Performance of mortars produced with recycled cement

Author: José Augusto Freire Rocha, jose.a.rocha@me.com

1 Introduction

Concrete is recognized as the most widely utilized construction material in the world, an annual production of 1 m3 per capita grossly estimated (Scrivener 2008). The ease of production and placement, the appropriate mechanical properties, the low cost and high availability of raw materials are some reasons justifying its success (Chuah et al. 2014).

However, concrete is currently responsible for producing 5 to 8% of the CO_2 emissions generated by man (Scrivener 2008).

Indicatively, a ton of CO_2 is emitted into the air per produced ton of Portland cement. These emissions result from limestone decarbonation (50-60%) and the burning of fuels used during the production of clinker (Scrivener 2008).

In order to move towards sustainable construction, the scientific community has played an important effort in the search for more economical solutions and, above all, aimed at reducing the environmental impact. Thus, various studies that have been developed to act at the level of aggregates, as in the case of the use of recycled aggregates, have an important role in the management of natural waste, but will never be a solution to solve the problem of concrete sustainability or in seeking to achieve an "environmentally friendly" concrete.

Industrial approaches for the production of low emission CO_2 cements are discussed by Gartner (2004). In the cement industry, the CO_2 reduction plan is essentially three main strategies (Kwon et al 2015.): The use of alternative fuels; the introduction of new technologies that optimize energy efficiency; the use of composite cements. In fact, numerous investigations have been conducted in order to promote a partial replacement of Portland cement with mineral additives (minerais (Yildiz 2005, Rafat 2004, Canan et al. 1996), mainly from industrial by-products.

Other more ambitious works, are aimed at re-using the cementitious matrix incorporated into existing mortar and concrete, allowing not only a response to the reuse of excess construction waste, but also a reduction of the production of Portland cement with direct consequences on the volume of CO_2 emissions.

Some authors like Mindess (2003), Revuelra (2008), Markéta et al. (2011) along with Sousa and Brown (2010) verify that a cementitious matrix has a rehydration capacity, when in their experiments on the study on the behavior of concrete in fire, verified that after cooling, is recovered part of the initial resistance lost during the heating is recovered. Other authors such as Xinwei et al. (2010) and Shui et al. (2008) were the most ambitious and their experiments demonstrate not only the rehydration capacity of a cementitious matrix, but as well as the possibility of using concrete and mortar, from the demolition for the production of recycled cement.

Using the thermal gravimetric analysis (TG), it is possible to notice some relevant transformations occurring in the concrete during its heating to high temperatures. In a TG analysis performed by Xinwei et al. (2010), the presence of four peaks relevant to mass loss is verified, Figure 2.4. The first two peaks occurring below 200ºC refers to the loss of free or capillary water. The third peak of about 472ºC and 500ºC corresponds to the dehydration of calcium hydroxide $Ca(OH)_2$. Finally, the last peak mass loss is due to the decomposition of C-S-H, occurring for values between about 682ºC and 775ºC (Xinwei et al. 2010).

For temperatures above 750°C the mass variation in cement paste is not obvious, since the temperature rise also affects the structure of the gross aggregate, consuming more energy (Figure 2.4). However, according to Shui et al. (2008), the mass variation in concrete samples is essentially due to the concrete because, after the complete dehydration and transformation of hydrated cement components, when the aggregates are heated and provided that there is no decarbonation, the mass remains significantly constant.

According to Canovas (1988), if the concrete is not subject to temperatures exceeding 500ºC, the rehydration process can recover up to 90% of initial mechanical properties after 1 year. The recovery of the greater part of resistance in concretes rehydrated after being subjected to 500ºC is also mentioned by Revuelra (2008). For higher temperatures, damage caused to the concrete is irreversible, the recovery of its strength being less effective (Neville 2002). Shui et al. (2008) confirms that cement rehydration occurs when it comes again in contact with water. However, the microstructure obtained after the formation of new rehydration product tends to be weaker due to the development in ordinary Portland cement.

