Frontiers in Mechanochemistry and Mechanical Alloying

INCOME2008
1-4 December, 2008

PRODUCTION AND PRACTICAL APPLICATION OF MECHANICALLY ACTIVATED FLY ASH-BASED BINDING MATERIAL

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Keywords: Mechanical activation, Fly ash, Fine grinding, Strength test, Pozzolanic activity.

Abstract

In this paper utilization of a mixture of mechanically activated fly ash and lime for producing an independent binding composition has been assessed involving determination of interrelationship(s) between the degree of activation of fly ash, the lime concentration and the resultant strength of the obtained concrete. Finally, pilot size experiments were conducted and a test road section was built to explore possibilities for the production of suitable binding composition from the mixture of fly ash and lime as well as the applicability such mixture forroad construction. Furthermore, present study deals with the comparison of the mechanical activation effect on the pozzolanic activity of deposited (brown coal) and recent (lignite) fly ash. Experimental results support the conclusion that the obtained binding material is suitable for construction of road bedding.

Introduction

The enormous amount of fly ash generating each year causes a serious environmental problem in most countries of the World. However, in the developed countries black coal fly ash is recovered in significant amount (60-80 % in the Western European countries) for the building and construction industry. An estimated 200 million tonnes of this byproduct is generated in China and 100 million tonnes in India each year; it might be a valuable raw material for binding material production. About 180 million m^3 fly ash is deposited in Hungary, 3.5 million tonnes of it is generated by coal fired power plant yearly and the fly ash is recovered in small amount and mainly in the cement industry. This situation in Hungary would change basically, if the fly ash and the quality of treated product could be controlled and guaranteed for users (mainly for civil engineers). Additionally, with the elimination of deposits we can save valuable field, the environmental risk and dusting can be reduced. Further advantage of the fly ash based binding material, the utilization instead of clinker, is that significant CO_2 emission reduction can be achieved, additionally big amount of limestone and clay raw material can be saved as well.

Preliminaries and Research Goal

In 2005, the experts of the Department of Process Engineering at the University of Miskolc and the Institute for Transport Sciences Kht. and H-TPA Innovation and Quality Investigations Co. Ltd. elaborated a project to improve the condition of roads in Hungary, especially in small villages. The aim is to build local roads at little cost and to reduce the considerable amount of unpaved roads using fly ash as binding material and wastes from the construction industry. The research work is supported by the GVOP-3.1.1.-2004-05-0113/3.0 project of the EU and the Republic of Hungary.

In a first stage of our investigations – physical and chemical - material properties of fly ash (three acidic and one alkaline type originating from combustion of various age coal) obtained from 4 various dumps have been characterized. In a next step systematic mechanical activation experiments - grinding - and measurements have been performed with various ashes to establish relations between grinding fineness (specific surface area), specific work input demand of grinding and activity. These results were shown in our previous study [9]. After summarizing major achievements of the first and second stages of the work (history) the present study deals with the research conducted in stages three and four. These are as follows:

- Comparison of the activation effect of quick lime and slaked lime mixed to acidic fly ash
- Determination of the compressive strength of concrete specimens containing fly ash based binding material after different grinding time.
- Carrying out of a pilot scale experiment to produce 4,4 tonnes binding material based on the elaborated process.
- Building of a test road section from the produced lime-ground fly ash binder and monitor the road.
- Finally, comparison of the mechanical activation effect on the pozzolanic activity of deposited (brown coal) and recent (lignite) fly ash, as well as experimental work and achievements extended for lignite fly ash are presented.

Materials

Primary experiments were conducted with fly ash from combustion of two various geological age (grade of coalification) coal, e.g. a brown coal and a lignite fly ash. Particle size distribution (Fig. 1) was determined by means of model Fritsch Analysette 22 laser particle size analyzer (x_{50} and x_{80} can be seen in Table 1). For determination of densities pycnometer method was applied (Table 2). For determination of specific surface area (Table 3) three different methods were used, namely: measurement with BET (Micrometrics TriStar 3000) and Blaine equipment as well as calculation from data on particle-size distribution.

