HYDRATION OF MECHANICALLY ACTIVATED MIXTURES OF PORTLAND CEMENT AND FLY ASH

GORDANA STEFANOVIĆ, ŽIVKO SEKULIĆ*, LJUBICA ĆOJBAŠIĆ, VLADIMIR JOVANOVIĆ*

Faculty of Mechanical Engineering, Aleksandra Medvedeva 14, 18000 Niš, Republic of Serbia,
**Institute for the Technology of Nuclear and Other Mineral Raw Materials,*
Franche d' Epere 86, 11000 Belgrade, Republic of Serbia

E-mail: z.sekulic@itnms.ac.yu

Submitted July 17, 2006; accepted May 25, 2007

Keywords: Fly ash, Mechanical activation, Activity, Cement

Fly ash (FA) can be used in cement mixtures with certain limitations. For experimental purposes, mixtures of Portland cement (PC) and FA were used. The content of FA in the mixtures was either 30 % or 50 %. The mechanical activation was performed in a vibrating mill with two rings, type MN 954/3, of different diameters. Due to the vibration motion, the working elements (which are significantly heavier than the sample) instigate simultaneously the grinding process and mechanical activation of the samples. The volume of the mill container was 2 dm³, the mass of sample 200 g and electromotor power 0.3 kW. The temperature of the mill container was 80°C, influenced by the vibrating process of the rings. The tested samples were characterized using XRD analysis (confirming changes at the structural level due to mechanical activation), differential thermal analysis (a shifting of the peak position for the decarbonisation process to lower temperatures after mechanical activation was observed) and thermogravimetry (confirming an increase of the total mass loss of the activated samples, which further indicates increased of reactivity of the mechanically activated mixtures). The experimental results of the compressive strength of the activated and non-activated mixtures and the changes of their specific surfaces area proved that the mixtures PC+FA had been mechanically activated during the grinding process. The highest increase of compressive strength was achieved in the early period of setting, which indicates an improvement in the early hydration of the mixture.

INTRODUCTION

Hydration of PC consists of simultaneous chemical reactions referring to the hydration of the individual clinker minerals (materials constituting PC). The reaction of alite and water is very often used for the purpose of presenting a model of the PC hydration process [1].

On the basis of the simplified model of alite hydration and the principles of the progress of pozzolanic reactions, it is possible to present the process of PC+FA hydration as a multi-phase process where early, medium and late periods of hydration can be distinguished. The degree of hydration of a PC and FA mixture is given by the change in content of $Ca(OH)_2$.

In the earliest period, after several minutes, the hydration of alite and belite from the Portland cement occurs:

$$2\cdot(3CaO\cdot SiO_2)+6H_2O=3CaO\cdot 2SiO_2\cdot 3H_2O+3Ca(OH)_2 \quad (C_3S_2H_3) \tag{1}$$

$$2\cdot(2CaO\cdot SiO_2)+4H_2O=3CaO\cdot 2SiO_2\cdot 3H_2O+Ca(OH)_2 \quad (C_3S_2H_3) \tag{2}$$

Elevated $Ca(OH)_2$ content in the cement paste causes instability of the concrete exposed to the action of soft water and acidic solutions, as well as to the action of high temperatures. After the early period of setting, there is a dormant period, during which the emission of hydration heat is relatively low. The physical changes in the cement paste during this period can be seen in its gradual hardening. After the dormant period, in the medium phase, the reaction accelerates and new hydration of the cement occurs. The maximum is reached 9-10 hours after the beginning of the reaction. The environment becomes progressively alkaline due to the increase of the $(OH)^-$ ion concentration, as a result of the generation of $Ca(OH)_2$. Fly ash negligibly activated in this early period, acts as an inert material and accelerates the setting of the cement paste by acting as a nucleus for the sedimentation of C–S–H, C–Al–H and $Ca(OH)_2$, which appear after the hydration of the cement [2,3].

The final formation of the structure of the cement paste occurs in the nucleation phase. In the late period, the cement paste hardens, while the *pH* value increases in the ores of the cement paste and it affects the dissolution of the molecules of amorphous SiO_2 [4]. $Ca(OH)_2$ created by the hydrolysis of alite and belite behaves as an activator of the latent hydraulic properties of fly ash and reacts in pozzolanic reactions with the active part of the fly ash (SiO_2, Al_2O_3). In this way, the negative influence of fly ash on the quality of the cement can be reduced or entirely neutralized:

$$2SiO_2+3Ca(OH)_2=3CaO\cdot 2SiO_2\cdot 3H_2O \quad (C_3S_2H_3) \quad (3)$$

$$3CaO\cdot Al_2O_3+CaSO_4\cdot 2H_2O+10H_2O=4CaO\cdot Al_2O_3.SO_3\cdot 12H_2O \quad (C_4ASH_{12}) \quad (4)$$

$$Al_2O_3+CaSO_4\cdot 2H_2O+3Ca(OH)_2+7H_2O=4CaO\cdot Al_2O_3\cdot SO_3\cdot 12H_2O \quad (C_4ASH_{12}) \quad (5)$$

$$Al_2O_3+4Ca(OH)_2+9H_2O=4CaO\cdot Al_2O_3\cdot 13H_2O \quad (C_4AH_{13}) \quad (6)$$

