



**INNOWACYJNA
GOSPODARKA**
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO



„Innowacyjne spoiwa cementowe i betony z wykorzystaniem popiołu lotnego wapiennego”
Projekt współfinansowany ze środków Europejskiego Funduszu Rozwoju Regionalnego
w ramach Programu Operacyjnego Innowacyjna Gospodarka, nr projektu: POIG.01.01.02-24-005/09

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AIR PERMEABILITY OF SUPERPLASTICIZED CONCRETE WITH 0.5 CLINKER FACTOR



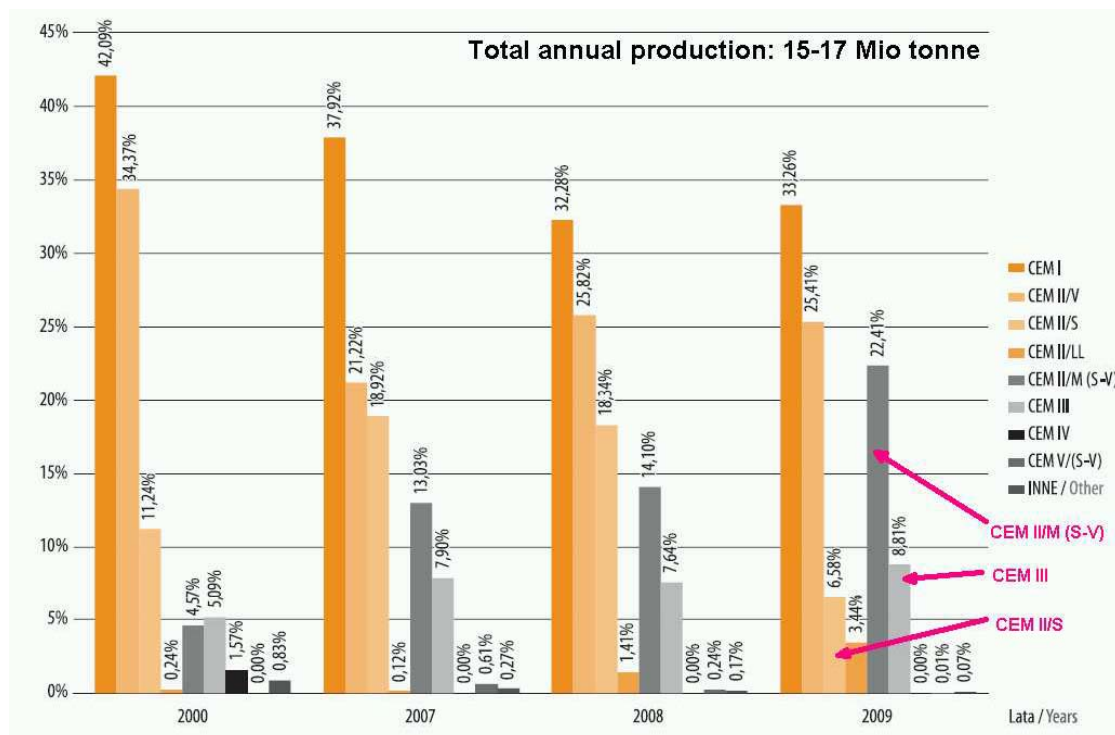
Institute of Fundamental Technological Research
Polish Academy of Sciences
Warsaw, Poland

Anna Maria Workshop, Nov. 10-12, 2010

THE CONCEPT

One of the tools for reducing carbon emissions due to cement consumption in concrete is a reduction of clinker share in cementitious material.

Blast furnace slag resources in Poland are fully utilized by cement industry.



The concept of significant reduction of clinker share in concrete is feasible by using high volume of coal ash or by **mixing coal ash** in concrete with slag blended cement, particularly **with CEM II B/S**.

TERNARY BINDERS IN CONCRETE

Ternary concrete mixtures including combinations of portland cement, slag and fly ash (or eventually silica fume) have been studied for decades.

The effect of slag in reducing the permeability of concrete is well known: generally, the higher the percentage of slag in a concrete mixture, the lower the permeability of the concrete. But the resistance to freezing/thawing +deicing salts is significantly reduced.

It is believed that high volume fly ash concrete due to its low permeability and high crack resistance should not exhibit any significant carbonation.