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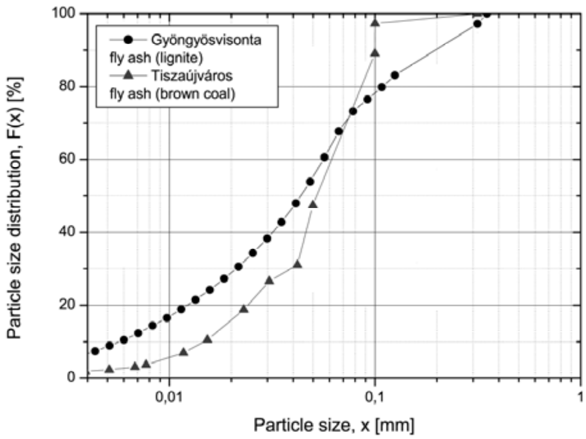


Figure 1. Particle size distribution of fly ash samples.

Table 1. Main particle size parameters of lignite and brown coal fly ash

Sample name	x_{50} [mm]	x_{80} [mm]
Gyöngyösvisonta fly ash (lignite)	0.042	0.107
Tiszaújváros fly ash (brown coal)	0.051	0.085

Table 2. Particle and bulk densities of fly ash samples

Origin of sample	ρ real [kg/m^3]	ρ bulk [kg/m^3]
Tiszaújváros (brown coal)	1893.35	860
Gyöngyösvisonta (lignite)	2033.34	1130

Table 3. Specific surface area of investigated fly ash samples

Origin of sample	Geological period of combusted coal	Specific surface area after BET [m^2/g]	Blaine fineness [cm^2/g]	Calculated specific surface area from F(x) [cm^2/g]
Tiszaújváros (brown coal)	Eocene	8.2	2724	2665
Gyöngyösvisonta (lignite)	Pannonian	-	-	4783

The significant differences shown in Table 3 between specific surface areas measured by BET and Blaine methods, respectively, can be attributed to the porous nature of fly ash.

Oxide components were determined by means of a Philips PW1410 RFA equipment. Results are shown in Table 4.

Table 4. Main chemical components of the fly ash samples.

Component	Tiszaújváros (brown coal) [m/m%]	Gyöngyösvisonta* (lignite) [m/m%]
SiO_2	59.06	60.70
Al_2O_3	26.14	11.10
Fe_2O_3	5.42	8.60
CaO	2.30	11.30
MgO	1.12	1.00
SO_3	0.25	5.00
L.O.I.	2.85	2.30

* Calculated from XRD results

The amorphous phase has very important role in the pozzolanic (C-S-H) reaction of fly ash [3]. For this reason, phase composition of the examined samples was determined by a Bruker D8 ADVANCE apparatus. The detailed results and XRD diagram of lignite based fly ash can be seen in Table 5 and Fig. 2, respectively.

Table 5. Phase composition of fly ash samples

Sample	Phase												
	Tridymite, SiO_2	Quartz	alpha-ristobalite	Akermanite	Anorthite, sodian	Rosenhahnite	Calcite	Sillimanite Al_2SiO_5	Albite, calcian	Maghemite Fe_2O_3	Hematite	Anhydrite	Amorph
Tiszaújváros (brown coal)	29	14					4	26		4			23
Gyöngyösvisonta (lignite)		27	1	4	13	3			5		5	5	37

