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Thermodynamic modelling of Portland cement clinkers.

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ABSTRACT
Research into thermodynamic modelling allows for product and process optimisation of Portland cement clinkers. Due to the magnitude and chemistry of clinker production, there is a great challenge in modelling such a complex system. The CALPHAD (CALculation of PHAse Diagrams) approach provides a method in overcoming this challenge, by constructing a model, step-by-step with increasing complexity, i.e., starting with the pure solids and liquid to modelling binary and ternary melts, and moving on to higher-order systems, and with the possibility to eventually embed mobility. This approach has had great success in the metals industry and has allowed for production optimisation for a variety of alloys. In this project, we have developed a thermodynamic database for the CaO-Al_2O_3-SiO_2-Fe-O-MgO system. This provides a much-needed update to the underlying thermodynamic data. In addition, prediction calculations made with our thermodynamic database are compared against technical clinkers analysed by XRD, XRF, and SEM-EDX. Future work will include developing further extensions to the thermodynamic database to include other elements such as sulfur to further model clinker diversity.

KEYWORDS: *Thermodynamic modelling, Clinker, Clinker prediction, CALPHAD, Characterisation*

1. Introduction

There is an immediate need to make Portland cement (PC) more environmentally friendly by optimising the clinker production process. There are huge potentials in the research of the high temperature chemistry within the cement kiln (Ludwig and Zhang (2015)), plenty of which related to efficiency has already been realised. Research into new clinker chemistries are mostly "trial and error" and would be aided by a thermodynamic model of the clinker production process, and with the growing pool of raw materials targeted for use in clinker manufacture. Thermodynamic models and databases have greatly aided the metals industry in material development, which have been rapidly developed using the CALPHAD that provides a step-by-step approach to rapidly develop thermodynamic databases through the calculation of phase diagrams. The effectiveness of the CALPHAD approach has been studied by De Noirfontaine et al. (2012), who reviewed the models of the CaO-$Al_2O_{3\backslash}$-SiO_2 system and carried out calculations in the clinkering zone. Barry and Glasser (2000), and Tazuddin et al. (2018) used commercial thermodynamic databases to carry out clinker predictions for synthetic clinkers and Tazuddin et al. (2020) was also able to study the effect of minor elements on clinker phase formation. Furthermore, Hanein et al. (2020) developed a stoichiometric thermodynamic database for PC and C$A clinkers and Meyer et al. (2016) developed a kiln simulator (KilnSimu) from a thermodynamic model with great success. As a part of this work, a thermodynamic database for the CaO-Al_2O_3-SiO_2-Fe-O-MgO system was developed. This includes the modelling of the main clinker phases: alite, belite, aluminate and ferrite. This database serves as a single source of thermodynamic data for the solid, liquid, solid solutions and the melt phases specifically created for PC clinkers. In this paper, we present the results of the clinker predictions resulting from the Scheil cooling calculations (Scheil (1942)) using the developed thermodynamic database. These values are compared with the analysis of 27 technical clinkers that were also analysed as part of this project. Finally, the power of the modelling work is presented through the comparisons of the calculated MgO content in the belite phase against the energy dispersive X-Ray (EDX) analysis of the clinkers.

2. Thermodynamic Modelling and Clinker analysis

The thermodynamic database for the CaO-Al_2O_3-SiO_2-Fe-O-MgO system that was developed in this work, made use of the latest 3rd generation CALPHAD function for the solid and liquid phases and the associate's

model for the melt phase. Novel fitting methodologies were used to fit the relevant parameters in the binary, ternary, and higher order systems; details on this approach are discussed in the $CaO\text{-}SiO_2$ assessment carried out by Abdul et al. (2022). Modelling of the full thermodynamic system was found not to be necessary and instead only the PC relevant ternary systems were modelled and combined to give the final database, this includes: $CaO\text{-}Al_2O_3\text{-}SiO_2$ (which contains C_3A, C_2S and C_3S), $CaO\text{-}Al_2O_3\text{-}Fe\text{-}O$ (which contains ferrite) and $CaO\text{-}MgO\text{-}SiO_2$ (which contains the substitution of MgO into C_2S). The thermodynamic database was used to carry out Scheil cooling calculations from 1500°C for a given clinker oxide composition. Scheil cooling is a set of equilibrium calculations that describes the rapid cooling of a melt like that which occurs in the cement kiln. This results in the calculated values of the precipitated clinker phases, which can be compared against experimental XRD data. Figure 1 presents a graph of a Scheil cooling precipitation that was conducted using the present thermodynamic work. The calculated values match closely with the values from Barry and Glasser (2000).

