

Formulation of Bogue Equations from Thermodynamic Modelling for Low-Carbon Dioxide Ferrite-Belite Clinkers [†]

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Abstract: In this study, limestone (LS), kaolin (K) and bauxite residue (BR) were considered as potential raw meal ingredients for the preparation of ferrite-belite (cement) clinkers. A forecast of the mineralogical composition for the different clinker composition, based on the major oxides, i.e., CaO (C), SiO₂ (S), Al₂O₃ (A) and Fe₂O₃ (F) was obtained using thermodynamic modelling (FactSage). A phase field schematic representation was established for the three-component raw meal. The data obtained therein were used to compute the Bogue equations for the ferrite-belite cements. Based on this assumption, i.e., only four simultaneous linear equations each containing four different variables (crystalline phases) were used to formulate Bogue type equations. It was established that with increasing LS content from 33 wt% to 64 wt% and BR content decreasing from 66 wt% to 35 wt%, CF was only present at an LS content between 33–47%, followed by gehlenite up to LS content of 53% and rankinite at a LS content of about 55 wt%. Moreover, C₃A and lime were present in place of gehlenite and rankinite beyond LS content of 55 wt%. However, the belite and ferrite phases remained present throughout the entire clinker composition. Overall, this study provides the basic understanding required for the development of low carbon ferrite-belite clinkers.

Keywords: bauxite residue; clinker; thermodynamic modelling; ferrite-belite cement; bogue equations; crystalline phases



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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 CO₂, which contribute to global warming [1]. The cement industry contributes around 8% of anthropogenic CO₂ emissions through limestone calcination, fuel burning in kilns, and high energy usage of raw mill for grinding leading to CO₂ emissions from electric consumption [2]. One strategy for reducing CO₂ 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 CO₂ 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 in tricalcium silicate formation (C₃S), which is the most reactive hydraulic phase in conventional cements. Dicalcium silicate (C₂S) crystallizes at a lower temperature than C₃S; however, its reactivity is lower than that of C₃S. 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 (AFt) phases [7]. Such types of low- CO_2 iron-rich cements whose clinker phase assemblage are mainly composed of belites, and ferrites also allows for the employment of secondary raw materials, typically industrial side-streams, in the manufacturing, 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 there 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. Hence, to develop a better mix design and control the quantity of the desired phases in the cement clinker, a calculation tool known as Bogue equations using the Taylor's method can be implemented [12]. Currently, a Bogue equation calculation tool, which is widely used by the industry to determine the clinker mineral content for other cement types, is lacking for this type of cement. In the present work, a set of three component raw meals, all containing limestone, kaolin and bauxite residue were incorporated to compute the modified Bogue formulations from the data obtained by thermodynamic modelling calculations (software package "FactSage" (GTT-Technologies, Aachen, Germany), predicting the phase assemblages. These phase assemblages were represented in a form of phase field schematic representation depicting the crystalline phases of the ferrite-belite clinker in dependence of the raw meal composition.

2. Materials and Methods

2.1. Experimental Method and Thermodynamic Calculation

The oxide compositions of the raw materials were derived using quantitative X-ray fluorescence, as shown in Table 1. The chemical composition of the BR from Mytilineos S.A. and the composition of commercially available limestone and kaolin were adapted for thermodynamic calculation. The loss on ignition was determined using thermal analysis. The data were incorporated in the thermochemical software package FactSage 8.0. (GTT-Technologies, Aachen, Germany) The databases *FToxid* and *FactPS* [13] were incorporated to model and predict the clinker phases formed after Scheil–Gulliver solidification from a selected clinkering temperature of 1260 °C and 1 atm of pressure.

Table 1. Chemical composition of raw materials (wt%) included in thermodynamic calculation.

	Limestone	Bauxite Residue	Kaolin
CaO	56.00	9.07	0.03
SiO ₂	0.18	8.20	45.10
Al ₂ O ₃	0.03	17.50	39.20
Fe ₂ O ₃	0.04	42.50	0.21
SO ₃	0.00	0.41	0.03
TiO ₂	0.00	5.87	1.66
MgO	0.32	0.16	0.06
Na ₂ O	0.00	4.29	0.03
K ₂ O	0.00	0.12	0.02
P ₂ O ₅	0.00	0.10	0.00
Cl	0.00	0.10	0.00
LOI	43.43	10.00	13.80

The chosen clinkering temperature is based on the maximum amount of belite, and ferrites formed in the equilibrium calculations. In the thermodynamic calculations, the crystalline phases formed from the four major common oxides (CaO, SiO₂, Al₂O₃ and Fe₂O₃) of the clinker were investigated in order to avoid the complexity of forming Bogue equations including other oxides. In this study, the LS content varied from 33 wt% to 64 wt%, BR constituted between 27 wt% to 65 wt% and kaolin from 1 wt% to 10 wt%. The sum of the raw materials in the mixtures added up to 100 wt%.