2 Methods

2.1. Concrete and cement paste preparation

Current concrete samples were produced, designated from original concrete (OC), which were intended to be representative of existing concrete elements, comprising a sufficiently hydrated cement matrix. In order to separate the influence of the aggregates and the hydrated paste in recycled cement production, samples were also produced with only paste (OP), subject to similar curing conditions. Both concrete and cement paste samples were produced with cement type CEM I 42.5 and an a/c ratio of 0.45.

Both the concrete and the cement paste were molded into cubic samples of 15 cm.

2.2. Crushing, grinding and milling of concrete and paste specimens

The sample size reduction was carried out in three phases. Initially, we used a jaw crusher. In the second phase, we used a stone crusher of smooth rollers and finally, to obtain the finest possible grain, the mixture was subjected to the action of grinding by a ball mill from which resulted the material with the granulometrics presented in Table 2.1.

Table 2.1 – Result of granulometric analysis after the third grinding phases

Sieve	1mm	250 μm	125 μm	63 μm	base
OC Retained [%]	7,3	46,5	37,3	8,4	0,5
OP Retained [%]	2,2	42,8	42,8	9,3	2,9

A further grinding was carried out for the production of mortars with this thinner binder, in order to understand the influence of granulometrics for these types of recycled binders. It is expected that the specific surface and the reactive capacity of the particles will increase with a diminishing grain dimension. The result of the granulometrics analysis after this further grinding phase is presented in Table 2.2.

Table 2.2 – Sieving result of the materials after the extra milling phase

Sieve	250 μm	125 μm	63 μm	Base
OC Retained [%]	1,1	3,4	49,8	45,8
OP Retained [%]	14,2	23,3	18,8	43,7

2.3. Test techniques and recycled cement production

After obtaining the materials already in the powder, they were subjected to a thermal gravimetric analysis (TG) with equipment (TG-DSC – Netzsch STA 409 PC Luxx) and X-ray diffraction with equipment (XRD - Panalytical X'PERT PRO).

According to the obtained results and data from the references, two preheating temperatures were selected to produce recycled cement, 350ºC and 650ºC, respectively. The initiation of the decomposition of calcium hydroxide (up to 350°C) is expected at these temperatures and dehydration of C-S-H (650°C).

To produce recycled cement, the binders were heated in the oven (TERMOCONTROL 3PR). For the heating of both recycled binders, two temperature parameters were used. The first to 100°C for 1 hour and the second at the highest temperature for 3 hours. The heating inside the furnace was at 20ºC/minute.

2.4. Mortars production

For the mortars production, we proceeded with the substitution of 0, 20, 50, 75 and 100% of ordinary Portland cement (OPC) with recycled cement originating from concrete (RCC) or paste (RCP), which correspond to the following mixtures: Reference mortar - RM (100% OPC); M20RCC (80% OPC +20% RCC); M50RCC (50% OPC +50% RCC); M75RCC (25% OPC +75% RCC); M100RCC (100% RCC); M20RCP (80% OPC +20% RCP); M50RCP (50% OPC+50% RCP); M75RCP (25% OPC+75% RCP); M100RCP (100% RCP).

For the production of mortars from recycled binders with finer grain, in order to evaluate the influence of grain size on the reactive capacity of recycled concrete, samples were molded with substitution percentages of 20, 60 and 100% of ordinary Portland cement (OPC) for a recycled cement originating from finer concrete (RCFC) or paste (RCFP), corresponding to the following mixtures: M20RCFC (80% OPC + 20% RCFC); M60RCCF (40% OPC + 60% RCFC); M100 RCFC (100% RCFC); M20RCFP (80% OPC + 20% CRFP); M60RCFP (40% OPC + 60% CRPF); M100RCFP (100% CRFP). The recycled binders obtained in this extra grinding phase were preheated only to 650°C.