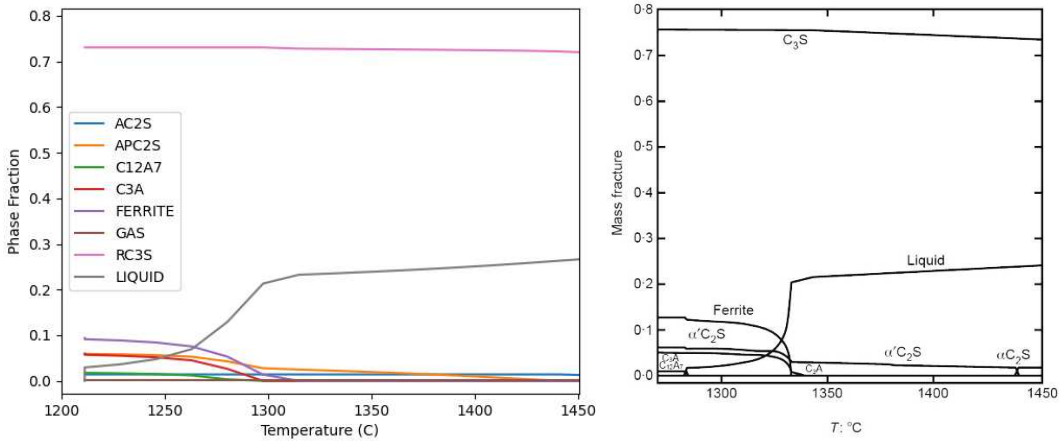

Figure 1 Accumulated phase fraction from the Scheil cooling calculation from 1450°C for the Barry and Glasser (2000) clinker composition (wt %): CaO 69, Fe_2O_3 3.6, SiO_2 22, Al_2O_3 5.4. (left) Results of the presently developed database. (right) Results of Barry and Glasser using MTDATA. Abbreviations are as follows, "AC2S": α-C_2S, "APC2S": α'-C_2S, "RC3S":C_3S (rhombohedral).

A total of 27 clinkers were received from industrial partners and analysed using X-ray diffraction (XRD) Rietveld analysis, X-ray fluorescence (XRF) analysis on molten beads XRF, and SEM-EDX mapping analysis, the methodology and full dataset is presented in a future paper. The EDX mapping analysis was carried out at various resolutions. High resolution (approx. 0.1µm step size) was used for characterisation of the ferrite phases and lower resolution (approx. 0.2µm step size) but large area analyses were used for belite characterisation respectively. In addition, Shim et al. (2021) collated the XRD and XRF analysis of 50 clinkers from literature, this provides a comparison of "historical" clinkers against the modern clinker dataset.

3. Results and Discussion

3.1. Clinker prediction

The difference (in weight %) of the calculated values of the clinker phases using the presently developed thermodynamic database, compared against the XRD analysis within the current clinker dataset and the dataset of Shim et al. is presented in Fig. 2. The figure shows that the calculated values of the belite, aluminate and ferrite phases are in good agreement with XRD values, especially for the clinkers in the dataset of Shim et al. There is a slight over-prediction in the alite phase, which is expected as the alite phase in the thermodynamic modelling was not modelled as a solid solution like the belite phase, this means the effects of MgO are not considered for alite formation. This requires further experimental work to accurately model this behaviour. A summary of the average error for the prediction of the 4 main clinker phases calculated using different calculation methods is presented in Table 1. The results confirm earlier conclusions by Taylor (1997), that the Bogue over-predicts the alite phase and under-predicts the belite phase. The modified Bogue is better at predicting the alite and belite phases but has poor prediction of the aluminate and ferrite phases. The calculations of Hanein et al. (2020) are generally in agreement with the experimental values for all clinker phases. Finally, the results of the thermodynamic database are favourable when compared against the previous calculation methods, with equal or better agreement for the prediction

of all clinker phases except alite, where values of alite match the predictions of the Bogue equation.

