Thus, this study investigated the effects of alkaline metals Na and K on the phase evolution of belite clinker during manufacturing. The clinker composition was predicted by thermodynamic modelling of samples synthesized experimentally in previous investigations [3], [10]. Operational aspects were analysed, including mineralogy evolution on heating and cooling, melt phase viscosity, and compatibility with findings from experimental investigations of reference studies.

2. Methodology

2.1. Thermodynamic modelling

Thermodynamic calculations were applied to evaluate the effects of alkali metals Na and K on belite clinker phase stability and melt phase viscosity during the clinkering process. FactSage version 8.2 software was used for the modelling, it which contains optimized parameters based on Gibbs free energy minimization of the solution phases for clinker equilibrium calculations [11]. Thermodynamic databases for gaseous components (FactPS) and oxides in solid, liquid, and solution phases (FToxid) were selected for calculating the phase assemblage during production [11], [12]. The system pressure was set at 1 atm. The processing was applied using Equilibrium and Viscosity modules and adopting the entire set of products available in the system. Calcium silicates were quantified as Ca_3SiO_5 (C_3S) and Ca_2SiO_4 (C_2S). Modelling utilizing FactSage considers solid solutions of calcium aluminium ferrites, including $Ca_3(Al,Fe)_2O_6$ ($C_3(A,F)$), $Ca_2(Al,Fe)_2O_5$ ($C_2(A,F)$), $Ca(Al,Fe)O_4$ ($C(A,F)$), and $Ca(Al,Fe)_3O_{10}$ ($C(A,F)_3$) [11]–[13]. Where, (Al,Fe) means Al and Fe are variable in the structure. The modelled solid solution $C_2(A,F)$ is mainly associated with the OPC ferrite content, $Ca_2(Al_xFe_{1-x})_2O_5$, often named C_4AF [1]. The tricalcium aluminate or C_3A ($Ca_3Al_2O_6$) content is included in the $C_3(A,F)$ solid solution, and the complementary content corresponds to intermediate phases in the development of C_4AF [12]. Thermodynamic modelling enabled quantifying other solids, including $Ca_3MgSi_2O_8$, MgO, CaO, and phases related to the chemical combination of alkali metals (K_2CaSiO_4, $KAlSiO_4$, K_2MgSiO_4, $KAlO_2$, $K_2Ca_6Si_4O_{15}$, $Na_2Ca_8Al_6O_{18}$, $Na_2Ca_3Al_{16}O_{28}$, Na_2CaSiO_4, $NaAlSiO_4$, Na_2MgSiO_4, $NaFeO_2$, Na_2SiO_3) [11]. The calculated liquid phase corresponded to the melt phase content formed during clinkering, and its viscosity was determined along the manufacturing simulations. The melt fraction was mainly developed through the melting of aluminates ($Ca(Al,Fe)_2O_4$, $Ca_2(Al,Fe)_2O_5$, $Ca_3(Al,Fe)_2O_6$, $Na_2Ca_8Al_6O_{18}$, and $KAlO_2$) from 1010 °C, reaching their maximum at the final clinkering temperature and then resolidifying during clinker cooling [1], [2]. This study

evaluates the effect of alkali metals (K and Na) on the phase stability of belite clinker during heating on clinkering and analysing melt phase viscosity.

2.2. Case study

The mineral composition of belite clinker raw meals synthesized experimentally in previous investigations was used as input for thermodynamic calculations [3], [10] (Table 1). Five samples were modelled. An undoped Portland belite clinker raw meal as a reference (B), two systems doped with 1.0 and 2.0 wt.% K_2O (B1.0K and B2.0K), and two with 0.5 and 1.5% Na_2O (B0.5Na and B1.5Na). The oxide composition was normalized to the sum of the main oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, and K_2O), and the clinkering temperature was 1365 °C.

Table 1. Raw meal oxide composition and chemical moduli of the modelled belite Portland clinker [3], [10].

