Recovering of Clinker Minerals from Hydrated Portland Cement Paste

Semion Zhutovsky and Andrei Shishkin

Abstract Recycling of concrete construction and demolition waste is necessary for the increase of sustainability and reducing the environmental impact of concrete construction because of the increasing rate of such waste production and its accumulation. Coarse aggregates can be partially recovered from concrete waste. However, it is not clear whether hydrated cement paste can be converted back to clinker. However, concrete waste fines, which are a mix of fine aggregates, coarse aggregate debris, and the hydrated cement paste, are currently not a part of the recycling process. The ability of hydrated cement paste to be recovered back to clinker minerals that have binder properties has not been studied systematically. In the current research, the phase transitions in hydrated cement paste heated to a temperature in the range from 600 and 1450 °C were investigated by means of X-ray diffractometry and thermal analysis. The experimental results demonstrate that hydrated Portland cement paste can be recovered back to clinker minerals. The recovered cement paste contains all the main clinker minerals similarly to the initial cement. The results provide evidence for the possibility of recycling hydrated cement and concrete into the cement clinker. The recycled clinker will potentially have a lower carbon footprint in comparison to original Portland cement.

Keywords Recycling · Clinker · Portland cement · Concrete waste fines

1 Introduction

The amount of concrete construction and demolition wastes is increasing constantly. Recycling of construction and demolition waste is necessary for saving natural resources, reducing the waste dump and landfill. The industry of concrete recycling has been steadily developed. European countries have goals to increase the reusing of waste construction materials up to 70% [1].

S. Zhutovsky (✉) · A. Shishkin
National Building Research Institute, Technion—Israel Institute of Technology, Haifa, Israel
e-mail: semionzh@technion.ac.il

The waste concrete contains hydrated cement paste and aggregates, but only the coarse aggregates are generally extracted now. Concrete waste fines which are a mix of fine aggregate, the residue of coarse aggregates and hydrated cement paste are out of recycling in industrial plants [2, 3]. The quality of recycled concrete aggregates is lower than that of natural ones, because of residual hydrated cement [4]. Using recycled aggregates has a negative effect on the properties of concrete [5, 6] that limit their maximum content in concrete.

On the other hand, recycled concrete fines could be used as a raw material in Portland cement production. Portland cement is used as a binder in construction for over a hundred years. Its production has a high environmental impact due to the exhaustion of natural resources and emissions of carbon dioxide. The use of recycled concrete fines for clinker production can potentially reduce its carbon footprint and save natural resources. The recycled concrete fines can replace up to 15% of raw materials, according to chemical and mineralogical limitations [7–10].

The fine aggregates often contain minerals used for cement production such as calcite and quartz. However, it is not clear whether hydrated cement paste can be recovered back to clinker minerals. It possible that the hydrated cement paste will prevent the formation of good clinker in the production process. Although the chemical composition of hydrated cement paste is equal to the chemical composition of Portland cement with the addition of water, the addition of pure hydrated cement paste to raw material at rates over 30% caused problems [4, 11].

Portland cement clinker is manufactured by heating of the raw materials in the rotary kiln to 1450 °C. In this high-temperature treatment process, major clinker phases are obtained: alite (C_3S) 50–70%, belite (C_2S) 15–30%, tricalcium aluminate (C_3A) 5–10%, and tetracalcium aluminoferrite (C_4AF) 5–15%. The main clinkering chemical reactions and their temperature ranges are well studied [12]. Alite forms at a temperature above 1300 °C in the liquid phase, tricalcium aluminate forms above 1000 °C through the intermediate phases, belite, and tetracalcium aluminoferrite form already near 700 °C. However, there is no clear answer to what phase transformations in hydrated Portland cement paste take place during high-temperature processing in the rotary kiln.

The hardened Portland cement paste is a product of hydration reaction, i.e. the reaction of cement with water. It mainly consists of calcium silicate hydrate (C–S–H) which is often referred to as cementitious gel and Portlandite ($Ca(OH)_2$, which is in cement chemistry notation CH). The cementitious gel has variable stoichiometry ($mCaO \cdot SiO_2 \cdot nH2O$, where m is about 1.7, and 1.4 < n < 4) with impurities and inclusions of aluminum, iron and sulfur.