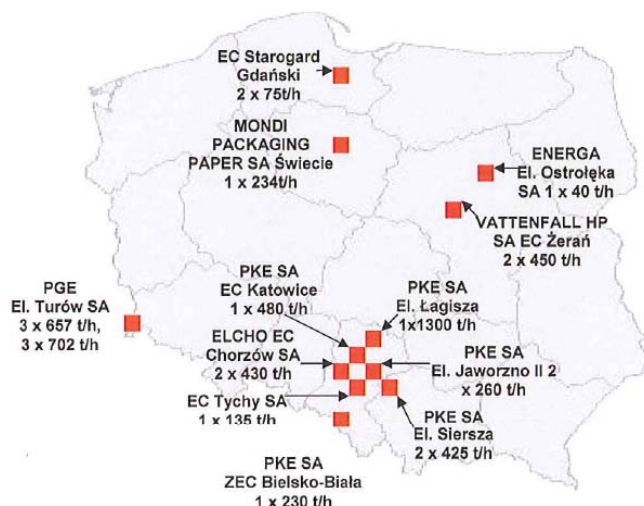
The reduction of permeability is most commonly reported as measured by the rapid chloride permeability test. The gas permeability of 50% clinker factor concrete mixtures is less documented.

COAL ASH RESOURCES

European (EU 27) production of coal combustion products : 100 Mio tonne/year

non-standard coal ash in Poland

FBC ash: about 2 Mio tonne/year
22 FBC boilers in power plants



High calcium fly ash : about 5 Mio tonne/year
3 brown coal mines – 3 large power plants

REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

- By this, all chemicals manufactured in or imported into the EU have to be registered at the **European Chemicals Agency (ECHA)**. The registration requires information on the properties and the potential risks of the substances; **no data → no trade**
- Producers or importers of coal combustion products (fly ash, bottom ash, boiler slag, etc) placed on the market as construction materials have to register their substances, i.e. provide comprehensive data incl. information about human toxicology and ecotoxicology of the substances.
- The substances are registered as mono-constituent, multi-constituent or UVCB-substance (Unknown or Variable composition, Complex reaction products or Biological materials).



Effective registration of FBC Ash with ECHA

september 2010

Substance Information

Substance name: [\[931-257-5\] Ashes from fluidized Bed combustion coal fired Power stations with and without co-combustion of secondary fuels \(biomass; other fuels - to be verified in view of ecotoxicological and toxicological tests\)](#)

Dossier content

Dossier submission remark

Remark: [Registration above 1000 tonne by Lead registrant](#)

Dossier information

Dossier UUID : [IUC5-8acc03ad-cac1-4c8f-8d31-97b420be96bf](#)

Dossier creator: -

Dossier subject

Name given by the dossier creator: [Dossier_FBC_Ash](#)

Submitting legal entity: [UTEX-CENTRUM Sp. z o.o.](#)

Submitting legal entity UUID: [ECHA-fd37b9ae-1021-44e0-abb9-5bfdd519e52b](#)

CHEMICAL SAFETY REPORT → no risk to humans and environment

Name and other identifiers of the substance

The substance **FBC Ash** is a UVCB (origin: inorganic) having the following characteristics and physical–chemical properties

IUPAC name:	Ashes from fluidized Bed combustion coal fired Power stations with and without co-combustion of secondary fuels (biomass; other fuels - to be verified in view of ecotoxicological and toxicological tests)
Description:	The residuum from the burning and desulfurization processes in Fluidized Bed Combustion boilers. The substance consists mainly of following oxides: silicon, aluminium, iron, calcium, titanium, sodium, potassium, magnesium and phosphorous and calcium sulphate as a residuum of desulfurization process.

Substance Identification Profile

Składnik	Min.	Max.
CaO (całkowite)	0,5	36
SO ₃	1	20
CaCO ₃	0	8
SiO ₂	10	76
Al ₂ O ₃	3	38
Fe ₂ O ₃	0,2	27
TiO ₂	0,2	8
MgO	0	8
Na ₂ O	0,01	4
K ₂ O	0,2	8
P ₂ O ₅	0,1	10,5

EXPERIMENTAL : Materials and mix design

Slag-blended cement CEM II/B-S 32.5N (slag content about 30%),

Slag cement CEM III/A 42.5N-HSR/NA (slag content about 57%),

according to European Standard EN 197-1.

FBC ash from fluidized bed combustion of brown coal or hard coal.

