Use of Bauxite Residue as Raw Material for Low-Carbon Ferrite-Belite Cements: Prediction of the Crystalline Phases Using Thermodynamic Modelling

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Abstract

In this study, thermodynamic modelling was carried out to predict the crystalline phase and provides a first stepping-stone to incorporate high amounts of BR in low-CO_2 cement manufacturing. As raw materials, 35-66 wt% bauxite residue (BR) in combination with 33-64 wt% of limestone (LS) and 1-10 wt% of kaolin (K) were chosen as raw materials for hydraulic low-CO_2 ferrite-belite (cement) clinkers. Thermodynamic modelling at a temperature of 1260°C was selected to predict the content of the crystalline phases for the different clinker composition, using the major oxides (i.e., CaO, SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and Na_2O). Increasing the BR content (decreasing LS content) led to high amounts of perovskite, gehlenite, iron-rich ferrites, and $CaO{\cdot}Fe_2O_3$ phases. Some of these crystalline phases i.e., perovskite, rankinite and gehlenite are hydraulically inactive; their content is thus aimed to be low. With increasing LS content (decreasing BR content), hydraulic phases such as belites, aluminium-rich ferrite phases, calcium aluminates and free lime dominate the clinker phase assemblage. The highest content of rankinite occurred at a similar LS and BR content of 45-50 wt%. In case of ferrite phases, if the ratio of alumina to iron oxide is equal to or greater than 1, the phases become more hydraulically active in comparison to ratios less than 1. In this study, the ratio of iron oxide to alumina reduces as the LS content is increased from 33-64 wt% and BR content decreased from 66-35 wt%, thus increasing the reactivity of ferrites. Moreover, at a LS content between 55-60 wt% and BR content varying from 35-42 wt%, equal proportions of iron oxide and alumina were obtained for ferrite phases which has positive impact on reactivity. Based on the thermodynamic calculation, the optimum raw mix to develop a favourable low-carbon emission ferrite-belite cement consists of a LS content of 57 wt%, a BR content of 38 wt% and a K content of 5 wt%. This mix design leads to reactive belites and ferrite, of 24 wt% and 63 wt%, respectively, with some minor inactive perovskite phases of about 3 wt%. Overall, this study provides a first stepping-stone to incorporate high amounts of BR in low-CO_2 cement manufacturing.

Keywords: bauxite residue, ferrite-belite cement, crystalline phases, thermodynamic modelling.

1. Introduction

The preservation of the environment, energy, and natural resources for future generations is one of the most pressing global challenges. The cement industry consumes a lot of energy and emits significant volumes of CO_2, which contribute to global warming [1]. The cement industry contributes around 8 % of anthropogenic CO_2 emissions through limestone calcination, fuel burning in kilns, and high energy usage of raw mill for grinding leading to CO_2 emissions from electric consumption [2]. One strategy for reducing CO_2 emissions in the cement manufacturing process is to minimize the limestone content in the cement. Cement with a reduced lime content results in a decrease in CO_2 emissions associated with the calcination of limestone [3]. Reduced lime content with alternative cementitious materials can result in a decrease in the required calcination or sintering temperature in the kiln for the manufacturing [4], but also leads to a reduction of tricalcium silicate formation ($Ca_3Si_2O_7$), which is the most reactive hydraulic phase in conventional cements. Dicalcium silicate (Ca_2SiO_4) crystallizes at a lower temperature than $Ca_3Si_2O_7$, however its reactivity is lower than that of $Ca_3Si_2O_7$. Similarly, ferrite phases of high iron cement clinker form at a much lower temperature than the calcium silicates of the Portland cement clinker[5]. The reactivity of ferrites depends on the Al/Fe ratio in the structure and is known that the higher the Al/Fe ratio, the higher the reactivity [6]. Moreover, ferrites have been found to be more reactive in iron-rich cement in comparison to OPC at a low sintering temperature, due to the absence of C_3A phase resulting in no competition between the two phases for reactivity with calcium sulphate to form ettringite, a hydration product of cement [7]. Such type of low-CO_2 iron-rich cements whose clinker phase assemblage is mainly composed of belites, and ferrites also allows for the employment of secondary raw materials, typically industrial side-streams, which would otherwise find little or no valorization.