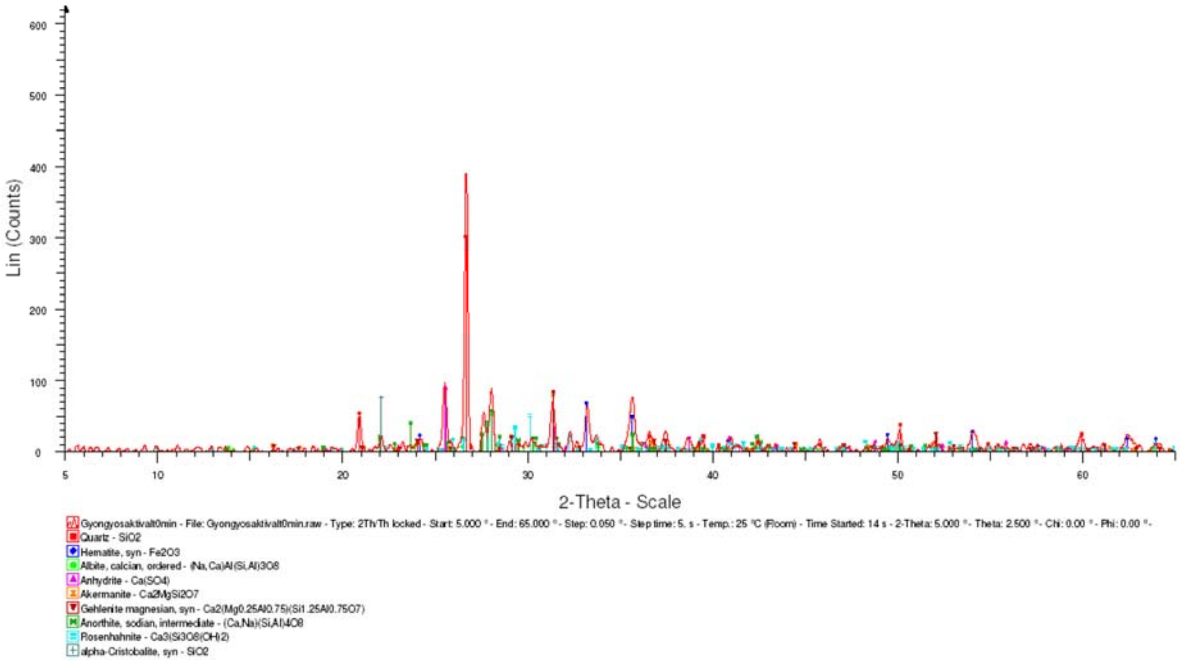


Figure 2. XRD diagram of raw fly ash from Gyöngyösvisonta (lignite fired)

Experimental

Since the most intensive effect of mechanical activation could be achieved in the case of fly ash from Tiszújváros – concluded from primary investigation [2,7-9], we decided to construct an experimental road section using fly ash from the Tiszaujvaros dump, lab- and pilot- scale milling experiments as well as strength tests were conducted with fly ash from Tiszaujvaros.

Laboratory Activation of Fly ash

For grinding, ball mill (ball filling ratio: 40 %, n = 81 min^{-1}, DxL = 305x305 mm) was used (see in Fig. 3). To determine specific work input demand of the grinding operation power input of the driving motor was monitored [4].

Figure 3. Laboratory ball mill used for mechanical activation

Pozzolanic activity measurement

Bearing in mind the intended use of grinds in road construction hydraulic activity of the material is characterized with an activity index (in compliance with the standard MSZ EN 450) [5]. The activity index refers to the measure of applicability of fly ash to replace cement. The activity index is interpreted as the percentage ratio of *fcp* compressive strength of a standard test piece made with 75 wt.% reference cement and 25 wt.% fly ash to the *fcc* compressive strength of a standard test piece made purely with reference Portland cement (Eq.1). Compressive strength measurements must be made under identical conditions. The activity index is expressed by the following formula:

$$PI = \frac{f_{cp}}{f_{cc}} 100 \qquad (1)$$

Specimens were made of a mixture of one part by weight binding material three parts by weight sand and had a water-cement ratio of 0.5. In every case 2 x 3 specimens (size of 40 mm x 40 mm x 160 mm) were used. Specimens were stored together with the moulds in an atmosphere of minimum 90 % relative humidity in water sealed storage vessel. After 24±2 hours, specimens were removed from the moulds, and after marking were immediately placed into water filled basin. Compressive strengths of specimens were measured after 28 and 90 days, respectively (MSZ EN 196-1) [6].