There are many studies on phase transformations in heat-treated concrete and hydrated cement paste at temperatures under 1000 °C [13, 14]. At these temperatures, the main decompositions stages take place with no further detectable phase transformations. The main decomposition stages include [12–15]: release of free evaporable water and partial decomposition of physically bound water between 30 and 120 °C; in the range between 110 and 170 °C decomposition of ettringite, gypsum, carboaluminate hydrates; between 180 and 600 °C dehydration of C–S–H; between 450 and 550 °C portlandite dehydration; and in the range between 700 and 900 °C calcium

carbonate decomposition. Nevertheless, there is no sufficient information about phase transformations in hydrated cement at the temperature between 1000 and 1450 °C, i.e. in the range of cement clinker mineral phases formation. One exception is maybe anhydrite decomposition with the SO_2 gas evaporation, which is known to take place at a temperature over 1200 °C and can be clearly seen in a thermogravimetric analysis [16].

There is some controversy in the literature about the high-temperature phase transitions in hydrated cementitious materials. The high-temperature X-ray diffraction (XRD) showed that C–S–H starts to decompose near 620 °C which is related to significant loss of strength. The characteristic amorphous C–S–H hump in XRD range of 25–40° 2θ completely disappears at 690 °C and a new strong crystalline peak of orthorhombic α′-Belite and Quartz appear [17].

Concrete structures exposed to fire have high mechanical damage and also chemical transformations [18]. It was reported that from 500 to 800 °C, due to the volume change of calcium silicate hydrate, cracks take place in the cement paste matrix and at about 1000 °C the hydrates including C–S–H and CH are transferred into crystalline phases completely [19]. The pore system increases rapidly after 400 °C with a graduate mass loss. The cement binder in concrete subjected to high temperatures save a partial regeneration ability [20]. At temperatures above 1200 °C, the binder in the concrete completely disintegrated [21].

Another study reports that the hump related to C-S–H around 29.35° 2θ disappeared above 500 °C accompanied by increased intensities of β-Belite (β-C_2S) peaks in paste samples after exposure to various temperatures for 6 h [22].

Some researchers claim that at the temperatures over 200 °C calcium silicate hydrate begins to form a "new nesosilicate", with CaO/SiO_2 ratio near 2, similar to a structure of Belite, but less crystalline [23]. At 750 °C C–S–H gel completely replaced mainly by this new phase. The process is reversible and a new C–S–H gel forms back due to hydration. The heating of 5-year old cement paste to various temperatures under 1000 °C, indicated β-belite and some alite are formed above 500 °C [24].

The high-temperature transformations of synthetic calcium silicate hydrate indicated that C–S–H transforms into β-Wollastonite ($CaSiO_3$) at 800–900 °C and into α-Wollastonite at 1220–1280 °C [25]. If CaO/SiO_2 ratio > 1 the competitive formation of Belite (C_2S) and Rankinite (C_3S_2) is increasing together with Wollastonite (CS).

Cement paste transformations in concrete during heating were also studied. C_2S polymorphs were found after thermal processing up to 900 °C in laboratory-prepared pastes [26]. Materials obtained at temperatures near 740 °C achieved higher early-age strengths due to the higher relative concentration of α′-belite, compared to the less reactive β-belite. The opposite results were obtained for 2-year-old laboratory-prepared cement paste pieces burned for 8 h under different temperatures [27]. High-temperature treatment (1100 °C) transformed the C–S–H into Wollastonite with a low content of Belite.

It can be seen that the information about high-temperature phase transitions in hydrated Portland cement paste is not sufficient and controversial. This is especially true for the temperatures above 1000 °C were the main clinker phases are forming.

The objective of the current research was to study the phase transitions in hydrated cement paste in the temperature range of 600–1450 °C. The study was carried out by means of X-ray diffractometry (XRD) and thermal analysis. The experimental results clearly demonstrate that hydrated Portland cement paste can be recovered back to minerals of clinker indicating high potential for recycling of hydrated cementitious materials.