2.2. Bogue Formulation

The Bogue calculation is, in principle, the solution of four linear simultaneous equations with four unknowns. Each equation of the Bogue calculation for the four primary oxide components (CaO, SiO₂, Al₂O₃ and Fe₂O₃) expressed as:

$$\sum a_{ij} \cdot x_j = b_i, \quad (1)$$

The summation expressed above is up to the four major phases considered in the calculation. The x_j refers to the weight percentage of phase j in the clinker, a_{ij} is the weight fraction of oxide component i in phase j and b_i is the percentage of oxide component i in the clinker. Hence, errors in the quantification of phases calculated by the Bogue equation can arise due to incorrect values for the coefficients a_{ij} or wrongly inputted weight fractions. In addition, deviations from the experimental values can also arise for not including other oxides such as TiO₂ and not applying correct deductions to the percentage of oxide b_i when considering phases composed of only CaO, SiO₂, Al₂O₃ and Fe₂O₃. To minimize these errors, correctly recording the weight fractions of the oxide component from the thermodynamic calculations through FactSage for instance can be a viable solution.

In this work, the Bogue formulation is based on a series of computations that involves a stepwise increment of the LS content by 1% for the same set of K content between 1–10%, that changes the chemical composition b_i and associating these changes to the different phase assemblages in the clinker. The computation method is schematically depicted in Figure 1.

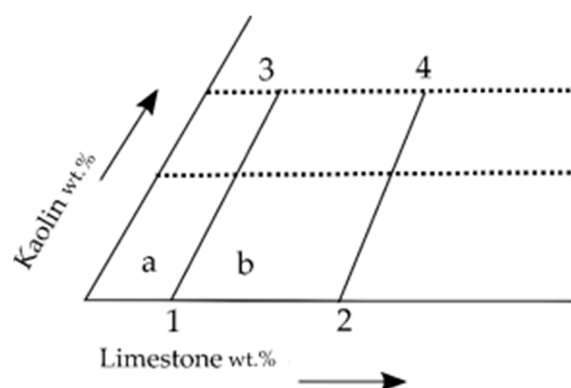


Figure 1. A depiction of phase field 1, 2, 3, 4 in the raw meal phase diagram with phase assemblage *b* within the area enclosed by 1, 2, 3, 4 and phase assemblage *a* outside the enclosed area.

As illustrated in Figure 1, an area corresponding to a three-component raw meal can be overlaid with a set of parallel lines and the computations are performed along each line constituting the kaolin (horizontal lines) and limestone (vertical lines). For instance, chemical compositions corresponding to the locations between 1, 2, 3, 4 are only “compatible” with phase assemblage *b* of all the possible phase assemblages obtained through thermodynamic calculations. This implies that the composition of raw meals corresponding to area 1, 2, 3, 4 will result in the formation of phases belonging to this phase assemblage.

3. Results and Discussion

Prediction of Crystalline Phases and the Phase Assemblage Based on the Raw Meal Composition

The crystalline phases obtained after cooling in FactSage from a clinkering temperature of 1260 °C are belite (C_2S), ferrite (C_4AF), gehlenite (C_2AS), rankinite (C_3S_2), CF, C_3A and lime. The weight fractions of the oxides of these individual phases are derived using thermodynamic calculations to set up the four linear simultaneous equations, as listed in Table 2. Depending on the raw meal composition and its corresponding phase assemblage, four types of crystalline phases are chosen, and four linear equations are formed. This is leading to the formulation of Bogue Equations to determine the crystalline phases.

Table 2. Weight fractions of the oxides in individual phases.

Crystalline Phases	wt. Fractions			
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
C_2S	0.651	0.348	0.000	0.000
C_4AF	0.461	0.000	0.209	0.328
C_2AS	0.408	0.219	0.371	0.000
C_3S_2	0.600	0.400	0.000	0.000
CF	0.259	0.000	0.000	0.740
C_3A	0.566	0.036	0.313	0.051
Lime	1.000	0.000	0.000	0.000

(C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.)