As the pozzolanic reactions progress, the fly ash particles lose their spherical form and become increasingly coated with a layer of the product, and after a period of 6 months they can no longer be identified [5]. During the hydration of cement with added FA, the same hydration products appear as after the hydration of Portland cement.

There are data supporting the fact that many types of cement with added fly ash have better mechanical properties than PC. The increased resistance to chemical attack of the cements with the added FA results from the lower content of $Ca(OH)_2$ in the cement paste and thus in the concrete. For the same reasons, Portland cement with added FA behaves better when exposed to high temperatures [6].

Therefore, there are many problems to be resolved in order to employ more fly ash in cement mixtures. The main problem lies in the insufficient activity of the particles of FA during the hydration reactions, which are important to establish the mechanical characteristics of cement [7]. Pozzolanic reactions are, in comparison to the hydration reactions of Portland cement, much slower and they occur to an observable extent only after one or two weeks. In addition, problems occur in case of the activities of alite and belite. In the early hydration period, the activity of belite decreases [8], as does the activity of alite in the dormant period and in the late hydration period [7]. As a result of this, cement pastes created by mixing fly ash and clinker have worse characteristics compared to pure PC, especially in the early period of setting.

There has been a series of attempts to increase the hydration activity of the individual components of cement and fly ash by varying the temperature [9,10,11], synthesis method [12] and additionally by adding certain activators [13]. Only a small number of papers deal with the influence of grinding on the hydration activity of the cement components, and there are even fewer on fly ash [7]. For this reason, this paper demonstrates how and to what degree mechanical activation of PC+FA mixtures affects the hydration process and the mechanical properties of the cement.

EXPERIMENTAL

For examining the influence of mechanical activation on mixtures of Portland cement and fly ash, gypsum from the Gruza bed, fly ash from Kragujevac and Portland cement clinker, which is a standard product of the Cement factory of Novi Popovac, were chosen. The mixture samples with 30 % and 50 % of fly ash content (PC30FA and PC50FA) were prepared. Their physical-chemical properties are presented in Table 1. Portland cement clinker and gypsum were ground to particle size 95 % <100 μm. Grinding of the samples was performed in a laboratory mill with balls, which simulates Portland cement production.

Mechanical activation of PC and cement mixtures (PC30FA and PC50FA) was performed in a vibrating ring elements mill (type MN 954/3). The activated components and mixtures were designated with the letter A: APC, APC30FA and APC50FA. The optimal time of activation was determined by monitoring the change of the specific surface during the course of the grinding of PC, FA and the cement mixtures in the period from 0 to 60 min. The results are presented in Figure 1.

With increasing activation time, the specific surface rose up to a certain value, after which it decreases. Simultaneously, the free surface energy also increased. However, if the activation time was too long, the surface energy increased to such an extent that agglomeration of the fine particles occurred due to the effect of surface adsorption, which resulted in a decrease in the specific surface. It was observed that, for all the examined samples, the maximum value of the specific surface was attained after 10 minutes which was chosen as the optimal activation time [14].

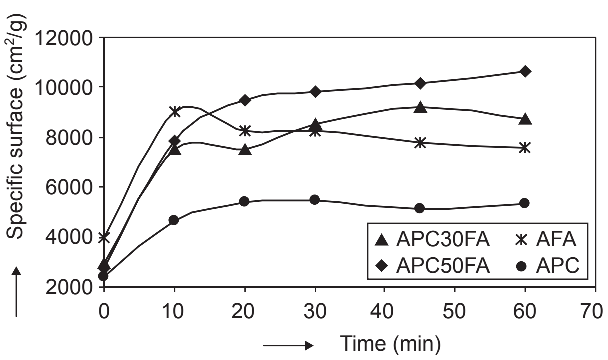


Figure 1. Change of specific surface of PC and the cement mixtures in dependence on the time of mechanical activation.

Standard prisms for compressive and bending strength tests were made after 2, 7 and 28 days of hardening from the non-activated and mechanically activated cement mixtures. Also the water consumption and setting time according to the standard testing method (EN 197-2) were determined. The results of the physical-chemical characteristics of the activated and non-activated samples are presented in Table 2.