Currently, iron-rich solid wastes are plentiful in a variety of metallurgical, chemical, and mining industries. The accumulated volume of these wastes, the bauxite residue (waste product of the Bayer process) being such a case, poses a big challenge for the industry with respect to managing them. Their possible incorporation in the manufacturing of high-iron cements[8, 9], hydraulic or alkali-activated [10], would be a breakthrough as it will offer a tangible solution [11]. Some studies on ferrite-belite cements have been conducted in this area already in the past [9]. The authors reported that the CaO-Fe_2O_3 and CaO-Al_2O_3-Fe_2O_3 phases are the primary phases of the high iron cement clinker, and that these phases are responsible for the cement's hydraulic properties and strength. However, progress in the manufacturing of high iron content ferrite-belite cement using bauxite residue have been slow since the dominant ferritic phases in the clinker hydrate slowly to develop mechanical strength. Nevertheless, such phases are preferred in contrast to the hydraulically inactive phases which do not contribute to the strength of cement at any extent. In the present work, a set of three component raw meals, all containing limestone, kaolin and bauxite residue were incorporated to predict the crystalline phase of the iron-rich cement using thermodynamic modelling. Prediction of these crystalline phases from thermodynamic modelling would provide a pre-assessment for the manufacturers on what phases are likely to form and how much BR can be incorporated.

2. Thermodynamic Calculations

The thermodynamic calculations were performed by FactSage 8.0 [12]. The databases *FToxid* (oxide database for slags, glasses, ceramics and refractories) and *FactPS* (pure substance database) were employed for stoichiometry solids, solutions and gases respectively. In the equilibrium calculation mode, the composition of the clinker in terms of their oxides were provided as the input data. These oxides were calculated from the chemical composition and the proportion of the raw materials chosen, to mimic the low-CO_2 ferrite-belite cements. The chemical composition of BR (content between 35-66 wt%) by Mytilineos S.A was considered in the calculations along with commercially available limestone (33-64 wt%) and kaolin (1-10 wt%). The chemical composition of the raw materials was obtained by quantitative X-ray fluorescence, listed in Table 1.

Table 1. Chemical composition of raw materials (%)

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	TiO_2	MgO	Na_2O	K_2O	P_2O_5	Cl	LOI
LS	56	0.1	0	0	0	0	0.3	0	0	0	0	43.4
BR	9.0	8.2	17.5	42.5	0.4	5.8	0.1	4.2	0.1	0.1	0.1	10
K	0	45.1	39.2	0.2	0	1.6	0	0	0	0	0	13.8

The next step was the selection of the solid solutions along with pure solids and gases. An *FToxid SlagA* oxide melt was chosen as the target phase in the non-equilibrium cooling, also known as Scheil-Gulliver solidification [13]. Thus, mimicking the cooling of the clinker after sintering at high temperature. In the case of aluminates, ferrites, and alumina-ferrites, two solutions are incorporated in the database known as $C_2(A, F)$ and $C_3(A, F)$ and for the belite phase, solutions of the belite phases such as α-C_2S and α'-C_2S were selected for the non-equilibrium calculation. In the Scheil-Gulliver cooling menu, a cooling step of 25°C was chosen. In the end, the clinkering temperature of 1260°C and the final terminating temperature of 700°C is provided as input in the final condition menu box. After pressing calculate option in the software, the output is provided, listing the quantification data of mineral phases formed at each temperature during cooling. Figure 1 represents the algorithm of the thermodynamic calculation.

