

RECOVERY POSSIBILITIES OF POWER PLANT FLY ASH FROM ZALĂU

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ABSTRACT This paper presents a detailed study on the properties of power plant fly ash from Zalău and the recovery possibilities in concrete slabs. The fly ash chemical and mineralogical composition, the particle size distribution and the thermal behaviour were established. The changes on the hardened concretes properties induced by the fly ash introduced in concrete compositions were studied. It was observed that 10 wt% replacement of cement by ash improved the mechanical features of the products.

Keywords: *fly ash, concrete, mortar*

INTRODUCTION

From economically point of view the use of fly ash has several advantages: the ash is an inexpensive raw material which introduced in compositions contributes to the manufacturing cost price decrease of the products, without compromising their quality. The ash use is justified by the construction products long-term mechanical strengths and durability improvement, therewith leading to increase their life cycle [1-3]

The study of the power plant fly ash recovery options as well as the establishment of the different products manufacturing technologies with this material require detailed knowledge of the fly ash properties and its complex characterization.

Knowing the properties of fly ash is important, being known the interdependence between the chemical-mineralogical composition, physical properties and hydraulic activity of ashes, which in turn influences the concrete products features. [4-6]

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RESULTS AND DISCUSSIONS

The granulation of power plant fly ash is of particularly interest regarding the preparation of concretes with imposed properties and appearance (the quality of sides and edges for example) by the local applications.

The results of the sieve analysis are presented in Table 1:

Table 1. Grain size distribution.

Fraction	Percent [wt %]
> 2mm	6,33
> 1mm	5,58
> 500µm	12,00
> 200µm	42,52
> 100µm	25,29
< 100µm	8,28

The average results of the chemical analysis obtained on replicate samples, are given in Table 2.

Table 2. The chemical composition of power plant ash from Zalău (%)

Major oxides (%)								
SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	L.I.
59,71	21,62	0,62	7,10	4,48	1,02	0,60	2,60	1,31

It notes an important content of main oxides: SiO₂, Al₂O₃, Fe₂O₃ and CaO.

The sum SiO₂+Al₂O₃+Fe₂O₃ amounts to 88,43%, which allows to classify the analysed fly ash in F class [3], for which the minimum percentage of these oxides is 70.0%. The ashes from this class result in the burning process of bituminous coal and anthracite and they are characterized by pozzolanic properties.

The calcium oxide content, an important parameter when using ash as additive in concrete, is of 4.48%; in this case the ash may be classified in type F, for which the CaO content is less than 8%.

In conclusion, the chemical composition of Zalău power plant fly ash is situated between the normal limits for this material. It notes that this material has a carbon content which slowly exceeds the recommended upper limit, which shows an incomplete process of preparation and burning of fuel in the thermoelectric power plant.

The mineralogical composition of the fly ash was determined by X-ray diffraction. The X-ray diffraction spectra, as it was recorded, are shown in Figure 1.