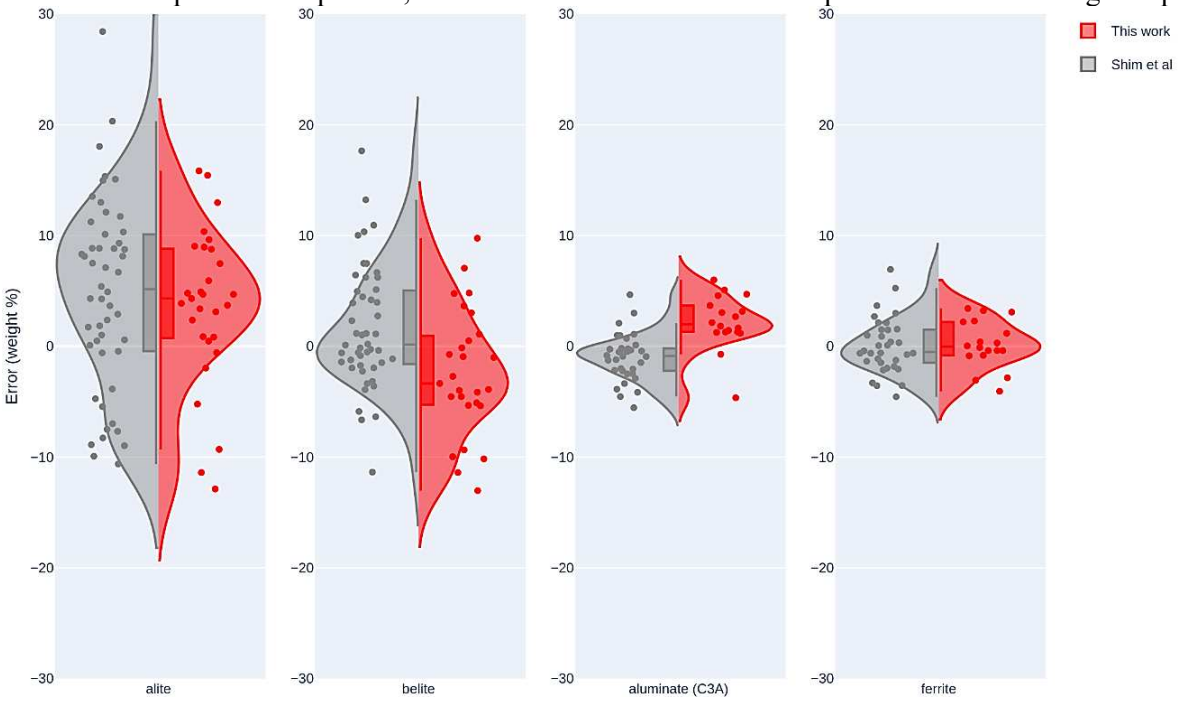

Figure 2 Violin plots of the error (in weight %) of the calculated values and the experimental XRD values of the present clinker dataset (this work) and the dataset of Shim et al (2021).

Table 1 Summary of the error in weight % between the calculated values of the clinker phases compared against the experimental XRD values of the present clinker dataset and the collated dataset of Shim et al. (2020).

Calculation	Bogue	Modified Bogue	Hanein et al. (2020)	This work
Alite (Present)	3.11 ± 6.95	-1.64 ± 7.38	-3.32 ± 6.32	3.62 ± 7.03
Alite (Shim et al.)	5.84 ± 7.50	-1.80 ± 8.04	0.911 ± 7.46	4.68 ± 8.63
Belite (Present)	-1.93 ± 6.75	2.18 ± 7.28	2.92 ± 6.26	-2.40 ± 5.69
Belite (Shim et al.)	-3.14 ± 8.10	-0.12 ± 8.75	0.569 ± 7.79	1.63 ± 5.49
Aluminate (Present)	0.981 ± 2.47	7.45 ± 6.21	3.70 ± 2.15	2.20 ± 2.40
Aluminate (Shim et al.)	-2.10 ± 2.67	3.73 ± 6.04	0.614 ± 4.20	-0.982 ± 2.11
Ferrite (Present)	0.130 ±1.83	-6.88 ± 9.40	0.130 ± 1.83	0.179 ± 2.15
Ferrite (Shim et al.)	0.15 ± 2.43	-5.64 ± 8.84	0.152 ± 2.43	0.038 ± 2.49