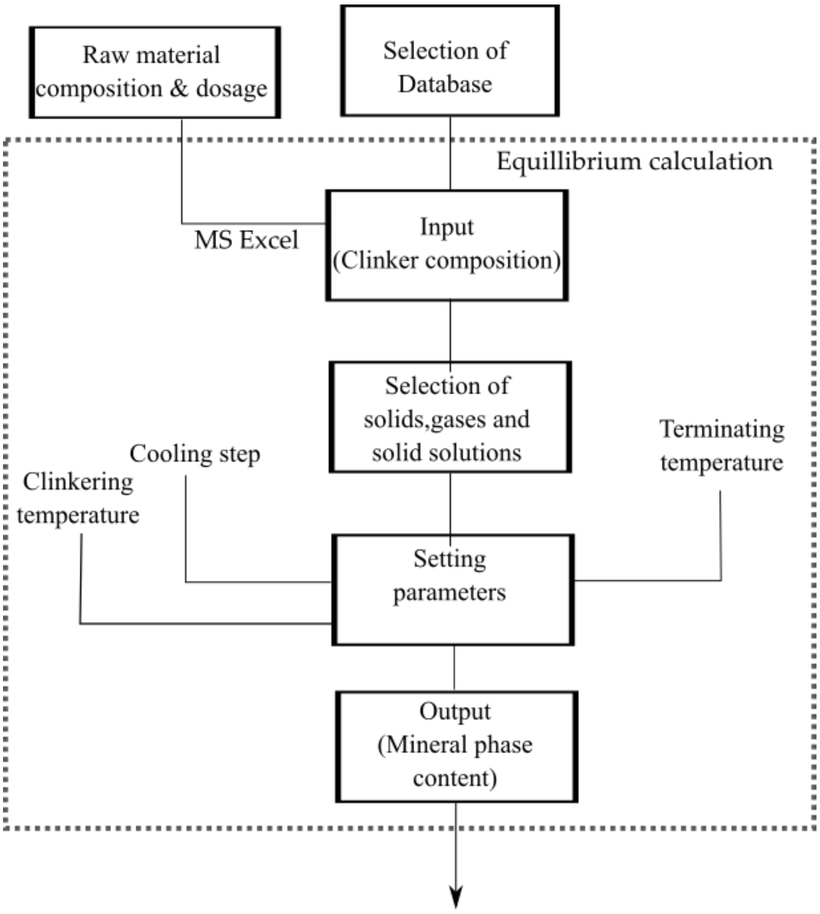
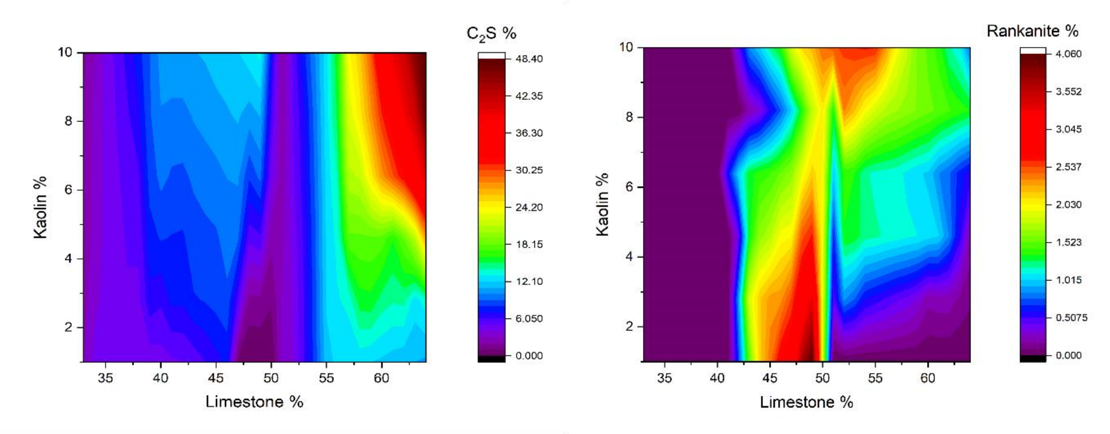


Figure 1. Algorithm for thermodynamic calculation in FactSage

3. Results and Discussions

After modelling the sintering at a target temperature and commencing Scheil-Gulliver cooling to 700°C, the crystalline mineral phases of the three component raw meal combinations were determined by phase equilibria calculations in FactSage. The crystalline phases that were formed in the thermodynamic calculations included – Ca_2SiO_4 (belite), $Ca_2(Fe_{2-x}Al_x)O_5$ (ferrite), $CaO{\cdot}Fe_2O_3$, $Ca_2Al_2SiO_7$ (gehlenite), $Ca_3Si_2O_7$ (rankinite), $Ca_3Al_2O_6$ and lime (CaO) for the raw meal consisting of LS, BR, and kaolin. According to Figure 2a, the percentage of Ca_2SiO_4 increased with increasing LS and kaolin content. The maximum amount of Ca_2SiO_4 reported was 48 wt% at a LS content of 63 wt%, kaolin content of 10 wt% and BR content of 27 wt%. This is due to the increased concentration of silica and calcium oxide from the kaolin and limestone respectively, that results in the formation of higher amount of belite phase. Meanwhile, the minimum content of Ca_2SiO_4 was obtained at an LS content varying between 48-50 % and kaolin content in the range of 1-10 %. A possible explanation to this phenomenon can be attributed to the presence of other high concentration phase composed of calcium oxide and silica i.e., the rankinite phase, as shown in Figure 2b. On the contrary, the content of rankinite in the clinker fluctuated with increasing LS content. Initially, no rankinite were observed for LS content up to 41 % and kaolin content between 1-10 % due to the higher demand of calcium oxide and silica by the corresponding phase. However, as the LS content increased from 45 to 50%, maximum rankinite of 4 % were reported for kaolin content between 1-6%. Nevertheless, beyond 50 % of LS content, the rankinite phases decomposes due to the accelerated formation of wollastonite for higher CaO/SiO_2 ratio with increased LS content [14]. In other words, rankinite transforms into wollastonite for higher LS content thus increasing reactivity.