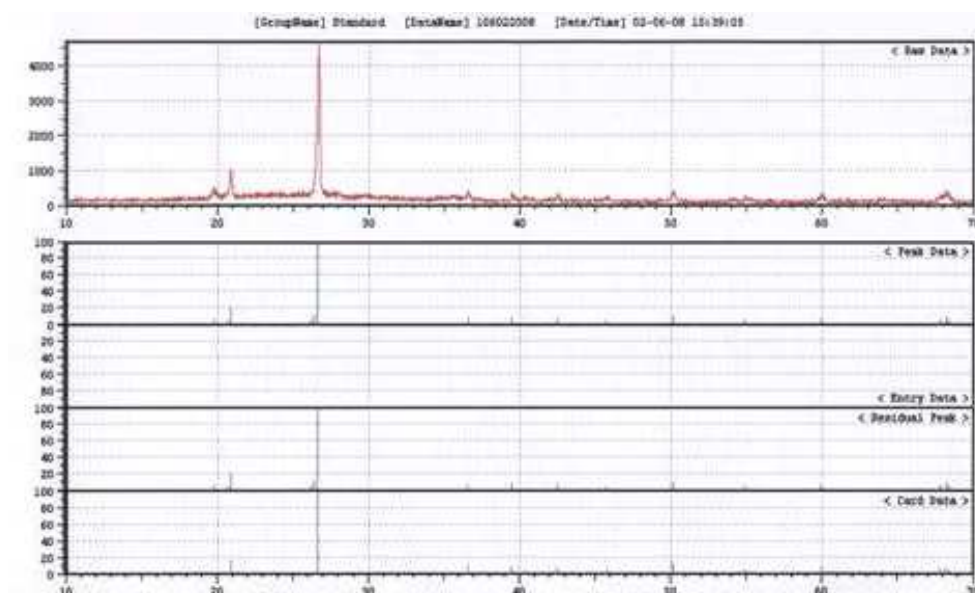


Figure 1. – The X-ray diffraction spectra

It notes a spectrum poor in reflexes, with a single mineral content. The X-ray spectra analysis established that the reflexes perfect match for quartz. Reflexes of other minerals were not recorded which indicate the presence of the silicon dioxide only in this mineralogical form. It is very interesting that minerals from clays, feldspars or iron oxides groups or other crystalline species that are possible to be present in ashes, derived from fossil fuels combustion as coal, are not revealed. Any crystalline form of carbon is not revealed, although the loss on ignition of the ash exceeds 10%. There is a small amount of vitreous phase, betrayed by the slightly lift, in the form of dome, of the spectra recorded between 18 and 30 degrees of 2θ angles.

For a more detailed study of the mineralogical composition the X-ray spectra of the fly ash sample, treated at 900°C for two hours was recorded. In Figure 2 are given the spectra performed under the same conditions as for original ash.

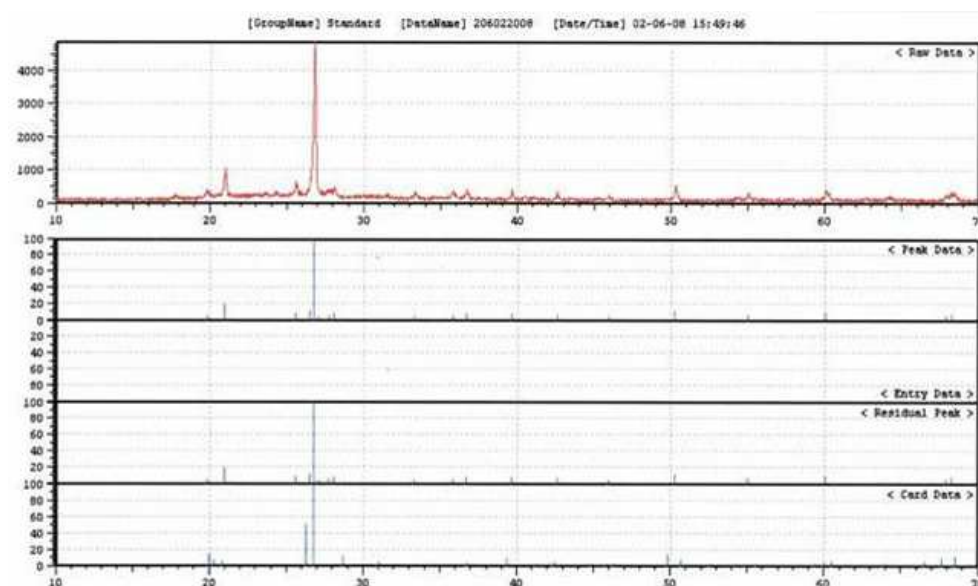


Figure 2. – The X-ray diffraction spectra of the calcinated ash

It notes the remarkable similarity of the two spectra, which leads to the conclusion that the minerals present are common and during the ash calcinations are not occurred essential changes in the mineralogical composition. The transformations of the minerals undergone during the coal combustion in the power plant at 1600°C, remained as definitive.

The stability related aspects of a material can be obtained with the aid of thermal analysis, especially for applications that allow operation at temperatures higher than the ambient temperature. In figure 3 is given the derivatogramm for Zalău power plant fly ash. The dried material was heated in device until the temperature of 1500°C.