According to measurement of strength after 90 days (Fig. 4) activity index of the Tiszaujvaros fly ash mechanically activated through 30 minutes grinding was 93.6 % compared to 57.4 % measured value of raw (not ground) fly ash. Experimental results suggest that pozzolanic activity of the investigated acidic fly ash can be reasonably controlled by grinding [1].

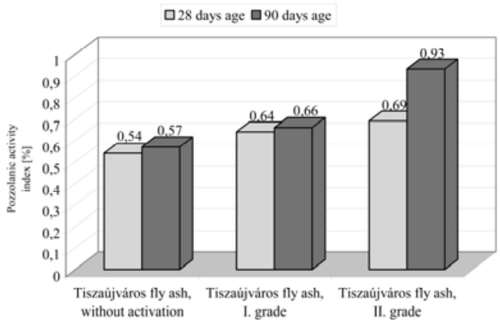


Figure 4. Activity index of activated and not-activated Tiszaújváros (brown coal) fly ash (I. grade activated: t=20 min; II. grade activated: t=30 min).

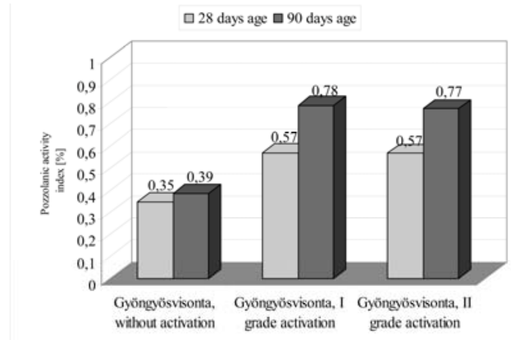


Figure 5. Activity index of activated and not-activated Gyöngyösvisonta (lignite) fly ash (I. grade activated: t=20 min; II. grade activated: t=30 min).

However, in the case of Gyöngyösvisonta fly ash (Fig. 5) 100 % relative difference could be observed between I. grade activated and not-activated state. Further extreme improvement (in the II. grade activated state) could not be seen, the values stagnated. The brown coal fly ash has higher initial pozzolanic activity which increased moderately in the activated state compared with lignite fly ash.

Figure 6 shows the comparison XRD diagram of not activated, 20 and 60 min activated Gyöngyösvisonta recent (lignite) fly ash. Based on this figure it can be concluded, that considerable amorphisation did not occurred during mechanical activation even after 60 min grinding time. Few changes in the XRD diagram can be explained by the particle shape orientation. Furthermore we observed that the crystallite size of quartz (determined by Scherrer equation) did not changed significantly after grinding.

To explore the reason of different activation behaviour between recent lignite and deposited brown coal fly ash we determined the specific surface area of ground fly ash by calculation from particle size data. These results can be seen in Table 6. It can be stated that notwithstanding the Tiszaújváros (deposited) fly ash has higher specific surface area (I. grade), the activity of lignite fly ash was higher after 90 days. However, if we compare the II grade activated state of the two different fly ash samples, it can be established that the higher specific surface area results in higher activity.

Table 6. Calculated specific surface area of lignite and brown coal fly ash samples (shape factor: 1,75)

	Gyöngyösvisonta (lignite) fly ash	Tiszaújváros (brown coal) fly ash
Not-activated	4783.27	2664.66
I. grade activated	6471.61	7931.16
II. grade activated	7210.28	8871.35

