The Assessment of Clinker and Cement Regenerated from Completely Recyclable Concrete

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Abstract

As the construction sector uses 50% of the earth's raw material and produces 50% of its waste, the development of more durable and sustainable building products is crucial. Nowadays, Construction and Demolition Waste (CDW) is already used as recycled aggregates in low-value concrete applications, since it is mostly inert material. On the other hand, the general trend today for the cement industries is the use of alternative raw materials for the production of cement clinker. From this and the above mentioned need for high-value recycling of CDW, the concept of completely recyclable concrete (CRC) has been developed. After demolition of a CRC-construction, the material cycle is closed as the concrete rubble is given a second life as raw material for cement production, without need for adjustments. Therefore, the concrete mixture is designed to be chemically equivalent to raw material for cement production by adequately incorporating limestone aggregates, different types of cement and industrial by-products. For this study, completely recyclable concrete was designed and produced. Within the design process, the chemical composition of the produced CRC was evaluated with the lime saturation factor, the silica modulus, the alumina modulus and the hydraulic modulus. In addition, the potential mineralogical composition was calculated according to the formulas of Bogue. Then, clinker was regenerated by burning ground CRC in a laboratory furnace by raising the temperature at a constant rate (15 °C/min) to 1350, 1400 and 1450 °C and maintaining it for 30 minutes. After burning, the clinker was immediately air-cooled by removing it from the furnace. The quality of the produced clinker and the influence of the burning temperature thereupon were investigated by determining the free lime content, and by microscopic and X-ray diffraction analysis. Based on these results, the ideal burning temperature was selected to produce cement. This cement was produced by grinding the clinker with calcium sulphate anhydrite. The hydration heat of cement pastes was measured in isothermal conditions and mortars were produced for compressive strength tests.

Originality

Sustainability is a major topic since years and the importance thereof is highlighted within the cement industry by the topic of the 13th ICCC, namely cementing a sustainable future. Within this trend towards a more sustainable production of cement, this research aims for a new approach towards concrete recycling, namely the development of Completely Recyclable Concrete (CRC) following the cradle-to-cradle (C2C) principle. In C2C production, all material inputs and outputs are seen as either technical resources or as biological nutrients. Biological nutrients can be composted or consumed and technical resources can be recycled or reused without loss of quality. Completely recyclable concrete (CRC) becomes such technical resource after demolition, namely an alternative raw material for cement production. By recycling CRC, a great deal of construction and demolition waste, which consists for about 40% of concrete, could be valorised. In addition, CRC is made chemically equivalent to cement raw materials by incorporating industrial by-products which reduces the clinker content of concrete and thereby its energy consumption and CO_2-emission.

Chief contributions

Within this research a new approach is studied towards a more sustainable construction. By designing a completely recyclable concrete (CRC), the production of clinker and cement out of concrete rubble is enabled, without need for adjustments. The unusual clinker and cement regenerated from CRC rubble is investigated within this study. Because the cement minerals within this regenerated clinker and cement are not necessarily the classic cement minerals, the influence on the formation and hydration of these minerals needs to be assessed. The standard quality tests are extended by microscopic and X-ray diffraction analysis, whereby a good picture of the clinker and its components was provided. The hydration process is on the other hand evaluated by recording the hydration heat of a cement paste in isothermal conditions and monitoring the setting with the ultrasonic through-transmission method.

Keywords: *Completely Recyclable Concrete, Cradle-to-Cradle, clinker regeneration, cement regeneration*

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1. Introduction

The European construction sector produces yearly around 850 million tons of waste, which represents 31% of the total waste generation (Fischer and Werge, 2009). Concrete itself accounts for 40% to 67% by weight of construction and demolition waste (CDW) (De Belie and Robeyst, 2007, ISO, 2005). These big numbers explain the efforts researchers are taking to develop the recycling of CDW, and concrete rubble in particular.

