Influence of Fine Fraction of Thermally Treated Concrete Waste on the Hydration and Hardening Processes of Portland Cement

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The main components of construction and demolition waste are concrete and masonry rubble and can be re-used in different applications such as road works, filling material in quarries or concrete manufacturing. The use of recycled concrete aggregate (RCA) as a substitute of natural aggregates in concrete production is limited to low amounts due to the decrease of mechanical properties and durability of concretes. This negative effect is mainly due to the lower strength and higher porosity specific for RCA as compared with natural aggregate, determined by the presence of adhered mortar/cement paste on the surface of natural aggregate. In this paper concrete rubble is thermally and mechanically treated in order to reduce the amount of adhered mortar/cement paste on the surface of natural aggregate and the separated fine material, called thermally treated fine fraction (TTFF), is used as supplementary cementitious material for portland cement preparation. The compressive strengths developed after 28 days of hardening by the mortars specimens in which portland cement was substituted with 10% and 25% TTFF are comparable with the one developed by portland cement. The data obtained by thermal analysis (TG/DTG), suggests a possible intensification of portland cement hydration process at early ages (2 days) in the presence of small amounts of TTFF (10-25%).

Key words: concrete waste, recycled concrete aggregate, fine fraction, thermal treatment, portland cement, hydration and hardening processes

The preparation for re-use, recycling and other form of material recovery of construction and demolition waste (CDW) represents an important research topic due to environmental, economical and legal aspects i.e. Waste Framework Directive - Directive 2008/98/EC and Landfill Directive - Directive 1999/31/EC.

According to European Commission report on management of C&D wastes [1] the main components of the CDW stream are concrete and masonry rubble. An usual way for the recycling of CDW (mainly of concrete and masonry waste) is re-processing into coarse and fine aggregate and re-use in different applications i.e. road works, as filling material in quarries or concrete manufacturing. The use of recycled concrete aggregate (RCA) and recycled masonry aggregate (RMA) as a substitute of natural aggregates into concrete production is the most valuable recycling method, opposite to the first two which are considered “down-cycling” [1].

However this option still requires the improvement of several technical aspects, mainly because the concrete produced with RCA/RMA is generally of lower quality (from mechanical and durability point of view) as compared with the one incorporating natural aggregate. The decrease of mechanical properties and durability of concretes with recycled aggregates is mainly due to the lower strength and higher porosity specific for RCA/RMA as compared with natural aggregate, determined by the presence of adhered mortar/cement paste (porous material) on the surface of natural aggregate (fig.1).

An improvement of recycled concrete aggregate quality can be achieved by thermal treatment at temperatures between 300-900°C combined with fast cooling; the mortar adhered on aggregate becomes friable and clean surfaces can be obtained by an abrasion treatment (crushing and/or sieving) [2-6]. The fine fraction of material contains a high amount of dehydrated cement paste (DCP) along with fine aggregate (sand). Depending on the thermal treatment temperature, DCP has a very complex composition consisting mainly in partially dehydrated products along with residual hydration products and unhydrated cement [5]. The DCP obtained by the thermal treatment of hardened cement paste requires a high amount of water for standard consistency and has a shorter setting time as compared with portland cement. Also, the rehydration capacity of DCP is influenced by the dehydration temperature, and the microstructure of rehydrated DCP becomes more compact with the increase of dehydration temperature [5].

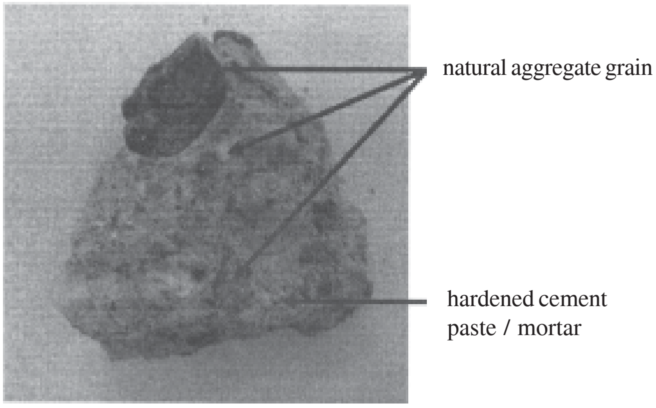

Fig. 1. Recycled concrete aggregate

The addition of portland cement [4,6,7], fly ash [6,7] or slag [7], to the fine fraction of preheated recycled concrete

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Table 1
COMPOSITION OF STUDIED BINDERS

% wt.	E	TTFF10	TTFF25	TTFF50
TTFF	-	10	25	50
Portland cement	100	90	75	50

aggregate, can significantly enhance its rehydrated strength. If this fine fraction is used as a substitute of portland cement, a decrease of compressive strength was recorded, especially for longer curing times; after 28 days of hardening, for a substitution rate of 60%, the compressive strength achieve 60% of the one assessed for portland cement and 80% for a substitution rate of 40% [4].