3.2. Belite and Ferrite substitution

Whilst the results of the clinker prediction are favourable, further calculations can be done with the thermodynamic database, where the previous calculations cannot predict. A cross-plot of the MgO/CaO ratios for selected belite clinker phases is presented in Fig. 3 and shows an almost linear relationship between the calculated and experimental values, showing good agreement in the prediction of MgO in the belite phase using the thermodynamic database. Furthermore, a similar cross-plot for the Al_2O_3/CaO ratio in ferrite, shows excellent prediction in clinkers with an alumina-poor ferrite phase (near C_4AF) and disagreements in the clinkers with alumina-rich ferrites (near C_6A_2F). This is due to the use of a simple sublattice model for the ferrite phase, which does not account for the substitution of Fe_2O_3 in other clinker phases.

4. Conclusion

A thermodynamic database was developed in this work, with a specific application of PC clinkers. The effectiveness of the developed models was shown through the prediction of real clinkers that were also analysed in this work. This resulted in a good prediction for the main clinker phases compared against the experimental values and the results are favourable against the more “traditional” calculation methods. Furthermore, the modelling of MgO in the thermodynamic database, allowed for the prediction of the MgO/CaO ratio in the belite phase, with these in good agreement with the EDX analysis. Similar predictions

were also made for the composition of the ferrite phase, which showed excellent predictions for alumina-poor ferrites. Further improvements in the ferrite model as well as the modelling of Fe_2O_3 substitution in the other clinker phase, would solve the issues with alumina-rich ferrites. The developed thermodynamic database shows promising results with regards to clinker phase and clinker substitution predictions. This database will be useful to the wider cement research community as it serves as a single open-source database for models and thermodynamic data for cement clinker. The thermodynamic database also has potential uses for modelling carbonation-hardening cements as it includes a full CaO-Al_2O_3-SiO_2 model. Furthermore, the oxygen dependence of iron is modelled in this system; this inclusion will make the addition of SO_3/SO_2 easier. Finally, minor elements like fluorine can be easily added to the current thermodynamic model, but the addition of molten salts and resolution of the volatilisation cycle will require more work. Future work will include extending the thermodynamic database to include other elements and species like SO_3, for further modelling of PC and other cement formulations such as calcium sulfo-aluminate based cements. The thermodynamic model/dataset developed here can also be combined with heat transfer and kinetic models to develop advanced thermal kiln models for cement production.

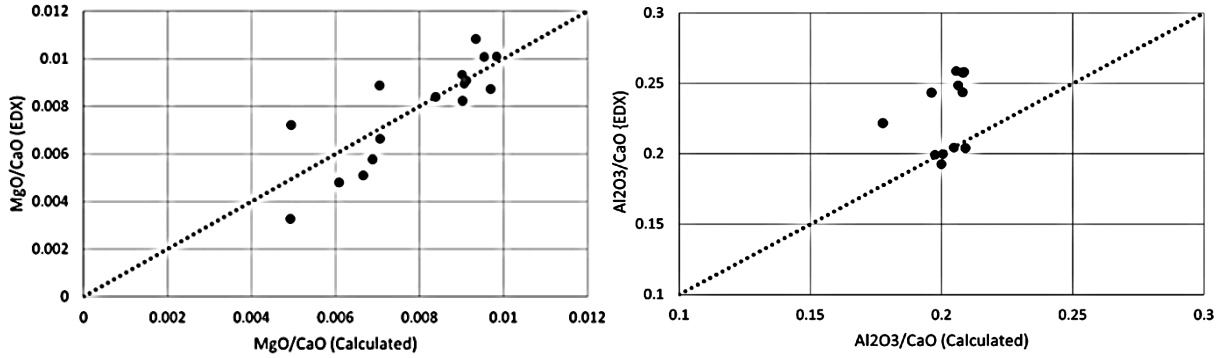

Figure 3 Cross-plot of the experimental and calculated values of the (left) MgO/CaO ratio in the belite phase and the (right)Al_2O_3/CaO ratio in the ferrite phase for selected clinkers in the clinker dataset. The dashed line represents the y=x relationship, indicating exact agreement.

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