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# APPLICATION OF WEATHERED GRANULATED BLAST FURNACE SLAG AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL IN CONCRETE

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The physical and chemical properties of cements with slag originated from the storage yards of different age, added as a supplementary cementing material are highlighted. The materials after 20-year storage, the crushed slag after approximately 2-year storage and the new slag from the ongoing production were compared. The materials supplied by the same metallurgical plant were characterized. The blended cements were produced by Portland cement clinker grinding with gypsum and slags added as 5 to 50% of binder mass. The standard properties of cements were examined, as well as some experiments related to the kinetics of hydration and hydration products were carried out. The addition of granulated blast furnace slag (GBFS) stored for a long time, as a component of cement, affects the properties of material in such a way that the early compressive strength is not specially altered but at longer maturing the strength decreases generally with the storage time and percentage of additive. This is related to the reduction of the vitreous component, as well as to the presence of weathered material of altered activity. At the additive content up to 50% the binder complying with the requirements of the European standards for CEM III/A or CEM II/(A,B)-S common cements can be produced. The cements with the old slag meet the requirements of EN 197-1 relating at least to the class 32,5. The role of calcium carbonate, being the product resulting from the slag weathering process, acting as a grindability and setting/hardening modifying agent, should be underlined.

*Keywords:* supplementary cementing materials (SCMs); old slag; slag weathering; compressive strength; heat of hydration; microstructure

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## 1. INTRODUCTION

### 1.1. CEMENT PRODUCTION ON THE WAY TO LOW CARBON FUTURE

The production of Portland cement clinker, because of high energy consumption and high emission of “technological” CO<sub>2</sub> accounts for up to 6–7% of global anthropogenic emission [1–5], contributing to the global warming. The problems of cement industry “on the way to low carbon future” have been discussed in many general reports and analytical works summarized for example in the comprehensive work presented by Schneider during the International Conference on Cement Chemistry in Prague [6]. A great impact is exerted by new regulations in the light of which carbon dioxide emissions in cement plants must be reduced by 30 percentage points by 2030, as compared to the level in 2005. In order to achieve the required level of emissions, cement manufacturers should reach for cements with a low so-called clinker factor [7-9]. Clinker factor reduction is the most efficient measure to reduce CO<sub>2</sub> emissions from cement production since it covers both the CO<sub>2</sub> from the raw materials and from fuel combustion.

The average global clinker factor was 0.65 in 2014 [6]; the European average clinker factor was 0.74 in 2016 [10], including countries like Ireland and Denmark which have a clinker factor of about 0.90, and the Netherlands, which have approx. 0.46 [11]. In Poland this value has been reduced to 0.75 according to the data from Polish Cement Association [13, 14].

Cement industry plays the key role in achieving the circular economy goals as it uses waste from other industries as supplementary cementing materials (SCMs) as well as the alternative fuels in the production process [6, 11, 14, 15].

The replacement of Portland cement by SCMs is widely adopted industrial practice. Furthermore, the development and characterization of SCMs has been an active research area for at least the past two decades [16 - 23].

Ground granulated blast furnace slag (GBFS) from pig iron production is one of the most commonly used and valuable SCMs [20, 21, 24 - 28]. Granulated blast furnace slag can be substituted up to high levels - even up to 95% in case of CEM III C according to the European 197-1 standard for common cement [6, 20, 21, 29]. The use of granulated blast furnace slag as main cement constituents is of great importance due to its high performance as compared to the other supplementary cementing materials. Moreover, GGBFS used in cement and concrete is well-known as concrete durability

enhancing component [20, 24 - 28]. Obviously, the slag "consumer" can accept the quality of offered slag or no. The metallurgical plant usually keeps his slag cooling procedure as confidential. However the shortage of slag in some countries forces the cement plants to look for the materials deposited many years ago.

## 1.2. ROLE OF SLAG COMPONENT IN CEMENT

Metallurgical slags are vitreous by-products derived from the smelting of metallic ores and usually consist of metal silicates and oxides, in some cases, sulfides and native metals. The composition varies widely depending on the initial ore content and different processing methods applied. Ground granulated blast furnace slag (GGBFS) from pig iron production is, among the other commonly used SCMs, the most active one. The granulation of molten slag is obtained by quenching using a high pressure water jets. The rapid cooling prevents crystallization producing a granular glassy material that, after grinding, has good hydraulic properties making it a Portland cement clinker substitute. Thousands of research projects and reports have been devoted to the role of GGBFS for over 50 years [24 -28].

According to the data published by Scrivener et al. [2] the amount of blast furnace slag available globally is only around 330 Mt/year and this availability has decreased from 17% of cement production in 1980 to only 8% in 2014. Despite the growth in steel production, the production of iron and slag is expected to diminish. Currently more than 90% of blast furnace slag is already used as an SCM either in cement component added in cement plants or as a component of concrete or other cement- based mixes [2].