In this paper TTFF was prepared by thermal treatment and mechanical processing starting from concrete rubble resulted in demolition operations. The influence on the mechanical strengths of mortars with low amounts of TTFF (10% up to 50%), used as a substitute of portland cement, was also assessed; the kinetic of cement hydration and hardening processes in TTFF presence was assessed by thermogravimetry and differential thermal analysis (TG/DTG/DTA).

Experimental part

TTFF was obtained by thermal treatment at 500°C and 700°C, for 60 min and rapid cooling of concrete rubble resulted in demolition operation. Two fractions of concrete rubble were used – fraction 2-10 mm and fraction 10-32 mm.

The composition of non treated and thermally treated concrete rubble was assessed by X-ray diffraction using a Shimadzu XRD 6000 with monochromatic radiation CuKα (λ= 1.5406 Å). A Shimadzu DTA-TG-50H instrument was used to obtain TG/DTG curves of fine fraction of as-received and thermally treated concrete rubble. The thermal analyses were conducted in air in the temperature range 20 - 1000°C with a heating rate of 10°C/min.

TTFF was obtained by the grinding of thermally treated material for 5 minutes in a laboratory planetary mill (Pulverisette) and sieving with 0.2 mm sieve.

The as-received concrete rubble and the aggregate recovered after applying the thermal and mechanical treatment were examined with regard to the water absorption; this parameter was determined by immersion in water for 24 h and the assessment of mass change [2].

The separated TTFF, from concrete rubble thermally treated at 700°C, was used as a substitute of portland cement (CEM 42.5R) to prepare mortar specimens for compressive strength assessment (table 1).

The compressive strengths developed by the binding systems were assessed on mortar specimens (prisms-15x15x60 mm) with binder/aggregate=1/3 and water to binder ratio of 0.5. The aggregate (sand) fulfilled the requirements of European norm (EN 196-1, 2006). The fresh mortars specimens were vibrated for 2 min then cured in humid air (R.H. 85%) the first 24 h, then demoulded and submerged in water at 20±2°C up to 90 days. At least four mortar specimens were tested in each experiment, for compressive strength assessment, using a hydraulic press TONITECH.

Cement pastes were prepared with water to binder ratio of 0.5, sealed in plastic-bags and stored 2 up to 28 days at room temperature. Hydration was stopped by ethanol washing and oven-drying at 60°C for 4 h. The hydrates formed in cement pastes were assessed by thermal (TG/DTG/DTA) analysis, using a Shimadzu DTA-TG-50H instrument. The microstructures of pastes hydrated 28 days, as well as of the TTFF powder, were examined by Scanning Electron Microscopy (SEM), on specimens coated with Ag layer using a HITACHI S2600N microscope.

Results and discussions

XRD patterns of fine fraction of concrete rubble, as-received (B) and thermally treated at 500°C (B500) and 700°C (B700) are presented in figure 2. As it can be seen, in the fine fraction (bellow 0.2 mm) of as-received concrete rubble, the main crystalline phases are quartz JCPDS [083-2465], calcite - JCPDS [083-0577] and small amounts of ettringite – $Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26}$ (JCPDS [072-0646)] and afwillite - $Ca_3Si_2O_6(OH)_2(H_2O)_2$ (JCPDS [073-2105]). The formation of afwillite at room temperature can occur by the crystallization of amorphous calcium silicate hydrates resulted by Ca_3SiO_5 hydration in specific condition [8, 9]. The presence of afwillite was also reported by Mymrin and Correa [10], in the composition of a construction material based on lime and concrete waste.

Thermal treatment at 500 and 700°C do not substantially modify the mineralogical composition assessed by XRD; the peaks characteristic for calcium silicates ($Ca_3Si_3O_9$ – JCPDS [074-0874], Ca_2SiO_4 – JCPDS [083-0464]) gradually increase with the temperature rise, suggesting their formation by the transformation of calcium silicates hydrates.

