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INFLUENCE OF HIGH-CALCIUM FLY ASHES ON THE CHLORIDE ION PENETRATION INTO CONCRETE

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Abstract
In this paper the resistance to chloride penetration into concrete containing various high-calcium fly ashes (HCFA) from brown coal combustion in power industry is examined. HCFA from Belchatow Power Plant was used as nonstandard concrete additive for partial replacement of cement in the mix. To evaluate the concrete resistance to chloride ion penetration the standard method of determination of chloride migration coefficient from non-steady-state migration test according to NT Build 492 was used. The range of investigation included fly ash grinded to specified specific surface as well unprocessed fly ash. Test results revealed a substantial improvement of the resistance to chloride penetration into concrete containing HCFA as partial replacement of Portland cement. The resistance was higher for increased replacement level and decreased water-to-cement ratio. Favourable effects of high-calcium fly ash are discussed in relation to *k*-factor concept.

Keywords: chloride penetration, high calcium fly ash, cement replacement

1.Introduction

Coal ash is a by-product of power generation in coal burning plants. Brown coal is used to produce over 30% of electricity used in Poland. Thus a significant amount of high calcium fly ash (HCFA) is generated, up to about 4 million ton per year. Possible use of high-calcium fly ashes in the composition of cement and in ready mix concrete would result in a number of environmental benefits (reduced consumption of cement clinker, reduced CO_2 emissions during cement production, saving natural resources, reduced landfill space and storage costs), which fit very well with the strategy of sustainable development. However, this type of ash is characterized by low silica contents, high content of free lime, an increased content of sulfur compounds. Therefore it does not meet the requirements defined in European standard EN 450-1. A large variability of chemical composition and grain size distribution can also be expected. At present HCFA is not in general use in European countries in spite of positive examples of its suitability provided by Greek researchers. It was shown [1] that in the case of cement replacement with HCFA, the compressive strength of concrete was increased if the content of active silica in the fly ash was higher than that in the cement. For overcoming drawbacks of HCFA composition and gradation different ash intermixtures were applied and synergy between the different types of fly ashes was found to be the main reason for the excellent strength performance of the mixtures [2]. It was also found that concrete specimens incorporating HCFA exposed to the long-term chloride ponding experiments exhibited significantly lower total chloride content for all depths from the surface [3]. The assessment of concrete resistance to chloride ingress is fundamental for durability of structures in XD and XS environmental exposure classes defined in EN 206-1. The objective of this investigation is to study the influence of fly ash from brown coal combustion in "Belchatów" power plant in Poland on the resistance of concrete to chloride ingress. This investigation is a part of a larger research program recently started in Poland in order to develop a suitable technology for use of high-calcium fly ash as a type II addition to concrete mix.

Chloride penetration resistance of concrete modified with standard siliceous fly ash was studied using slow and rapid testing methods [4]. The Rapid Chloride Migration (RCM) test described by Luping and Nilsson in 1992 [5] (also known as test according to NT Build 492 standard) is becoming the standard test for this purpose. The principle of the test is based on active chloride migration enhanced by an electric field over a saturated concrete sample [6]. The criteria for evaluating the resistance of concrete against chloride penetration are presented in Table 1 on the basis of the chloride migration coefficient determined according to NT Build 492 standard. The criteria are not yet well established for specific structural applications in different European countries.

Table 1 Evaluation of resistance to chloride ingress in concrete

Chloride migration coefficient D_{nssm}	Resistance to chloride penetration
$< 2 \times 10^{-12}$ m^2/s	Very good
$2 - 8 \times 10^{-12}$ m^2/s	Good
$8 - 16 \times 10^{-12}$ m^2/s	Acceptable
$> 16 \times 10^{-12}$ m^2/s	Unacceptable

2. Experimental program

2.1 Materials and specimens

The investigation included threeseriesof concrete mixtures modified with high-calcium fly ashes used for partial replacement of cement in the mix.

Following materials were used:

- cement: CEM I 42.5R and CEM I 42.5 HSR NA,
- high-calcium fly ashes from Belchatów Power Plant collected at three different dates during 6 months period (the chemical composition of fly ashes is shown in Table 2),
- aggregates: sand 0-2 mm, amphibolite gravel 2-8 mm and 8-16 mm,
- water reducing admixtures: Glenium SKY 591 and BV-18,
- tap water.