2 Materials and Test Methods

2.1 Materials

In the present study, cement paste with water to cement ratio of 0.68 was investigated. It was produced using standard Portland cement of CEM I 52.5 N type. The cement paste was mixed in a pan mixer and cast into 1-inch cube molds, which were demolded at the age of 1 day. The curing was carried out in a lime solution until 28 days.

2.2 Methods

The hydrated cement paste was crushed into pieces of approximately 15 mm and burned in a high-temperature bottom-loading laboratory furnace. Burning was performed to the temperatures between 600 and 1450 °C. The samples were air quenched after removing them from the furnace.

Thermal analysis included thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC). Thermal analysis was carried out in the Netzsch STA 449 F5 Jupiter instrument. The oxidizing atmosphere of dry air at the flow rate of 80 ml/min was used. For thermal analysis samples were ground below 45 μm size. The ground samples were put in a platinum crucible and tested in the temperature range from 25 to 1500 °C at the heating rate of 10 °C/min.

The mineral composition was determined by means of XRD. For this purpose Malvern PANAlytical EMPYREAN X-ray diffractometer was used with the following configuration: Goniometer radius of 240 mm, an X-ray source was CuKα1,2 ($\lambda = 1.5408$ Å) with the X-Ray generator operated at a voltage of 45 kV and a current of 40 mA. The optical configuration of XRD was as follows: the incident beam optics included a 10 mm mask, 0.04 rad Soller slit along with ¼° divergence and 1° anti-scatter fixed slits; the diffracted beam optics consisted of 8 mm anti-scatter fixed slit and 0.04 rad Soller slit. The detector was PIXcel 3D detector used in a 1D continuous scan mode. The scan was performed using Brag-Brentano θ–θ

geometry, between 10 and 70° 2θ. Timestep of 80.32 s with a step size of 0.013° 2θ was used resulting in a total measurement time of 25.22 s. The quantitative analysis was performed by means of Rietveld refinement using HighScore Plus software.

3   Results

The results of thermal analysis of hydrated cement paste, which include TGA and DSC are shown in Figs. 1 and 2, respectively. Four mass loss steps can be identified in the TG curve in Fig. 1, with the corresponding DTG peaks. The first step in the range of 90–300 °C is associated with the decomposition of AFt and AFm phases partially overlapping with the dehydration of calcium-silicate-hydrate (C–S–H) gel. The second step is associated with portlandite dehydration in the range of 400–500 °C. The third step in the temperature range of 600–750 °C is caused by the decomposition of calcite and accompanied by the emission of CO_2 gas. The last fourth step between 1250 and 1400 °C is associated with the final decomposition of sulfates with the emission of gaseous SO_2. The DSC peaks corresponding to these steps can be seen in Fig. 2. In addition to these endothermic peaks, the solid–liquid transition can be identified in the DSC heating curve, as well as the liquid–solid transition at 1250 °C that is clearly seen in the cooling curve in Fig. 2. Some additional small DSC peaks that are associated with clinkerization reaction can be seen in the vicinity of 1300 °C.