The samples of the cement mixtures were analysed on a "PHILIPS" X-ray diffractometer, model PW-1710, with a curved graphite monochromator and scintillation counter. The thermal changes of the samples were monitored on a differential thermal analysis instrument, Netsch STA 409EP. The samples were thermally treated in the temperature range from 20°C to 1000°C.

RESULTS AND DISCUSSION

On the basis of the experimental results presented in Table 2, it can be observed that the compressive strength of the cement mixtures decreased with increasing content of fly ash. The compressive strength of the non-activated mixtures was always lower than the compressive strength of pure Portland cement, regardless of the composition of the mixture.

Table 1. Compositon and physical characteristics of the employed raw materials.

Compounds	Portland cement (wt.%)	Gypsum (wt.%)	Fly ash Kragujevac (wt.%)
SiO_2	22.54	4.33	40.40
Al_2O_3	6.11	1.53	16.50
$(Fe_2O_3)_u$	2.26	0.99	5.69
CaO	65.27	33.08	27.70
MgO	2.93	2.01	1.93
Na_2O	0.32	-	1.17
K_2O	0.38	-	1.84
SO_3	-	47.33	2.65
Pozzolanic activity			9.5 MPa

Since fly ash has a lower reactivity than Portland cement, its presence in a mixture negatively affected the early strength. To confirm the influence of the mechanical activation on the hydration capacity of a mixture of PC and FA, the compressive strength of the activated and non-activated mixtures with 30% and 50% content of fly ash was investigated, as well as the compressive strength of the activated and non-activated Portland cement. The mechanical activation of PC, PC30FA and PC50FA showed an improvement of the hydration process: the compressive strength in all three cases significantly increased (up to three times) at day 28 of curing at 20°C.

Mechanical activation led to an increase of the specific surface area, i.e., to an increase of the active surface which can participate in the reactions of hydration during the binding and hardening processes. However, an increase in the specific surface area during the mechanical activation led to an increase in the free surface energy, due to the increase of the reactivity the fly ash and clinker particles in the hydration reactions [8]. The kinetics of these reactions can be significantly changed after mechanical activation, in the sense of their acceleration, which further causes the significant increase in the compressive strength achieved after 7 and 28 days of setting.

Comparing the compressive strength of the activated and non-activated Portland cement, it can be observed that the mechanical activation resulted in an improvement in the compressive strength characteristics, by several times (Table 2). In the earliest period of setting, this ratio was almost 4 (24.2/6.3 = 3.84), and with the passage of the setting time, it dropped to 36.5/15.9 = 2.3 and 44.6/24.2 = 1.84. It is obvious that this increase was not only caused by the increase of in the specific surface area. The increased PC activity resulted from either an acceleration of alite hydration or an increase of the early belite hydration, or both.

For cement mixtures, the influence of the mechanical activation is even higher (APC30FA: 16.3/2.8 = = 5.82; 36.6/7.6 = 4.82; 52.6/15.7 = 3.35; APC50FA: 20.9/1.9 = 11.00; 34.7/6.3 = 5.51; 51.3/14.7 = 3.49),

Table 2. Physical-mechanical characteristics of activated and non-activated cement mixtures.

Characteristics	APC/PC	APC30FA/PC30FA	APC50FA/PC50FA
Compressive strength (MPa)			
2 days	24.2/6.3 = 3.84	16.3/2.8 = 5.82	20.9/1.9 = 11.00
7 days	36.5/15.9 = 2.30	36.6/7.6 = 4.82	34.7/6.3 = 5.51
28 days	44.6/24.2 = 1.84	52.6/15.7 = 3.35	51.3/14.7=3.44
Setting time (hour)			
initial	0.2/4.00	0.2/7.20	0.4/4.45
final	1.0/5.15	1.0/9.30	2.15/8.35
Water consumption (%)	30.0/27.00	31.6/36.00	32.0/37.00
Specific surface area, By Blaine (cm^2/g)	4635/2427	7535/2978	7852/2780

which indicates a significant increase in the activity of the fly ash. It was found that the increase was the highest in the earliest period of setting, in the mixture with the higher content of FA. This indicates that the pozzolanic reactions were accelerated. Also, the starting and termination time of the concrete binding was reduced (Table 2). Namely, for APC, the start of binding was reduced from 4 h to 0.2 h, and the end from 5.15 h to 1 h. For the mixtures, this reduction was even more prominent, i.e., for APC 30FA, the start was reduced from 7.2 h to 0.2 h and the end from 9.3 h to 1.0 h, while for APC50FA the start was reduced from 4.45 h to 0.4 h and the end from 8.35 h to 2.15 h.

