Engineering the phase composition of akermanitic carbonatable clinkers to achieve high CO_2 reactivity

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Introduction

Global implementation of carbonation-cured construction materials will facilitate the transition of the construction sector into a CO_2-storing activity.[1] The current feedstock of resources that enables this in an environmentally and economically sound process is limited to steel slags[2], in other words limited to 300 Mt/y while a demand for cementitious materials of 4000 Mt/y must be satisfied.[3] Mine tailings and carbonatable clinkers are being investigated to close this gap, but while tailings are not sufficiently reactive to process economically,[4,5] the carbonatable clinkers make elaborate use of $CaCO_3$ and its associated emissions which are not easily compensated in the subsequent carbonation process. The benefits of both streams converge when producing clinkers with a high content of akermanite $Ca_2MgSi_2O_7$. Being engineered from Mg-silicate residues such as mafic tailings or ferronickel slag, they can hold a large fraction of uncarbonated material in the raw meal, while the reactivity towards CO_2 is greatly enhanced.[6] This new system however still holds many unknowns in terms of phase relations, elemental distributions, and their relation to reactivity. Recent work elucidates the phase relations that govern the composition around akermanite. The presence of diopside, forsterite, merwinite, and pseudowollastonite could thereby be pre-estimated from simple equations. The present paper intends to provide further insights into the effect of alkali additions on the burnability and reactivity of akermanitic clinkers.

Material and methods

The clinker raw meal uses a ferronickel slag as main component. This was more elaborately discussed in previous work.[6] The chemical composition of the slag is repeated in Table 1. The slag can be described as a Mg-silicate with high Fe content.

Table 1: Chemical composition of the starting slag.

	FeO	SiO_2	CaO	Al_2O_3	MgO	Others
wt%	15.4	50.5	2.7	5.1	25.1	1.2

The slag is blended with reagent grade $CaCO_3$ and Na_2CO_3 powders. Thermodynamic simulations were carried out in the Equilibrium module of FactSage 8.2 using chemical composition of the slag from Table 1, assuming the $CaCO_3$ and Na_2CO_3 are 100% pure. A pO_2 of 0.1 was imposed. Experimental synthesis of the clinkers was carried out on Pt trays in a box furnace (heating and cooling at 3°C/min, dwell time 30 minutes). Before clinkering, the raw meal blends were pressed to a cylinder. Naming of the clinkers was carried out based on the $CaCO_3$ and Na_2CO_3 dosage in the raw meal, indicated with a number and “Cc” and “Nc”, respectively. The clinkers were investigated using X-ray diffraction (XRD) on a PANalytical Empyrean with a Co tube. Identification and Rietveld refinement was carried out using the HighScore X’pert Plus software and PDF-4 database. The amorphous content was estimated from external standards measured 2 days before the measurement of the samples. Carbonation experiments were carried out at 10 bar, 60 °C, 100% CO_2, > 90% relative humidity. Before carbonation, the clinkers were mixed with 8 wt% moisture and pressed into 23 mm diameter cylinders using 150 kg/cm^2. The resultant height was 22-24 mm.

Results and discussion

FactSage simulations to predetermine clinker formulations

The equilibrium phase composition of akermanitic clinkers with varying $CaCO_3$ (Cc) and Na_2CO_3 (Nc) dosage is first simulated with FactSage. Figure 1 focuses on the melt and akermanite concentration. As the appearance of 10-20 wt% of melt is the cause of industry-relevant kinetics of the Portland clinkering process, this was the target in this study as well. Figure 1 shows that the addition of 2-4 wt% of Nc can establish this melt content, independent from the Cc dosage. The maximum akermanite that can be formed decreases with the addition of 4 wt% Nc.