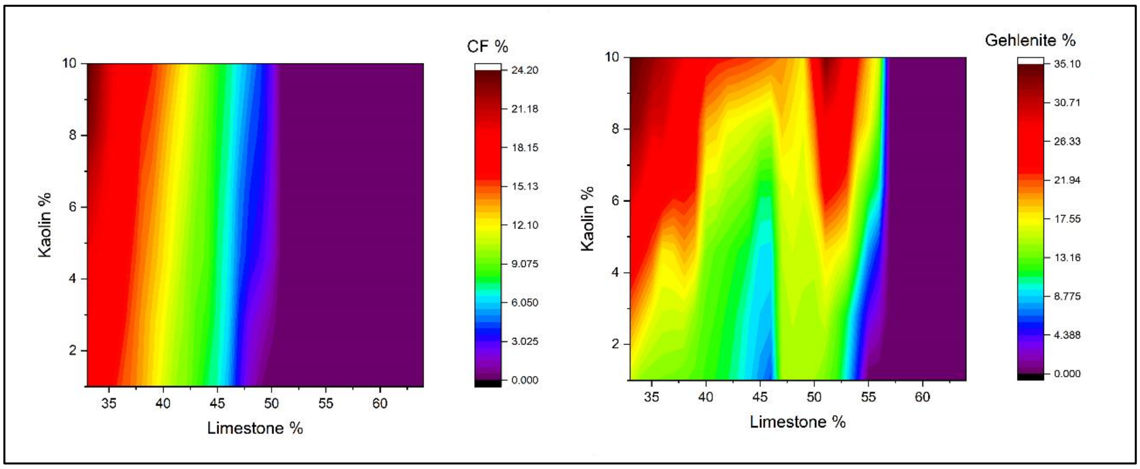


(a) (b)

Figure 2. (a) prediction of belite and (b) rankinite phase based on limestone-kaolin-bauxite residue composition by thermodynamic modelling (Ca_2SiO_4 and $Ca_3Si_2O_7$ abbreviated as C_2S and rankinite).

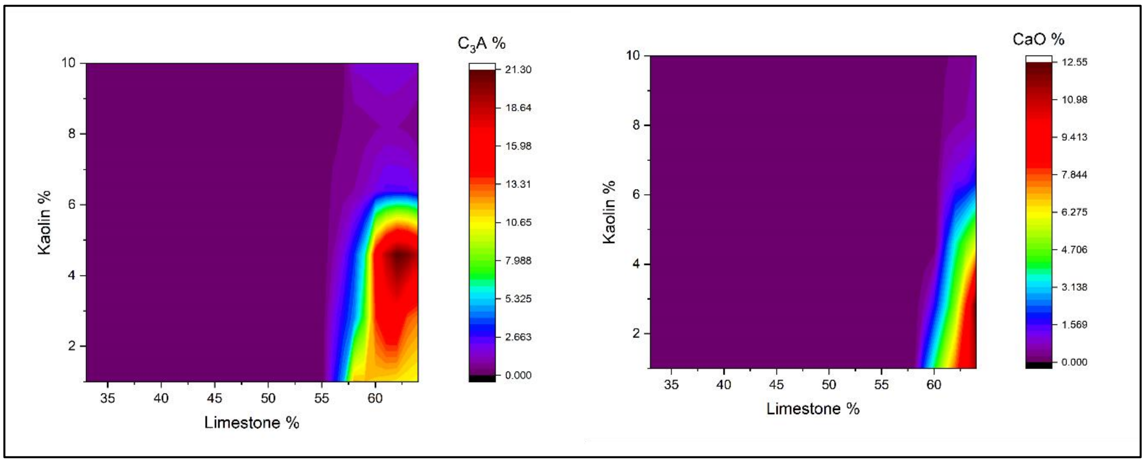
High content of bauxite residue in the raw meal led to the presence of gehlenite and $CaO\cdot Fe_2O_3$ at high proportions. For instance, the bauxite residue content varying between 55-62 wt% at a LS content of 35 wt% reported a maximum percentage of hydraulically inactive gehlenite and reactive $CaO\cdot Fe_2O_3$ phase corresponding to 35 % and 24 % respectively in the clinker. This outcome could be caused by the presence of high dosage of the bauxite residue in the clinker containing Al_2O_3 and Fe_2O_3. The formation of $CaO\cdot Fe_2O_3$ depends more on the bauxite residue content in contrast to that of gehlenite (Figure 3) due to the percentage of $CaO\cdot Fe_2O_3$ phase gets reduced with increasing LS content and decreasing BR content. In contrast, for gehlenite, significant amount of these phases is formed even at a higher LS content between 50-55 wt% but at a kaolin content of 6-10 wt%. Thus, the formation of gehlenite depends on the kaolin content.