Oxides (wt.%)	B	B1.0K	B2.0K	B0.5Na	B1.5Na
CaO	62.90	62.44	61.83	62.68	62.06
SiO_2	25.04	24.85	24.60	24.94	24.69
Al_2O_3	6.35	6.30	6.24	6.32	6.26
Fe_2O_3	5.24	5.20	5.14	5.22	5.16
MgO	0.07	0.07	0.06	0.07	0.07
Na_2O	0.13	0.13	0.12	0.50	1.50
K_2O	0.27	1.01	2.01	0.27	0.26
LSF	76	76	76	76	76
SM	2.16	2.16	2.16	2.16	2.16
AM	1.21	1.21	1.21	1.21	1.21

LSF: Lime saturation factor; SM: Silica modulus; AM: Alumina modulus.

The publications were chosen based on the following criteria: It presented the raw meal composition obtained by X-ray fluorescence spectrometry (XRF); it detailed temperature conditions and heating rate during clinkering; it was published in a peer-reviewed journal; it addressed the synthesis of belite Portland clinker; it details a reliable quantification of the mineralogical composition of clinker obtained by X-Ray diffractometry combined with the Rietveld method (XRD/Rietveld); it fixed the chemical moduli to highlight the effect of alkali metals eliminating interference concerning the proportions of the clinker principal oxides. Lime Saturation Factor (100CaO / (2.8SiO_2+1.65Al_2O_3 + 0.35Fe_2O_3)), Silica Modulus (SiO_2/(Al_2O_3 + Fe_2O_3)), and Alumina Modulus (Al_2O_3/Fe_2O_3) were considered as chemical parameters [14]. The parameters, trends, and results observed in the thermodynamic modelling were experimentally validated based on the five belite clinker samples produced in the previous studies [3], [10].

3. Results and discussions

3.1. Clinker composition after cooling

Table 2 presents the predicted composition of the clinkers after cooling, calculated by thermodynamic modelling and obtained experimentally by XRD/Rietveld as reported in previous investigations [3], [10]. The reference sample results evidence the accuracy of thermodynamic modelling as a predictive method. Tricalcium silicate and calcium aluminium ferrite (Ca_x(Al,Fe)O_{x+3}) showed an absolute variation of at most 1.54 wt.% between the techniques, being within the error limit of the experimental method utilized (XRD/Rietveld) [15]. The dicalcium silicate (Ca_2SiO_4) varied by 4.75 wt.%. This difference can be attributed to minority phases modelled in thermodynamic calculations but not detected in XRD. C_2S is the most representative phase in belite clinker (60.5 wt.%), and, consequently, it receives the highest error associated with phases not quantified in XRD/Rietveld. Thermodynamic simulations assume maximum recrystallization of the melt phase during cooling. However, alterations in the clinker manufacturing process can modify the cooling conditions and promote the formation of non-crystalline phases and, therefore, are not detectable by XRD [16]. The decline of C_2S content in the presence

of 2.0 wt.% K_2O and 1.5 wt.% Na_2O was comparable to the experimental data, decreasing by about 6 and 12 wt.%, respectively. The Ca_3SiO_5 (C_3S) prediction presented approximate values with the same tendency to increase as higher alkali contents were added.

$Ca_x(Al,Fe)O_{x+3}$ comprises the sum of $C_3(A,F)$ and $C_2(A,F)$. It decreased as alkali metals were added and had a more significant effect on the Na-doped clinker. However, the experimental results of the doped samples differ from the modelled one, having considerable amounts of $Na_2Ca_8Al_6O_{18}$ (C_3A-o). Cubic tricalcium aluminate ($Ca_3Al_2O_6$) incorporates Na atoms, deforming the crystalline structure until it becomes orthorhombic [17]. C_3A-o is an undesirable compound in Portland clinker because, when combined with sulphates, it tends to promote the instant-setting effect of hydrated cement [18]. The difference between quantification by modelling and DRX of the doped samples suggests that $C_3(A,F)$ destabilization by incorporating Na and forming C_3A-o occurred predominantly in the experiments. It can also be attributed to the redistribution of Na in other minor phases verified in the modelling, decreasing the dopant availability for the composition of C_3A-o. The main compounds containing potassium were $KAlO_2$ and $K_2Ca_6Si_4O_{15}$. For sodium, in addition to C_3A-o, the modelled phases included $Na_2Ca_3Al_{16}O_{28}$, Na_2CaSiO_4, $NaAlSiO_4$, and $NaFeO_2$.

Table 2. Belite clinker composition at clinkering up to 1365 °C followed by rapid cooling obtained by thermodynamic modelling (Model.) and XRD/Rietveld (Exp.) [3], [10]. n.d.: not detected.