For the composition of the mortar, it was decided to use a trace volume, of 1:3 proportions of 35-65% of fine and coarse sand, respectively, leading to mixing and with greater bulk, a/c ratio of 0.6, with the exception of RPC mortar with thermal treatment, which were produced with a/c varying from 0.6 to 0.81, for the reasons stated in 3.3 and, in order to provide acceptable workability.

Samples with recycled cement at room temperature correspond to the material not subjected to any heat treatment, i.e. only original concrete (OC) or original paste (OP), which should function essentially as a filer effect.

In accordance with NP EN 196-1, for each composition we used prismatic molds measuring 40x40x160 mm. After demolding, the samples were stored in a humid curing chamber with RH> 95%, until the testing age. The mortars produced with 100% recycled concrete were not subjected to preheating were stored in the dry curing chamber, due to poor binding capacity. For each composition 9 samples were produced in order to test 3 prisms for flexural and subsequently compression at 7, 28 and 90 days of age.

Note that recycled cement originating from concrete (RCC) contains only about 22.2% of the weight in the mass corresponding to the cement, and the other 77.8% relating to the aggregate, acting only by filer effect, which has mechanical implications, as seen later on.

3 Results and discussion

3.1. Thermogravimetric analyses

Considering the curve regarding the derived from the evolution of the mass loss depending on the temperature, the three most important peaks stand out. The first peak occurs at temperatures below 200°C (113ºC for RCC and 144ºC and RCP), which must be related to the loss of free or capillary and some adsorbed water in the hydration products. Similar results were reported by Xinwei et al. (2010).
A second peak is identified for temperatures between 470 and 550ºC (498ºC for RCC and 536ºC for RCP), which should be related to the dehydration of the calcium hydroxide, $Ca(OH)_2$. This phenomenon is also identified by Xinwei et al. (2010).

In the case of recycled cement from paste, we identify a third peak at about 813ºC corresponding to the culmination of the progressive dehydration of the C-S-H, initiated to temperatures of about 450-500ºC. Shui et al. (2008), Ma Xinwei et al. (2010) and Choi (2014) report the presence of this peak for values between about 650 and 800°C.

Regarding the recycled cement from the concrete, there is an evident peak to 930ºC which will combine the culmination of the dehydration of the C-S-H with the progressive phenomenon of decarbonizing the existing $CaCO_3$ in crushed limestone aggregates. The mass loss due to this phenomenon starts with greater relevance to temperatures above about 800°C. In general, the decarbonation is identified for temperature ranges between about 700 and 900ºC (Markéta et al. 2011).