XRD analysis

Relative indicator of the changes in the crystal structure of PC minerals and cement mixtures is the intensity of the diffraction maxima. The XRD patterns of the non-activated and activated samples of Portland cement, as well as of the cement mixtures with the different contents of fly ash are presented in Figures 2, 3 and 4.

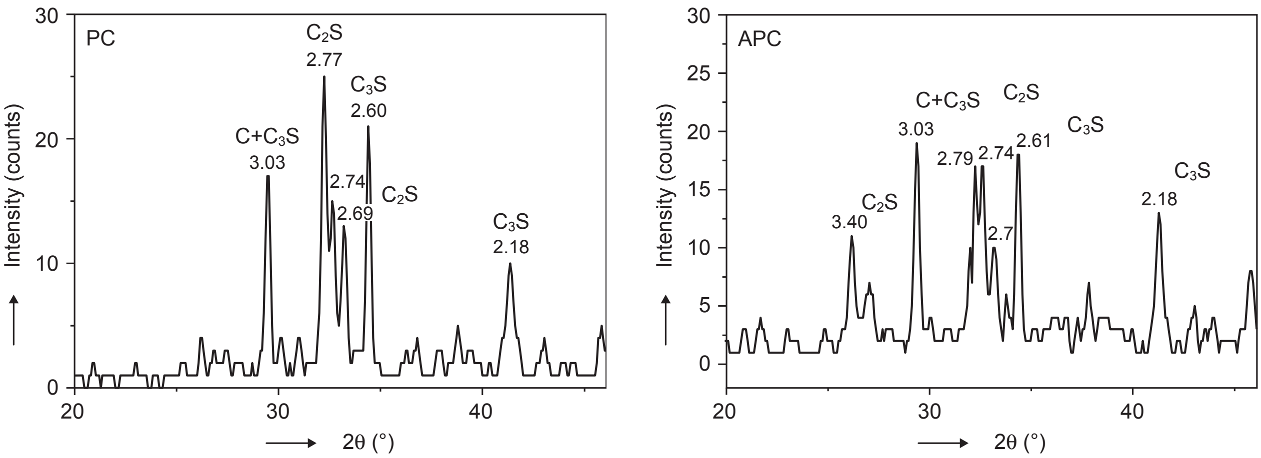
In Figure 2, one can observe that the diffraction maximum of alite was reduced in the activated Portland cement (APC), (2.6 Å). The diffraction maximum of alite and of residue of calcite can be observed at (3.03 Å). The diffraction maximum of belite did not decrease (2.74 Å).

In the cement mixtures containing 30% of ash (Figure 3), both alite and belites were activated (A 2.60 Å, B 2.74 Å). For this mixture, a peak referring to quartz was identified. The decrease of the diffraction maximum indicates mechanical activation of the fly ash, which can be related to the breakage of Si–O–Si chains, leading to the amorphisation of the material.

In the mixture with the high content of fly ash (PC50FA), the highest peak was detected for quartz (Figure 4). After mechanical activation, the diffraction maximum of the cement mixtures is reduced, which indicates the fly ash and quartz inside it.

The relative intensities of the key diffraction maxima for the observed mineral phases in the treated cement mixture before and after the mechanical activation are presented in Table 3.

The comparison of the values of the diffraction maxima of the basic phases before (I_0) and after (I_A)



a) b)

Figure 2. X-ray diffraction patterns of: (a) "PC" and (b) "APC" powder samples.

Table 3. Intensities of the diffraction maxima of the basic phases in PC and PC+FA, before and after mechanical activation.

d value (Å)		PC/APC intensity before MA I_0	PC/APC intensity after MA I_A	PC/APC $(I_0-I_A)/I_0$ (%)	PC30FA/APC30FA intensity before MA I_0	PC30FA/APC30FA intensity after MA I_A	PC30FA/APC30FA $(I_0-I_A)/I_0$ (%)	PC50FA/APC50FA intensity before MA I_0	PC50FA/APC50FA intensity after MA I_A	PC50FA/APC50FA $(I_0-I_A)/I_0$ (%)
2.60	C_3S	42	32	24	40	20	50	70	49	30
2.74	C_2S	50	28	44	16	12	25	95	86	9,5
3.05	C_3A				30	27	10	116	93	20
3.36	Quartz				25	18	28	16	11	31
4.28	Quartz							76	48	37

mechanical activation leads to the conclusion that, due to the mechanical activation, changes of the phase microstructure in Portland cement and the cement mixtures had occurred. Namely, the decrease of the intensity of the diffraction maxima, calculated as I_0-I_A/I_0, in alite in APC was 24%, in APC10FA 40%, in APC30FA 50% and in APC50FA 30%. For belite, the decrease calculated in APC30FA was 25% and in APC50FA 9.5%. For quartz, the decrease was 28% in APC30FA and 37% in APC50FA. From the previous results, it can be proposed, that due to mechanical activation to a higher fineness of the cement mixture relative to the reference system enabled a higher degree of hydratation and an improved formation of the hydrate phase than those observed in the reference cement and the cement/FA systems without mechanical activation. The XRD pattern of gypsum is shown in Figure 5.