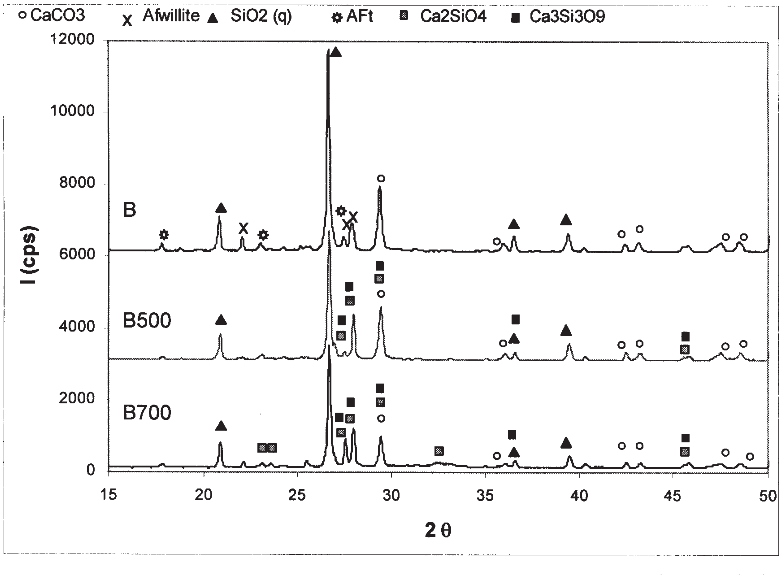

Fig. 2. XRD diffractograms of recycled aggregate (B) and recycled aggregate thermally treated at 500°C (B500) and 700°C (B700)

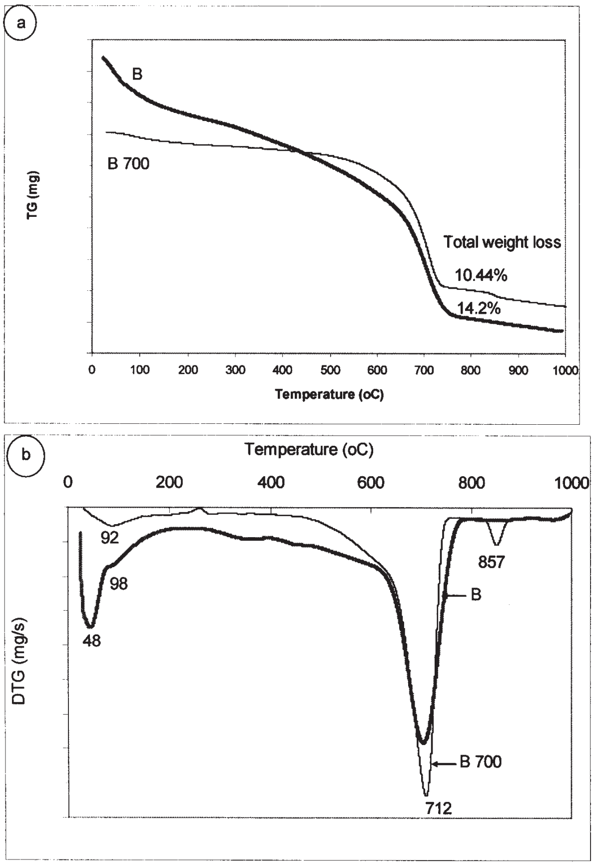

Fig. 3. TG (a) and DTG (b) curves of recycled aggregate (B) and recycled aggregate thermally treated at 700°C (B700)

The TG and DTG curves, of the concrete rubble, as-received or thermally treated are presented in figure 3, and weight losses corresponding to different temperature domains are shown in figure 4.