The recorded curves do not show pronounced thermal effects. The residual carbon combustion occurs in a narrow temperature range of 400°-610°C, with a maximum of the DTA curve at 410,38°C, in a broad exothermic effect. The thermal effects curve presents an endothermic effect with a maximum at 1250,22°C. This occurs without a change in weight – recorded on TGA curve - and is assigned to the ash soaking itself, a process that occurs in the temperature range of 1120°-1270°C.

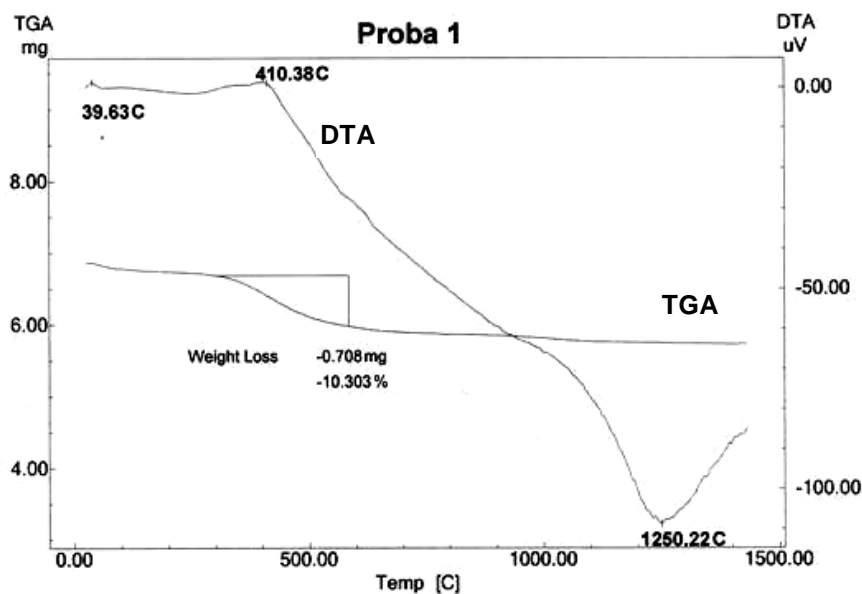


Figure 3. – Thermal behaviour of the ash

In conclusion, the fly ash presents a thermal resistance up to 410°C, when begins the residual carbon burning.

After 28 days of hardening the density and water absorption of the concrete compositions were determined.

The results are shown in the figures nr 4 and 5.

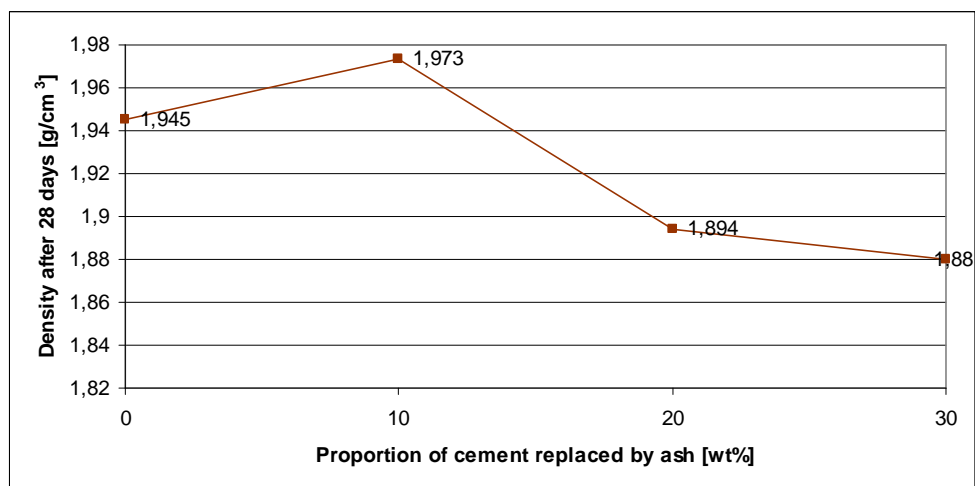


Figure 4. Density variation in function of cement replaced by ash.