According to TGA the Portlandite content of 14.4% and calcite of less than 3% was determined. The calculated amount of decomposed anhydride according to TGA
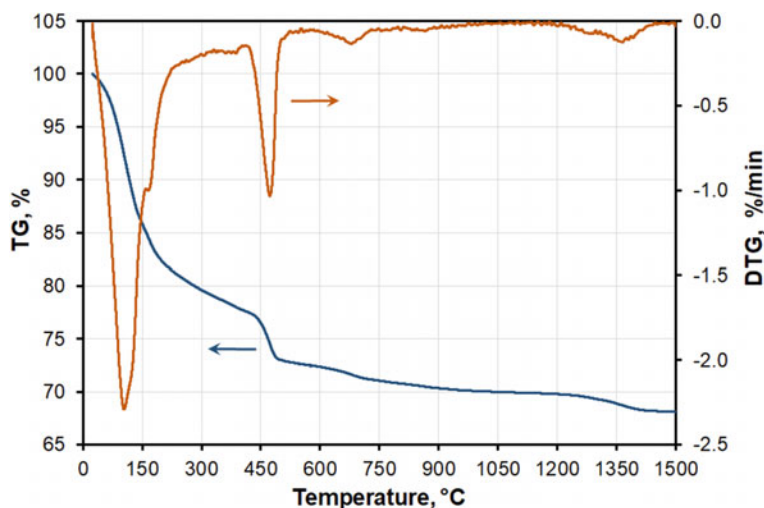
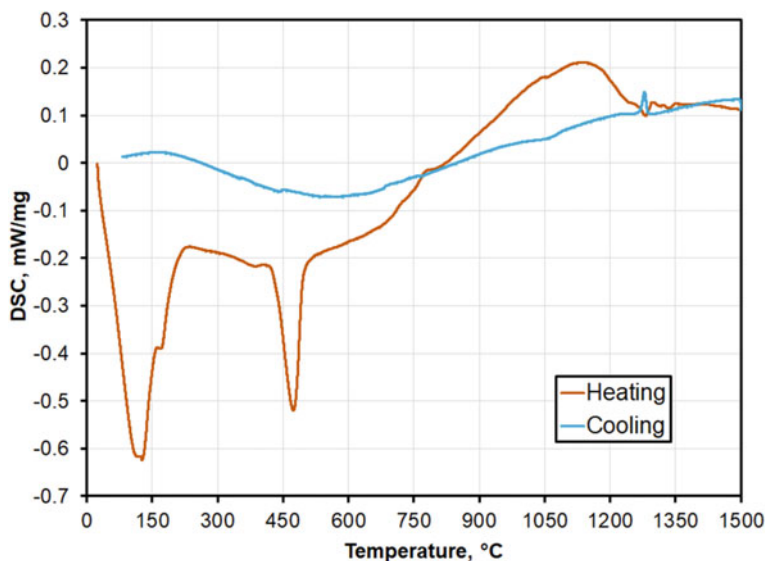**Fig. 1**   Thermogravimetric analysis of hydrated cement paste

Fig. 2 Differential scanning calorimetry of hydrated cement paste

was about 2.0 that indicates that some sulfates from the original cement still remained in the burned material in form of anhydrite.

The change of the content of alite, belite and free lime with the burning temperature as determined by XRD is shown in Fig. 3. Belite and fee lime were formed in the process of C–S–H decomposition. It can be seen in Fig. 3 that alite starts to form after 1200 °C, at which point the amount of belite and free lime decreases correspondingly.

It should be noted that belite can be present in different polymorphic forms. Changes in the content of different belite polymorph types as a function of burning temperature are demonstrated in Fig. 4. Rietveld refinement for α′ and β belite polymorphs was performed using ICSD 98-008-1097 and ICDD 04-007-9746 references, respectively. The α′-belite has an orthorhombic crystal system. The β-polymorph is monoclinic and forms from α′-belite during cooling. Reversible transformation between this polymorphs generally takes place near 670 °C [12].

