# The hydration of cement regenerated from Completely Recyclable Concrete ☆

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## HIGHLIGHTS

- A hydration study on cement regenerated from Completely Recyclable Concrete.
- Experimental results on recycled cement are compared with a cement hydration model.
- Reaction kinetics are very similar for recycled and traditional cement.
- Hydration product assemblages are very similar for recycled and traditional cement.

## ARTICLE INFO

## ABSTRACT

This paper presents a study of the hydration reactions of a cement regenerated from Completely Recyclable Concrete by thermogravimetric analysis and X-ray powder diffraction/Rietveld analysis. The experimental results for the hydration reactions of the clinker phases in the regenerated cement were compared to a hydration model for OPC. A good agreement between the experimental and modeling results was observed. Therefore in terms of both reaction kinetics and hydration product assemblages the hydration of cement regenerated from CRC is concluded to be very similar to the hydration of OPC.

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## 1. Introduction

Concrete is due to its strength, flexibility in design and relatively low cost a popular construction material. Each year the cement and concrete industry produces worldwide up to 3 and 10 billion tons, respectively [1,2]. Due to this popularity, cement and concrete manufacturing has a big impact on the environment. Enormous amounts of primary natural resources are used for aggregate and cement production. For instance, 15 billion tons of aggregate is produced annually [3], of which around 42% is used in concrete [4] and of which only 8% is recycled [5]. Another problem arising from the global success of concrete is the production of concrete demolition waste, which represents 12–21% of the total waste generated in the European Union [6,7]. Last but not least,

the production of the main component of Ordinary Portland Cement (OPC), namely Portland clinker, releases about 0.85 kg $CO_2$ per kg clinker. This is on the one hand due to the calcination of limestone, the main material source for clinker production. On the other hand important quantities of fuels are combusted as a temperature of 1400–1450 °C is reached in the production process [8]. In total the cement industry is estimated to emit 5-7% of the global $CO_2$ emissions [9].

Worldwide, many studies in the field of concrete research are dealing with the reduction of the environmental impact of cement and concrete; e.g.:

- The replacement of Portland clinker and cement by industrial byproducts such as metallurgical slags [10] and fly ashes [11] or waste products such as ground glass powders [12–15] with pozzolanic or latent hydraulic properties to reduce the use of primary materials and the $CO_2$ emissions.
- The use of industrial by-products (e.g. metallurgical slags and fly ashes) [16–18] or waste materials (e.g. municipal solid waste incineration ash [19,20], mining waste [21,22], refinery residues

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[23], sewage sludge [24], refuse glass [12,25]) as raw materials for clinker production to reduce the use of primary materials and $CO_2$ emissions.

- Use of (concrete) demolition waste as recycled aggregate in concrete by which a waste material becomes a valuable material to replace primary resources [26–29].

The above mentioned recycling opportunities often arise from the search for new synergies between usually unrelated industrial partners. Producers of waste materials on the one hand, desire their waste products to be optimally used as material resources at the end of their life cycle. On the other hand producers are encouraged to improve the resource efficiency of their manufacturing process by the incorporation of waste materials. To take recycling to a higher level of efficiency, the interests of both partners should be joined and the 'design for reincarnation' principle, also known as the Cradle-to-Cradle (C2C) concept [30], should be applied.

When applying this idea on the production of concrete, it is easily noticeable that the raw materials used for concrete and cement production share common base components. Hence the idea emerged to design a Completely Recyclable Concrete (CRC) as a technical resource for cement production by designing the chemical composition of CRC to be similar to that of the cement raw material mix. Hereby concrete waste becomes a valuable material for cement production. To obtain the desired raw meal composition, the concrete should contain limestone aggregates, and can also contain waste materials such as metallurgical slags or fly ash [31,32] which additionally reduces the environmental impact of the CRC. Prior studies have shown that the performance and durability characteristics of such CRC comply with international specifications [32,33]. Moreover, life cycle assessment indicated that the overall environmental impact of the CRC can be lower than regular concrete by 25–60%, provided that transportation costs remain limited [34]. Preliminary studies have shown that the properties of the eventually regenerated clinker and cement were comparable to reference cements of similar composition [32,35]. The clinkering reactions during firing of Completely Recyclable Concrete were studied in detail earlier [36].

We acknowledge that some logistic and other practical issues will arise when taking the CRC concept into practice. And we are aware that there will be no future where only CRC concrete is produced and later on used as cement raw material. Nevertheless, we are certain that CRC can be a part of the solution in lowering the environmental impact of the cement and concrete industry. A well-considered tracking system will be required, but should be feasible for integrated cement and concrete producers. Furthermore, the CRC concept for concrete will have its benefits for some applications, e.g. for concrete structures that are exposed to serious pollutions, whereof the toxic elements can be decomposed to harmless elements within the clinkering process. The issue that OPC production asks very strict limits towards raw material composition (see Section 2.1) will solve itself as we are aware that no future clinker production plant will be fed with CRC only. Nonetheless, by aiming for a 100% use of CRC in laboratory studies, the potential of CRC use in the clinkering process is maximized. Finally, it should be mentioned that also the use as such of today's concrete and demolition waste in the cement clinkering is studied in our laboratories [37–39].