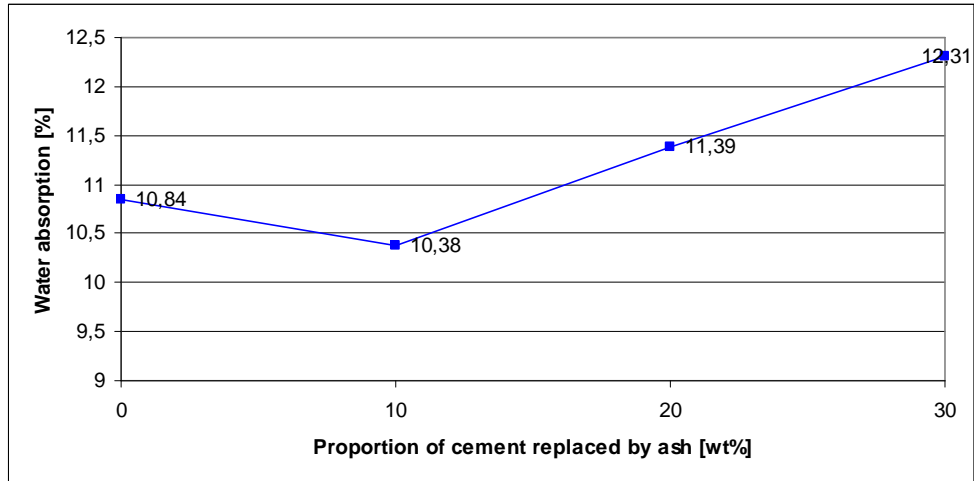


Figure 5. Water absorption variation in function of cement replaced by ash.

The flexural and compressive strength of the compositions were determined after 28 days of hardening. In the figure 6 and 7 is presented the evolution of the strength in function of proportion of cement replaced by ash.

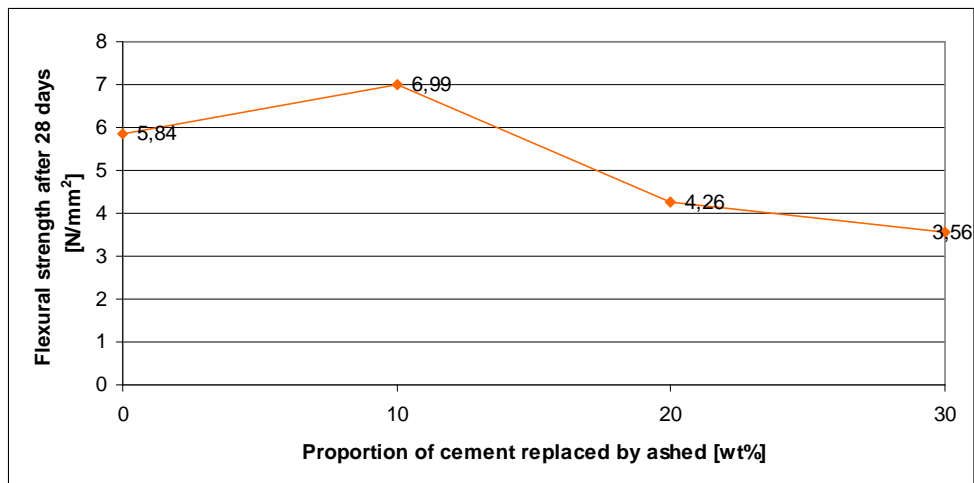


Figure 6. Flexural strength variation in function of proportion of cement replaced by ash.

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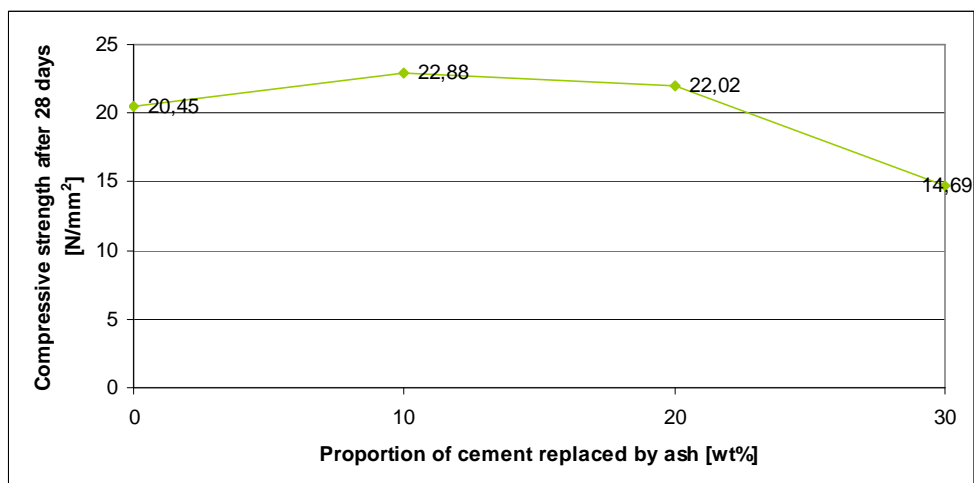