Composition (wt.%)	B		B 1.0K		B 2.0K		B 0.5Na		B 1.5Na	
	Model.	Exp.	Model.	Exp.	Model.	Exp.	Model.	Exp.	Model.	Exp.
Ca_2SiO_4	60.45	65.20	56.96	62.30	53.50	59.60	56.11	63.20	47.36	53.80
Ca_3SiO_5	14.74	13.20	18.12	15.40	21.32	17.60	18.21	14.90	25.01	20.60
$Ca_x(Al,Fe)O_{x+3}$	22.83	21.60	21.75	13.60	19.02	12.50	20.24	19.40	15.10	8.20
$Ca_3MgSi_2O_8$	0.07	n.d.	0.12	n.d.	0.00	n.d.	0.57	n.d.	0.55	n.d.
CaO	0.00	n.d.	0.00	0.35	0.88	n.d.	0.00	n.d.	0.00	n.d.
$Na_2Ca_8Al_6O_{18}$	0.85	n.d.	0.46	8.30	0.32	10.30	2.84	2.50	7.03	17.40
$Na_2Ca_3Al_{16}O_{28}$	0.29	n.d.	0.01	n.d.	0.00	n.d.	0.45	n.d.	0.75	n.d.
Na_2CaSiO_4	0.09	n.d.	0.25	n.d.	0.27	n.d.	0.61	n.d.	2.18	n.d.
$NaAlSiO_4$	0.00	n.d.	0.00	n.d.	0.00	n.d.	0.03	n.d.	0.10	n.d.
$NaFeO_2$	0.03	n.d.	0.01	n.d.	0.00	n.d.	0.05	n.d.	0.18	n.d.
$KAlO_2$	0.55	n.d.	2.04	n.d.	3.97	n.d.	0.46	n.d.	0.16	n.d.
$K_2Ca_6Si_4O_{15}$	0.02	n.d.	0.22	n.d.	0.61	n.d.	0.35	n.d.	1.25	n.d.
Others	0.07	n.d.	0.05	n.d.	0.11	n.d.	0.04	n.d.	0.17	n.d.
Melt	0.01	n.d.	0.01	n.d.	0.00	n.d.	0.04	n.d.	0.14	n.d.

3.2. Phase evolution during clinkering

Figure 1 shows the composition of belite clinkers during manufacturing, comprising heating from 1000 to 1365 °C and cooling until the maximum resolidification of the melt phase. Adding alkali metals increased the formation of C_3S and free CaO, reducing the C_2S content throughout the production. The C_3S content alteration is generally associated with modifying

the CaO/SiO$_2$ proportions in the clinker raw meal, besides the chemical moduli LSF, AM, and SM. However, all these parameters were fixed for the analysed samples (Table 1). In this context, the increase in free CaO was related to the destabilization of C$_3$(A,F) in the presence of K$_2$O and Na$_2$O. This effect was observed in previous investigations on alkali metals, in which C$_3$A was decreased in the dopped clinker [3], [9], [10].

C$_3$(A,F) destabilization provided free CaO to the system. Part of CaO was combined with C$_2$S in forming C$_3$S from 1300 °C onwards. The C$_3$(A,F) Al and Fe oxides then composed the melt phase, increasing its value throughout the production. The systems started from similar C$_2$S contents (70 ± 2 wt.%), which then reacted with free CaO to form C$_3$S and reach 60.4 wt.% (B), 53.5 wt.% (B2.0K) and 47.4 wt.% (B1.5Na) of C$_2$S after the rapid cooling. The decrease of C$_2$S by about 6 and 12 wt.% in the presence of 2.0 wt.% K$_2$O and 1.5 wt.% Na$_2$O, respectively, were reported in experimental results by Morsli et al. [3] and De la Torre et al. [10].

The C$_2$S evolution increased during the cooling step (1365 °C), corresponding to about 3 wt.% (B), 15 wt.% (B2.0K), and 8 wt% (B1.5Na). This change was associated with the recrystallization process, in which part of the CaO and SiO$_2$ dissolved in the melt phase resolidifies as C$_2$S α'. It is noteworthy that the alkali metals extended the temperature range of additional C$_2$S formation, occurring on cooling to 1120 °C (B), 1050 °C (B2.0K), and 1000 °C (B1.5Na).