In general, recycling has an environment-friendly image: it reduces the demand upon new resources, it cuts down on transport as well as production energy costs, and it recycles waste which would otherwise be lost as landfill (Edwards, 1999). Nevertheless, e.g. Recycled Concrete Aggregates (RCA) still suffer a low acceptability, caused by a lack of trust in the quality of these products and compared to natural aggregates the higher cost (F.I.R., 2005). Therefore it is important that designers think ahead, and consider already in the design process the recycling of the waste produced by their products. This idea is better known as the Cradle-to-cradle (C2C) concept, which is worldwide promoted by McDonough and Braungart (2002). In C2C production, all material inputs and outputs are seen either as technical resource or as biological nutrients. Biological nutrients can be composed or consumed and technical resources can be recycled or reused without loss of quality.

To enable this idea for concrete, one can look at the raw materials used for concrete and cement production and it is seen that they have common raw materials. From here, the idea aroused to design Completely Recyclable Concrete (CRC) as a technical resource for cement production. This is done by designing the chemical composition of CRC to be similar to that of cement raw materials. If CRC is then used on a regular basis, a closed concrete-cement-concrete material cycle will arise, which is completely different from the current life cycle of traditional concrete.

2. Materials & Methods

2.1. Design for reincarnation

From a predesign state, Completely Recyclable Concrete is intended to be recycled as raw material within the cement production. This makes it necessary to aim for a chemical composition of CRC similar to those of a cement raw meal, of which the requirements are well known. If a cement raw meal is heated to about 1450 °C, traditional Portland clinker with hydraulic properties is formed. If this clinker is milled with calcium sulphate, Ordinary Portland Cement is produced. Portland clinker exists for about two thirds of calciumoxide (CaO), which makes it necessary to incorporate limestone aggregate into CRC. The second most important oxide is siliciumdioxide (SiO_2), which is found in sand and fly ash. The other components, Al_2O_3 and Fe_2O_3, can be provided by porphyry aggregates, copper slag or calcium aluminate cement.

In the first step of the design of CRC, the chemical composition of the concrete materials is determined (see Table 1). With this information, it is possible to design the CRC using parameters normally used for the assessment of traditional cement raw meals. These parameters are the lime saturation factor (LSF), the silica modulus (SM), the alumina modulus (AM) and the hydraulic modulus (HM). The LSF is the ratio of the lime available in the raw meal, to the lime chemically necessary to react with the present SiO_2, Al_2O_3 and Fe_2O_3 (Taylor, 1997):

$$\mathrm{LSF} = \frac{\mathrm{m}(CaO)}{2.8m(SiO_2) + 1.2m(Al_2O_3) + 0.65m(Fe_2O_3)} \quad (1)$$

with m(x) the mass percentage of the element in the raw meal. Unlike the LSF, which has a theoretical basis, the other parameters are empirical (Taylor, 1997). Where the SM has a major influence on the formation of the melt, the AM only has a significant effect on clinker formation at low temperatures. The HM is used to evaluate the hydraulic activity regarding the strength development of the cement (Shih et al., 2003). These parameters for the designed CRC are given in Table 2, together with the boundaries found in literature. It is seen that almost all parameters meet these limits, only the AM is exceeding the limits of Galbenis and Tsimas (2006).

Table 1: Chemical composition of used concrete raw materials

Concrete materials	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**Na_2O-equivalent**
Limestone sand [kg/m³]	51.88	2.68	0.12	0.22	1.46	-
Limestone aggregate 2/6 [kg/m³]	43.13	15.48	1.54	0.57	0.94	0.38
Limestone aggregate 6/20 [kg/m³]	43.86	15.42	1.2	0.45	0.84	0.30
CEM I 52.5 N [kg/m³]	63.43	18.9	5.77	4.31	0.89	0.95
Fly ash [kg/m³]	2.42	47.99	33.5	3.8	0.47	1.26