As it can be seen on the DTG curve of fine fraction of concrete rubble (B) two effects associated with weight loss are present:

- the first effect in the temperature range 20-200°C corresponds to humidity and water loss from calcium silicates hydrates, as well as ettringite (AFt) [6,11];

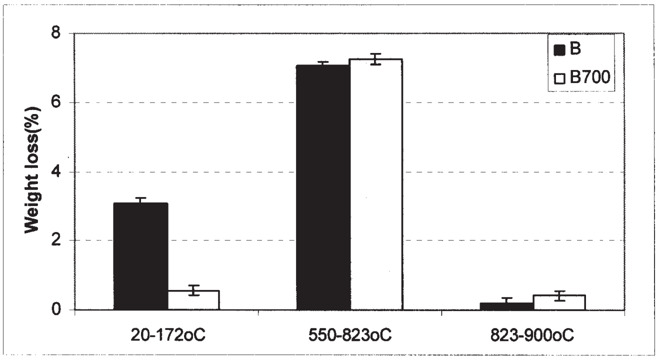

Fig. 4. Weight loss assessed on TG curves

- the second effect corresponding to the temperature range 600-800°C can be associated mainly with the decarbonation of calcite present in the material [6, 11-13].

For the material thermally treated at 700°C, beside the large effect with maximum at 857°C, a small effect with weight loss is recorded between 800-900°C; this effect can be attributed to the decomposition of $CaCO_3$. The presence of this effect, on the DTG curve, at higher temperatures (>750°C) suggests a higher crystallinity degree or/and the presence of large crystals formed during the thermal treatment at 700°C [12]. The increase of the weight loss corresponding to 550-823°C range along with the decrease of weight loss corresponding to 20-172°C range (fig.4) correlated with the information obtained by XRD, suggests that afwillite is dehydrated with C_2S, SiO_2 and CaO formation, as reported by Moody [14], and CaO is converted in calcite by subsequent carbonation process. Alonso and Fernandez [15] report also that at temperature above 200°C, C-S-H is dehydrated and forms a new phase ("nesosilicate") with $CaO/SiO_2 \cong 2$ assimilated with C_2S structure but with lower crystallinity degree.

The XRD identification of CaO, in B700 specimen, was not possible probably due to its low amount or/and rapid conversion in $CaCO_3$.

The visual aspect of concrete rubble (fractions 2-10 mm and 10-32 mm), before and after thermal treatment at 700°C and mechanical processing (milling and sieving) is presented in figure 5 and 6.

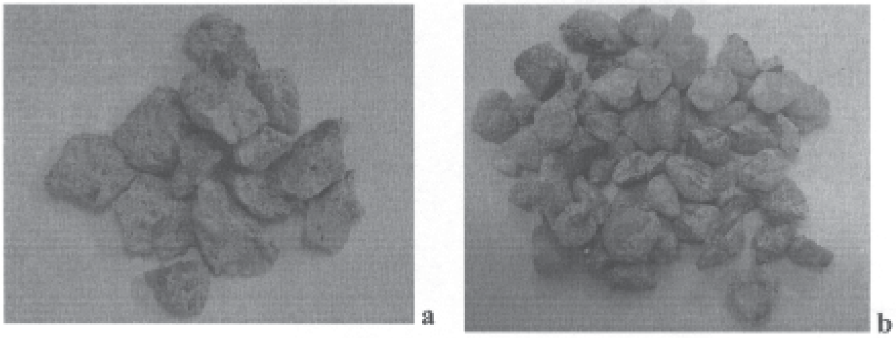

Fig. 5. Fraction 2-10 mm: a) as-received; b) after thermal and mechanical treatment.

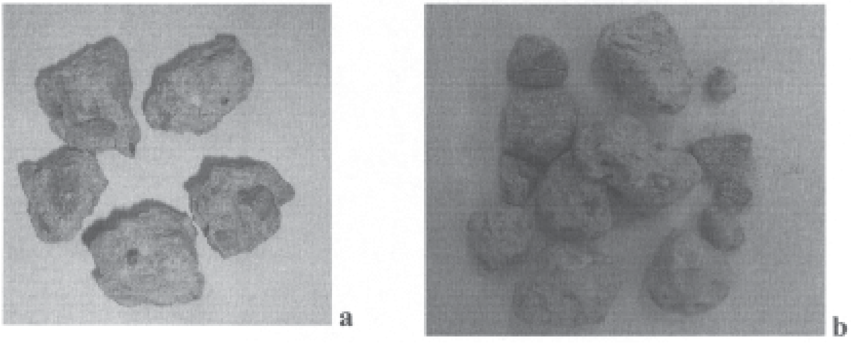

Fig. 6. Fraction 10-32 mm: a) as-received; b) after thermal and mechanical treatment