Alkali co-processing reduced the C$_3$(A,F) stability in the clinker. For B2.0K, this decrease was associated with an increase in C$_2$(A,F) by about 3 wt.% and other complementary phases containing potassium, including KAlO$_2$, K$_2$Ca$_6$Si$_4$O$_{15}$, K$_2$CaSiO$_4$, K$_2$MgSiO$_4$, and K$_2$Ca$_2$Si$_2$O$_7$. Experimental studies on synthesizing K-doped clinkers reported potassium aluminate as a product of the clinkering and associated with silicates combined with K$_2$O [19]–[21]. In this sense, thermodynamic modelling corroborated the experimental analyses, presenting possible potassium-doped calcium silicates as minor phases.
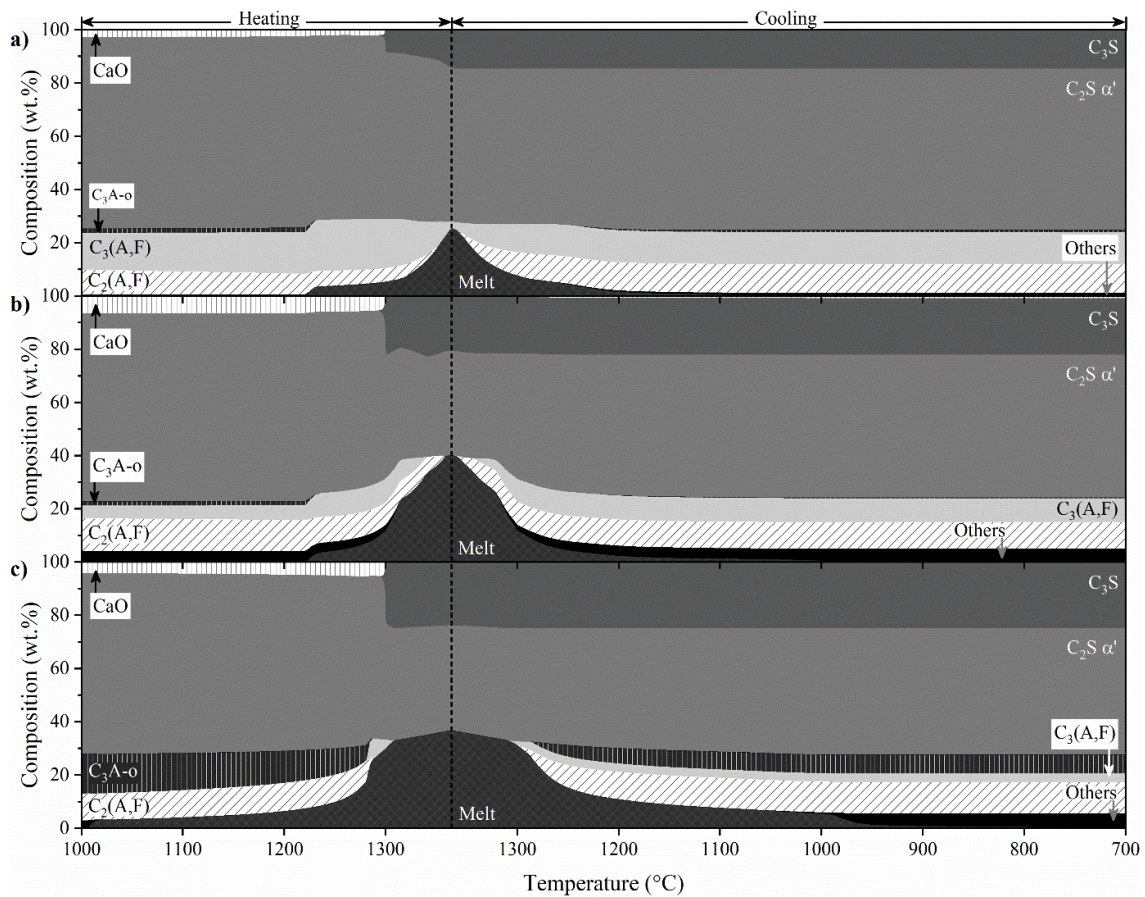

Fig. 1. Normalized mass distribution of belite clinker solid and melt phases during clinkering up to 1365 °C followed by rapid cooling (Scheil-Gulliver method) obtained by thermodynamic modelling. a) Reference (B), b) 2.0 wt.% K$_2$O (B2.0K), c) 1.5 wt.% Na$_2$O (B1.5Na).

