Crystallinity of Cement Clinkers: Application of Rietveld Refinement

Problem

The quantitative determination of the phases in cement clinker has important implications for the reactivity and grindability of clinker. Both these properties are sensitive to the relative amount of various constituents (alite, belite, aluminate, ferrite, alkali sulfates, periclase, free lime, etc.). Therefore, an accurate estimation of the phase content is of high relevance in cement production. One of the most commonly used methods to estimate the phase contents in clinker is the Bogue method. This simple technique uses the results of quantitative chemical analysis (e.g. x-ray fluorescence, XRF), and calculates the approximate amount of the clinker phases based on formulas for the distribution of specific oxides among alite, belite, aluminate and ferrites. The limitations of this method are that it assumes ideal compositions for the primary phases, does not estimate other components, and does not take into account any material that has failed to crystallize as it cools to ambient temperature. More accurate techniques based on x-ray methods, like the Rietveld refinement, bear the potential to provide a more accurate assessment of the quantitative composition of clinker, including any amorphous content.

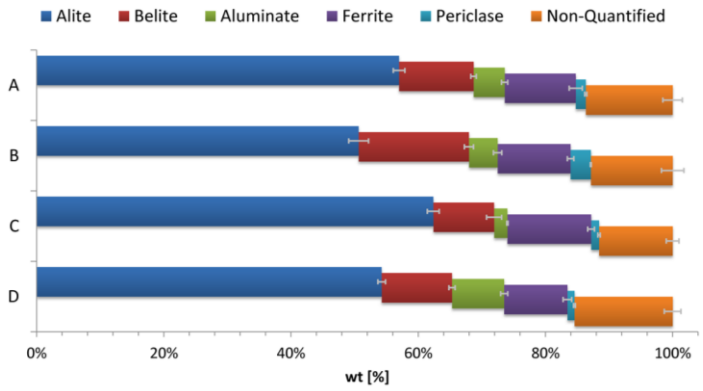

Fig. 1: Results of the quantitative analysis with Rietveld Refinement of selected industrial clinkers (A-D). Error bars represent 95% confidence intervals. Amorphous content determined with the External Standard Method (ESM), Corundum (Al_2O_3) NIST: SRM 674.

Approach

We studied the composition of four different industrially produced clinkers. The Rietveld refinement was applied, following ASTM C1365-06 recommendations, in order to estimate the weights of the major crystalline phases (see Figure 1). The amorphous content of the clinker, along with the content of any non-detected crystalline phases, and any mis-fitted clinker phase patterns, is also shown as "non-quantified." A portion of this non-quantified material may be amorphous material, which has not been rigorously studied in the literature. Future work will include vigorous reliability and robustness testing.

Findings

The experimental results obtained with the Rietveld refinement show a significant fraction of unidentified phases, which can reach up to 15% by weight. Despite the non-quantified material being significantly lower in mass than alite, which is the most abundant component, the amount is comparable to that of belite, aluminate and ferrite. Therefore, it may have substantial impact on the hydraulic properties and grindability of clinkers.

Impact

Using the Rietveld method, we provide evidence that the presence of non-quantified material is significant in the studied samples of industrial clinker. This material likely affects grindability and reactivity, and our strategy allows one to quantify systematically its content, which has the potential to permit more complete characterization and therefore better estimates of performance and grindability.

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