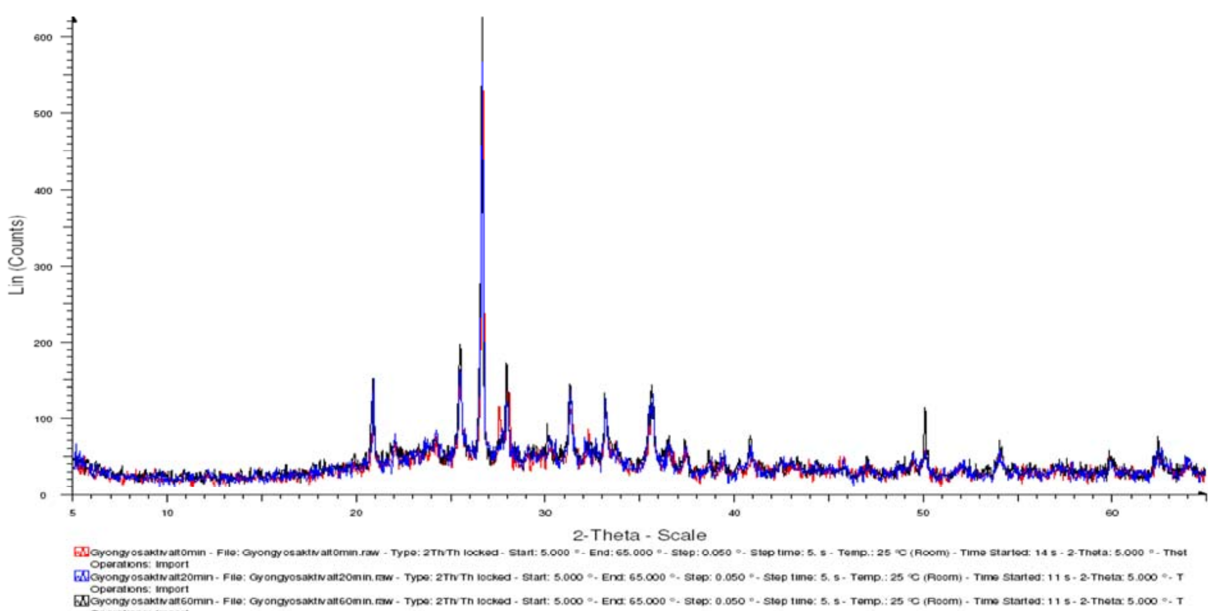


Figure 6. XRD diagram of activated (20 and 60 min grinding time) and not-activated lignite fired fly ash from Gyöngyösvisonta

Compressive strength of concrete specimens made by using fly ash – lime binder for the planning and construction of road

In this series of measurements real (cylindrical) compressive strength of various binder content mixtures was investigated according to MSZ EN 12390-3:2002. Frost-resistance and splitting strengths have also been measured. Various fly ash (brown coal) - lime binding mixtures were prepared using non-activated, activated-I (t = 20 min. grinding time) and activated-II (t= 30 min. grinding time) fly ash, respectively. Concrete test-pieces made with such binder mixtures were then tested at representative ages for strength (Fig. 7). In respect of economics of fly ash based binder, major issues are the quantity of powdery calcium-oxide or lime-hydrate to be mixed in as well as the achievable strength of the product. For this reason, binder mixtures were made using CaO and $Ca(OH)_2$, respectively.

Results (Fig. 8) clearly suggest that application of $Ca(OH)_2$ is more preferable in comparison to CaO. The difference is explained by the fact that CaO at first reacts with water to form $Ca(OH)_2$ In case of using CaO, formation of C-S-H chemical bonds in the pozzolanic reaction would require significantly larger amounts of water.

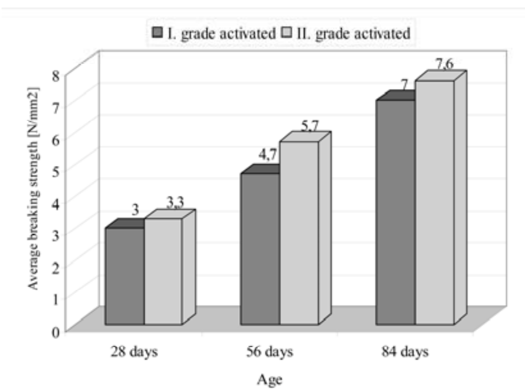


Figure 7. Rupture test results obtained with specimens prepared with binding material from Tiszaujvaros fly ash (I. activated, t=20 min; II. activated, t=30 min (t = grinding time).Dosage: 170 kg binder/m3 concrete; fly ash to lime-hydrate ratio in binder: 3 to 1).

