A HYDRATION STUDY BY XRD/RIETVELD ANALYSIS OF CEMENT REGENERATED FROM COMPLETELY RECYCLABLE CONCRETE

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Abstract

In today's cement and concrete research, mineralogical quantification of (un)hydrated cement samples by X-ray Diffraction/Rietveld analysis becomes more and more important. As the results from XRD/Rietveld analysis are becoming increasingly more accurate, it became a widely used tool to study the hydration of cementitious materials besides other techniques e.g. isothermal calorimetry or thermogravimetric analysis. To quantify amorphous or non-identified phases, an internal standard might be added to estimate these so-called 'other' phases. Compared to unhydrated samples which are almost completely crystalline, it has a higher significance in hydrated samples, as certain cement hydrates, such as C-S-H, hydrogarnet, hydrotalcite, AFm, etc., are often poorly crystalline. Within the development of Completely Recyclable Concrete (CRC – a concrete designed for reincarnation within the cement production following the Cradle-to-Cradle Principle) the hydration of the regenerated cement was assessed by XRD/Rietveld analysis. Within this study it was found that the particle size distributions of the sample and the internal standard should not be underestimated within the quantification of the 'other' phases.

Keywords: *X-ray diffraction, Cement hydration, amorphous material*

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1. INTRODUCTION

In today's society, concrete is a popular building material: it is strong, gives flexibility in design and comes with a relatively low cost. However, like all materials, it also comes with an environmental cost. About 42% [1] of the 15 billion tons [2] of aggregates produced each year are used in concrete, of which only 8% are recycled aggregates [3]. This use of enormous amounts of natural raw materials is the first environmental problem of the concrete industry. Indeed, at the end of a concrete's life cycle, there is the waste production. 12-21% of the total waste generated in the European Union is concrete demolition waste [4, 5]. These numbers are the motivation for many researchers to work towards a more sustainable construction by resource efficiency and recycling.

To optimize product-recycling opportunities, the Cradle-to-Cradle (C2C) concept was developed [6]. In C2C production all material inputs and outputs are either seen as biological nutrients or as technical resources. Biological nutrients can be composted or consumed whereas technical resources can be recycled or reused without loss of quality. Applying this idea to the production of concrete, a Completely Recyclable Concrete (CRC) was designed [7, 8]. In order to make CRC a valuable technical resource for cement production, without need for ingredient adjustments, the concrete mixture should be chemically equivalent to a traditional cement raw meal. The primary ingredient for CRC is limestone aggregate as a source for CaO, the main ingredient for Portland cement production. Besides natural raw materials, such as limestone and porphyry aggregate, industrial by-products like fly ash and copper slag are preferably used for CRC production.

In the laboratory regeneration process (see 2.1) only small amounts of cement could be regenerated. For this reason the quality of the regenerated cement was assessed by XRD/Rietveld analysis, requiring only a limited amount of sample. The hydration process of the regenerated cement was compared with the one of an Ordinary Portland Cement.

2. MATERIALS & METHODS

2.1 The Cement Regeneration Process

An overview of the cement regeneration process from CRC applied in this study is given in Fig. 1. Within the regeneration process, the industrial cement manufacturing process was simulated in the laboratory.

CRC rubble from compressive strength tests was used for the preparation of the cement raw meal. Before grinding the concrete in a planetary ball mill during 4 min at 300 rpm, it was broken in a jaw crusher (resulting particle size <10 mm). Afterwards the resulting powders were mixed with water to form a paste that was brought into a perforated PVC-plate. By drying, at least 1 day at room temperature or 2 hours at 60 °C, small tablets (d = 5 mm, h = 5 mm) were formed. After removing the tablets from the perforated plate, a raw meal was ready to be sintered.