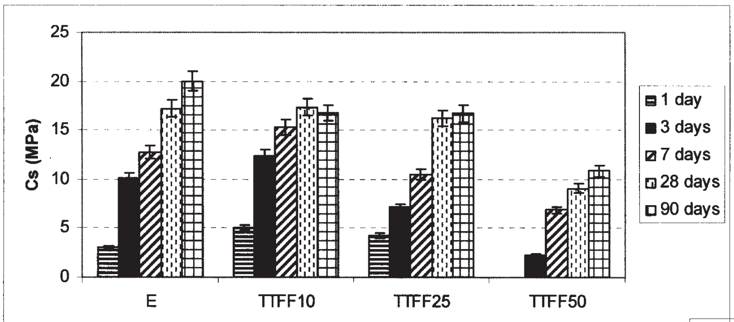

Fig. 7. Compressive strengths of mortars without/ with different amounts of TTFF

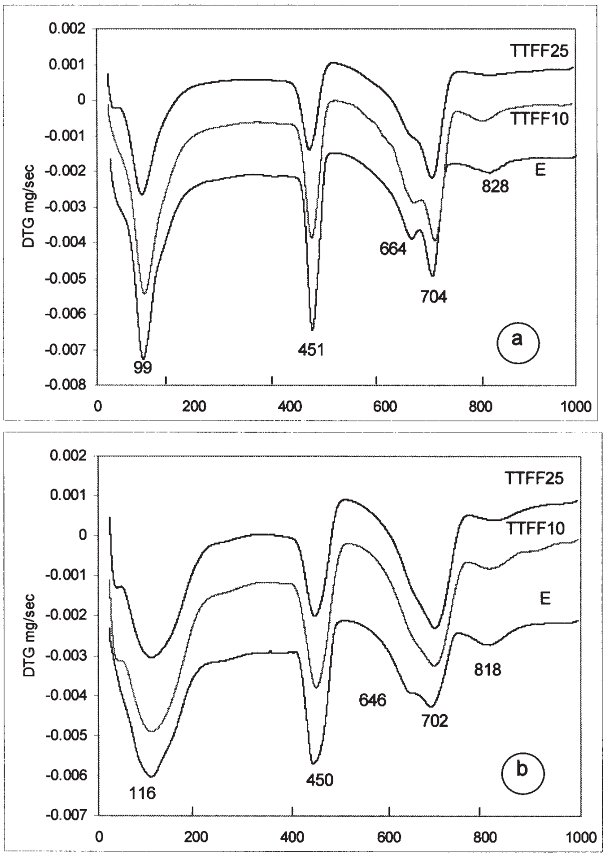

Fig. 8. DTG curves of pastes cured for: a) 2 days; b) 28 days

As it can be seen the amount of cement mortar/paste (TTFF) separated by the applied treatment is higher for the smaller fraction (2-10 mm) as compared with the bigger grains (10-32 mm).

The values of water absorption (A) assessed on the thermally and mechanically treated materials are comprised between 4.6 to 5.7 % representing a reduction with more than 45% with reference to the as-received concrete rubble (A=9.7%). Still, these values are higher as compared with the one of natural aggregates (≅1%), therefore an increase of the time of abrasion process is recommended.

The compressive strength assessed on mortars prepared without/with different amount of TTFF (as a substitute of portland cement - table 1) are presented in figure 7. As it can be seen the substitution of portland cement with low amounts of TTFF (10%) determines an increase of the compressive strengths values at early ages (1 up to 7 days) as compared with the mortar based on portland cement (E). The cement substitution with higher amount of TTFF (50%) determines an important decrease of the compressive strengths, for all the studied hardening times, due to the so called "dilution effect" – replacement in a higher amount of active component (cement) with a less reactive material (TTFF). It is also important to notice that after 28 days of hardening, the compressive strengths of mortars with 10 and 25% TTFF are comparable with the one recorded for portland cement mortar (E).

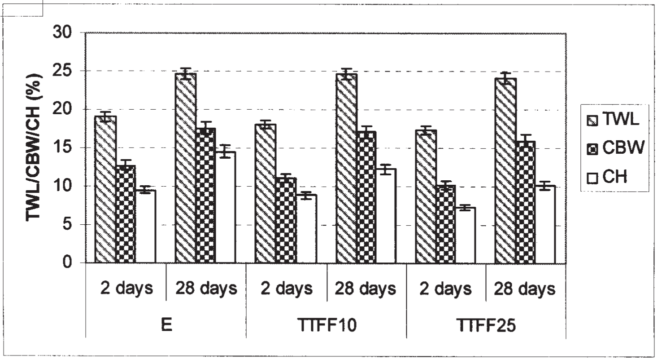

Fig. 9. Total weight loss (TWL), chemical bound water (CBW) and portlandite (CH) amount assessed after 2 and 28 days of hydration

Information regarding the kinetic of hydration and hardening processes, as well as on the nature of formed hydrates, was obtained by thermogravimetric analysis (TG/DTG). According to Dweck et al. [13] the identification of main hydrates and carbonated phases can be better assessed from their dehydration/decompositions effects identified on DTG curve, as compared with endo-effects assessed on differential thermal analysis (DTA).