For raw meal mixtures with high LS content i.e., LS $\geq$ 60 wt%, the presence of C_3A and lime could also be identified along with belite and ferrite. In the case of $Ca_3Al_2O_6$, the highest percentage of 21 wt% was found for a LS content of 63 wt% and a BR content of 42 wt%. Similarly, the amount of lime increased for a LS content higher than 60 wt% and reaching up to levels beyond 12%, as shown in Figure 4. Some of the lime formation could be excess due to the reduced melt formation at a lower clinkering temperature (1260°C) with increasing LS content. However at higher clinkering temperature (around 1400°C) , most of the lime present reacts with solid solution of belite in the melt, leading to the formation of Ca_3SiO_5 (hydraulic active phase) which doesn't exist in our case [15]. The presence of free lime can be detrimental to the cement since it reacts with water, significantly reducing the performance of the cement [16]. Thus, a higher clinkering temperature would be required to increase the lime content in the melt and reduce the free lime content [15].



(a) (b)

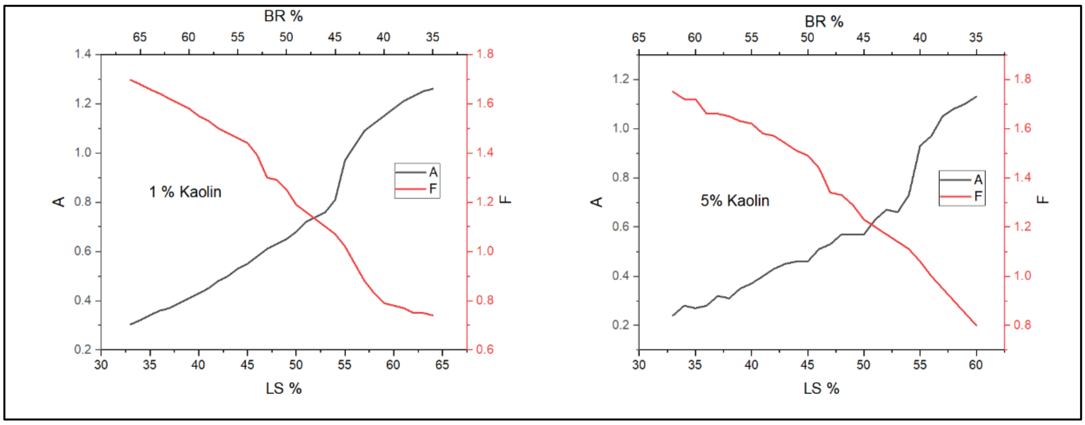
Figure 3. (a) prediction of $CaO \cdot Fe_2O_3$ and (b) Gehlenite phase based on limestone-kaolin-bauxite residue composition by thermodynamic modelling ($CaO \cdot Fe_2O_3$ abbreviated as CF).



(a) (b)

Figure 4. (a) prediction of $Ca_3Al_2O_6$ and (b) CaO based on limestone-kaolin-bauxite residue composition by thermodynamic modelling ($Ca_3Al_2O_6$ abbreviated as C_3A) .

The ferrite $Ca_2(Fe_{2-x}Al_x)O_5$ in the ferrite-belite clinkers have a varying Al/Fe ratio i.e., as LS content increases and BR content decreases, the ferrite becomes enriched in alumina since the content of Al_2O_3 is increased. In terms of change in the kaolin composition, results indicate that for significant change in the kaolin content (1 % and 5 % in this case), the change in the content of Fe_2O_3 and Al_2O_3 in the ferrite phase is minute, as shown in Figure 5. This indicates that the ratio Fe_2O_3/Al_2O_3 in the ferrite phase is dependent on the type and quantity of BR added to the raw feed, in contrast to the change in kaolin composition, which had a minor effect on the ratio of Fe_2O_3/Al_2O_3. Hence, the type of BR incorporated can influence the reactivity of ferrites in the cement.