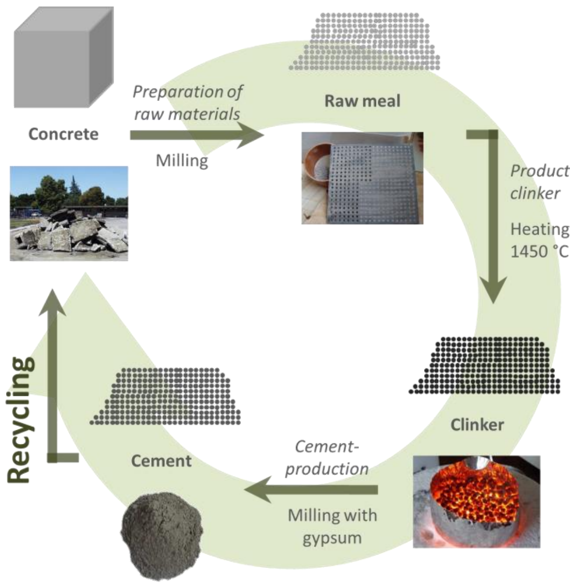

Fig. 1: Overview of the clinker regeneration process from CRC

In the industry, the raw meal would then be burned in a rotary kiln tube and thus gradually heated by shifting down towards the flame at the end of the furnace. In this study, a high temperature electric furnace (Carbolite BLF 1800) was used for simulating the burning process. The raw meals were gradually (10 °C/min) heated up to 1450 °C followed by a dwell time of 60 min. After burning, the clinkers were immediately air-cooled by removal from the furnace.

In the final step of the regeneration process, cement is produced by milling the clinker with calcium sulphate. The clinkers were first ground in a planetary ball mill during 4 minutes before adding 3.8 wt% calcium sulphate (2/3 $CaSO_4.{}^1/_2H_2O$ + 1/3 $CaSO_4$). Together with the calcium sulphate the clinker was ground an additional 2 minutes to obtain the regenerated cement powder (Blaine SSA 350 m²/kg). The mineralogy of the CRC clinker and OPC cement are given in Table 1. The OPC cement (CEM I 52.5 N) had a fineness of 380 m²/kg (Blaine SSA).

Table 1: Mineralogy of CRC clinker and OPC cement obtained by XRD/Rietveld analysis [wt%]

Mineral	**CRC clinker**	**OPC cement**
Alite	70.2	52.5
Belite	13.6	18.2
Ferrite	9.2	10.9
Aluminate	2.8	5.0
Calcite	0.9	2.5
Periclase	0.9	
Gypsum		0.4
Anhydrite		2.2
Other	2.5	8.4

2.2 Arresting the Hydration Process

To study the hydration process of the regenerated cement in time by XRD analysis, it was necessary to stop hydration after predetermined time periods (1, 3, 6 and 9 hours and 1, 2, 3, 7 and 28 days). For this purpose small amounts of paste (w/c = 0.4) were introduced into 125 ml conical PP-containers, resulting in discs (d = 45 mm, h = about 5 mm). Once closed, these containers were stored in a climate chamber (20 °C, RH >95%).

Solvent Exchange (SE) was used to stop the hydration process. The benefit of SE is the reduced damage to the pore structure, nonetheless it might partly dehydrate the C-S-H and ettringite phases [9]. Also, the solvent might be sorbed into the cement phases. The use of isopropanol as solvent is preferred, as it causes the least reaction in cement [9].

The method used for solvent exchange is based on [10]. The samples were crushed and ground with a mortar and pestle to obtain a powder. About 15 g powder was submerged in about 200 ml isopropanol for 15 min. After filtering and washing with isopropanol and diethylether, the powder was dried for about 8 min at 40 °C.

2.3 XRD Analysis of Hydrated Cement Pastes

XRD analysis was performed on cement pastes for which hydration was stopped as described earlier. In preparation of the measurement, the samples were crushed and ground using a mortar and pestle to achieve a powder with a maximum grain size of 74 µm (mesh 200). The internal standard approach was selected for absolute phase quantification and estimation of the amorphous or non-identified phase content by XRD analysis [11, 12]. A 20 wt% ZnO internal standard was added to the untreated clinker powder. Finally the powders were side-loaded into sample holders to reduce preferred orientation effects. Samples were measured in θ-2θ geometry over an angular range of 5-70 °2θ (CuKα radiation) using a 0.02 °2θ step size and 1 s/step counting time.

Topas Academic V4.1 software was used for Rietveld refinement [13]. Overall, the refined parameters were the measurement specific or global zero error and cosine Chebyshev function of 12 polynomial terms and the phase specific scale factors, unit cell parameters and Lorentzian peak shape broadening parameters. During Rietveld refinement, the clinker minerals alite, belite, aluminate and ferrite, gypsum, anhydrite and the hydration products portlandite, ettringite and kuzelite (a crystalline calcium monosulfoaluminate) were considered. Other hydration products, such as C-S-H, hydrogarnet, hydrotalcite and other AFm phases (calcium monosulfoaluminate and calcium hemi- or monocarboaluminate) are (often) poorly crystalline [14-16] and are therefore comprised within the 'other' fraction.