In this paper the hydration process of cement regenerated from Completely Recyclable Concrete is studied. The hydration of a cement paste was stopped at different ages and the samples were then studied by X-ray diffraction (XRD) and thermogravimetric (TG) analysis. The hydration heat was registered by isothermal calorimetry. The obtained results were subsequently compared to an established hydration model [40]. The physical performances

of regenerated cement mortars such as workability and compressive strength will not be handled within this paper.

## 2. Experimental procedure

### 2.1. Materials

A Completely Recyclable Concrete was designed to have the chemical composition of a cement raw material. Upon heating this raw mix to 1450 °C, a traditional Portland clinker with hydraulic properties is formed. The main constituents of a Portland clinker are lime (CaO, 60–67%), silica ($SiO_2$, 17–25%), alumina ($Al_2O_3$, 2–8%) and iron oxide ($Fe_2O_3$, 0–6%) [41]. Due to the high lime content required, limestone aggregates need to be used in CRC. Additionally porphyry (diorite) aggregate (rich in $SiO_2$ and $Al_2O_3$) and copper slag (high in $Fe_2O_3$ and $SiO_2$) were used as aggregates. The binder consisted of a combination of CEM I 52.5 N and fly ash (containing $SiO_2$ and $Al_2O_3$) with a cement to fly ash ratio (by mass) of 3. The concrete also contained a small amount of limestone filler (Table 1).

The chemical compositions of the raw materials and the produced clinker were determined by X-ray Fluorescence (XRF) analysis, of which the results are presented in Table 1. A rather good agreement was found between the real clinker composition and the expected clinker composition based on the chemical analysis of the raw materials.

CRC cubes were produced and cured in the laboratory according to NBN B 15-001 (2004). The produced cubes were crushed in a jaw crusher and ground in a planetary ball mill. Afterwards the resulting powders were mixed with water to form a paste that was introduced into a perforated PVC-plate. By drying at 60 °C for about 2 h, small pellets (diameter = 5 mm, height = 5 mm) were formed. After removal of the pellets from the perforated plate, the raw mixture was ready to be sintered. A high temperature electric furnace (Carbolite BLF 1800) was used for heating the raw meal to 1450 °C at a constant rate (10 °C/min) followed by a dwell time of 1 h. After heating, the clinkers were immediately air-cooled. In the final step of the cement regeneration process, the clinkers were ground in a planetary ball mill during 4 min. Subsequently, the clinkers were milled with 2% $CaSO_4$, using a mixture of anhydrite (about 30%) and hemihydrate (about 70%), for an additional 6 min to obtain a cement with a specific surface area of about 400 m²/kg.

### 2.2. Analysis

For the hydration study cement pastes were prepared with a water to cement ratio of 0.4. About 10 g of the cement paste was mounted into glass vials, which were then placed in an isothermal calorimeter (TAM AIR) at 20 °C to measure the hydration heat during the first 7 days of hydration. Since mixing occurred outside the calorimeter, the first hydration peak could not be registered entirely. Because this peak only amounts to a few percent of the total heat liberated [42] it will not be considered in further analysis.

Small amounts of paste were introduced into 125 mL conical PP-containers, resulting in discs with a diameter of about 45 mm and 5 mm high. Once closed, these containers were stored in a climate chamber (20 °C and RH > 95%). At specified ages (1 h, 3 h, 6 h, 9 h, 1 d, 2 d, 3 d, 7 d, 28 d) hydration was stopped by freeze drying or by solvent exchange.

When using freeze drying (FD), the cement paste discs were crushed, placed in aluminum sample holders and submerged in liquid nitrogen for about 2 min. Subsequently, the samples were dried in a Mini Lyotrap Freeze Drying machine (LTE Scientific Limited) until constant mass. If Solvent Exchange (SE) was used, 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 (method based on Winnefeld and Lothenbach [43]). Before analysis 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).

Thermogravimetric (TG) analysis was carried out using a Netzsch STA 449F3 apparatus. The measurements were executed on about 50 mg of powdered cement paste with a nitrogen gas flow of 50 mL/min and a heating rate of 10 °C/min up to 1050 °C. The weight loss between 400 and 520 °C was attributed to the dehydroxylation of portlandite ($Ca(OH)_2$) [44]. The limited mass loss in the range of 600–780 °C was considered to be due to the release of carbon dioxide, from carbonated portlandite [45]. The portlandite contents $m(Ca(OH)_2)$ (wt%) presented in this paper were corrected for this:

$$m(Ca(OH)_2) = WL(Ca(OH)_2)\frac{M(Ca(OH)_2)}{M(H_2O)} + WL(CaCO_3)\frac{M(Ca(OH)_2)}{M(CO_2)} \qquad (1)$$

with $WL(Ca(OH)_2)$ en $WL(CaCO_3)$ the weight loss between 400–520 °C and 600–780 °C respectively (in wt%) and $M(Ca(OH)_2)$, $M(H_2O)$ and $M(CO_2)$ the molar masses of $Ca(OH)_2$, $H_2O$ and $CO_2$.

For X-ray Diffraction (XRD) analysis, a 10 wt% ZnO internal standard was added to the powdered cement paste. This enables absolute phase quantification and estimation of the amorphous or non-identified phase content by XRD analysis [46,47], hereafter called the 'other' fraction or part. To reduce the effects of preferred orientation, the powders were side-loaded into the sample holder. The XRD data were