

# SYNTHESIS OF A HYDRAULIC BINDER FROM A Ca-Si BASED METALLURGICAL RESIDUE THROUGH HIGH TEMPERATURE POST-TREATMENT

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## Introduction

Ordinary Portland cement (OPC) is traditionally used as the binder material in the construction sector; however, OPC has a high embodied energy. The measure used to compare the emissions from various greenhouse gases based upon their global warming potential, ranges up to 0.97 kg of CO<sub>2</sub> emitted per kilogram of produced OPC.<sup>1</sup> Overall, OPC production contributes approximately 5–7% of global anthropogenic CO<sub>2</sub> emissions. The key causes are attributed to: (i) calcination of limestone, one of the key ingredients, which leads to formation and release of CO<sub>2</sub>; and (ii) high energy consumption during manufacturing, including heating raw materials within a rotating kiln at temperatures greater than 1400°C.<sup>2</sup>

Alternative cements to OPC have been proposed for reducing greenhouse gas emissions. Several materials, such as blast furnace slag and fly ashes, are already used in the production of blended cements. This provides substantial advantages by a) reducing CO<sub>2</sub> emissions while b) delivering similar or better properties than original (100%) OPC.<sup>3</sup> The aim of this work is to further extend this family of alternative materials by exploring the possibility of converting a Ca-Si-rich metallurgical residue (MR) with approximately 20 wt% amorphous carbon into a hydraulic binder. For this purpose, the MR was heated to 1350°C without any additions in a first step. In a second step the initial chemistry of MR was adapted towards a “classical” OPC clinker composition. Eventually, the feasibility of the process was demonstrated in an upscaled experiment.

## Materials and Methods

The as received MR powder was pelletised with and without addition of CaCO<sub>3</sub> followed by sintering. The mixture design was performed based on the Bogue equations, in which the approximate proportions of the four main minerals (C<sub>3</sub>S, C<sub>2</sub>S,

C<sub>3</sub>A, C<sub>4</sub>AF) were determined. Approximately 100 g of pellets were heated up to both 1350°C (MR without CaCO<sub>3</sub>) and 1450°C (MR mixed with CaCO<sub>3</sub>) in a bottom loading furnace (AGNI ELT 160-02) using a Pt crucible. The high temperature treatment consisted of 3 main steps: heating (5°C/min), isothermal step for 1.5 h (1350°C or 1450°C) and air quenching. The temperatures were chosen based on FactSage® calculations, which predicted a similar portion of liquid phase (< 20%) for the respective chemistries. Sintered materials were milled to a specific surface of about 4500 cm<sup>2</sup>/g using a vibratory ring mill (Retsch, RS200).

The as received material as well as both treated samples were characterised by means of X-ray fluorescence spectrometry (XRF, Philips PW 2400) and X-Ray diffraction analysis (XRD, Bruker 2D PHASER). XRD patterns were collected in the 2θ range of 10 – 70° with step size of 0.02°, step time of 0.6 s, and CuKα radiation of 30 kV and 10 mA. 10 wt% of ZnO was added as internal standard. Both heat treated samples were subjected to thermogravimetric measurements (TA Instruments, SDT Q600) in air, 10 °C/min up to 1300 °C. Isothermal calorimetry was performed on samples mixed with gypsum (TA Instruments, TAM Air) keeping the solid/liquid mass ratio at 0.5. Upscaling experiments were performed using a sinter pot. Approximately 40 kg of granulated material mix was covered with a 1 cm layer of coke dust, which was ignited by a gas burner. The sintering reaction was controlled by air suction pressure (Δp), which was kept stable at 0.01 bar.

## Results and Discussion

The as received MR consisted mainly of Ca, Si, Fe and Al, whereas S, Ti, Mg and V were present in minor quantities. SEM analyses revealed 5 types of particles, differing in shape, composition and mineralogy. The mineralogical composition was rather complex with 12 crystalline phases identified in the structure. Surprisingly, the amorphous content comprised about 40 wt%. It was expected that the C present in the material would be in an amorphous form, however this was estimated to be close to 20 wt%. EDS analyses revealed, that the rest of the amorphous fraction mainly consisted of Ca, Si and Fe.