3. RESULTS & DISCUSSION

3.1 The Effect of Sample Preparation

The presented manual grinding of the samples was necessary to preserve the hydration products sensitive for rough grinding techniques such as a planetary ball mill. Due to the lower fineness of the samples, the accuracy of the

Rietveld analysis is reduced [17]. Furthermore, it seemed that the amount of ZnO was overestimated. This was observed after testing an unhydrated sample for which both preparation methods were followed (see Table 2). To both samples, 20% of ZnO was added, while the refinement of the XRD patterns resulted in ZnO contents of 20.9 and 23.9 wt% for respectively the ideal sample preparation using a ball mill and the manual soft preparation procedure.

Table 2: Effect of sample preparation on the quantification by Rietveld analysis [wt%]

Mineral	**Ball mill**		**Mortar and Pestle**	
	With ZnO	*Normalized*	*With ZnO*	*Normalized*
Zincite	20.9	-	23.9	-
Alite	52.9	66.9	52.7	69.3
Belite	10.5	13.3	9.6	12.7
Ferrite	7.1	8.9	6.7	8.8
Aluminate	2.1	2.7	2.0	2.6
Calcite	0.3	0.3	0.2	0.3
Bassanite	2.3	3.0	2.5	3.2
Anhydrite	1.3	1.6	1.3	1.7
Aphthitalite	0.6	0.7	0.5	0.6
Syngenite	1.3	1.7	0.3	0.4
Periclase	0.7	0.9	0.2	0.2

The difference between both measurements might be explained by a ‘rocks in dust effect’ (see Fig. 2), whereby the coarse clinker or cement particles are covered by the fine zincite particles, resulting in an overestimation of the ZnO content. After normalization of the results (without ZnO), it is seen that the effect on the quantification of the different phases is acceptable, keeping in mind the accuracy of XRD/Rietveld analysis (see Table 3 [16]), but obviously the effect becomes more significant for phases present in lower amounts.

Fig. 2: Visualisation of the 'rock in dust effect'

As a correction for this effect during quantification of the hydrated samples, the amount of ‘other’ phases was calculated using the ZnO content measured for an unhydrated sample that followed the preparation procedure of a hydrated sample (only manual grinding), instead of the ZnO content added to the sample. However for future assessments of the cement hydration process using XRD/Rietveld analysis an external standard method for quantification as described in [18] will result in a more accurate quantification.

Table 3: Typical values and accuracies for the determination of phases present in anhydrous cement [wt%] by XRD/Rietveld analysis [16]

Phase	**Typical value with accuracy**
Alite	60 ± 2.0
Belite	15 ± 1.5
Ferrite	4 ± 0.6
Aluminate	4 ± 0.6
Free lime	1 ± 0.3
Periclase	1 ± 0.3
Gypsum	2 ± 0.3
Hemihydrate	2 ± 0.3
Anhydrite	2 ± 0.3
Portlandite	1 ± 0.3
Calcite	1 ± 0.3
Quartz	1 ± 0.3

3.2 The Cement Hydration Process

The hydration of the calcium silicate phases as determined by XRD/Rietveld analysis is presented in Fig. 3. It is seen that alite and to a smaller extent also belite are consumed to form portlandite. Also a C-S-H gel is formed, but due to its poorly crystalline nature, an indication of the formation of this C-S-H gel can only be obtained from the increasing amount of ‘other’ phases quantified using an internal standard. This amount of ‘other’ phases however also contains the poorly or non-crystalline hydration products from the hydration of aluminate and ferrite, namely the AFm phases (calcium monosulphoaluminate and calcium hemi- or monocarboaluminate) and hydrogarnets.

Initially, after 1 hour of hydration, the alite content is about 70 and 55 wt% for CRC and OPC cement respectively. Up to one day, most of the alite hydrates and thereafter hydration slowly continues to result in alite contents of about 10 wt% after 28 days. The amount of belite slowly decreases in time. In disregard of the differences in mineralogy of the cements, the variation on the amount of portlandite and ‘other’ phases is rather limited. After 28 days of hydration the cement pastes contain about 20 wt% of portlandite and about 50 wt% of other phases.