Table 2: Values of LSF, SM, AM and HM of CRC

	Designed CRC	**Limits (Desired limits)** *(Galbenis and Tsimas, 2006)*	**Limits** *(Taylor, 1997)*
LSF [-]	0.94	0.66-1.02 (0.92-0.96)	0.92-0.98
SM [-]	2.66	1.9-3.2 (2.3-2.7)	2.0-3.0
AM [-]	3.62	1.3-2.5 (1.3-1.7)	1.0-4.0
HM [-]	2.16	1.7-2.3 (~2)	-

In this study the accurate chemical composition of CRC is achieved by using limestone aggregates, as lime stone is the main ingredient within the manufacturing of Portland clinker. Fly ash was used as cement replacement to provide the necessary SiO_2 and Al_2O_3. The mixture proportions of the produced CRC are presented in Table 3. The influence of the cement replacement on the properties of concrete will not be discussed within this paper.

Table 3: Concrete mixture proportions
FA/B = fly ash to binder ratio; W/B : water to binder ratio

Concrete materials	**CRC**
Limestone sand [kg/m³]	614.2
Limestone aggregate 2/6 [kg/m³]	378.0
Limestone aggregate 6/20 [kg/m³]	666.5
CEM I 52.5 N [kg/m³]	292.5
Fly ash [kg/m³]	191.4
Water [kg/m³]	180.0
FA/B [-]	0.40
W/B [-]	0.40

2.2. Regeneration of cement

An overview of the regeneration of cement is given in Figure 1. First, the designed CRC was produced and cured in the laboratory according to NBN B 15-001 (2004). At the age of one month, the produced concrete cubes were crushed in a jaw crusher and ground in a laboratory mill until a powder with a specific surface area of approximately 450 m²/kg was obtained. After mixing the resulting powders with water, small tablets (d=5mm, h=5mm) were formed in a perforated PVC-plate by drying at room temperature for 24 hours.

Clinker was produced in an electric furnace by heating the raw meal up to 1350, 1400 and 1450 °C at a constant rate (15 °C/min) and maintaining this temperature for 30 minutes. After burning, all clinkers were air-cooled. The regenerated cements were produced by grinding the clinker burned at

1450 °C in a laboratory mill with calcium sulphate anhydrite. The necessary amount of $CaSO_4$, 4.52%, was determined by the following formula:

$$\mathrm{m}(CaSO_4) = \frac{\mathrm{M}(CaSO_4)}{\mathrm{M}(SO_3)}[0.6\mathrm{m}(Al_2O_3) - \mathrm{m}(SO_3)] \quad (2)$$

where: m(x) is the mass percentage and M(x) is the molar mass of the element in the clinker.

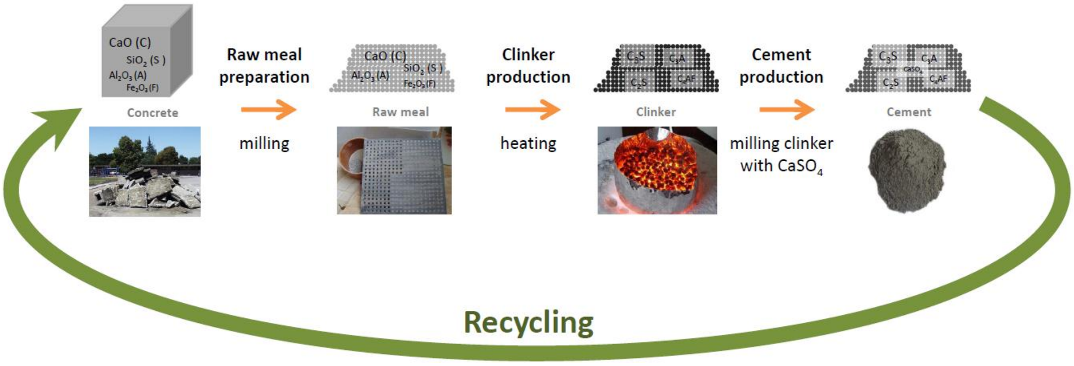

Figure 1: Regeneration process of cement out of Completely Recyclable Concrete

2.3. Testing of clinker and cement properties

The quality of the produced clinkers was evaluated by determining the free lime content. The ethylene-glycol method based on BS EN 196-2 and EN 196-2 was used to determine this parameter. Also a microscopic analysis was performed. The clinker sections were etched with HF and then observed using a light microscope. An X-ray diffraction analysis was executed based on Stutzman and Leigh (2002), using a Thermo Scientific ARL X'TRA Powder Diffractometer and the FullProf Suite software (Rodriguez-Carvajal, 1990) for Rietveld analysis.

