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

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

1. Juenger, M.C.G., et al., Advances in alternative cementitious binders. Cement and concrete research, 2011. 41(12): p. 1232-1243.
2. Andrew, R.M., Global CO_2 emissions from cement production. Earth Syst. Sci. Data, 2018. 10(1): p. 195-217.
3. Iacobescu, R.I., et al., Hydraulic and leaching behaviour of belite cements produced with electric arc furnace steel slag as raw material. Ceramics-Silikaty, 2013. 57(2): p. 126--132.
4. Lawrence, C.D., 9 - The Production of Low-Energy Cements, in Lea's Chemistry of Cement and Concrete (Fourth Edition), P.C. Hewlett, Editor. 1998, Butterworth-Heinemann: Oxford. p. 421-470.
5. Nayak, B., Process for manufacturing of high iron hydraulic cement clinker, U.S.P.a.T. Office, Editor. 2004, Council of Scientific and Industrial Research: India.
6. Wang, H., D. De Leon, and H. Farzam, C_4AF Reactivity-Chemistry and Hydration of Industrial Cement. ACI Materials Journal, 2014. 111(2): p. 201-210.
7. Sharp, J.H., C.D. Lawrence, and R. Yang, Calcium sulfoaluminate cements—low-energy cements, special cements or what? Advances in Cement Research, 1999. 11(1): p. 3-13.
8. Hertel, T., et al., Boosting the use of bauxite residue (red mud) in cement - Production of an Fe-rich calciumsulfoaluminate-ferrite clinker and characterisation of the hydration. Cement and Concrete Research, 2021. 145: p. 106463.
9. Arino Montoya, D., et al. Low-Carbon Footprint Cements Incorporating High Volumes of Bauxite Residue. in Proceedings of 35th International ICSOBA Conference. 2017. Hamburg, Germany.
10. Hertel, T. and Y. Pontikes, Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud) – Putting things in perspective. Journal of Cleaner Production, 2020. 258: p. 120610.
11. Pontikes, Y. and G.N. Angelopoulos, Bauxite residue in cement and cementitious applications: Current status and a possible way forward. Resources, Conservation and Recycling, 2013. 73: p. 53-63.12. Bale, C.W., et al., FactSage thermochemical software and databases. Calphad, 2002. 26(2): p. 189-228.
12. Gulliver, G.H., The quantitative effect of rapid cooling upon the constitution of binary alloys. J. Inst. Met., 2021. 9.

13. Tajuelo Rodriguez, E., et al., Thermal stability of C-S-H phases and applicability of Richardson and Groves' and Richardson C-(A)-S-H(I) models to synthetic C-S-H. Cement and Concrete Research, 2017. 93: p. 45-56.
14. Ariño Montoya, D., et al., Revisiting the iron-rich “ordinary Portland cement” towards valorisation of wastes: study of Fe-to-Al ratio on the clinker production and the hydration reaction. Materials and Structures, 2021. 54(1): p. 30.
15. Kaewmanee, K., et al. (2013). "Effect of free lime content on properties of cement–fly ash mixtures." Construction and Building Materials 38: 829-836.