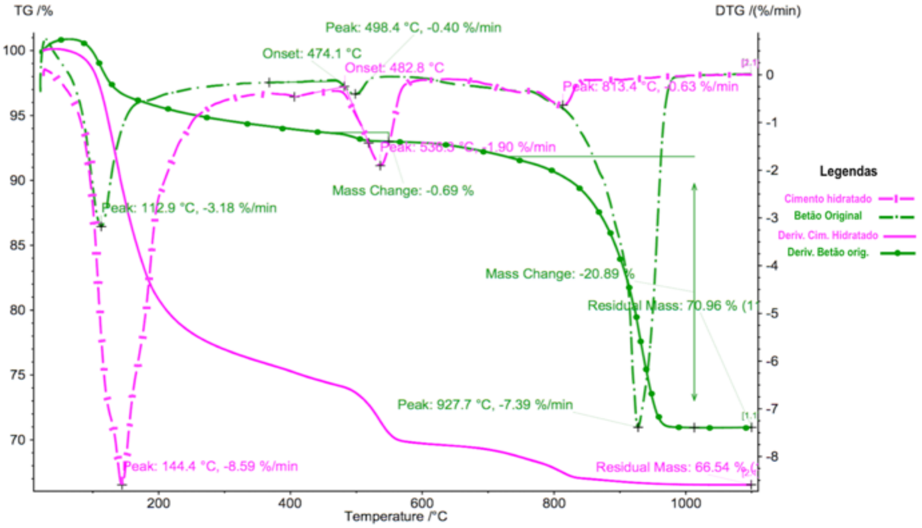

Figure 3.1 – Thermogravimetric analysis

3.2. XRD analyses

Regarding the RCC heated to 350°C, there has been the elimination of the peaks relating to ettringite, which are usually unstable at lower temperatures (Mindess 2003, Metha 1996). The decomposition of compounds such as ettringite and gypsum, for temperatures below 200°C there are also reports by

Markéta et al. (2011) and Sui et al. (2009). The portlandite (CH) is maintained for this level of temperature.

With regard to the RCC subjected to 650°C, the main differences consist in the disappearance of portlandite peaks and the appearance of peaks that indicate the presence of CaO and dehydrated C-S-H. The presence of lime is expected, since in this temperature there has already occurred a great part of the dehydration of portlandite, with a transformation of $Ca(OH)_2$ in CaO and any possible decarbonation of the calcite present in the mixtures. Note also the diffraction peaks corresponding to the presence of calcium silicates, which must be derived from the dehydration and transformation of hydrated calcium silicates.

In the RCP heated to 350°C the presence of portlandite and the dehydration of the aluminates and iron-hydrated calcium aluminates becomes more evident, also identified for the RCC. It is emphasized that, compared to the hydrated cement, to leave the identification of the presence of C-S-H. The referred transformations are demonstrated by the appearance of peaks relative to the presence of silicates and aluminates or iron-hydrated calcium aluminates. However, for the 350°C threshold, the amount of these anhydrous compounds is still not significant.

Regarding the RCP heated to 650°C, there is a clear decrease in the amount of portlandite, accompanied by the increased free lime content, demonstrating the gradual dehydroxylation of $Ca(OH)_2$ in CaO. Given the RCC heated to 650°C, the presence of *larnite* (C_2S) is clearer, which is a calcium silicate mineral and the diffraction peaks related to the formation of the remaining dehydrated compounds of the cement, some already identified in samples subjected to 350°C, in particular silicates and aluminates or iron-hydrated calcium aluminates, Figure 3.2.