Aggregates: crushed limestone 2/8mm and 8/16 mm, or crushed granite 2/8mm and 8/16mm, pit sand 0/2mm.

Chemical admixtures: water reducer/retarder; superplasticizer.

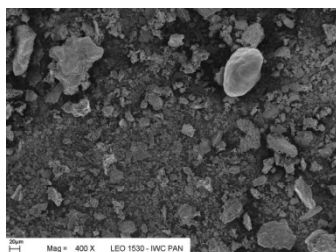
Concrete mix designed with **constant** water to (cement+FBC ash) ratio, the slump of about 150mm.

Variable: the amount of chemical admixtures required to achieve the target slump.



Chemical composition of FBC ashes

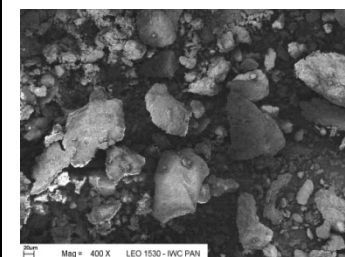
hard
coal



grain size [μm]:
mainly below 1
max 80
min below 1

Test parameters	FBC FA Katowice	FBC FA Turow	EN 450-1 requirements
SiO_2 , [% by mass]	47.46	36.47	the sum of contents $\text{SiO}_2 + \text{Al}_2\text{O}_3 +$ $(\text{Fe}_2\text{O}_3) \geq 70$
Al_2O_3 , [% by mass]	23.29	28.40	
CaO , [% by mass]	7.48	15.95	*)
SO_3 , [% by mass]	3.56	3.80	not more than 3.0
Cl^- , [% by mass]	0.08	0.03	not more than 0.10
CaO free, [% by mass]	0.35	4.75	not more than 1.0 or 2.5 and **)
MgO , [% by mass]	3.10	1.65	not more than 4.0
Fe_2O_3 , [% by mass]	7.53	4.40	-
Loss on ignition, [% by mass]	3.30	2.73	≤ 5 : Category A 2-7: Category B 4-9: Category C
Unburned carbon content by TGA-DTA, [% by mass]	0.3	-	-

brown
coal



grain size [μm]:
mainly 4-5
max 120
min below 1

*) the content of reactive calcium oxide $\leq 10.0\%$

**) soundness : the expansion in accordance with EN 196-3 not greater than 10mm

EXPERIMENTAL : Specimens and test methods

Curing of specimens:

- cubes 150mm: standard moist curing
- slabs 100x500x500mm : standard moist curing for 28 days, later - indoor laboratory exposure