(a) (b)

Figure 5. (a) stoichiometry of A and F in $Ca_2(Fe_{2-x}Al_x)O_5$ phase at 1% kaolin and (b) 5% kaolin. Here A and F abbreviates to Al_2O_3 and Fe_2O_3, respectively.

Figure 6 displays the percentage of calcium alumina-ferrites formed based on the dosage of raw material constituents. It was revealed that the maximum percentage of ferrite (74%) was obtained for LS content of 55 wt% and a BR content of 44 wt%. However, for lower LS content below 40 wt% and BR content between 54-60 wt%, the ferrite content reduced to less than 30 wt% due to the minor amount of CaO present in the clinker, leading to the presence of unreacted iron-rich crystalline minerals from the BR such as hematite.

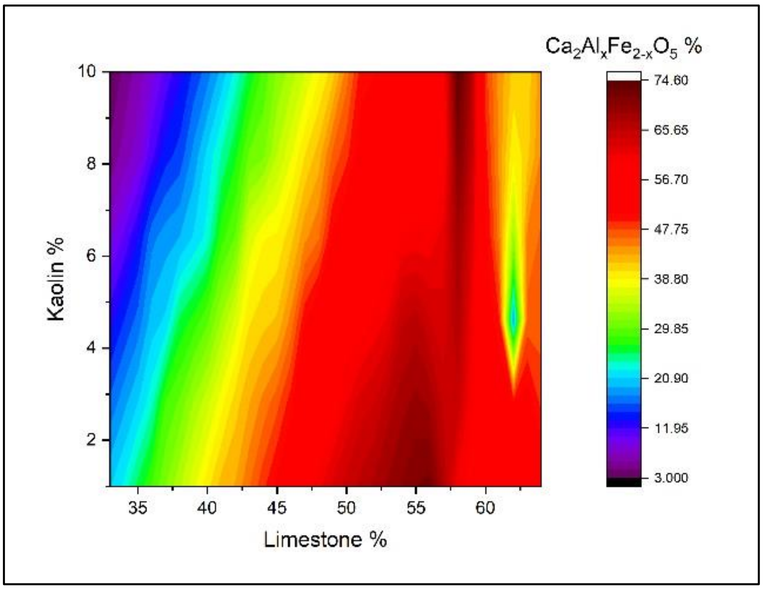


Figure 6. Prediction of $Ca_2(Fe_{2-x}Al_x)O_5$ based on limestone-kaolin-bauxite residue composition by thermodynamic modelling.

Overall, to develop a low-CO_2 ferrite-belite cements, certain crystalline hydraulic inactive phases will coexist with the hydraulically active phases. However, the proportions of these inactive phases can be minimized by selecting the correct proportion of the raw materials. For instance, at a higher LS content beyond 55%, the content of unreactive phases such as rankinite and gehlenite decreases. Nevertheless, a higher LS content would also lead to presence of free lime which is detrimental to cement and may not form the reactive Ca_3SiO_5 when operating at lower sintering temperature. Hence, to aim an optimum mixture for such cement would depend on the correct dosage of the raw materials. In this case, LS content of 57 wt%, a BR content of 38 wt% and K content of 5 wt% would be favorable as these clinker composition forms majority of belites and ferrites without any presence of free lime.

4. Conclusion

The types of crystalline phases formed depend on the composition of the ferrite-belite clinker incorporated in the thermodynamic calculations. Prediction of these crystalline phases provides an estimate on the major phases formed that are responsible for the reactivity and the mechanical properties of these type of cement. Thus, these calculations would assist the cement producers to check what phases to expect when incorporating high amounts of BR. Based on the thermodynamic calculation, to develop a favourable low-carbon emission ferrite-belite cement, the composition of the raw mix consists of a LS content of 57 wt%, BR content of 38 wt% and K content of 5 wt%. This mix design leads to reactive belites (responsible for the later age strength in cements) and ferrite (Al/Fe equal to 1), of 24 wt% and 63 wt%, respectively with some minor hydraulic inactive perovskite phases of about 3 wt%. These selected mixtures will be further investigated for experimental analysis to confirm the reliability of thermodynamic calculations and to assess the reactivity and mechanical properties. Moreover, the existing clinker mix composition require less limestone due to the replacement of bauxite residue in the cement clinker, leading to the valorization of bauxite residue in building materials at bulk.

5. References

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