Figure 7. Compressive strength variation in function of proportion of cement replaced by ash.

It is a known fact that the mechanical strength of the mortars and concretes with ash content is lower after 28 days and a beneficial effect it is observed only after 56 or 91 days. To demonstrate the evolution of the strength, mechanical tests were repeated after 56 days (fig. 8 and 9).

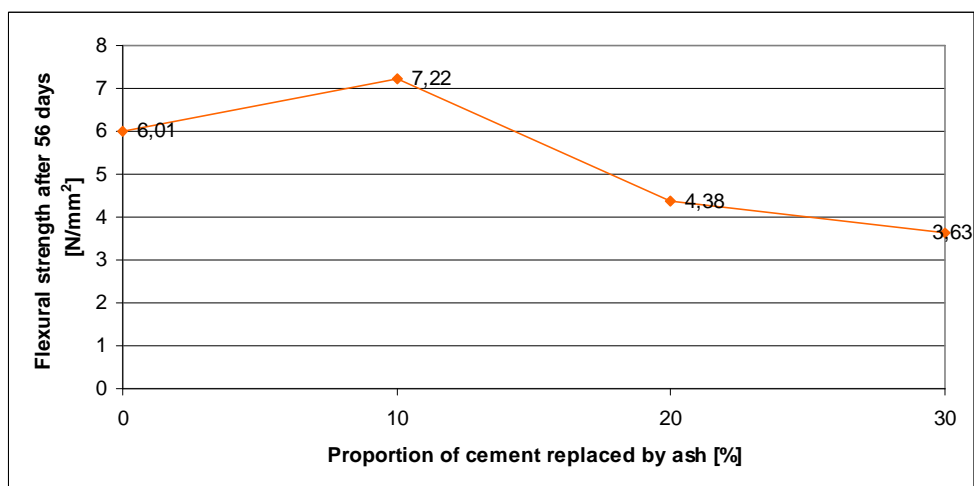


Figure 8. Flexural strength variation in function of proportion of cement replaced by ash.

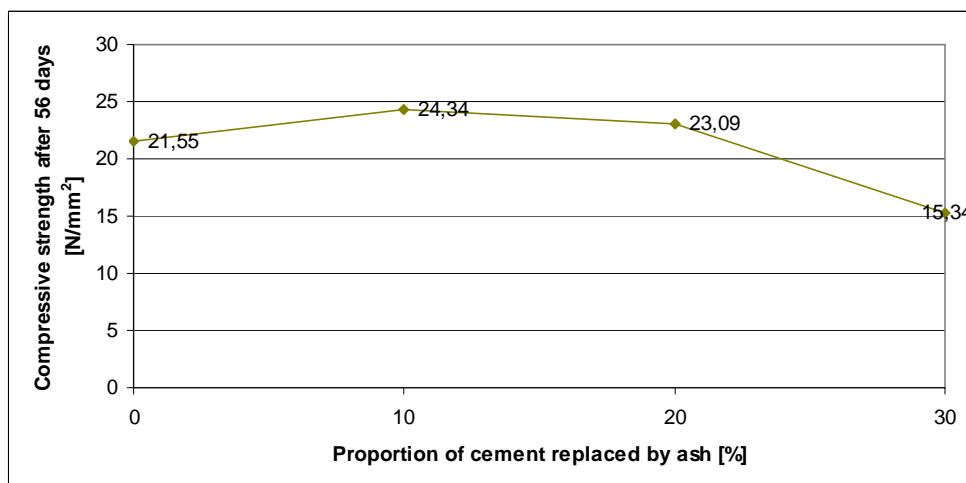


Figure 9. Compressive strength variations in function of proportion of cement replaced by ash

From the figures presented above it can be concluded that it is possible to use ashes in concrete compositions, respectively a part of the cement can be replaced by ashes. The replacement of cement in proportion of 10, 20 and 30 wt% was experimented (composition 2, 3 and 4).