The characteristic feature of fly ash composition is the content of CaO, SO_3 and SiO_2 within the range 22-31%, 3.0-4.5%, 34-40%, respectively. High-calcium fly ash was used both in unprocessed form (as collected) and after grinding in laboratory mill during 10 to 28 minutes. No grinding was performed for "S2" ash because of its high specific surface in the as-collected form. Physical properties of fly ashes are given in Table 3.

Table 2 The chemical composition of high-calcium fly ashes determined using XRF method

Component	Fly ash sampling date and batch designation		
	16.03.2010, S1	19.05.2010, S2	28.06.2010, S3
LOI	2.56%	3.43%	1.85%
SiO_2	33.62%	35.41%	40.17%
Al_2O_3	19.27%	21.86%	24.02%
Fe_2O_3	5.39%	6.11%	5.93%
CaO	31.32%	25.58%	22.37%
MgO	1.85%	1.49%	1.27%
SO_3	4.50%	4.22%	3.07%
K_2O	0.11%	0.13%	0.20%
Na_2O	0.31%	0.16%	0.15%
P_2O_5	0.17%	0.16%	0.33%
TiO_2	1.21%	1.22%	1.01%
Mn_2O_3	0.07%	0.06%	0.06%
SrO	0.20%	0.17%	0.16%
ZnO	0.02%	0.02%	0.02%
CaO_{free}	2.87%	1.24%	1.46%

Table 3 Physical properties of high-calcium fly ashes before and after processing

Batch	Fly ash designation	Density [g/cm^3]	Fineness – the residue on sieve 45μm [%]	Specific surface by Blaine [cm^2/g]
S1	S1-N : unprocessed	2.62	38.0	2860
	S1-10M: grinded 10 min	2.77	23.0	3500
	S1-28M: grinded 28 min	2.75	10.5	3870
S2	S2-N: unprocessed	2.58	35.4	4400
S3	S3-N: unprocessed	2.64	55.6	1900
	S3-20M: grinded 20 min	2.71	20.0	4060

Concrete specimens were manufactured at constant water to binder ratio using variable HCFA content for partial replacement of cement. The design of concrete mix was based on the prediction of compressive strength and for this purpose the efficiency factor *k* was assumed: *k*=0.4 for HCFA type "S1" and "S2" and *k*=0.7 for HCFA type "S3". The cement replacement level was 15% and 30%. The use of HCFA addition induced a significant increase of water demand for concrete mixes. To maintain the target slump of concrete mixtures (class S2 to S3) the amount of water was kept constant and the content of water reducing admixtures was adjusted.

The composition of concrete mixtures made with assumed water-to-binder ratio and high-calcium fly ashes content is shown inTable 4.

2.2 Test methods

The compressive strength of concrete was determined on 150 mm cube specimens after up to 90 days. The strength tests were performed according to PN-EN 12390-3:2009 standard. The chloride migration coefficient was determined on concrete specimens after 56 days of standard wet curing. The testing procedure was in accordance with NT Build 492 standard.