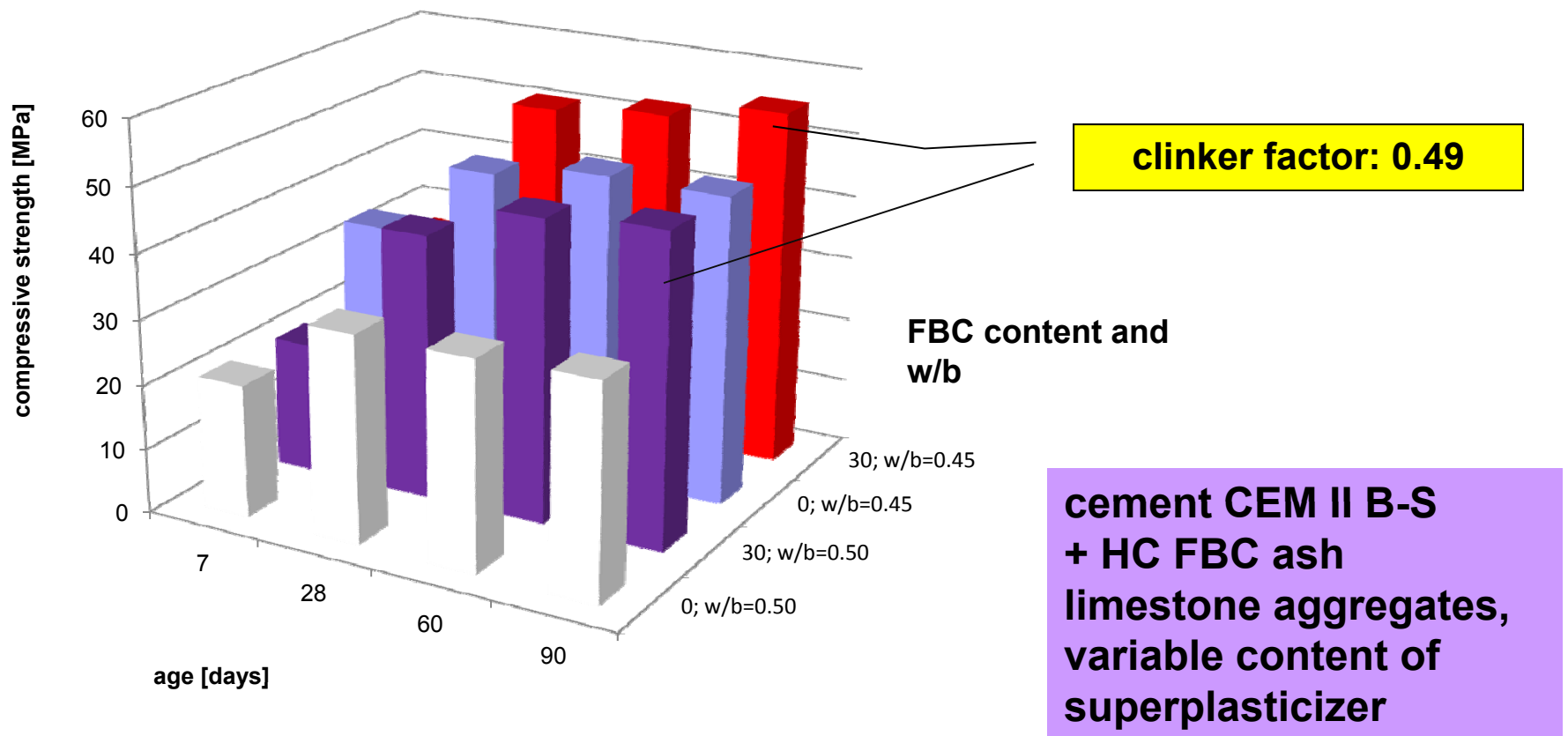
Tests:

- Standard test method for determination of compressive strength on cube specimens
- Air permeability test on slab specimens using Torrent apparatus