Adding 1.5% Na enhanced C_3A-o in place of $C_3(A,F)$ up to about 1285 °C. From that point on, Na migrates to the melt fraction, and the Ca and Al atoms start to compose $C_3(A,F)$, which in turn is melted at 1300 °C. Although C_3A-o and $C_3(A,F)$ are not simultaneously stable during heating, the phases coexisted during cooling below 1285 °C. The phases are concurrent. Consequently, $C_3(A,F)$ partially formed from 1300 °C. At temperatures below 1285 °C, C_3A-o was gradually recrystallized, and the $C_3(A,F)$ formation stopped.

Although the stability of $C_2(A,F)$ was altered on heating, the alkali metals do not seem to affect the phase stability during cooling, reaching values similar at the end of production (11 ± 1 wt.%). However, the melting temperatures of this phase were altered, being exhausted in heating at 1352 °C (B), 1358 °C (B2.0K), and 1291 °C (B1.5Na). This behaviour may be associated with the change in melting point reported in previous studies on the effect of alkali metals on clinkering [2], [10].

In the reference sample, the melt phase developed from 1230 °C due to the complete melting of C_3A-o and partial melting of $C_2(A,F)$, reaching its maximum (26.17 wt.%) at the highest clinkering temperature (1365 °C). At this point, the system contained $C_3(A,F)$ (1.73 wt.%) as the only remaining aluminate. For B2.0K, although the system contained similar amounts of Al_2O_3 and Fe_2O_3, the amount of melt phase increased. Melt formation started with the decomposition of C_3A-o, followed by $KAlO_2$, $C_3(A,F)$, and $C_2(A,F)$, respectively. At 1365 °C, the system comprised calcium silicates (59.62 wt.%) and a melt phase (40.38 wt.%), which tended to recrystallize as the system cooled. Na notably altered the melt phase behaviour, starting at a lower temperature (1010 °C) as a result of the melting of Na_2CaSiO_4 and $K_2Ca_6Si_4O_{15}$, followed by the depletion of C_3A-o, $C_2(A,F)$, and $C_3(A,F)$ up to 1307 °C. The system then remained with the maximum melt phase (36.95 wt.%) up to 1365 °C. Changing the melt content from 26.17 wt.% (B) to 40.38 wt.% (B2.0K) and 36.95 wt.% (B1.5Na) may cause severe implications during manufacturing on an industrial scale. The liquid content in the clinker for OPC is generally limited to 22%, in order to avoid melting during clinkering and consequent adherence and damage to the refractory lining of the kilns [2]. However, it is noteworthy that, in addition to content, the viscosity of the melt phase also plays a crucial role in the stability of clinker nodules during manufacturing [1]. In general, the lower the melt phase viscosity, the lower the content limit needs to guarantee the stability requirements of the systems [1], [2].