Table 4 Composition of concrete mixtures

Designation of the concrete mixture	Water-binder ratio	HFCF designation	HFCF content [%]	Type of cement	Cement content [kg/m^3]
C1/0.45	0.45	none	0	CEM I 42.5R	359
C1/S1-N/15/0.45		S1-N	15		305
C1/S1-N/30/0.45		S1-N	30		250
C1/S1-10M/15/0.45		S1-10M	15		310
C1/S1-10M/30/0.45		S1-10M	30		257
C1/S1-28M/15/0.45		S1-28M	15		306
C1/S1-28M/30/0.45		S1-28M	30		255
C1/0.55	0.55	none	0	CEM I 42.5R	323
C1/S1-N/15/0.55		S1-N	15		272
C1/S1-N/30/0.55		S1-N	30		226
C1/S1-10M/15/0.55		S1-10M	15		275
C1/S1-10M/30/0.55		S1-10M	30		228
C1/S1-28M/15/0.55		S1-28M	15		277
C1/S1-28M/30/0.55		S1-28M	30		228
C2/0.45	0.45	none	0	CEM I 42.5 HSR NA	366
C2/S1-N/15/0.45		S1-N	15		312
C2/S1-N/30/0.45		S1-N	30		251
C2/S2-N/15/0.45		S2-N	15		304
C2/0.55	0.55	none	0	CEM I 42.5 HSR NA	328
C2/S1-N/15/0.55		S1-N	15		278
C2/S1-N/30/0.55		S1-N	30		226
C2/S2-N/15/0.55		S2-N	15		277
C1/0.50	0.5	none	0	CEM I 42.5R	340
C1/S3-N/15/0.50		S3-N	15		296
C1/S3-N/30/0.50		S3-N	30		237
C1/S3-20M/15/0.50		S3-20M	15		295
C1/S3-20M/30/0.50		S3-20M	30		239
C1/0.60	0.6	none	0	CEM I 42.5R	308
C1/S3-N/15/0.60		S3-N	15		265
C1/S3-N/30/0.60		S3-N	30		218
C1/S3-20M/15/0.60		S3-20M	15		265
C1/S3-20M/30/0.60		S3-20M	30		219
C2/0.50	0.5	none	0	CEM I 42.5 HSR NA	343
C2/S3-N/15/0.50		S3-N	15		290
C2/S3-N/30/0.50		S3-N	30		239
C2/S3-20M/15/0.50		S3-20M	15		295
C2/S3-20M/30/0.50		S3-20M	30		240
C2/0.60	0.6	none	0	CEM I 42.5 HSR NA	312
C2/S3-N/15/0.60		S3-N	15		265
C2/S3-N/30/0.60		S3-N	30		222
C2/S3-20M/15/0.60		S3-20M	15		265
C2/S3-20M/30/0.60		S3-20M	30		223

Cylindrical specimens of diameter of 100mm were sliced into 50 mm high specimens and before testing the side surfaces were protected against infiltration. Specimens saturated in

$Ca(OH)_2$ solution were placed between two chambers, one of which was filled with catholyte (10% NaCl solution) and the second with anolyte (0.3 molar solution of NaOH). Between the cathode and the anode the electrical voltage was set to 30V. After the measurement of current passing through the sample the duration of test was set. After finishing the ion migration process the specimens were split into two parts in order to determine the depth of chloride ions penetration. For this purpose the concrete section was sprayed with silver nitrate solution (0.1M$AgNO_3$) (Figure 1). On the basis of the measured depth of chloride ions penetration and Fick's second law the chloride migration coefficient D_{nssm} was determined.

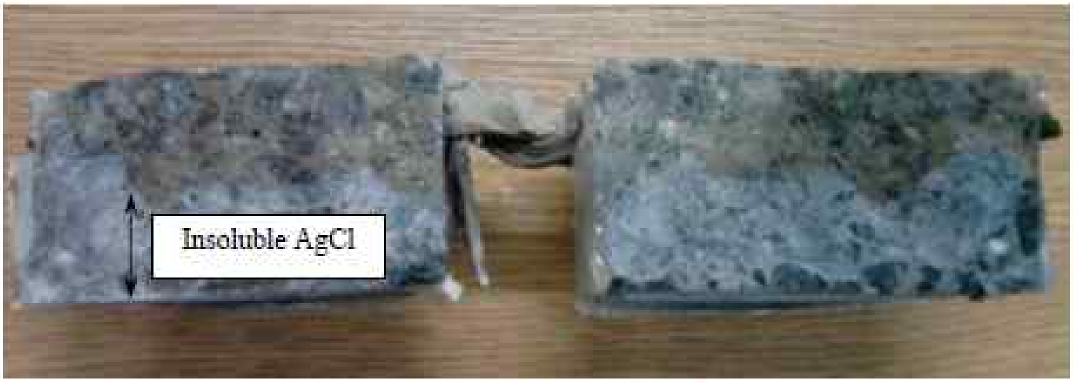

Figure 1: Section view of concrete specimen split after the chloride migration test and after spraying the surface with $AgNO_3$ solution

3 Test results and discussion

Test results of chloride migration coefficient D_{nssm} and the compressive strength data are shown in Table 5 as average values for three specimens tested for each concrete mix. The major influence of the water to binder ratio on D_{nssm} is seen. For a close investigation of HCFA effects the test results are illustrated in Figures 2 to 5.

It is seen that increasing content of fly ash form Belchatow power plant generally decreased the chloride migration coefficient of concrete containing Portland cement CEM I 42.5 R. Such a reduction of D_{nssm} improved the category of resistance from "acceptable" to "good" or from "unacceptable" to "acceptable". For w/b=0.60 the reduction of D_{nssm} was marginal and did not improve the category of chloride penetration resistance. Grinding of HCFA was found to improve its performance but not significantly.