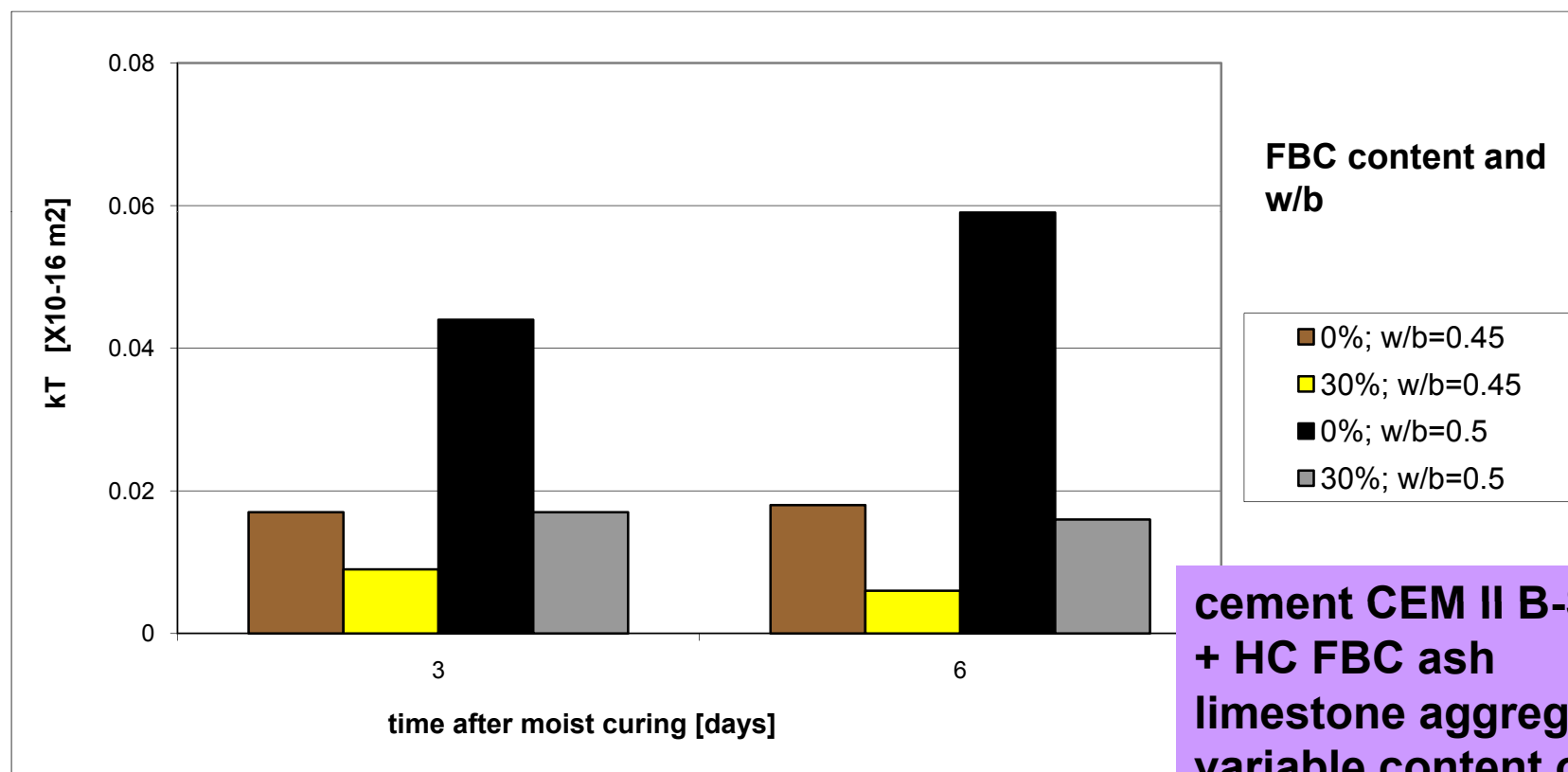




Compressive strength of concrete

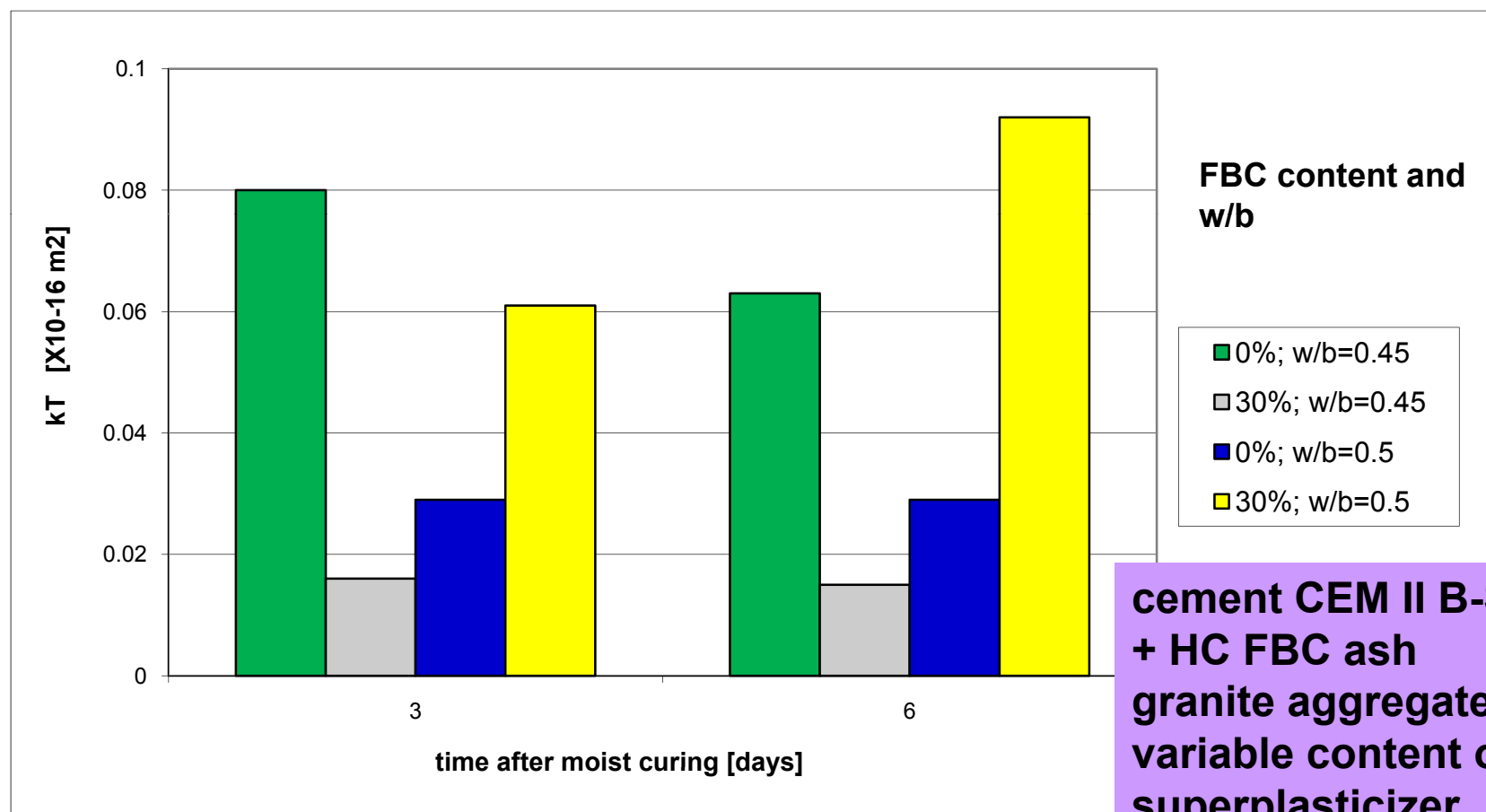


Coefficient of air permeability (Torrent) of concrete



**cement CEM II B-S
 + HC FBC ash
 limestone aggregates,
 variable content of
 superplasticizer**

Coefficient of air permeability (Torrent) of concrete



EXPERIMENTAL : Materials and mix design -part 2

Cement CEM I 42.5R

High calcium fly ash :

Chemical composition of HCFA [%]

LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	CaO _w
2,56	33,62	19,27	5,39	31,3	1,85	3,91	0,11	0,31	0,17	1,21	2,87