The hydration heat was measured on cement pastes with a w/c ratio of 0.4 with an isothermal calorimeter (TAM AIR). The regenerated cement was tested by a compressive strength test according to NBN EN 196-1 (2005) on standard mortars.

3. Results & Discussion

3.1. Quality of the regenerated clinker

Table 4 presents the free lime (fCaO) content of the clinkers burned at different temperatures. To prevent the expansion of free lime in cement, the free lime content should be less than 3% (BBG, 2006), which is the case for all burning temperatures. It is seen that higher burning temperatures result in a lower fCaO content, whereby more alite should be formed. Assuming all the fCaO is reacting with belite to produce alite, the additional amount of alite formed can be calculated based on the molar mass ratio of alite to fCaO, being 4.071. According to these calculations, burning at 1450 °C instead of 1350 °C should result in the formation of an additional amount of 3.14m% alite, which is rather a small amount.

The microscopic analysis shows a porous heterogeneous clinker (see Figure 2) , which indicates an unsatisfying burning process. The alite crystals are rather small, and here and there belite crystals appear in clusters or between alite crystals. Remarkable is that the clinker burned at 1350 °C seems to contain less belite as the clinker burned at 1400 and 1450 °C while they are originating from the same raw material. It is possible that exposure time to HF-vapour was unsatisfactory for the clinker burned at 1350 °C, which will not colour the belite crystals blue. Also noticeable is the absence of an interstitial material nicely surrounding the alite and belite crystals within the clinker burned at 1400 and 1450 °C, although XRD analysis and Bogue calculations based on chemical analysis prove that large amounts of aluminate should be present (see below). Within further research the burning process should be studied more in detail to improve the clinker quality. Probably keeping the maximum temperature for longer than 30 minutes will lower the porosity and will result in a homogenous clinker of good quality.

Table 4: Free lime content (fCaO) of regenerated cements burned at different temperatures