3.3. Viscosity of the melt phase during clinkering

Figure 2 shows the viscosity evolution of the clinker melt during manufacturing. The results corroborate the range reported for ordinary clinker at the maximum firing temperature, reaching about 0.16 Pa.s [14], [22]. During heating, the maximum viscosity was reached at the onset of melt formation, reaching 0.56 (B and B2.0K at 1230 °C) and 1.39 Pa.s (B1.5Na at 1010 °C). This behaviour agrees with the findings of previous studies, which verified an increase in melt viscosity in Na-doped systems in the absence of SO_3 [23].
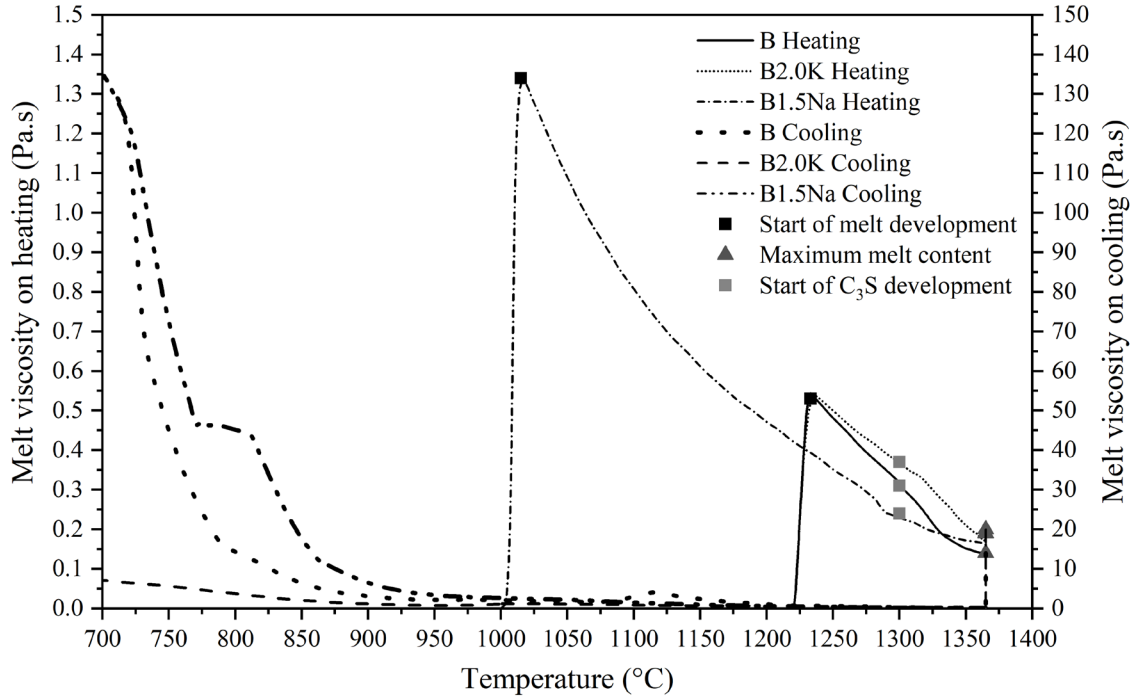
Fig. 2. Viscosity of melt phase during clinkering up to 1365 °C followed by rapid cooling obtained by thermodynamic modelling. a) Reference (B), b) 2.0 wt.% K_2O (B2.0K), c) 1.5 wt.% Na_2O (B1.5Na).

The starting point of melt phase development in a pure $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system was reported at 1338 °C when the mixture reached its eutectic point [14]. However, previous studies reported that impurities in the raw meal, including Na_2O, K_2O, MgO, and SO_3, could shift the eutectic point to 1280 °C [14]. The rise of the melt phase is a crucial parameter, as it delimits its degree of infiltration into the pores of the refractory lining of cement kilns, thickening the surface, altering the modulus of elasticity, and turning the lining brittle [22]. After the beginning of the liquid phase development at 1230 °C, the increase in temperature at 135 °C decreases the viscosity of the clinker liquid phase by 75% (B), 70% (B2.0K), and 60% (B1.5Na). It corroborates the previous studies that verified a 70% reduction in the liquid viscosity in this clinkering zone [14].

Previous investigations have reported that decreasing melt viscosity can improve CaO diffusion and its reaction with C_2S to form C_3S [1], [24]. For the analysed systems, the development of C_3S started when the viscosity reached the limit values of 0.31 (B), 0.37 (B2.0K), and 0.23 Pa.s (B1.5Na). The highest C_3S amount was reached at 1365 °C when the melt content was maximum, and the viscosity of the systems reached 0.15 ± 0.02 Pa.s. In this context, the viscosity was associated with the diffusion potential of elements in the melt phase and may indicate the necessary conditions for the development of the clinker compounds.

On cooling below 785 °C, the melt phase content of system B reduces sharply due to the solidification of $K_2Ca_6Si_4O_{15}$ and $KAlSiO_4$, promoting an increase in the viscosity rate. Similar behaviour occurs for B1.5Na after 915 °C, in which Na_2CaSiO_4 is crystallized. The system is then maintained at a constant viscosity, which is increased after 770 °C when $Ca(Al,Fe)_3O_{10}$ and Na_2MgSiO_4 are solidified. For the B2.0K system, the solidification of the phases is gradually distributed during cooling so that the melt phase viscosity remains below 10 Pa.s, although its entire content is solidified.