Aggregates: crushed amphibolite 2/8mm
and 8/16 mm, pit sand 0/2mm.

Chemical admixtures: water
reducer/retarder; superplasticizer.

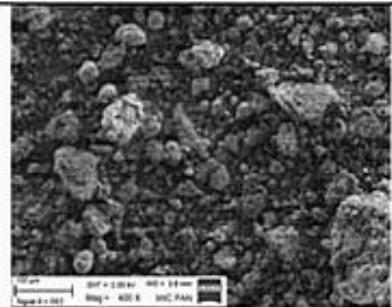
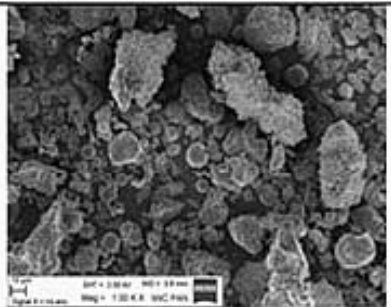
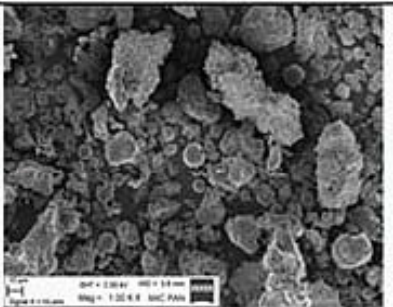
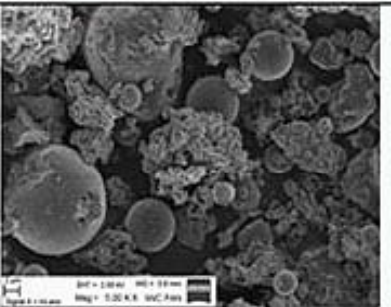
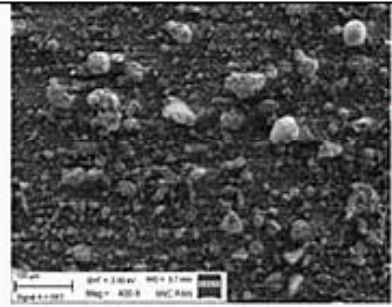
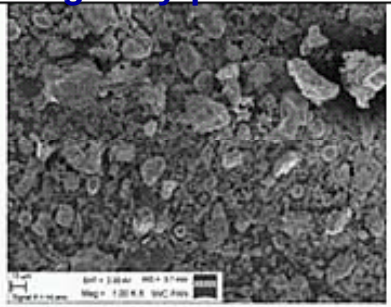
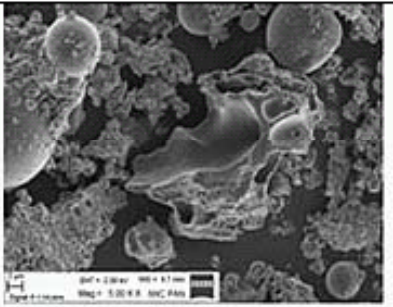
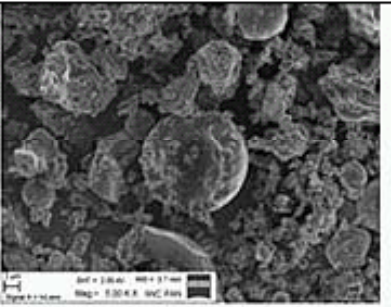
Concrete mix designed with **constant** water
to binder ratio, assuming $k=0.4$