The burning of hydrated cement paste at the temperatures below 900 °C followed by fast cooling resulted in high content of α′-belite and low content of β-belite. The burning at the temperatures higher than 900 °C the content of α′-belite reduces and content of β-belite reduces with the increase of temperature, while total belite content stays at the same level until the formation of alite begins. This fact was also noticed in some other studies [26, 28]. It is interesting to note that with the formation of alite after 1200 °C α′-belite appears again. The appearance of different belite polymorphs at different temperatures can be caused by certain impurities and by the certain rates of cooling that may stabilize α′-belite [28]. Similar behavior of belite polymorphs heated to 1250 °C with the subsequent fast cooling was reported in the literature [29].
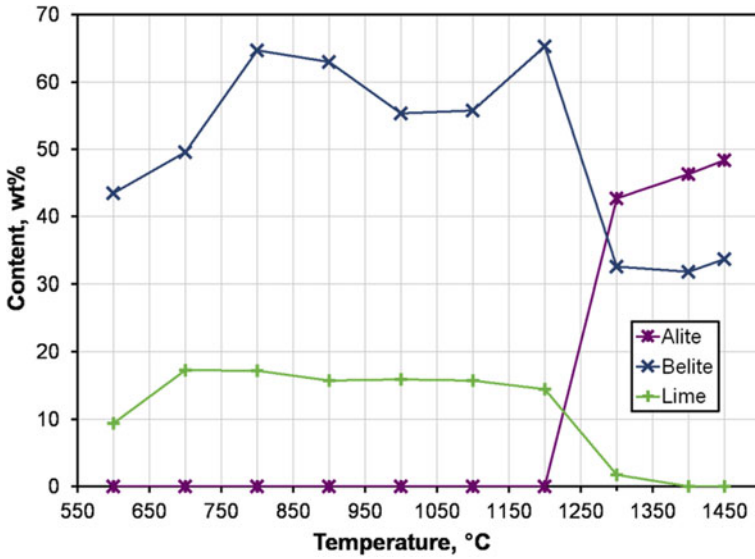
Fig. 3 Content of alite, belite and free lime as a function of burning temperature
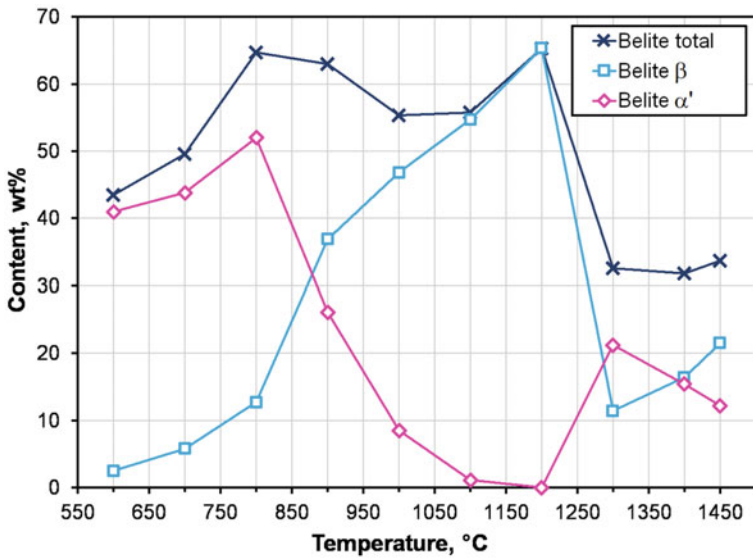

Fig. 4 Changes of belite type as a function of burning temperature

The content of aluminate and ferrite phases as a function of burning temperature is shown in Fig. 5. Brownmillerite (C_4AF) was present throughout the whole tested range of burning temperatures. Its content increases with the increase of burning temperature up to 1300 °C and then slightly decreases. Aluminates initially appeared in the intermediate forms of mayenite ($C_{12}A_7$) until 1200 °C and ye'elimite ($C_4A_3\$$) from 900 to 1200 °C. Tricalcium aluminate C_3A formed after 1200 °C. This sequence is similar to the formation of the phases during ordinary Portland clinker production, except ye'elimite formation, which appears due to the relatively high content of sulfates, though ye'elimite also sometimes can be found in Portland cement clinkers [13].

The ferrite (C_4AF) content in the burned cement paste is slightly higher than in the initial cement, while tricalcium aluminate (C_3A) content is somewhat lower. C_3A content reaches its maximum of 3.1% at the temperature of 1300 °C and then slightly decreases similarly to ferrite. This can be caused by aluminum and iron partially entering the structure of alite. No crystalline silica oxides were found after heating up to any temperature.