The DTG curves of cement pastes without and with 10% and 25% TTFF, after 2 and 28 days of hydration, are presented in figure 8. The effects identified in all hardened pastes can be attributed as follows [11-13]:

- a large effect in the 20-220°C range, is due to the water loss from hydrates formed by cement hydration i.e. calcium silicates hydrates (C-S-H) and ettringite (AFt);
- the large effect corresponding to 430-500°C range is attributed to the decomposition of calcium hydroxide (portlandite) also formed by cement hydration;
- two superposed effects with maximum at 646°C/664°C and 702°C/704°C and the small one with the maximum at 828°C/818°C are attributed mainly to the CO_2 release during decomposition of calcite with different crystallization degrees and grain sizes [12].

In figure 9 is presented the evolution vs. time of total weight loss TWL (assessed on TG curve between 20-1000°C), chemical bound water (CBW) and portlandite amount (CH). Chemical bound water (CBW) was determined based on the weight loss recorded on thermogravimetric curve (TG) between 20-500°C and represents the water bound in hydrates formed by portland cement hydration i.e. C-S-H, portlandite (CH), ettringite (AFt) [11, 16-18]. The portlandite amount was calculated based on the weight loss, recorded on TG curve, between 400-500°C [11,17].

As expected the TWL, CBW and CH amounts increase for all specimens with the increase of the curing time due to the cement hydration process; the amount of CBW and

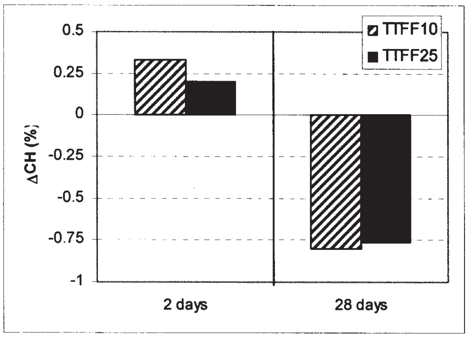

Fig. 10. The difference between experimentally determined $Ca(OH)_2$ – CHe and theoretically calculated $Ca(OH)_2$ – CHt *vs*. time for specimens with TTFF