Variable: the amount of chemical admixtures
required to achieve the target slump.

Physical properties of HCFA [%]

Grinding time [min]	% retained on 45µm sieve	Specific surface Blaine [cm ² /g]
0	38%	2860
10	23%	3500
28	10,5%	3870

High calcium fly ash: grain shape before and after grinding

			
BII/0, 400x Pow.wł. 4400 cm ² /g Zawartość szklowa = 46,64%	1000x ←specific surface ← glassy phase	1000x	5000x
			
BII/15, 400x Pow.wł. 6410 cm ² /g Zawartość szklowa = 40,31%	1000x ←specific surface ← glassy phase	5000x	5000x

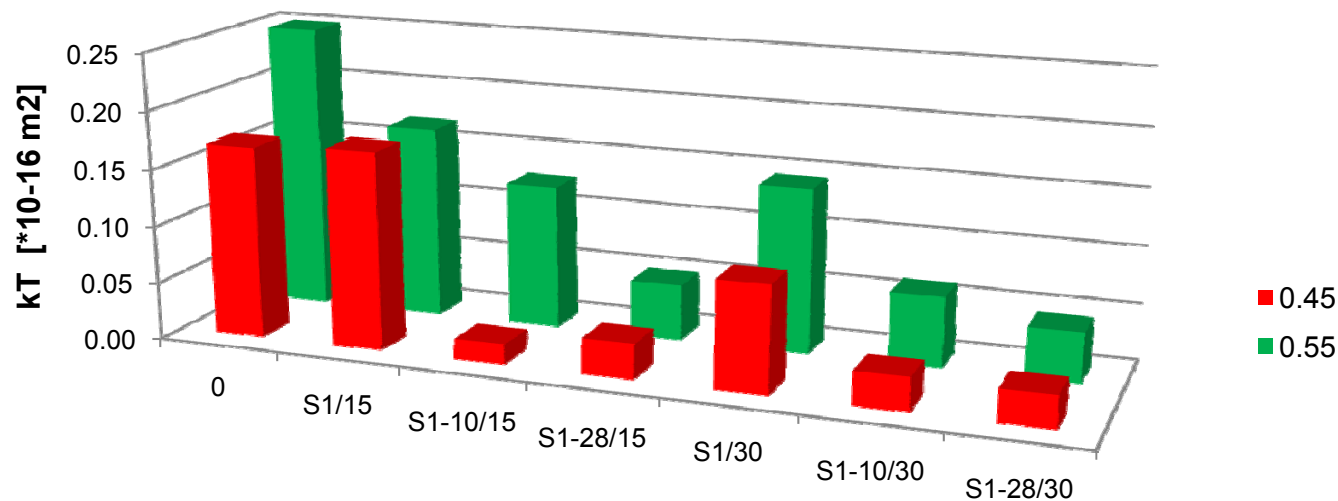


Coefficient of air permeability (Torrent) of concrete

cement CEM I 42.5 R

HCFA (15% or 30% replacement with $k=0.4$)

significant increase of superplasticizer



CEM I ; 15% & $k=0.4$; 30% & $k=0.4$

moist curing



CONCLUSIONS

- Reduction of clinker factor below 0.50 feasible using slag blended cement CEM II B-S and FBC ash addition with increased content of superplasticizer
- Tests revealed increased compressive strength and decreased air permeability coefficient for FBC ash addition
- Use of HCFA for major replacement of CEM I at $k=0.4$ was disturbed by increased water demand
- Decreased kT for increased grinding time of HCFA