The high performance of GBFS also means that the proportion of additional main cement constituents can be increased significantly compared to the simultaneous use without SCMs and beyond the compositions previously standardized. The inclusion of such cements in the revised European cement standard EN 197-1 is expected to take the form of CEM II/C and CEM VI cement [20], [29].

While the lower clinker factors are desirable and technically possible, the regional availability of basic supplementary cement materials has become the limiting factor. This relates particularly to the availability of slag type material on the market which should be taken into account. The limited regional availability can make difficult for cement producers to source GBFS for their cement production [30, 31].

In Poland cement industry uses approximately 5 Mt/year of by-products, among them the ground granulated blast furnace slag [14]. However, up to now the granulated blast furnace slag is supplied

by the only one steel producing plant. The supply of slag in this case is significantly smaller than the demand, hence there are many problems related to the shortage of this material [19, 20]. Therefore the limitation of GGBS current production became an indication for testing old slag.

### 1.3. APPLICATION OF WEATHERED SLAGS FROM OLD DEPOSITS

Many publications have dealt with the use of fresh-made granulated blast furnace slag as a cementitious material but less work has been done about the use of old, weathered slag. In fact, there are only contributions of Brazilian authors, Battagin and Pecchio [32]; it seems worthwhile to remind their work. They, in turn, relate to the Japanese authors - Hiroshima and Igarashi [33] who studied the effect of weathering of GBFS and concluded that there was a loss of 28-day compressive strength and an increase of setting times of cements containing "old" slag.

On the other hand, the Brazilian cement manufacturers have reported an improvement of slag grindability. It is generally agreed that slag reactivity is due to both its characteristics and to some external factors. Inherent characteristics of slag is related to operational conditions of blast furnace, temperature and viscosity of molten slag, granulation process and installation, etc, as it was postulated in many works [24, 25]. External factors are imposed to slag by means of handling, storage and grinding. For practical purposes and quality control the authors summarize, as slag inherent characteristics, their chemical composition and glass content decreasing with time of storage. The authors [32] relate to some earlier reports in which the partial devitrification of slag glass is not discussed as only detrimental phenomenon [34, 35].

For 7-day compressive strength test the mixes with slag replacement from 20% to 60% showed that the higher the slag replacement, the higher the strength loss for both weathered and new slags compared to the reference. However the strength loss was higher for weathered slags [32]. A different behavior was found for 28-day compressive strength tests. The mixes containing weathered slags exhibited a strength loss for all slag replacement while the mixes containing new slags presented a strength gain of 10% to 15% with replacement from 30% to 50%. For some slag replacement, mixes presented strength loss up to 40% by comparing new and weathered slags from a single source [32]. Finally, by raising the slag replacement, a change of setting time, that is the time range between the standard initial and final setting time, for both weathered and news slags was observed. By comparing weathered and new slags there was a slight decrease of initial setting time and a shortening of final setting time for mixes containing weathered slag (up to 85 minutes). The blends with the old slag

showed lower hydration heat [32]. From the results of tests carried out in this investigation the following conclusions have been drawn:

- Slag weathering is linked to the hydration/carbonation/oxidation process that causes a loss of slag reactivity;
- By comparing the cements with weathered and new slags originating from one source a decrease of heat of hydration as well as a decrease of strength development for the materials with weathered slag is observed.

The special dryers installed with aim to valorize the materials from the old deposits - mainly fly ash - have been put into use in cement plants a couple years ago. However, the results of detailed studies dealing with the implementation of the old, recovered materials are not commonly available. The research aimed in reuse the abandoned power plant landfills have been carried out in Spain. The report focused on the physical and chemical characterization of different fractions of wastes (fly ash and slag) was presented by Puertas et al. [36].

The present study shows the properties of cements with slag originated from the storage yards of different age, added as a supplementary cementing material. These slags were examined in order to apply them on a large scale production. The standard measurements were accompanied by some experiments relating to the kinetics of hydration and characterization of hydration products.

## **2. EXPERIMENTAL**

### **2.1. METHODS**

The chemical composition of slag, clinker and gypsum was determined with the help of XRF spectrometer equipped with a goniometer Thermo model ARL9800-043. The loss of ignition, the content of chlorides, free lime, sulfates, calcium oxide and other oxides, and also the insoluble residue were analyzed in accordance with the EN 196-2: 2005 standard. The vitreous phase content in slags was examined with help of microscopic method, on the basis of Polish PN-B-19707:2013-10 standard. Specific surface area of cement was determined according to the EN 196-6:2010. The compressive strength tests were carried out in accordance with the procedure described in EN 196-1: 2006.

Soundness determination of cements was performed according to EN 196-3:2005+A1. The setting time for cement pastes with a standard consistency was tested in accordance with EN 196-3: 2006 standard.

The investigation of hydration kinetics was done with the non-diabetic - non-isothermal differential calorimeter BMR constructed by the Institute of Physical Chemistry, Polish Academy of Sciences, further modified by the authors. This method is very sensitive and the small samples (binder - 5g; mixed with 2.5g distilled water; w/c=0.5g respectively). The samples were placed in the polyethylene string bag, subsequently an appropriate amount of water was added and the pastes were homogenized (about 10 seconds), and then immediately placed in the measuring chamber of the apparatus. The rate of heat emission was measured vs. time and the data were calculated to give the total heat evolved vs. time.