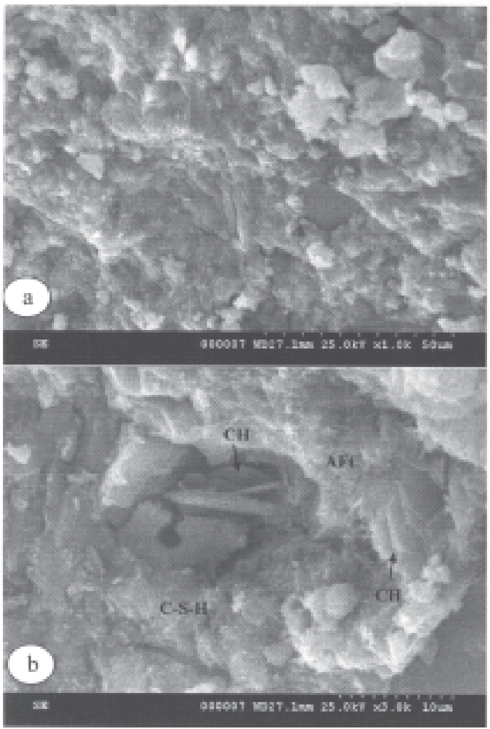

Fig. 11. SEM micrograph of cement paste (E) hydrated 28 days: a) x1000; b) x3000

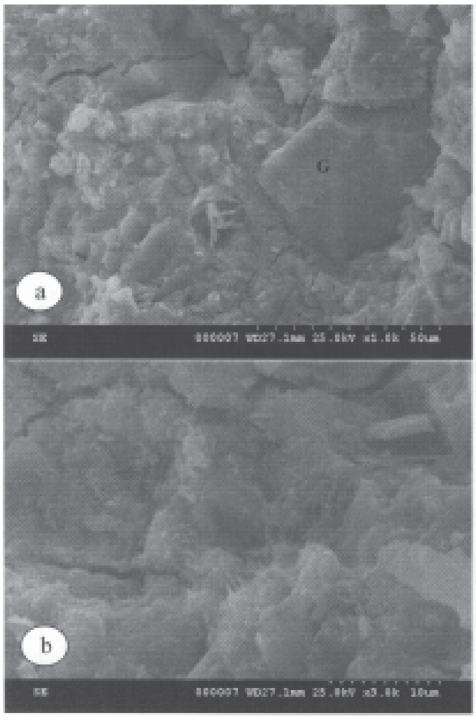

Fig. 12. SEM micrograph of cement paste with 25%TTFF hydrated 28 days: a) x1000; b) x3000

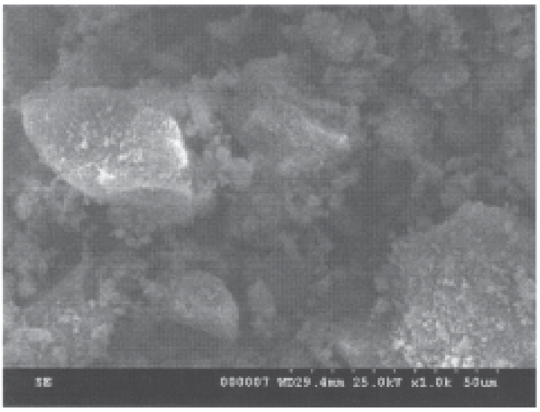

Fig. 13. SEM micrograph of TTFF (x1000)

CH slightly decreases with the increase of the cement substitution rate with TTFF, suggesting a decrease of the amount of formed hydrates mainly in the system with a higher amount of TTFF (TTFF25).

In figure 10 is presented the difference between experimentally determined $Ca(OH)_2$ - CHe (obtained by TG data processing) and $Ca(OH)_2$ theoretically calculated on the basis of hydrolysis of existing portland cement fraction within the sample (CHt) [11, 18]. Positive values of ΔCH can suggest either an intensification of portland cement hydration process with supplementary $Ca(OH)_2$ formation, or/and the hydration of small amounts of CaO formed by the thermal treatment of fine fraction of concrete rubble; both processes contributes to the development of early strengths and could explain the higher values of compressive strengths registered after 2 days for 10%TTFF and 25%TTFF mortars as compared with E.

The microstructure of cement pastes without/with 25%TTFF was assessed by scanning electron microscopy - SEM (fig.11 and 12). SEM micrograph of cement paste (E) hydrated for 28 days, shows a dense matrix (fig.11a) in which phases with different morphologies can be observed – hexagonal plates attributed to portlandite crystals (CH), fibers/needles generally attributed to ettrigite (AFt) and C-S-H with a foil like structure [6, 16].

The microstructure of TTFF25 paste (fig.12) is less dense, as compared with E paste, and big angular grains (G) are embedded in the cement matrix. These grains have approximately similar size and morphology as some of those assessed in TTFF (fig. 13). This less compact and coherent structure, specific for the cement pastes with a high amount of TTFF (>25%), can also contribute to the lower values of compressive strengths of these specimens.

Conclusions

Adequate thermal and mechanical treatment of concrete rubble permits beside the increase of recycled aggregate quality (i.e. decrease of water absorption) the separation of fine fraction (TTFF). TTFF obtained by thermal treatment of concrete rubble at 700°C followed by crushing and sieving, consists mainly in quartz, calcite and calcium silicates.

Small amounts of TTFF (10-25%) can be used as supplementary cementitious material (SCM) for portland cement preparation without an important decrease of the compressive strengths values. The compressive strengths developed after 28 days of hardening of mortars specimens with 10% and 25% TTFF are comparable with the one developed by portland cement.

The cement substitution with higher amount of TTFF (50%), determines an important decrease of the compressive strength values, for all the studied hardening times, mainly due to the so called “dilution effect” – replacement in a higher amount of active component (cement) with a material with lower reactivity (TTFF). The less dense microstructure of cement pastes with TTFF (as compared with portland cement paste) contributes also to the decrease of the compressive strengths values.

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