The hydration of aluminate and ferrite phases is presented in Fig. 4. While the aluminate phases will dissolve completely,

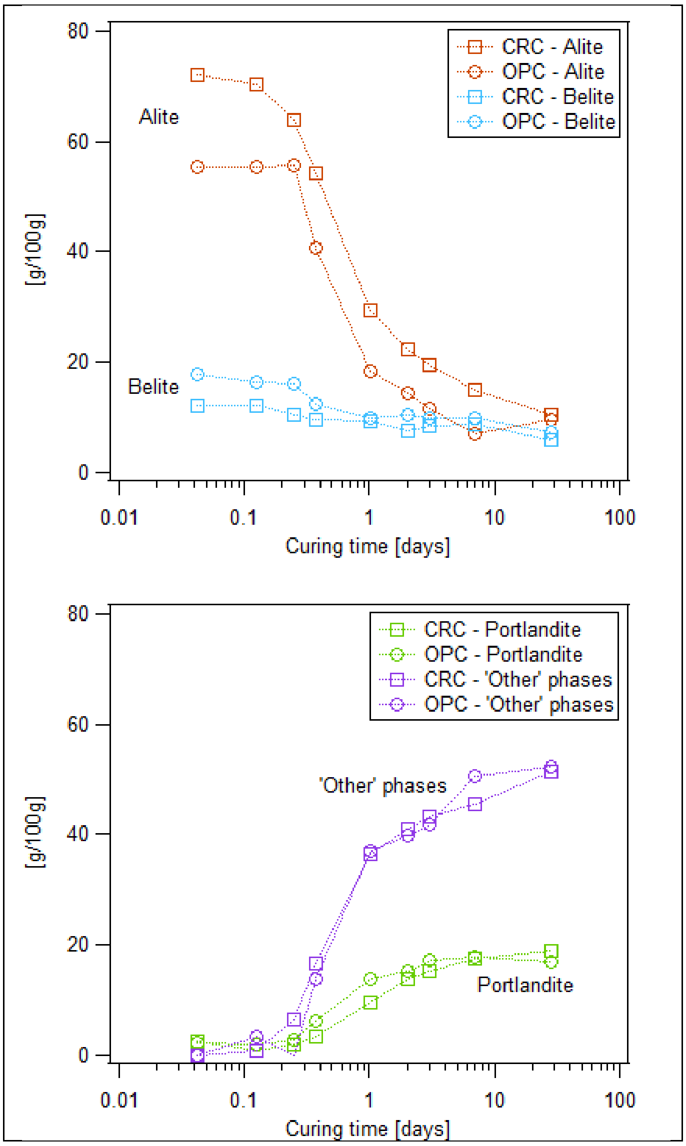

Fig. 3: XRD/Rietveld results of hydrating CRC and OPC cement pastes after arresting hydration using solvent exchange: overview of the hydration of the calcium silicate phases

the ferrite phase will decrease from 7 and 11 wt% after 1 hour of hydration up to 4 and 6 wt% after 28 days of hydration for CRC and OPC cement respectively. Aluminate was observed up to 1 day of hydration for CRC cement and up to 3 days for the commercial OPC.

Upon hydration of the aluminate phase, and to a smaller extent also the ferrite phase, gypsum is consumed within the first day for the formation of ettringite. The calcium sulphate added to the CRC cement (2/3 hemihydrate and 1/3 anhydrite) immediately formed gypsum upon contact with water, while for the commercial cements anhydrite remained present in the hydrating cement pastes up to 9 hours. For all cements ettringite remained present up to 28 days. After one week kuzelite, a crystalline calcium monosulphoaluminate, was observed in the CRC sample. For the commercial cement low amounts were detected from 9 hours onwards.