In Figure 2, the phase fields are represented by a set of boundary lines. These phase fields are numbered from 1–11, each representing a phase assemblage. Based on the phase field representation, the phase assemblage is identified for the corresponding selected mixture. For example, at a LS content of 36 wt% and Kaolin content of 5 wt%, the corresponding phase assemblage is $Ca_2Al_2SiO_7$ -CF- $C_4A_{0.27}F_{1.70}$ - C_2S represented as “1” in Figure 2. The weight fractions of these phases are obtained from Table 2 to form four sets of simultaneous linear equations for the formulation of Bogue equations. The phase assemblages in dependence of the raw meal composition are listed in Table 3. In Figure 2, points A, B, C and D represent the solid solutions of ferrites that are deviating from C_4AF chemistry lying between the intersecting regions, as shown in Table 3. It was identified that at point C, the chemistry of A–F in the ferrite is 1:1, i.e., C_4AF (4 CaO·Al₂O₃·Fe₂O₃) at an LS content of 55–56 wt% and K content of 3 wt%. Thus, the intersection points behind C (LS content < 55 wt% and K content between 1–10 wt%) and ahead of C (LS content > 56 wt% and K content between 1–10 wt%) represented the F > A (iron-rich ferrites) and A > F (aluminum-rich ferrites) ferrite phases, respectively.

Table 3. Phase assemblages of each phase fields and intersection points.

Field No.	Phase Assemblage	Intersection Point	Phase Assemblage
1	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.27}F_{1.70}$ - C_2S	A	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.47}F_{1.40}$ - C_2S
2	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.34}F_{1.64}$ - C_2S	B	$C_4A_{0.63}F_{1.25}$ - $Ca_3Si_2O_7$ - $Ca_2Al_2SiO_7$ - C_2S
3	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.39}F_{1.51}$ - C_2S	C	C_4AF - C_2S - $Ca_3Si_2O_7$ - C_3A
4	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.45}F_{1.45}$ - C_2S	D	$C_4A_{1.20}F_{0.83}$ - C_2S - C_3A -C
5	$Ca_2Al_2SiO_7$ -CF- $C_4A_{0.50}F_{1.36}$ - C_2S		
6	$C_4A_{0.58}F_{1.32}$ - $Ca_3Si_2O_7$ - $Ca_2Al_2SiO_7$ - C_2S		
7	$C_4A_{0.67}F_{1.20}$ - $Ca_3Si_2O_7$ - C_2S $Ca_2Al_2SiO_7$		
8	$C_4A_{0.82}F_{1.07}$ - C_2S - $Ca_3Si_2O_7$ - $Ca_2Al_2SiO_7$		
9	$C_4A_{1.03}F_{0.90}$ - C_2S - $Ca_3Si_2O_7$ - C_3A		
10	$C_4A_{1.15}F_{0.85}$ - C_2S - C_3A -C		
11	$C_4A_{1.25}F_{0.75}$ - C_2S - C_3A -C		

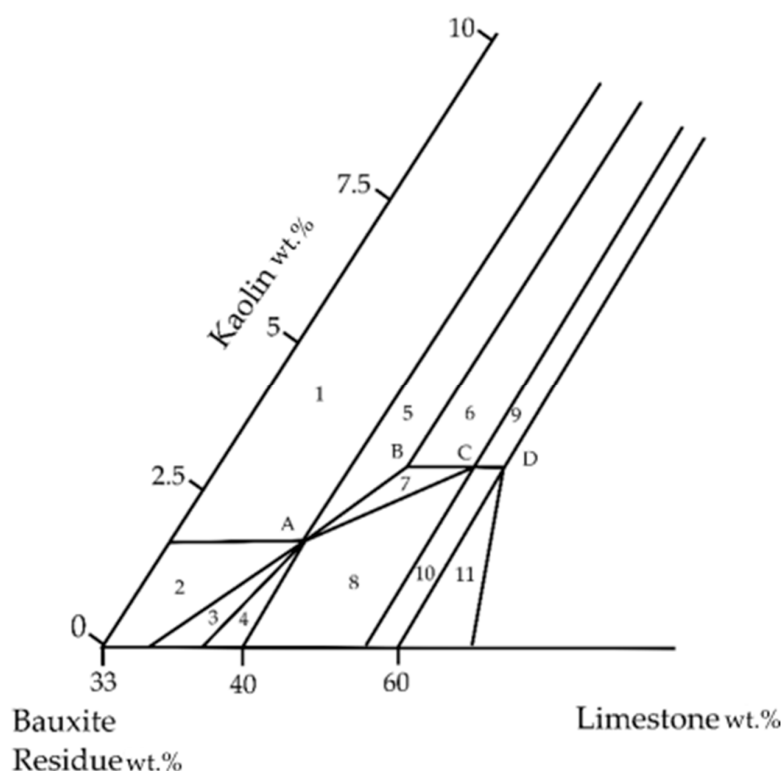


Figure 2. Phase field diagram of limestone-bauxite residue-kaolin based on FactSage. Here, Bauxite residue is 100-LS wt%-K wt%.