DTA analysis

The decrease of the melting temperature of certain minerals and the temperatures of characteristic reactions can prove an increase in the reactivity of activated mixtures. The reception of energy during mechanical activation leads to changes in the crystal structure, which causes a reduction of the reaction enthalpy and, therefore, a reduction of the decomposition temperature [15].

The DTA curves of PC and the cement mixtures with a mass content of fly ash of 30% and 50%, both before and after the mechanical activation, are presented in Figure 6. Comparing the DTA curves of the samples before and after mechanical activation, several effects can be observed. The endothermic effect at 141°C, 135°C and 141°C is related to the loss of water

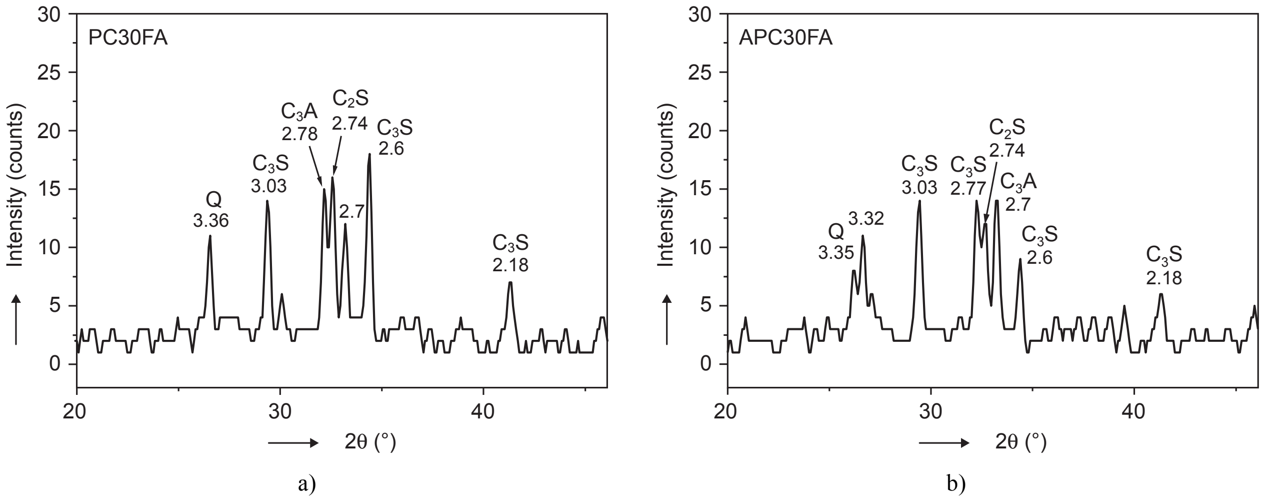


Figure 3. X-ray diffraction patterns of: a) "PC30FA", b) "APC30FA", powder samples.