4. Conclusions

According to the results of this study, the following conclusions can be drawn:

Thermodynamic calculations allowed the accurate modelling of the belitic clinker composition. The modelling results agreed with the findings of previous experimental studies, which reported an increased melt viscosity and the decrease of C_2S by about 6 and 12 wt.% in the presence of 2.0 wt.% K_2O and 1.5 wt.% Na_2O. The modelling differed from the experimental results regarding the $CaO-Al_2O_3-Fe_2O_3$ phases, mainly due to the simulation of new compounds containing dopants not quantified by the experimental method.

The co-processing of K_2O and Na_2O in clinker extended the temperature range of dicalcium silicate formation on cooling and increased the tricalcium silicate content. $Ca_3(Al,Fe)O_6$ was destabilized in Na-doped clinkers, resulting in orthorhombic tricalcium aluminate (C3A-o) and minor phases, including $Na_2Ca_3Al_{16}O_{28}$, Na_2CaSiO_4, $NaAlSiO_4$, Na_2MgSiO_4, $NaFeO_2$, and Na_2SiO_3. For K-doped samples, it increased $Ca_2(Al,Fe)O_5$ and potassium silicates as minor phases ($K_2Ca_6Si_4O_{15}$, K_2CaSiO_4, K_2MgSiO_4, and $K_2Ca_2Si_2O_7$).

The viscosity of the melt phase is related to the mobility degree of the oxides in the liquid. It represents the diffusion potential of the elements in forming the clinker phases. In this sense, the results suggest that viscosity indicates the necessary conditions for forming clinker compounds. The alkali metals enhanced the highest melt content and decreased its viscosity at the maximum clinkering temperature (1365 °C). The highest C_3S content was promoted for all the samples when the melt viscosity reached around 0.15 Pa.s, suggesting that viscosity may play a crucial role in clinker mineralogy during manufacture.

Thermodynamic modelling allowed the understanding of the phase assemblage evolution during the manufacture of belite clinker doped with alkali metals. However, additional studies are needed to investigate the effect of other classes of impurities from alternative materials co-processed in the industry and the influence of melt viscosity on phase transitions during clinker manufacturing.

Acknowledgements

References

[1] P. Hewlett and M. Liska, *Lea's chemistry of cement and concrete,* 5th ed. Oxford: Butterworth-Heinemann (Elsevier), 2017. doi: 10.1016/C2013-0-19325-7.

[2] J. I. Bhatty, F. M. Miller, and S. H. Kosmatka, *Innovations in Portland cement manufacturing,* 2nd ed. Skokie: Portland Cement Association, 2011.

[3] K. Morsli, Á. G. De La Torre, S. Stöber, A. J. M. Cuberos, M. Zahir, and M. A. G. Aranda, "Quantitative phase analysis of laboratory-active belite clinkers by synchrotron powder diffraction," *Journal of the American Ceramic Society,* vol. 90, no. 10, pp. 3205–3212, Oct. 2007, doi: 10.1111/j.1551-2916.2007.01870.x.

[4] S. P. Deolalkar, *Designing Green Cement Plants.* Oxford: Butterworth-Heinemann (Elsevier), 2016. doi: 10.1016/c2014-0-00783-6.

[5] Y. Zhang, J. Wang, L. Zhang, C. Li, H. Jiang, X. Ba, D. Hou, "Study on the preparation and properties of high-belite cementitious materials from shield slag and calcium carbide slag," *Constr Build Mater,* vol. 355, Nov. 2022, doi: 10.1016/j.conbuildmat.2022.129082.

[6] W. Kurdowski, *Cement and concrete chemistry.* Springer, 2014. doi: 10.1007/978-94-007-7945-7.

[7] P. K. Mehta and P. J. M. Monteiro, *Concrete: Microstructure, properties and materials,* 4th ed. New York: McGraw-Hill Professional Publishing, 2013.

[8] S. Krishnan, F. Zunino, S. Bishnoi, and K. Scrivener, "Characterisation and hydration kinetics of β-C2S synthesised with K2SO4 as dopant," *Cem Concr Res,* vol. 167, May 2023, doi: 10.1016/j.cemconres.2023.107119.

[9] A. Gies and D. Knöfel, "Influence of sulfur on the composition of belite-rich cement clinkers an the technological properties of the resulting cements," *Cem Concr Res,* vol. 17, pp. 317–328, 1987, doi: 10.1016/0008-8846(87)90114-1.