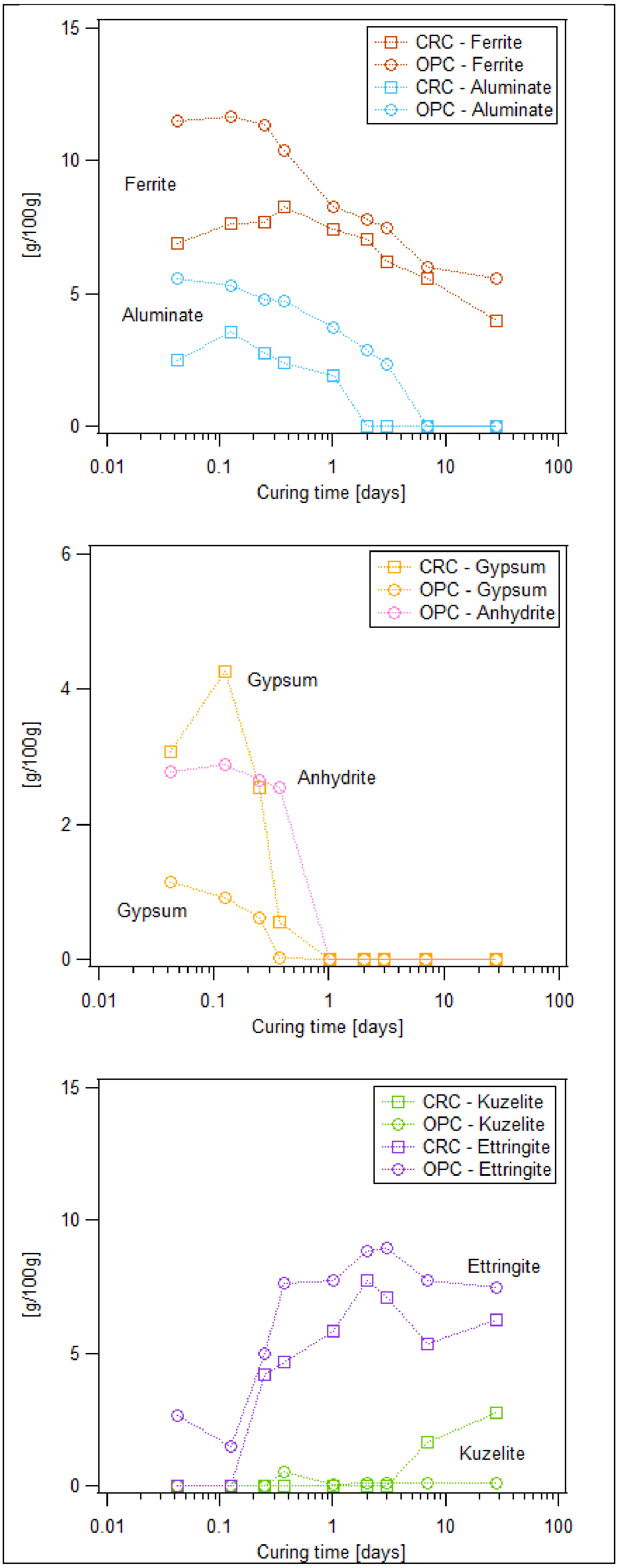

Fig. 4: XRD/Rietveld results of hydrating CRC and OPC cement pastes after arresting hydration using solvent exchange: overview of the hydration of the aluminate and ferrite phases

4. CONCLUSIONS

The phase changes upon hydration were visualized using XRD/Rietveld analysis. It was found that the particle size distribution of the measured sample affects the quantification using an internal standard (20 wt% ZnO). An external standard method could be used in the future to avoid the effect of the particle size distribution on the quantification of the different phases.

In general it can be concluded that the CRC cements have a hydration process similar to the commercial cements that were used as reference. In both cases the calcium silicate phases (mainly alite and more slowly also belite) dissolve to form crystalline portlandite and poorly crystalline C-S-H, the latter is considered in the ‘other’ phases. The aluminate phase, and to a smaller extent also the ferrite phase, dissolve to form ettringite consuming calcium sulphate. In case of the CRC cement crystalline kuzelite (an AFm phase) was observed after 7 days of hydration.

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BIOGRAPHIES

Mieke De Schepper received her master degree in civil engineering in 2009 from Ghent University (Belgium). Currently she is finishing her PhD on Completely Recyclable Concrete at the Magnel laboratory for Concrete Research (Ghent University).

Klaartje De Buysser received her PhD degree from Ghent University (Belgium) in 2007. Since 2009 she is professor at the faculty of science at Ghent University (SCRiPTS research group). Her research interests are transparent, conductive oxides, thermoelectric materials and electrospinning of ceramic fibres.

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Nele De Belie is professor in Durability of Cement Bound Materials at Ghent University (UGent) since 2000. She is technical director of the Magnel Laboratory for Concrete Research and leads the research group Concrete and Environment that has activities in the broad field of cement and concrete related to durability and sustainability.