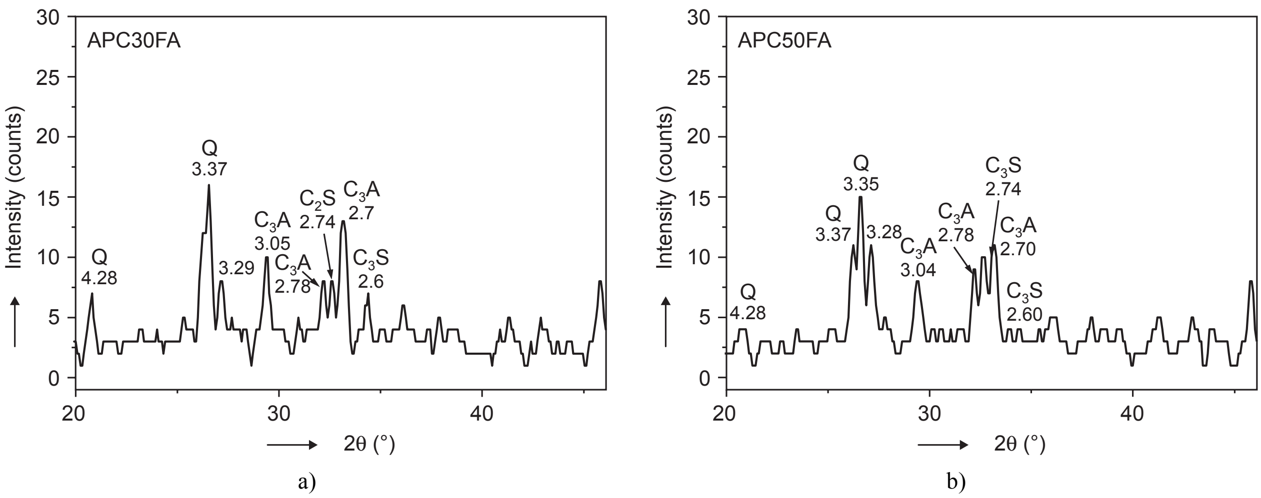


Figure 4. X-ray diffraction patterns of: a) "PC50FA", b) "APC50FA" powder samples.

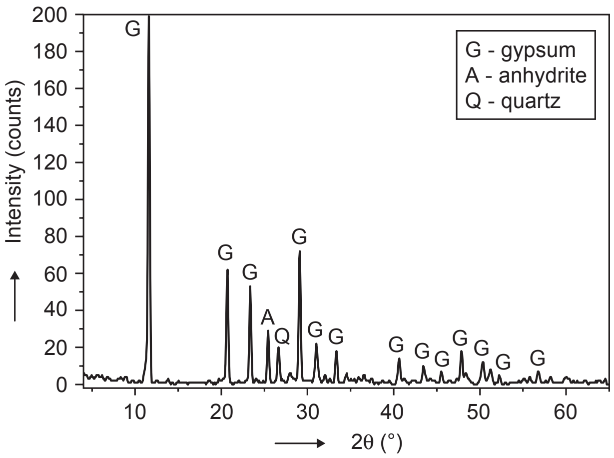


Figure 5. X-ray diffraction patterns of gypsum.

from the gypsum (Figure 6a). Figure 6b shows, that the temperatures of water loss from gypsum took place at lower temperatures (127°C, 135°C and 126°C) for the mechanically activated samples, which indicates the increased reactivity of the activated samples.

The endothermic effect at about 750°C corresponds to the decarbonisation of $CaCO_3$, which is present in Portland cement clinker. The temperature of this effect after activation is shifted from 769°C to 708°C for the sample activated with 30% of fly ash and from 765°C to 710°C for the sample with 50% of fly ash, indicating that the gypsum and ash had an increased reactivity due to mechanical activation and, thus, the decomposition of $CaCO_3$ unfolded at a lower temperature.

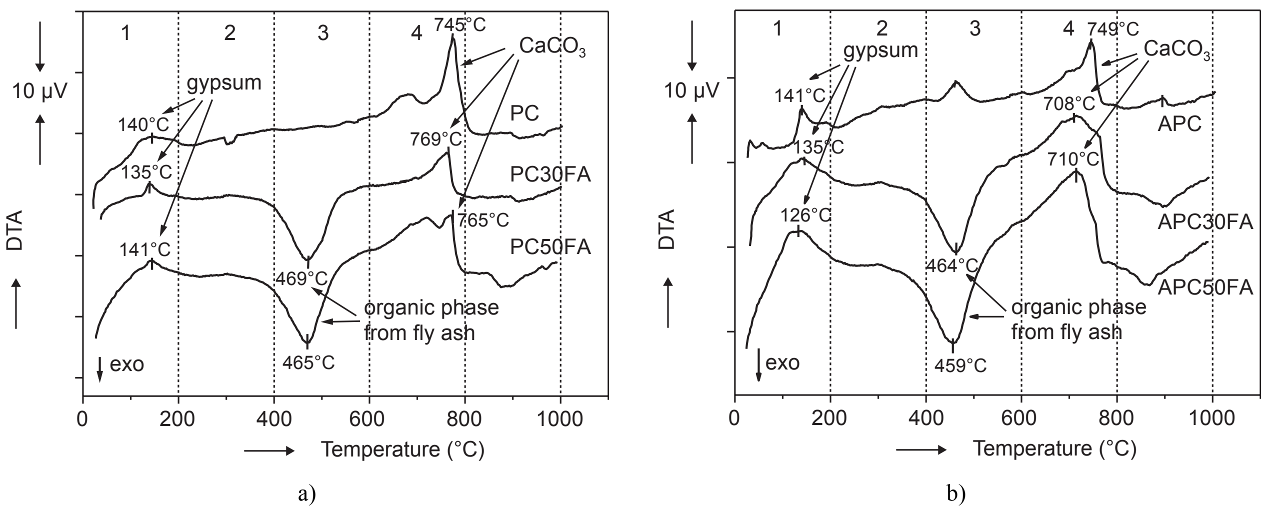


Figure 6. DTA curves of samples of the PC and the cement mixtures of PC with 30% and 50% content of fly ash, before and after mechanical activation.