[10] Á. G. De La Torre, K. Morsli, M. Zahir, and M. A. G. Aranda, "In situ synchrotron powder diffraction study of active belite clinkers," *J Appl Crystallogr,* vol. 40, pp. 999–1007, Nov. 2007, doi: 10.1107/S0021889807042379.

[11] C.W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. E. Gheribi, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M-A. V. Ende, "Reprint of: FactSage thermochemical software and databases, 2010–2016," *CALPHAD,* vol. 55, pp. 1–19, 2016, doi: 10.1016/j.calphad.2016.07.004.

[12] B. Hökfors, D. Boström, E. Viggh, and R. Backman, "On the phase chemistry of Portland cement clinker," *Advances in Cement Research,* vol. 27, no. 1, pp. 50–60, Jan. 2015, doi: 10.1680/adcr.13.00071.

[13] T. Hanein, F. P. Glasser, and M. N. Bannerman, "Thermodynamic data for cement clinkering," *Cem Concr Res,* vol. 132, Jun. 2020, doi: 10.1016/j.cemconres.2020.106043.

[14] P. Sengupta, *Refractories for the cement industry.* Springer International Publishing, 2020. doi: 10.1007/978-3-030-21340-4.

[15] P. R. Matos, J. S. Andrade Neto, R. D. Sakata, A. P. Kirchheim, E. D. Rodríguez, and C. E. M. Campos, "Strategies for XRD quantitative phase analysis of ordinary and blended Portland cements," *Cem Concr Compos,* vol. 131, Aug. 2022, doi: 10.1016/j.cemconcomp.2022.104571.

[16] P. M. Suherman, A. van Riessen, B. O'Connor, D. Li, D. Bolton, and H. Fairhurst, "Determination of amorphous phase levels in Portland cement clinker," *Powder Diffr,* vol. 17, no. 3, pp. 178–185, Sep. 2002, doi: 10.1154/1.1471518.

[17] A. P. Kirchheim, D. C. Dal Molin, P. Fischer, A. H. Emwas, J. L. Provis, and P. J. M. Monteiro, "Real-time high-resolution X-ray imaging and nuclear magnetic resonance study of the hydration of pure and Na-doped C3A in the presence of sulfates," *Inorg Chem,* vol. 50, pp. 1203–1212, Feb. 2011, doi: 10.1021/ic101460z.

[18] A. P. Kirchheim, V. Fernàndez-Altable, P. J. M. Monteiro, D. C. C. Dal Molin, and I. Casanova, "Analysis of cubic and orthorhombic C3A hydration in presence of gypsum and lime," *J Mater Sci,* vol. 44, pp. 2038–2045, Apr. 2009, doi: 10.1007/s10853-009-3292-3.

[19] E. Atallah, F. Defoort, A. Pisch, and C. Dupont, "Thermodynamic equilibrium approach to predict the inorganic interactions of ash from biomass and their mixtures: A critical assessment," *Fuel Processing Technology,* vol. 235, Oct. 2022, doi: 10.1016/j.fuproc.2022.107369.

[20] B. Samet and S. L. Sarkar, "The influence of calcium sulfate form on the initial hydration of clinkers containing different alkali combinations," *Cem Concr Res,* vol. 27, no. 3, pp. 369–380, 1997, doi: 10.1016/S0008-8846(97)00030-6.

[21] L. Kacimi, M. Cyr, and P. Clastres, "Synthesis of α'L-C2S cement from fly-ash using the hydrothermal method at low temperature and atmospheric pressure," *J Hazard Mater,* vol. 181, no. 1–3, pp. 593–601, Sep. 2010, doi: 10.1016/j.jhazmat.2010.05.054.

[22] M. A. Muhammed, A. A.-H. A. Amir, and F. A. Shukur, "Corrosion mechanism of refractory bricks lining the cement kiln," *The Iraqi Journal for Mechanical and Material Engineering,* vol. 9, no. 2, 2009.

[23] H. F. W. Taylor, *Cement chemistry,* 2nd ed. London: Thomas Telford, 1997.

[24] Y. Hu, W. Li, S. Ma, Q. Wang, H. Zou, and X. Shen, "The composition and performance of alite-ye'elimite clinker produced at 1300 °C," *Cem Concr Res,* vol. 107, pp. 41–48, May 2018, doi: 10.1016/j.cemconres.2018.02.009.