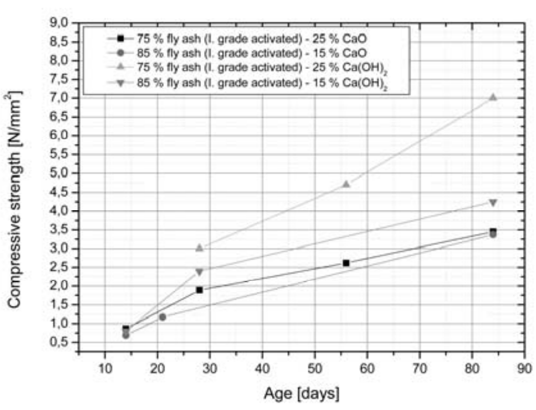


Figure 8. Compressive strength of various ratio Tiszaújváros (brown coal) fly ash to CaO or $Ca(OH)_2$ binders vs. time

Pilot-scale Production of Fly Ash/lime Binder

Pilot-scale production mainly aimed at manufacturing a quantity of the binder sufficient for construction of the experimental road section. Preparation of the Tiszaújváros (brown coal) fly ash consisted of drying and grinding of the raw ash followed by mixing the grinds with lime. Flow-sheet of the pilot experiments is shown in Fig. 9. The nearly 8 ton raw fly ash was extracted directly from the Tiszaujvaros dump was dried for 2 to 3 days at ~ 50 ^oC under the rotary kiln of a cement plant from initial moisture content of 21.79 % to a final moisture content appropriate for grinding (<3 %).

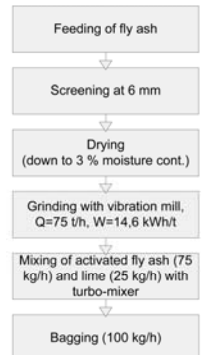


Figure 9. Steps of pilot plant scale fly ash preparation

Pilot-scale grinding experiment were performed using model 20U PALLA vibration mill (Fig.10). Prior to grinding the raw feed material was screened on 5 mm granular size screen to remove coarse foreign matter (clay, grass and other organic materials). For grinding the upper section of the mill body was used. Size and filling rate of the steel grinding balls in the upper grinding space were Ø15 mm and 67 %, respectively. Fly ash feed rate was 75 kg/hour. Specific grinding work input was $W_{specific}$ = 14.6 kWh/ton. Feed rate of lime-hydrate to the mixer was 25 kg/hour resulting in 100 kg/hour combined mass flow rate of the binding material. Parameters of dried fly ash fed into the vibration mill and those of the obtained grinds are shown in Table 7.

Figure 10. Equipment used in pilot scale experiments 1) 20 U PALLA vibration mill, 2) bucket elevator, 3) Vibration feeder, 4) Turbo-mixer

Table 7. Particles related parameters of brown coal fly ash feed and obtained grinds

	x_{50} [µm]	x_{80} [µm]	Calculated specific surface area from F(x), [cm^2/g]
Feed	40.34	61.04	3085.16
Grinds	32.05	51.59	6121.75

Construction and Investigation of the Experimental Road Section

Using 4.4 tonnes of produced fly ash (brown coal) - lime binding mixture having the above indicated properties a 30 m long experimental road section was constructed for the purposes of strength tests on large sample. The experimental section was suitable for monitoring variation of road properties under real weathering conditions. Placing was made after on-site mixing onto suitably prepared earthwork surface. Each layer was inspected for plate bearing test and density. On top of the bed layer made with fly ash based binder periodic measurements were performed to monitor characteristic secondary consolidation of the fly ash based binder. Pictures of the road construction are shown in Fig. 11.

Figure 11. Construction of the experimental road section

Despite certain scattering of obtained E2 (Plate loading test) values it is obvious that load bearing capacity of the constructed experimental road layer met requirements specified for road bedding and improvement layers (Fig. 12). The higher compaction factor is deemed to be a consequence of complications in water-draining. Such problems shall of course be eliminated in large scale road construction projects.

On-site samples of the mixture were compacted in a standard method under laboratory conditions using "Proctor" rammer. Size 100 x 150 mm specimens were produced.