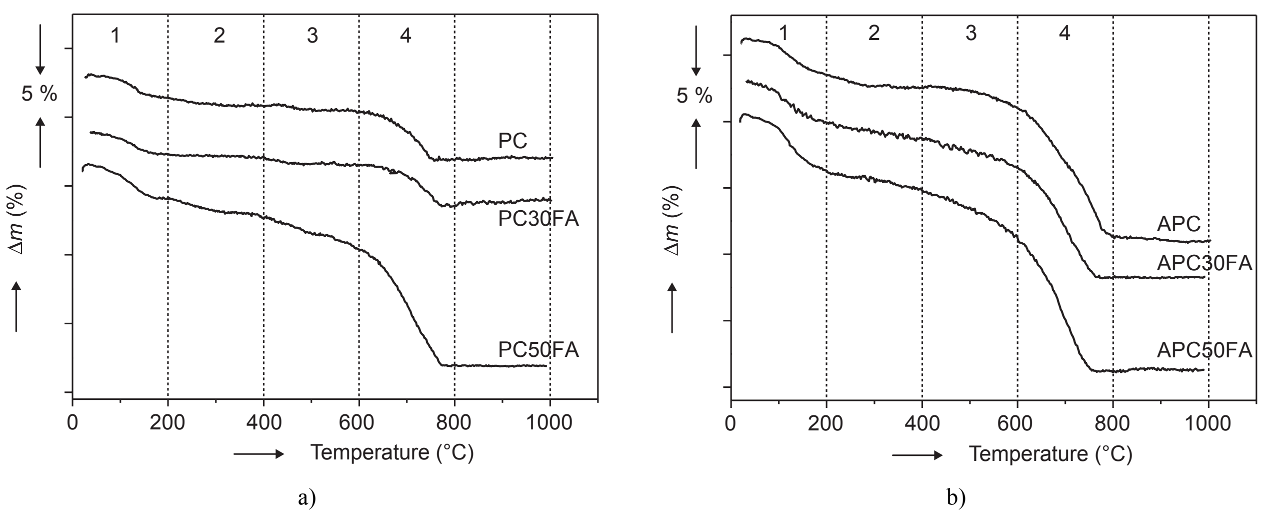


Figure 7. TG curves of samples of PC and mixtures of PC with 30% and 50% content of fly ash, before and after mechanical activation.

On the basis of the results of the DTA analysis of cement mixtures, it can be concluded that mechanical activation changes the properties of gypsum and fly ash.

Thermogravimetry

The TG curves of the tested samples are presented in Figure 7. Additionally, the mass losses of the cement mixtures in different temperature ranges are presented in Table 4. Comparing the TG data, an increase of mass loss in the cement mixtures after the mechanical activation was observed. Thus, for the temperature interval 110-220°C related to the loss of water, the largest difference appeared in the mixtures with 50% of FA. The highest difference of the mass loss between the activated and non-activated mixtures was in the temperature interval 550-800°C, which indicates $CaCO_3$ decomposition.

The increased reactivity of the cement mixture determined by DT and TG analysis influences the course of the hydration process and the concrete setting process. Namely, apart from the basic hydration reactions which occur in these cases, there are also secondary, pozzolanic reactions with the participation of fly ash. Since it was established that fly ash had also been activated, the pozzolanic reactions proceed more efficiently, leading to an improved final quality of the cement pastes, which can be seen from the results of the mechanical characteristics.

CONCLUSIONS

During the mechanical activation of PC+FA mixtures, alite, belite and quartz from the cement mixtures were activated. These components in the tested samples mostly affect the direction, rate and range of the hydration process.

The mechanical activation of PC+FA mixtures is an effective way for increasing their hydration characteristics and increasing their early compressive strength.

The increased reactivity of the cement mixtures after the mechanical activation, determined by the XRD, DT and TG analyses, affects the course of the hydration and setting processes of the cement pastes. Namely, apart from the basic reactions of alite and belite, which are accelerated, pozzolanic reactions are also accelerated and become more efficient. Thus, the increased reactivity of the active portion of fly ash permits the addition of high concentrations of fly ash in cement mixtures (up to 50%).

Acknowledgement

This paper is the result of the project No 6706 which has been financed by the Ministry of Science and Environmental Protection of the Republic of Serbia in 2005-2007.