<table>
<tr><th>Burning temperature [°C]</th><th>fCaO [m%]</th><th colspan="2">Additional alite formed [m%]</th></tr>
<tr><td>1350</td><td>1.00</td><td rowspan="2">1.59</td><td></td></tr>
<tr><td>1400</td><td>0.61</td><td rowspan="2">1.55</td></tr>
<tr><td>1450</td><td>0.23</td><td></td></tr>
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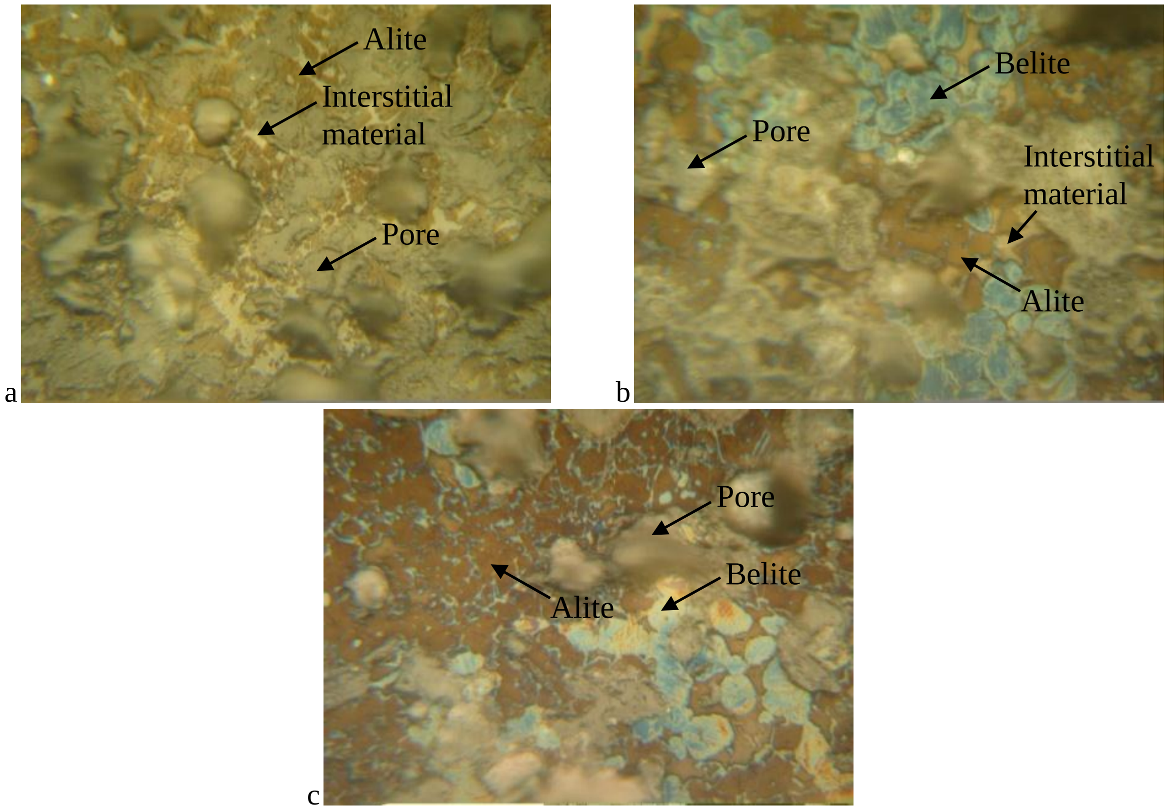

Figure 2 : Micrographs of clinker regenerated from CRC burned at 1350 °C (a), 1400 °C (b) and 1450 °C (c). The clinker section is etched with a HF-vapour and observed with light microscopy. The height of the images is 180 µm.

An overview of the mineralogical composition of the CRC is given in Table 5. The mineralogical composition achieved by Bogue calculations on the designed chemical composition and on the results of a chemical analysis on the clinker burned at 1450 °C show a good similarity. In this table it is also seen that alite is the main phase, as it should be in a good clinker. The amount of aluminate phase is high compared with Taylor (1997), and the amount of ferrite is rather low.

Comparing the Bogue calculations with the Rietveld analysis, were alite, belite, aluminate and ferrite were considered, it seems that within the Bogue calculations the amounts of alite and ferrite are overestimated and the aluminate content is underestimated. Taylor (1997) already suggested that the results from Bogue calculations can differ from the true phase composition, mainly because the composition of each clinker phase differs considerably from those of the pure compounds. On the other hand, the high content of alite and belite makes it harder to detect aluminate and ferrite by X-ray diffraction. To check the accuracy of the Rietveld analysis for minor phases, e.g. ferrite, the method of selective extractions described by Stutzman and Leigh (2002) could be used within further research.

Table 5: Overview of the mineralogical composition of the clinker by (1) Rietveld analysis of X-ray diffraction patterns of clinker burned at 3 temperatures, (2) Bogue calculation on the designed chemical composition, and (3) Bogue calculation on the chemical analysis of the clinker burned at 1450 °C

	XRD			Design	Chemical analysis	Literature
	1350 °C	*1400 °C*	*1450 °C*			*Taylor (1997)*
Alite	47.71	51.88	50.85	53.50	56.52	50-70
Belite	27.53	24.88	24.46	25.52	24.54	15-30
Aluminate	21.61	21.76	21.83	15.30	14.24	5-10
Ferrite	3.15	1.48	2.86	5.68	4.7	5-15