4. Conclusions

In this study, the Bogue equations for the ferrite-belite cements incorporating bauxite residue were derived from thermodynamic modelling using FactSage (GTT-Technologies, Aachen, Germany). The designed equations are a tool to calculate the phases present in the clinker based on the input provided by the raw material composition of the clinker. Within this design toolbox, a desired solid solution of the ferrite phases could be targeted in the Bogue equation. The established relationship between the compositions of raw mixtures and the mineralogical compositions of the burnt raw mixes thermodynamically modelled by FactSage (GTT-Technologies, Aachen, Germany) could provide the foundation for the design and manufacturing of ferrite belite clinkers based on bauxite residue. Experimental data are currently collected to confirm these theoretical calculations or have the equations adjusted to reflect real data more accurately.

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References

1. Juenger, M.C.G.; Winnefeld, F.; Provis, J.L.; Ideker, J.H. Advances in alternative cementitious binders. *Cem. Concr. Res.* **2011**, *41*, 1232–1243. [[CrossRef](#)]
2. Andrew, R.M. Global CO₂ emissions from cement production. *Earth Syst. Sci. Data* **2018**, *10*, 195–217. [[CrossRef](#)]
3. Iacobescu, R.I.; Koumpouri, D.; Pontikes, Y.; Angelopoulos, N. Hydraulic and leaching behaviour of belite cements produced with electric arc furnace steel slag as raw material. *Ceram. -Silik.* **2013**, *57*, 126–132.
4. Lawrence, C.D. 9—The Production of Low-Energy Cements. In *Lea's Chemistry of Cement and Concrete*, 4th ed.; Hewlett, P.C., Ed.; Butterworth-Heinemann: Oxford, UK, 1998; pp. 421–470.
5. Nayak, B. *Process for Manufacturing of High Iron Hydraulic Cement Clinker*; U.S.Pa.T. Office, Ed.; Council of Scientific and Industrial Research: New Delhi, India, 2004.
6. Wang, H.; De Leon, D.; Farzam, H. C₄A_F Reactivity-Chemistry and Hydration of Industrial Cement. *ACI Mater. J.* **2014**, *111*, 201–210.
7. Sharp, J.H.; Lawrence, C.D.; Yang, R. Calcium sulfoaluminate cements—low-energy cements, special cements or what? *Adv. Cem. Res.* **1999**, *11*, 3–13. [[CrossRef](#)]
8. Hertel, T.; Bulck, A.V.D.; Onisei, S.; Sivakumar, P.P.; Pontikes, Y. Boosting the use of bauxite residue (red mud) in cement—Production of an Fe-rich calciumsulfoaluminate-ferrite clinker and characterisation of the hydration. *Cem. Concr. Res.* **2021**, *145*, 106463. [[CrossRef](#)]
9. Arino Montoya, D.; Katsiotis, M.; Giannakopoulos, G.; Iacobescu, R.I.; Pontikes, Y. Low-Carbon Footprint Cements Incorporating High Volumes of Bauxite Residue. In Proceedings of the 35th International ICSOBA Conference, Hamburg, Germany, 2–5 October 2017.
10. Hertel, T.; Pontikes, Y. Geopolymers, inorganic polymers, alkali-activated materials and hybrid binders from bauxite residue (red mud)—Putting things in perspective. *J. Clean. Prod.* **2020**, *258*, 120610. [[CrossRef](#)]
11. Pontikes, Y.; Angelopoulos, G.N. Bauxite residue in cement and cementitious applications: Current status and a possible way forward. *Resour. Conserv. Recycl.* **2013**, *73*, 53–63. [[CrossRef](#)]
12. Taylor, H.F.W. Modification of the Bogue calculation. *Adv. Cem. Res.* **1989**, *2*, 73–77. [[CrossRef](#)]
13. Bale, C.W. FactSage thermochemical software and databases. *Calphad* **2002**, *26*, 189–228. [[CrossRef](#)]