Additionally, construction mixtures with planned binder dosages were reproduced under lab conditions, too. Results indicate that after 63 days consolidation both on-site produced and laboratory made mixtures meet Class CB1 strength requirement. However, Class CB-2 requirement (5.5 N/mm^2) is only met by the laboratory made mixture.

Relying on the progress of consolidation, it may be stated that the rate of secondary consolidation becomes significantly lower after 63 days. Consequently, parameters measured at the "age" of 63 days sufficiently characterize the investigated mixture. Measured strength of cylindrical specimens made of on-site mixture was mostly around 4.7 N/mm^2.

Conclusions

Tendency of the obtained results and some local non-homogeneities found in on-site produced mixtures do not allow us to come to explicit conclusions. However, simultaneous laboratory results (6 N/mm^2 strength at the age of 63 days) suggest that through appropriate construction technology and mixing process the binding material consisting of acidic fly ash and lime mixed with sandy gravel can meet requirements specified for bedding layers of surface pavement.

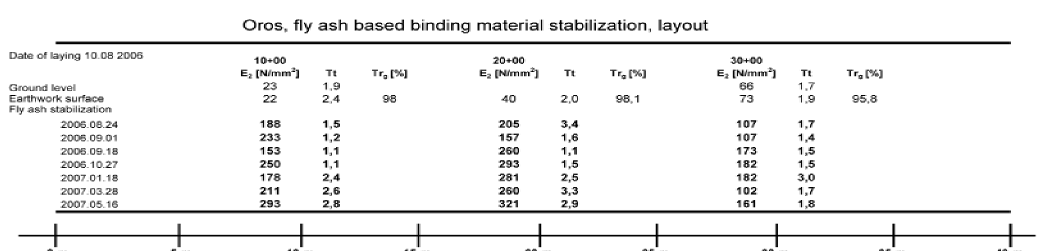
From the laboratory compressive strength results of concrete specimens, 7.6 N/mm^2 value obtained after 84 days.

The application of $Ca(OH)_2$ is more preferable in comparison to CaO. The difference is explained by the fact that CaO at first reacts with water to form $Ca(OH)_2$. In case of using CaO, formation of C-S-H chemical bonds in the pozzolanic reaction would require significantly larger amounts of water.

The brown coal fly ash (with lower amorphous contant: 23 %) had higher initial pozzolanic activity – in not-activated state - than that of lignite fly ash (amorphous phase: 37 %). However, mechanical activation by milling had more intensive positive effect on activity of lignite fly ash than that of brown coal fly ash.

Frost resistance (F25) of mixtures was investigated at age of 84 days. The investigation involved 25 times repeated freezing/melting out cycles with specified number of specimens. Results indicated that such mixtures met relevant requirements on resistance to weathering.

Of course, there are road categories and functions where meeting of neither the above referred criteria nor the extremely high strength requirement (with consideration to the wide scattering of values due to weak reproducibility of on-site mixtures) is necessary. In such cases the binding material dealt with herein used at ratios suitably selected for function of the road to be constructed (influence of dosages on strength of the mixture should be counted with) may competitively replace mixtures made with cement binder.



Oros, fly ash based binding material stabilization, layout

Date of laying 10.08 2006	10+00 E_2 [N/mm^2]	Tt	Tr_g [%]	20+00 E_2 [N/mm^2]	Tt	Tr_g [%]	30+00 E_2 [N/mm^2]	Tt	Tr_g [%]
Ground level	23	1,9					66	1,7	
Earthwork surface	22	2,4	98	40	2,0	98,1	73	1,9	95,8
Fly ash stabilization									
2006.08.24	188	1,5		205	3,4		107	1,7	
2006.09.01	233	1,2		157	1,6		107	1,4	
2006.09.18	153	1,1		260	1,1		173	1,5	
2006.10.27	250	1,1		293	1,5		182	1,5	
2007.01.18	178	2,4		281	2,5		182	3,0	
2007.03.28	211	2,6		260	3,3		102	1,7	
2007.05.16	293	2,8		321	2,9		161	1,8	

Figure 12. Load carrying capacity measurements on the experimental road section

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