The density increases slowly by replacing 10% of cement, after that a decrease is observed, every sample densities being under the density of the standard composition. The water absorption is in agreement with the results obtained for the densities. The water absorption decrease from 10,84 % for the standard composition to 10,38% for composition 2 with 10wt% ash. For the other compositions the value of absorption increases to 12,31 %, while the ash proportion was increased to 30 wt%.

The values for the mechanical strength state the observations at the density and absorption determination. Thus an increase in strength, both flexural and compressive, was observed for the composition no. 2 with 10 wt% ash. While the ash content was increased the mechanical strength decreased and it is situated below the standard composition strength.

The mechanical test after 56 day of hardening shows that the strength increase is higher for the compositions with ash.

Microscopic images of the studied concretes were realised. In all samples it can be distinguished the presence of binder, which is the basis of the concrete pieces, giving their size and shape. The binder is composed of Portland cement, whose chemical components re-crystallized, immediately and in time, in the form of gels of hydrated calcium silicate crystals or fine granules of calcium hydroxide by reaction with water.

Microscopic sections were prepared to be examined by transmission. The sections were prepared from the composition containing 10% fly ash and from the standard composition.

For both sample (standard and experimental sample) a highly uniform matrix can be observed, in the finely ground cement, hardened by water, fine particles of crystalline silicate components are dispersed. Especially quartzite crystals are present, in smaller proportions feldspar and limestone and rarely inclusions of mica contained by the sand introduced as aggregate. The particle content is clear and every mineral exhibit specific optical characteristics.

Unevenly distributed small and rare pores are present, more often in the standard sample (Figure 10a-11a).

In the figures 10b-11b intensely colored, small and isolated granules of fly ash can be observed. They are placed between the aggregate particles, increasing the mass compactness. All granular phases are well connected and embedded by the binder matrix

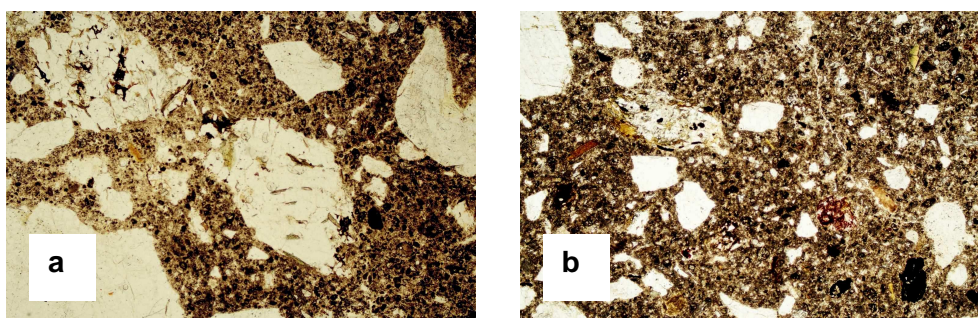


Figure 10. – Samples of slabs in natural polarized light
a - standard concrete slab, b – concrete slab with 10% fly ash

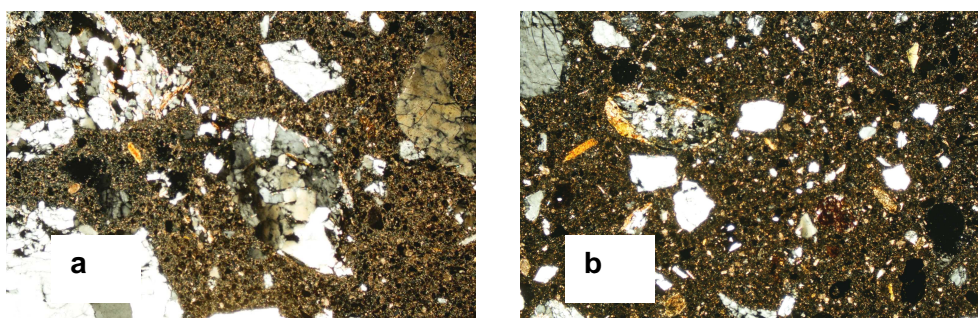


Figure 11. - Samples in transmitted (refracted) polarized light
a - standard concrete slab, b – concrete slab with 10% fly ash

CONCLUSIONS

It can be concluded that the Zalău power plant ash can be used in concrete compositions. 10 wt% replacement of cement by ash brings both economical and qualitative benefits.