The results demonstrate the complete recovery of hydrated pastes to the new Portland cement clinker by thermal treatment. Numerous phase transformations occur throughout the studied temperature range during the burning. But the major clinker phases have been formed in this process indicating high potential for recycling. The mineral compositions of the original Portland cement used in the preparation of cement paste and clinker recycled from hydrated cement paste by burning at 1450 °C as obtained using the XRD quantification are given in Table 1. The XRD scans of original cement and recycled clinker are given in Fig. 6 for comparison.
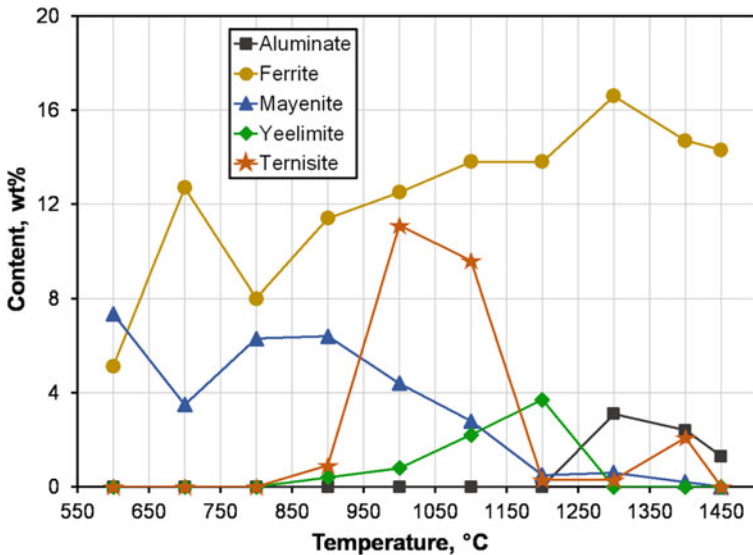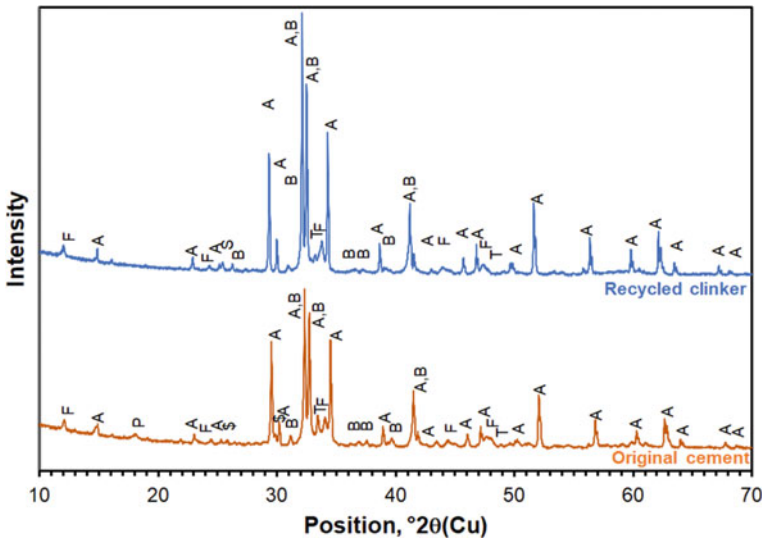

Fig. 5 Content of aluminate and ferrite phases as a function of burning temperature

Table 1 Mineral composition of original cement and recycled clinker, % wt

	Alite C_3S	Belite C_2S	Ferrite $C_4(AF)$	Alumnate C_3A	Anhydrite $C\$$	Bassanite $C\$H_{0.5}$
Original cement	55.2	20.3	13.9	4.4	0.0	6.6
Recycled clinker	48.4	33.7	14.3	2.4	2.3	0.0

Fig. 6 Comparison of XRD scans of original cement and recycled clinker

In can be seen in Table 1 that the recycled cement paste has slightly lower alite and slightly higher belite, though the percentage of the reactive α'-belite is high (36.2% of total belite). The content of the ferrite phase is slightly higher, and the content aluminate phase is slightly lower.

It can be clearly seen that the clinker recovered from the hydrated cement paste has high quality. A certain amount of anhydrite is left in the recycled clinker from the decomposition of basanite that was present in the original cement, but this may be corrected by the adjustment of the added gypsum at the stage of cement production.

4   Conclusions

The paper presents the study of phase transformations in hydrated cement paste during burning at the temperatures of 600–1450 °C. The results of the research demonstrate that clinker minerals can be recovered from hydrated cement paste

by heat treatment. This indicated a high potential for recycling of concrete and mortar waste. Since hydrated cementitious materials have lower embedded carbonated content than a limestone used in clinker production, such recycling can reduce CO_2 emissions in the process of Portland cement production.

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