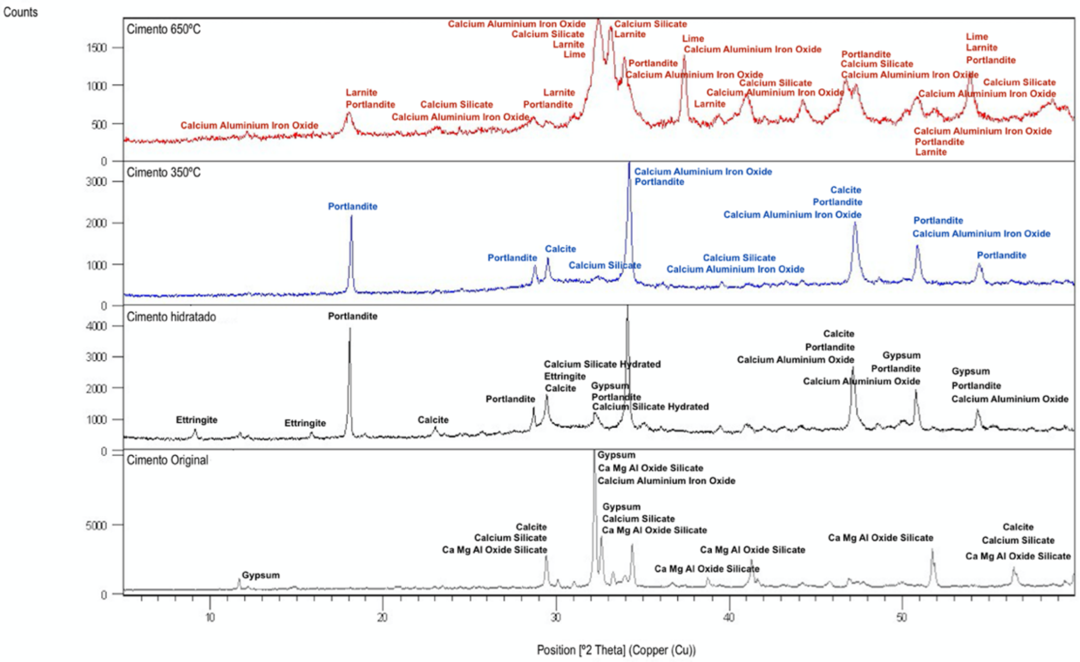

Figure 3.2 – XRD results for cement matrix

3.3. Characterization of the fresh pulp produced with RCC and RCP

The results of the tests according to NP EN 445 (2008) indicate that the RCC, regardless of having been subjected to different temperature parameters, has a negligible influence on the workability of the pastes produced. However, the recycled cement from the grinding and heating of the paste significantly affects the fluidity of the mixtures, verifying that this phenomenon tends to increase by increasing the RCP processing temperature. This may be a reason attributable to the obtained study results, water absorption able to occur in recycled cement particles with the consequent reduction of free water for the workability of the mixture. In analyzing the setting time in accordance with NP EN 197-1 (2001), the results show that the reactivity of the pastes tends to increase significantly when the binders are pre-heated to 650°C.

The initial setting time of the RCC and RCP was less than 30 minutes, which translates into a minor adequate value for its application in work. This phenomenon should be associated with the fact that the recycled cement does not provide sufficient sulfate content to satisfy the dehydrated calcium aluminate, meanwhile forming in the binders previously subjected to 650ºC. To increase the workability of the pastes, it was decided to add about 1.5% gypsum for the RCP and 0.5% for the RCC, both preheated to 650°C.

This fast setting time also contributes to the loss of the mixture’s plasticity. Another factor that can contribute to increased water demand is related to the greater percentage of free lime present in RCP heated to greater temperatures, which will require its extinction.

3.4. Mechanical strength of mortars

In RCC and RCP mortars, both the compressive and flexural resistance, when the percentage of the recycled cement added to the mixture is greater, the lower the resistance obtained.

At 90 days the M100RCC mortar presents a flexural 0.14, 0.20 and 0.27 MPa for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively. In the compression, these mortars have resistances of 0.26, 0.52 and 0.59 MPa for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively.

The extra grinding effect has little influence on RCC mortars. The mortars with 100% RCFC have an increased flexural resistance of 0.27 to 0.34 MPa at 90 days. Regarding compressibility, the resistance value increased from 0.59 to 0.91 MPa.

At 90 days the M100RCP mortar have a flexural resistance of 0.33, 0.34 and 0.86 MPa for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively. In compression, these mortars have resistances of 0.66, 0.66 and 2.49 MPa for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively.

The effect of the extra grinding plays an important role in RCFP mortar, Figure 3.3. Mortars with 100% RCFP show an increase in flexural resistance of 0.86 to 2.55 MPa at 90 days. And in relation to compression, the resistance value rose from 2.59 to 8.49 MPa.

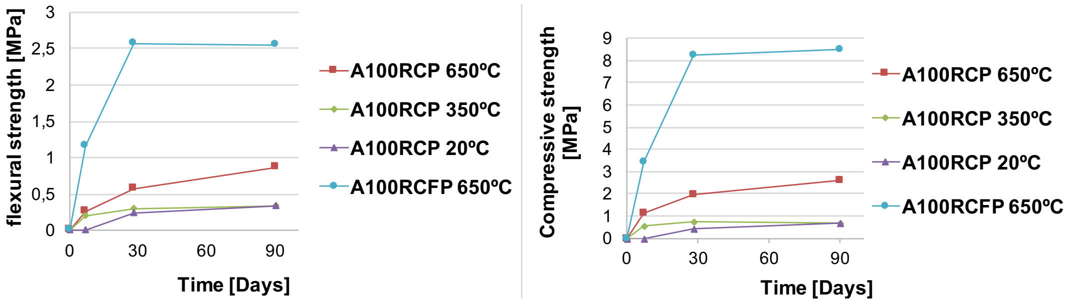

Figure 3.3 – Compressive strength and flexural strength of mortar specimens produced with RCP and RCFP