Effects of HCFA addition in concrete containing sulfate resistant cement CEM I 42.5R HSR NA were positive. A reduction of D_{nssm} due to fly ash addition improved the category of chloride penetration resistance of concrete. Unusual effects observed for "S3" fly ash at w/b=0.60 can be associated with a high scatter of test results.

It is obvious that the assumed *k*-factor for the compressive strength is not adequate for chloride penetration resistance of concrete. However, the relationship between the compressive strength and the chloride migration coefficient should be analysed to get a better understanding of the results.

Table 5 The coefficient of chloride migration and the category of resistance to chloride ion penetration

Designation of concrete mixtures	Chloride migration coefficient D_{nssm} [x 10^{-12} m^2/s]		Category of resistance to chloride penetration	Compressive strength [MPa]	
	Average value	Standard deviation		f_{c28}	f_{c90}
C1/0.45	10.13	1.0	Acceptable	60.8	68.1
C1/S1-N/15/0.45	7.88	0.1	Good	62.1	68.9
C1/S1-N/30/0.45	3.76	0.3	Good	60.2	73.7
C1/S1-10M/15/0.45	5.44	0.3	Good	66.0	78.3
C1/S1-10M/30/0.45	3.42	0.5	Good	72.7	81.7
C1/S1-28M/15/0.45	6.37	1.2	Good	66.9	76.4
C1/S1-28M/30/0.45	3.85	0.7	Good	70.7	77.9
C1/0.55	23.73	4.13	Unacceptable	43.4	48.7
C1/S1-N/15/0.55	12.36	0.8	Acceptable	50.5	57.7
C1/S1-N/30/0.55	8.1	2.0	Acceptable	54.2	64.2
C1/S1-10M/15/0.55	17.79	4.0	Unacceptable	46.7	58.1
C1/S1-10M/30/0.55	10.37	2.3	Acceptable	57.6	67.4
C1/S1-28M/15/0.55	12.22	1.17	Acceptable	53.3	63.3
C1/S1-28M/30/0.55	5.52	0.3	Good	58.6	71.6
C2/0.45	11.96	0.5	Acceptable	62.0	75.6
C2/S1-N/15/0.45	6.34	0.4	Good	61.5	79.1
C2/S1-N/30/0.45	4.04	0.1	Good	62.9	75.1
C2/S2-N/15/0.45	5.04	0.2	Good	64.3	74.3
C2/0.55	21.91	1.3	Unacceptable	48.8	55.4
C2/S1-N/15/0.55	10.3	0.8	Acceptable	51.8	66.1
C2/S1-N/30/0.55	7.88	0.9	Good	46.3	58.8
C2/S2-N/15/0.55	7.76	0.8	Good	55.1	62.8
C1/0.50	20.79	3.1	Unacceptable	44.4	53.2
C1/S3-N/15/0.50	8.17	0.8	Acceptable	47.8	62.1
C1/S3-N/30/0.50	10.95	2.4	Acceptable	43.7	54.1
C1/S3-20M/15/0.50	12.0	0.9	Acceptable	47.3	58.1
C1/S3-20M/30/0.50	5.17	0.4	Good	42.5	57.8
C1/0.60	26.0	1.1	Unacceptable	34.4	40.4
C1/S3-N/15/0.60	22.80	1.2	Unacceptable	35.9	46.4
C1/S3-N/30/0.60	20.86	3.4	Unacceptable	28.0	37.8
C1/S3-20M/15/0.60	12.10	2.2	Acceptable	40.6	49.4
C1/S3-20M/30/0.60	7.59	0.5	Good	42.3	52.7
C2/0.50	23.09	2.2	Unacceptable	52.4	58.6
C2/S3-N/15/0.50	22.87	2.4	Unacceptable	42.6	52.6
C2/S3-N/30/0.50	21.85	2.0	Unacceptable	37.4	45.8
C2/S3-20M/15/0.50	19.61	1.5	Unacceptable	49.6	58.6
C2/S3-20M/30/0.50	17.65	5.4	Unacceptable	39.2	55.9
C2/0.60	28.5	1.7	Unacceptable	34.4	40.4
C2/S3-N/15/0.60	31.63	2.6	Unacceptable	29.1	40.8
C2/S3-N/30/0.60	27.44	2.4	Unacceptable	24.4	33.9
C2/S3-20M/15/0.60	25.42	2.1	Unacceptable	33.6	44.9
C2/S3-20M/30/0.60	23.04	2.0	Unacceptable	32.5	47.7