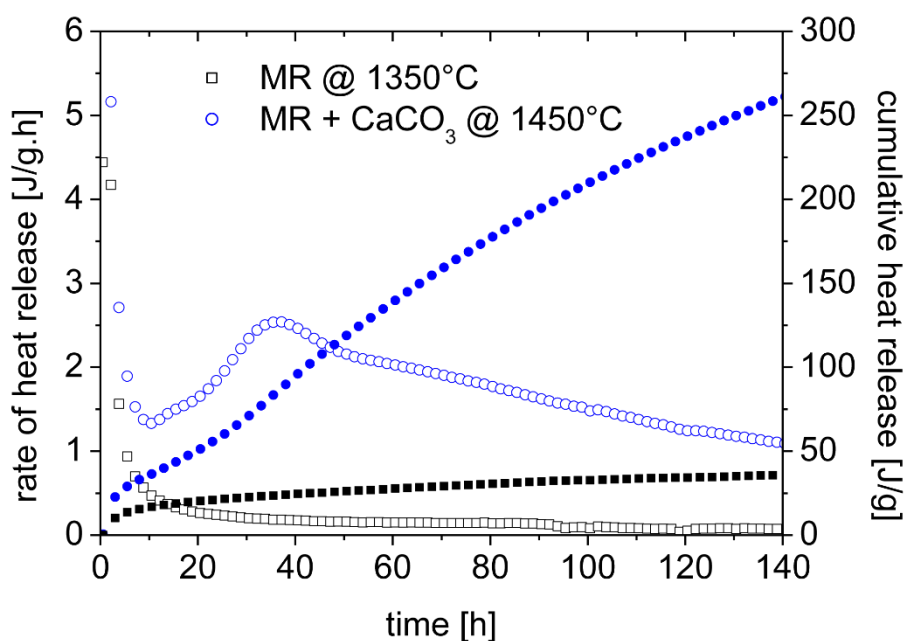
The temperature treatment at 1350°C resulted in a significant change in mineralogy. The amorphous fraction disappeared completely. This was partially due to the removal of C, which reacted with oxygen from the surrounding atmosphere to form CO/CO<sub>2</sub>. Additionally, the structure of treated MR also contained significantly higher amounts of gehlenite and belite. The latter is particularly relevant, as belite is the second most abundant phase in OPC. From the other three OPC phases, C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF, only C<sub>3</sub>A is present and in limited quantity (2 wt%).

**Table1:** Mineralogical composition of as-received and treated MR, in wt%

Phase name	Formula	As-received	MR @ 1350°C	MR + CaCO <sub>3</sub> @ 1450°C	Sinter pot
Gehlenite	Ca <sub>2</sub> AlSiO <sub>7</sub>	11	36	4	-
Quartz	SiO <sub>2</sub>	11	9	4	< 1
Portlandite	Ca(OH) <sub>2</sub>	13	-	-	2
Belite	β-Ca <sub>2</sub> SiO <sub>4</sub>	12	35	20	25
C <sub>2</sub> S-gamma	γ-Ca <sub>2</sub> SiO <sub>4</sub>	-	6	1	6
Lime	CaO	5	-	< 1	-
Hatrurite	Ca <sub>3</sub> SiO <sub>5</sub>	-	-	27	9
C <sub>3</sub> A	Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	-	2	8	3
C <sub>4</sub> AF	Ca <sub>4</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>10</sub>	-	< 1	5	12
Jasmundite	Ca <sub>22</sub> Si <sub>8</sub> O <sub>36</sub> S <sub>2</sub>	-	-	15	4
Calcite	CaCO <sub>3</sub>	< 1	3	6	25
Bredigite	Ca <sub>7</sub> MgSi <sub>4</sub> O <sub>16</sub>	-	4	4	-
Phases lower than 2 wt%	TiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub> , CA <sub>2</sub> , C <sub>12</sub> A <sub>14</sub> , Fe	Fe <sub>3</sub> O <sub>4</sub> , CA, Fe	C <sub>12</sub> A <sub>14</sub> , Fe	-	-
Amorphous/undetected		40	< 1	3	13

From Table 1 it can be seen that the addition of calcite and increase in T effectively stimulates the formation of a significant amount of C<sub>3</sub>S. The amounts of C<sub>2</sub>S and C<sub>3</sub>A are rather close to the predicted mix design, whereas the amount of C<sub>4</sub>AF is substantially lower. Furthermore, the high amount of free lime originally present in MR is eliminated, which is important for the volume stability of the produced building materials.

Figure 1 presents the heat release of both samples when mixed with water. The MR shows a substantially lower heat release than the MR+CaCO<sub>3</sub>. Also, no clear peak was visible in this sample. This could be due to the slow reaction of the belite and gehlenite phases. The results are in good agreement with those published by Doval *et al.*<sup>4</sup>, who observed a very slow and gradual heat release when a C<sub>2</sub>S and C<sub>2</sub>AS sol-gel was mixed with water. The hydration reaction of sintered MR doped with CaCO<sub>3</sub>, however, resulted in a significantly higher heat release. A clear double peak is visible due to the hydration of C<sub>3</sub>A, C<sub>3</sub>S and, later, C<sub>2</sub>S. In this case, the reaction of the C<sub>2</sub>S phase is enhanced by the presence of C<sub>3</sub>S, as stated by Taylor<sup>5</sup>. The 28<sup>th</sup> day compressive strength of mortar prepared from CaCO<sub>3</sub> doped MR equalled almost 30 MPa, which is close to the category of CEM I 32.5N.



**Figure 1:** Reaction heat generated by sintered samples when mixed with water. Results are expressed per g of solid

The feasibility of the upscaling process was demonstrated in a sinter pot experiment. The reached temperatures varied throughout the sample in the range of 800 - 1250°C. The final sinter product was relatively heterogeneous and two parts could be distinguished (well sintered and not sufficiently sintered). Still, even in the well sintered part, the amounts of  $C_3S$  and  $C_2S$  were lower than expected resulted in a compressive strength of slightly below 20 MPa. Also, higher amorphous content indicated that the C present in the as received material was not completely burnt out.

## Conclusions

It has been shown that MR can be converted into a hydraulic binder and its reactivity can be improved by doping with  $CaCO_3$ . A sinter pot experiment proved that the process can be upscaled, although some optimisation is needed. Still, the reactivity of this material is promising and the produced material can be used, already in its current stage, for certain applications, *e.g.* the production of paving tiles.

## References

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