3.5. Ultrasound and dynamic elasticity modulus test

The obtained results from the ultrasound (Vus) experiments corroborate the mechanical characterization analysis performed at 3.4. It confirms that increasing the percentage of OCP for RCC or RCP leads to the reduction of Vus, since there is a decrease in the volume mass and stiffness of mixtures associated with increased porosity. However, once again it is confirmed that the heat treatment of the recycled binders at higher temperatures leads to lower losses of propagation velocity for the ultrasound.

The reference mortar at 90 days of age has a Vus of 4407.7 m/s. At the same age, the M100RCC mortars have a Vus of 25, 35.4 and 42.7% of the reference value for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively.

In ultrasound, the extra grinding effect also has little influence on RCC mortars. The mortar with 100% CRFB reveal an increase of 42.7 to 52% of the reference mortar value, equal to 2292.2 m/s.

The M100CRP mortars have a Vus of 31.7, 42.3 and 62.1% of the reference value for the samples molded with the binder without heat treatment, heated to 350°C and 650°C, respectively. When the RCFP is used, the mortar with 100% of the recycled binder showed an increase of 62.1 to 73.6% of the reference mortar value, equal to 3245.4 m/s.

Regarding the dynamic elasticity modulus, at 90 days of age, the reference mortar shows a value of 37.7 GPa. At the same age, M100RCC mortars have values 5.4, 6.0 and 9.6% of the reference value for the molded samples with this binder without heat treatment, heated to 350°C and 650°C, respectively.

The mortars with 100% RCFC (finer grain) show an increase from 9.6 to 13.9% from the reference mortar, which is equivalent to 5.2 GPa.

The M100RCP mortars have modulus values of 6.9, 10.2 and 25.9% of the reference value for the molded samples with the binder without heat treatment, heated to 350°C and 650°C, respectively.

When the RCFP is used, mortars with 100% of this binder increase from 25.9 to 45.6% of the reference mortar, equivalent to 17.2 GPa.

4. Conclusions

The X-ray diffraction analysis shows that when the RCC is heated to different temperatures the majority of the diffraction peaks correspond to the presence of calcite and quartz from the aggregates. Only at 650°C we verify some diffraction peaks of calcium silicate, resulting from the dehydration and transformation of hydrated calcium silicates, although at very low levels. It is also to 650ºC that Portlandite is dehydrated to originate free lime.

In the samples of the recycled cement from paste heated at 350°C there was found the dehydration of the aluminates or iron-hydrated calcium aluminates, keeping in mind the portlandite. We also verified the beginning of the dehydration of the C-S-H, while still in very small quantities. For the 650°C threshold we verified a marked reduction of portlandite contents and the onset of manifestations of CaO and also an increased amount of calcium silicates resulting from the dehydration and transformation of C-S-H. Naturally, the cement hydration products were always less evident in the RCC, as the aggregates occupy a significant fraction of this mixture. From this study it is concluded that the recycled cements subjected to 650ºC show the greatest potential for rehydration without entailing high CO_2 emissions during its heating processing.

The pastes produced from the recycled cement heated to 650°C present the initiation of setting times of less than 30 minutes and there was a need to add 1.5 and 0.5% for RCP and RCC gypsum mixtures, respectively.