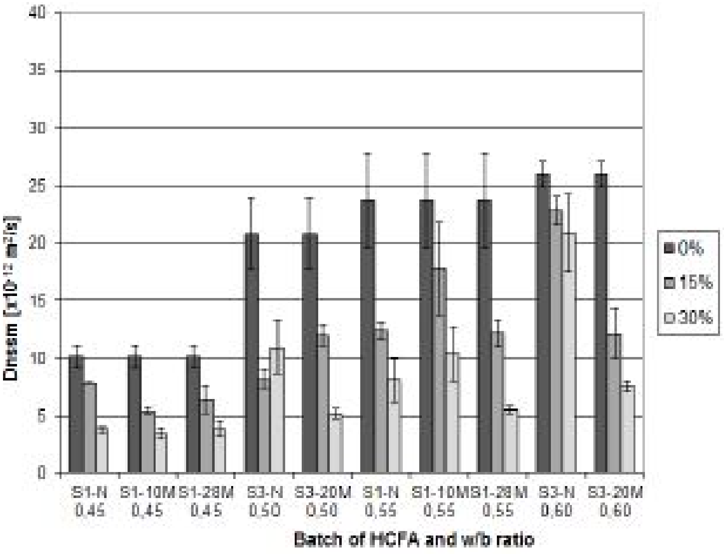

Figure 2: The influence of HFCA type and content on the chloride migration coefficient D_{nssm} for concrete made with CEM I 42.5R for w/b =0.45, 0.50, 0.55 and 0.60

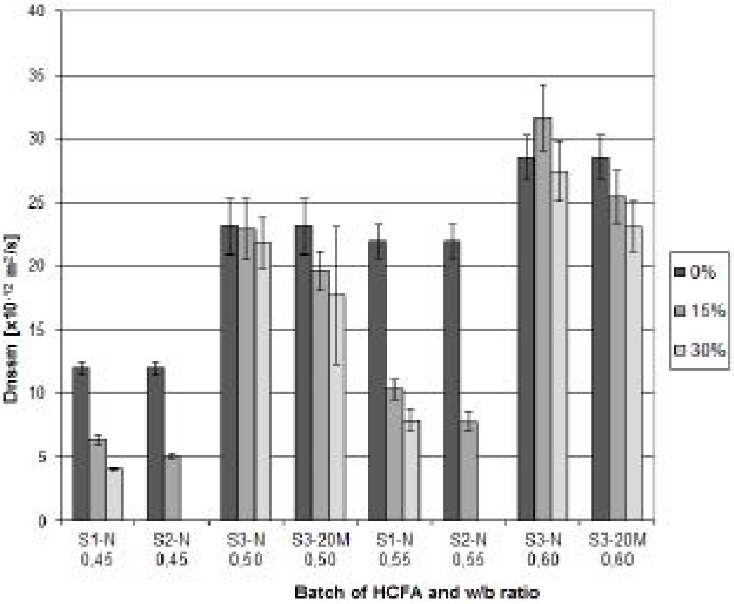

Figure 3: The influence of HFCA type and content on the chloride migration coefficient D_{nssm} for concrete made with CEM I 42.5R HSR NA for w/b =0.45, 0.50, 0.55 and 0.60

Assumed k=0.4 (the same as for standard siliceous fly ash) was found to underestimate the efficiency of HCFA from the batch "S1" and "S2". Therefore for the next series k=0.7 was assumed and such a coefficient seems to be correct for the strength estimation.

The relationship between D_{nssm} and w/b for mixes without fly ash is close to linear. It is well described using the following empirical formula with $R^2 = 0.84$:

$$D_{nssm}\ [x10^{-12}\ m^2/s] = 99 \cdot w/c - 31.20. \qquad (1)$$

The relationship between D_{nssm} and f_{c90} shown in Figure 4 is close to linear. The empirical relationship is approximated using the following formula with $R^2 = 0.72$:

$$D_{nssm}\ [x10^{-12}\ m^2/s] = -0.55 \cdot f_{c90}\ [MPa] + 47. \qquad (2)$$

Using one of well known formulas, eg. Feret's formula, for the strength of concrete the formula (2) can be transformed to include explicitly the *k*-factor used for the strength design and the content of water, cement and fly as in such a way as it was shown in [7].