Ashes fill in the minute voids that no other part of the mix can fill, thus creating a denser and less absorptive concrete with improved mechanical features. On short term mechanical strengths are lower than plain concrete, after 28 days they equalized and after a long period of hydration products with ashes presents 15-20% higher mechanical strength than classic concrete. Ashes use – recovered wastes – reduces the natural resources use. They also reduces the energy-intensive production of other concrete ingredients, leading to energy saving and “greenhouse gas” emission decrease. Replacing one tone of cement with fly ash it would save enough electricity to power an average home for 24 days, and reduce carbon dioxide emissions equal to a two months use of an automobile.

The enormous quantities and the increasingly wider using opportunities, promoting economic, technical and ecological criteria, make the fly ash an important industrial by-product whose recovery is a national necessity.

EXPERIMENTAL SECTION

Chemical analysis was performed by disaggregating the sample by alkaline fusion of the fine grounded and calcined in platinum crucible. The silica gel was filtered out and separate from the filtrate by double insolubilisation and the oxidic constituents of the mineral mass were determined by complexometric techniques. The second stage in power plant ash composition analysis consisted in careful measurements of the contents of secondary elements. The finely pulverized material, fully passed through a sieve no. 0063 was subjected to mineralization in a mixture of aqua regia and hydrofluoric acid for 30 minutes in a microwave facility and the residual material was filtrated. The contents of the secondary elements were measured by the ELAN DRC II spectrophotometer produced by the Perkin Elmer Company.

The mineralogical composition of the ash was investigated with a SHIMADZU 6000 X-ray diffractometer, using CuK_α radiation (40.0 kV, 30.0 mA).

The thermal behaviour of the ash was investigated by a SHIMADZU derivatographe.

In this experimental works (4) compositions of concrete were prepared replacing the cement with different amounts of ash. In the table 3 are presented the proportions of the raw materials used in the compositions. The first composition, without ash is the standard composition. The hardened concrete characteristics were investigated.

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From the experimentally realized monolithic pieces, some of them with standard composition, without fly ash, others with the addition of 10% ash, thin sections were prepared for microscopic investigations. The used method of investigation was polarizing microscopy in transmitted light with a Yenapol microscope.

Table 3. Concrete compositions

	1	2	3	4
CEM I 42,5 R %	40	36	32	28
Ash %	0	4	8	12
Sand 0-4 %	45	45	45	45
Gravel 4-8 %	15	15	15	15
+ Water %	18,30	18,30	18,30	18,30

The aim was to highlight the role of the ash granules as dispersed phase in the concrete matrix.

REFERENCES

1. Gao Pei-wei, Lu Xiao-lin, Lin Hui, Li Xiaoyan, Hou Jie, *Fuel*, **2007**, 86, 1208.
2. Tsong Yen, Tsao-Hua Hsu, Yu-Wen Liu, Shin-Ho Chen, *Construction and Building Materials*, **2007**, 21, 458.
3. L. Széll, V. Cetea, A. Tóth, L. Gagea, C. Roman, M. Roman, A. Gog, *Studia Universitatis Babeş-Bolyai Chemia*, **2009**, LIV, 1, 59
4. Serdar Aydın, Halit Yazıcı, Hüseyin Yigiter, Bülent Baradan, *Building and environment*, **2007**, 42, 717.
5. N.P. Rajamane, J. Annie Peter, P.S. Ambily, *Cement & Concrete Composites*, **2007**, 29, 218.
6. Takeshi Yamamoto, Tsutomu Kanazu, Masateru Nambu, Takao Tanosaki, *Fuel*, **2006**, 85, 2345.