References

1. Jawed J., Skalny J., Young J. F.: *Hydration of Portland Cement*, Pergamon Press, London, 1988
2. Fraay A.L.A., Bijin J.M., de Haan Y.M.: Cem.Concr.Res. *19*, 235 (1989).
3. Pitersen H.S.: Mat.Res.Soc.Symp.Proc. *176*, 139 (1990).
4. Browers H.J. H., Van Eijk R.J.: J.Mater.Sci. *37*, 2129 (2002).
5. Vagelis P.: Cem.Concr.Res. *29*, 1727 (1999)
6. Đorđević S.: *Građevinski materijali-poznavanje i ispitivanje*, Građevinski fakultet Niš, 1995.
7. Ma W., Brown W.P.: Cem.Concr.Res. *27*, 1237 (1997).
8. Jinyu Z.L., Yueming F., Jlazhl J.: 9th Int. Con. Chem. Cem., New Delhi, Vol. III, (1992) p. 51.
9. Yueming F., Suhong Y.: Cem.Concr.Res. *29*, 467 (1999).
10. Hanehara S., Tomosawa F., Kobayakawa M., Hwang K.: Cem.Concr.Res. *31*, 31 (2001).
11. Hassett D., Eylands K.: Fuel *76*, 807 (1997).
12. Yazici H., Yigiter H., Aydin S., Baradan B.: Cem.Concr. Res. *36*, 409 (2006).
13. Brough A. R., Atkinson A.: Cem.Concr.Res. *32*, 865 (2002).
14. Ćojbašić Lj., Stefanović G., Sekulić Ž.: Facta Universitatis *3*, 117 (2005).
15. Sekulić Ž., Popov S., Đuričić M., Rosić A.: Mat.Lett. *39*, 115 (1999).

Table 4. Mass loss before and after mechanical activation (%).

	Mass loss (%)				
	1	2	3	4	5
	20-200°C	200-400°C	400-600°C	600-800°C	20-1000°C
Sample	Water mass loss from gypsum	Without significant change	Combustion of organic phase from FA	$CaCO_3$ Decarbonisation	Sum
PC	1.59	0.62	0.47	3.42	6.10
APC	2.65	0.94	1.63	9.50	15.15
PC 30 FA	1.58	0.26	0.53	2.94	5.31
APC 30 FA	3.23	1.02	2.31	8.17	14.73
PC 50 FA	2.51	1.25	2.26	8.44	14.46
APC 50 FA	4.28	1.45	3.46	10.13	19.32

HYDRATACE MECHANICKY AKTIVOVANÉ SMĚSI PORTLANDSKÉHO CEMENTU A POPÍLKU

GORDANA STEFANOVIĆ, ŽIVKO SEKULIĆ*, LJUBICA ĆOJBAŠIĆ, VLADIMIR JOVANOVIĆ*

Faculty of Mechanical Engineering,
Aleksandra Medvedeva 14, 18000 Niš, Republic of Serbia,
**Institute for the Technology of Nuclear*
and Other Mineral Raw Materials,
Franche d' Epere 86, 11000 Belgrade, Republic of Serbia

Popílek (fly ash, FA) lze v cementových směsích používat s jistým omezením. Pro experimentální účely byla použita směs portlandského cementu (PC) a FA. Obsah FA ve směsi byl 30% nebo 50%. Mechanická aktivace byla prováděna na vibračním mlýně se dvěma kroužky typu MN 954/3 s různými průměry. Díky vibračnímu pohybu provádí pohyblivé části (které jsou výrazně těžší než vzorek) mletí a zároveň mechanickou aktivaci vzorku. Objem komory vibračního mlýnu byl 2 dm^3, hmotnost vzorku 200 g a výkon elektromotoru 0,3 kW. Teplota v komoře mlýnu byla 80°C a byla ovlivňována vibracemi kroužků. Zkoumané vzorky byly dále podrobeny analýze s pomocí XRD (potvrzeny změny na strukturální úrovni vlivem mechanické aktivace), diferenciální teplotní analýzy (po mechanické aktivaci pozorován posun píku procesu dekarbonizace k nižší teplotě) a termogravimetrie (potvrzen nárůst celkové ztráty hmoty aktivovaného vzorku, který také vykazuje zvýšení reaktivity). Experimentální výsledky pevnosti v tlaku aktivované a neaktivované směsi a změny specifického povrchu prokázaly, že směs PC+FA byla během mletí mechanicky aktivována. Nejvyššího nárůstu pevnosti v tlaku bylo dosaženo na začátku tuhnutí, což značí zlepšení počáteční hydratace směsi.