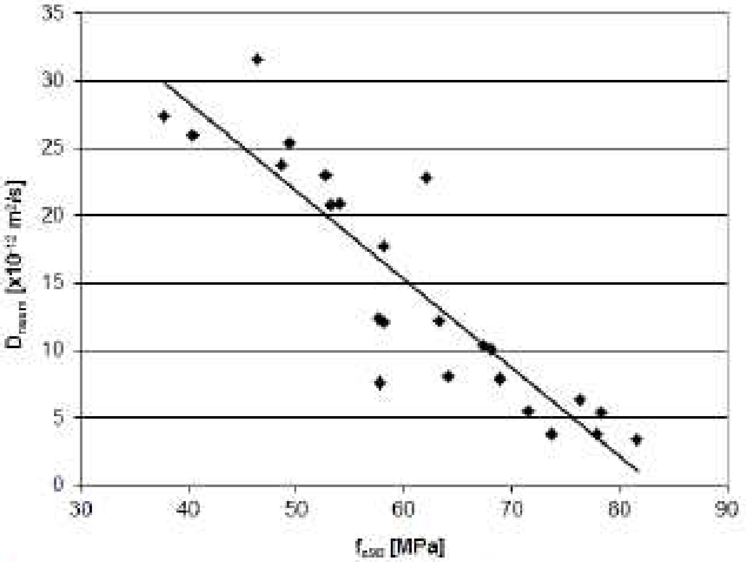

Figure 4: The relationship between average values of chloride migration coefficient and compressive strength for concrete made with CEM I 42.5R

Compilation of efficiency factors from a variety of references in the literature [8] for the strength and the chloride penetration resistance demonstrated the marked differences between the effectiveness of fly ashes for the various performances. The k-factor related to the strength efficiency is usually much higher than the recommended values in EN 206-1) and the chloride penetration resistance efficiency is expected to be about 2. Since a number of various k-factors is needed for various types of exposure conditions the meaning of water-to-binder ratio is no longer valid. There is an obvious need for more sophisticated approach to characterize the efficiency of fly ashes, especially beyond standard siliceous ashes, for the performance of concrete exposed to chloride exposure environment

4 Conclusions

The following conclusions can be drawn on the basis of performed research.

1. Increasing content of high calcium fly ash form Belchatow power plant significantly decreased the chloride migration coefficient of concrete containing Portland cement.

2. Grinding of HCFA was found to provide only slight improvement of its performance in respect to chloride penetration.
3. The relationship between the chloride migration coefficient and the compressive strength of concrete at 90days was found to be close to linear relationship.

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References

[1] Papadakis, V.G 2000: *Effect of fly ash on Portland cement systems Part II: High-calcium fly ash*, Cement and Concrete Research 30: 1647-1654

[2] Antiohos, S.K. . Tsimas, S. 2007: *A novel way to upgrade the coarse part of a high calcium fly ash for reuse into cement systems*, Waste Management 27: 675-683

[3] Papadakis, V.G. 2000: *Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress*, Cement and Concrete Research 30: 291-299

[4] Gjorv, O.E. 2009:*Durability Design of Concrete Structures in Severe Environments*, London and New York: Taylor & Francis

[5]Luping, T. Nilsson, L.O., 1992: *Rapid determination of the chloride diffusivity in concrete by applying an electric field*, ACI Materials Journal 89: 49-53

[6]Rooij, M.R. van Dalen, S.M. Bouwmeester, W.j. Koenders E.A.B. 2006: *Experimental excercises with the RSM-Method*, Canada, 2nd International Symposium on Advances in Concrete through Science and Engineering

[7] Glinicki, M.A. Nowowiejski, G. Gibas, K. 2011: *Strengthening efficiency of nonstandard addition of fluidized bed ash in concrete*, Hong Kong : RILEM International Conference on Advances in Construction Materials through Science and Engineering (in print)

[8] Bentur, A. Mitchell, D. 2008: *Material performance lessons*, Cement and Concrete Research 38: 259–272

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