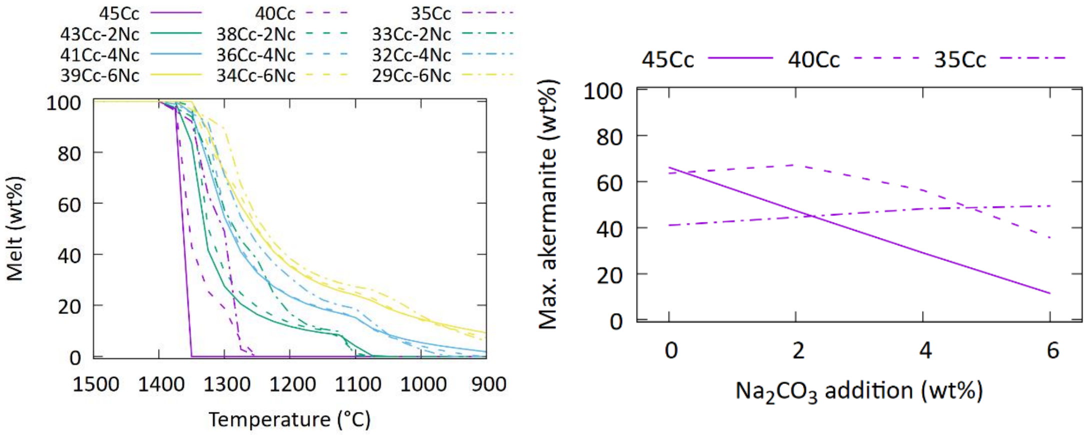

Figure 1: FactSage equilibrium simulations with resultant wt% of melt and maximal akermanite content in clinkers with varying $CaCO_3$ (Cc) and Na_2CO_3 (Nc) dosage.

Experimental validation of the increased burnability proceeds with 2Nc formulations. Figure 1 shows that the required content of Cc to achieve maximal akermanite content shifts downwards to 40Cc.

Experimental phase composition and reactivity

The phase compositions of clinkers using 43Cc and 40Cc-2Nc formulations are compared in Figure 2. The phase composition of 40Cc-2Nc clinkered at 1150 °C was similar to 43Cc clinkered at 1200 °C, with an akermanite content of approximately 60 wt%. When clinkering the 43Cc formulation at 1150 °C, the akermanite content decreased to 50 wt%. This suggests that the burnability has slightly increased with Nc addition.

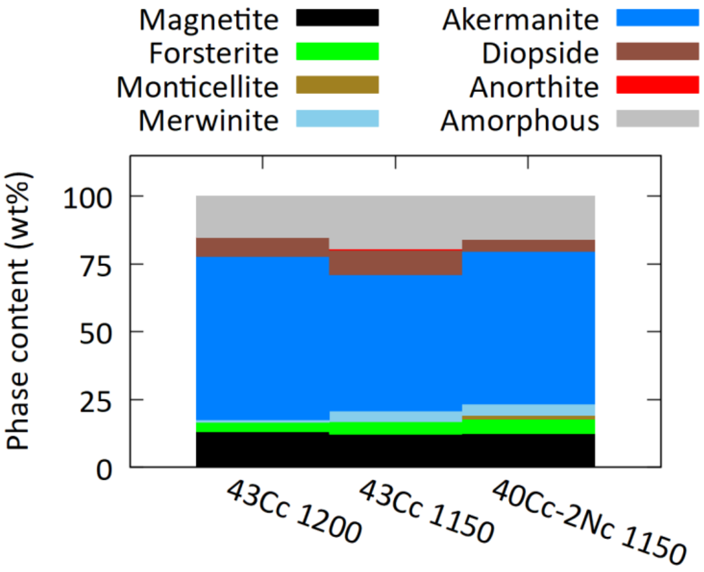

Figure 2: Phase composition of akermanitic clinkers determined using XRD.

The performance of the clinkers in the carbonation process is shown in Figure 3. The CO_2-uptake was not influenced by the clinker composition or clinkering temperature. The compressive strength was better for the better burnt clinkers, showing > 90 MPa for the cylinders from 43Cc clinkered at 1200 °C and 40Cc-Nc clinkered at 1150 °C, while only < 80 MPa was achieved for 43Cc clinkered at 1150 °C. This is in line with the observed importance of the akermanite phase for compressive strength in previous work.[6] However, further confirmation is required and the repeatability needs to be tested (please note the lack of error bars on Figure 3).

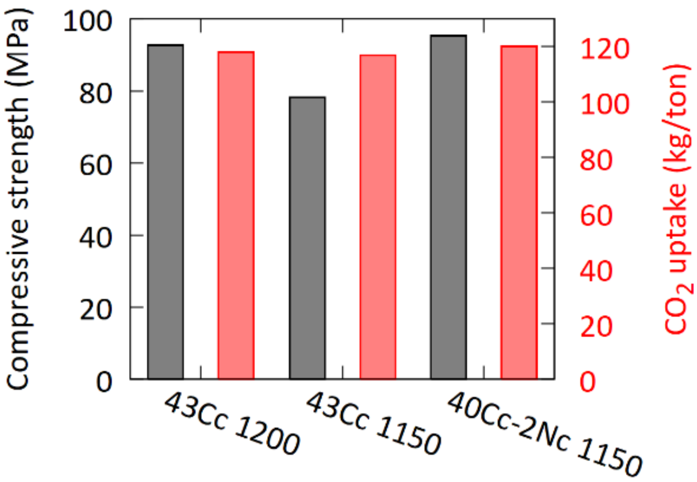

Figure 3: Compressive strength and CO_2 uptake of carbonated akermanitic clinkers.

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