3.2. Quality of the regenerated cement

In Figure 3, the heat production rate and the cumulative heat production of the cement regenerated from CRC are compared with those of an Ordinary Portland cement. The very first hydration peak due to the first hydration reactions at the moment of mixing the samples will be neglected in this paper. Then the first peak observed is likely caused by the hydration of alite, similar to the hydration of CEM I 52.5 N. As it is seen in Figure 3, this peak is not as high for cement from CRC as for CEM I 52.5 N. However, after 7 days the cumulative heat production of cement from CRC (295.08 J/g) is approaching the one of CEM I 52.5 N (312.98 J/g).

The reactions causing the three small peaks indicated with an arrow in Figure 3 need to be identified by further study. XRD-analysis before and after these peaks could be performed to identify the reactions at these moments of hydration.

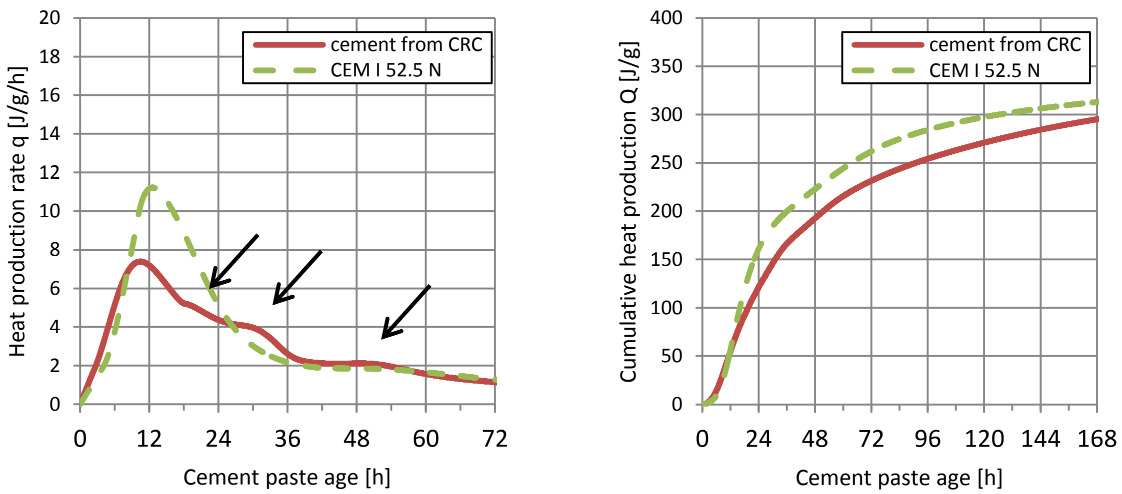

Figure 3: The heat production rate q (left) and cumulative heat production Q (right) of cement pastes with W/C = 0.4 under isothermal conditions (20 °C)

The compressive strength at 28 days of mortars produced with regenerated cement was found to be 45.88 ± 1.94 MPa. This result is good keeping in mind the relatively low specific surface area of 2591 ± 281 cm²/g (Blaine, according to NBN EN 196-6 (1991)), which should reach 4800 cm²/kg for a cement strength class 52.5.

4. Conclusions

This paper proves that a cement with a good strength can be regenerated from CRC. Nevertheless some aspects of the regeneration and hydration process should be studied more in detail. First of all the burning process should be improved to produce a homogeneous clinker with good quality. The fineness of the cement produced by this clinker should be increased, e.g. by wet grinding if dry grinding would not fulfil the requirements, what will result in higher strengths. Also the influence of the type and the amount of calcium sulphate added to the cement should be studied more in detail as it will influence the hydration process of the regenerated cement.

After all, there is a need for high level recycling applications for concrete rubble and from this study it seems that the development of Completely Recyclable Concrete can be a solution. As CRC is designed to be recycled, CRC rubble is not a waste material, but instead a valuable material for the cement production.

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