The results of the mechanical experiments show that the greater the percentage of recycled cement added to cement mixtures, the smaller the resistance, but this mechanical resistance tends to be higher when the binder is preheated to higher temperatures. The best resistance results were obtained with recycled concrete from a finer granulometry (RCFC and RCFP). Mortars with 100% RCFC at 90 days have resistances of 0.34 and 0.91 MPa for flexural and compression, respectively. With respect to the results from the analysis of the ultrasound and the dynamic elastic modulus of the mortars with 100% RCFC at 90 days, there is recovered 52 and 13.9% of the reference mortar, respectively.

Mortars with 100% RCFP at 90 days have resistances of 2.55 and 8.49 MPa for flexural and compression, respectively. With respect to the results of the analysis for the ultrasound and the dynamic elastic modulus of the mortars with 100% RCFP at 90 days, there was recovered 73.6 and 45.6% of the reference mortar, respectively.

Overall, it was possible to demonstrate that the existing concrete recycling is possible, and there can be produced mixtures of binders of reasonable efficiency and rehydration capacity without involving large energy consumption and the significant generation of CO_2 emissions into the environment.

References

Canan, Tasdemir, Mehmet A. Tasdemir, Frank D. Lydon, e Ben I. G. Barr. "*Effects of silica fume and aggregate size on the brittleness of concrete*." Cement and Concrete Research, Volume 26, Issue 1, January, 1996: pp 63-68.

CANOVAS, M. F. "Patologia e Terapia do Concreto Armado". Ed. PINI. São Paulo, 1988.

Chuah S, Pan Z., Sanjayan J., Wang C. and Duan W. "*Nano reinforced cement and concrete composites and new perspective from graphene oxide*". Construction and building materials, 73:113-124, 2014.

Gartner E. Industrially interesting approaches to ''low-CO2'' cements. Cem Concr Res 2004.

Kwon Eunhee, Jaecheol Ahn, Bongsuk Cho, Dongcheon Park “A study on development of recycled cement made from waste cementitious poder”, 2015.

Markéta Chromá, Pavel Rovnaník, Dita Vořechovská, Patrik Bayer, Pavla Rovnaníková – “Concrete Rehydration after Heating to Temperatures of up to 1200°C”. Brno University of Technology, CZECH REPUBLIC, 2011.

Mehta P.K., P. J. M. Monteiro, “Concrete - Microstructure, Properties and Materials”, McGraw- Hill, Third Edition, 1996, ISBN 0-07-146289-9.

Mindess, Sidney, J.Francis Young, and David Darwin. “Concrete”. Second edition. Edited by Prentice Hall, Pearson Education, Inc, 2003.

NEVILLE, A. M. “Properties of concret”; Fourth edition, 2002.

Rafat, Siddique. “*Performance characteristics of high-volume class F fly ash concrete*.” Cement and Concrete Research, vol 34, 2004: pp 487-493.

Revuelra Manuel Bustillo. “Hormigones y Morteros”. Fueyo Editores, Madrid, 2008.

Scrivener Lothenbach, B., G. Le Saout, E. Gallucci. “Influence of lime-stone on the hydration of Portland cements”, 2008.

Shui Zhonghe , Dongxing Xuan, Huiwen Wan, Beibei Cao – “*Rehydration reactivity of recycled mortar from concrete waste experienced to thermal treatment*” (Wuhan University of Technology, China), 2008.

Sousa e Moreno JR “*Assessment of the influence of the type of aggregates and rehydration on concrete submitted to high temperatures*”, 2010.

Xinwei Ma, Han Zhaoxiang, and Li Xueying; “Reactivity of Dehydrated Cement Paste from Waste Concrete Subjected to Heat Treatment”, Harbin Institute of Technology, China, 2010.

Yildiz, Oner, A., S. Akyuz, e R. “*An experimental study on strength development of concrete containing fly ash and optimum usage of fly ash in concrete*.” Cement and Concrete Research, vol 35, 2005: pp 1165-1171.