The hydrated samples were crushed, ground with acetone and dried to produce the specimens for XRD and DTA/TG analysis. XRD data were collected by the Philips PW 1050/70 diffractometer with Cu K $\alpha$  radiation generated at 35kV and 16 mA. Thermoanalytical and thermogravimetric data were obtained as a function of temperature by a simultaneous Thermal Analyser STA 449F3 Jupiter (Netzsch). Around 40 mg of sample powder was placed into the corundum crucible and heated in the air atmosphere at the heating rate 15 K/min from 40 to 1000°C.

Microstructure observations of cement pastes were carried out with the usage of electron scanning microscope FEI Nova NanoSEM 200, with spectrometer LINK ISIS 300 by Oxford Instruments allowing for chemical composition identification in micro areas (SEM/EDS). The device for the back scattered electron (BSE) analysis of polished sections (produced as a result of appropriate treatment), was also attached to the microscope.

## 2.2. MATERIALS

Portland cement clinker - the material was collected directly from the current production in cement plant. The samples were collected every 2 hours for a period of 4 days. Then the separated sample of material was homogenized and reduced by coning and quartering method. The total amount of material for testing was 100kg.

Three types of granulated blast-furnace slag materials were prepared for testing. Firstly, granulated slag from current production was used from the one pig iron and steel producing plant - denoted as "new" (N). Then, the slag stored on the company's waste heap, collected over a period of about two

years - denoted as “crushed” (K). The last sample was prepared from the blast furnace slag stored in the heap for about 20 years - the “old” slag (S). Second and third slag were pre-crushed in a jaw crusher. The slag materials were charged randomly from deliveries. Three samples from a cone of material were taken from each selected car. Then the all slag samples of given type were homogenized and reduced using the quartering method. Finally, each sample was then dried in a laboratory dryer for 12 hours at 80°C.

Natural gypsum was collected from deliveries to the cement plant. The material was then crushed in a laboratory mortar, dried in a laboratory drier at 45°C for a period of 12 hours and homogenized. A representative part was separated by quartering. The chemical composition of clinker and slag components is shown in Table 1.

Table 1. Chemical composition of materials

Sample	LOI [%]	CaO [%]	SiO <sub>2</sub> [%]	Al <sub>2</sub> O <sub>3</sub> [%]	Fe <sub>2</sub> O <sub>3</sub> [%]	MgO [%]	SO <sub>3</sub> [%]	Cl [%]	Na <sub>2</sub> O [%]	K <sub>2</sub> O [%]	CaO free [%]
New slag (N)	1.25	40.5	38.7	7.7	0.6	6.32	0.31		0.45	0.55	
Crushed slag (K)	2.03	40.2	37.98	7.78	0.56	6.35	0.36		0.54	0.53	
Old slag (S)	4.24	40.42	36.38	5.39	2.64	5.4	0.32		0.35	0.63	
Clinker	0.0	66.26	21.81	5.1	3.48	1.64	0.36	0.01	0.1	0.18	0.77

One can notice that the iron oxide residue in the old slag material is over four times higher; this could be presumably due to the modification of metallurgical process throughout the years, and/or perhaps to the different composition of the blast furnace charge. The activity factor  $((\text{CaO} + \text{MgO}) / \text{SiO}_2)$  is in the range from 1,21 (new slag) through 1,23 (crushed slag) to 1,26 (old slag).

### 2.2.1. CHARACTERISTICS OF SLAGS

The vitreous component content in slags was determined by standard microscopic method and the percentage of this component (as % by weight) was 95.7; 80.4 and 69.9 for the new slag (N), crushed slag (K) and old slag (S) respectively. These differences are undoubtedly the effect of slag granulation process used in the metallurgical plant 20 years ago and nowadays; the de-vitrification cannot be excluded as well. It should be underlined that the vitreous phase content in these slag materials is within the 67% limits recommended by the EN 197-1 standard for common cements. The nature of slags was studied with help of XRD methods. XRD patterns of slags show a very high, broadened

“shoulder” attributed to the amorphous nature. The residue of crystalline phases: quartz and calcite is also detected as weak peaks, particularly in case of the old slag. The hydration and subsequent carbonation in “older” slags is the result of reactions with water originating from the granulation process and also from the external sources (rain); water allows to transform the slag material into hydrates.  $\text{Ca}(\text{OH})_2$  is leached out and finally reacts with carbon dioxide. The calcium carbonate contents in slag samples, as determined by thermogravimetric analysis, are as follows: 1.8% for the new slag, 4.4% for the old slag and 2.5% for the crushed “intermediate” material respectively. The amount of absorbed water is between 0.89% (new), through 1.03% (crushed) to 2.14% (old).

### 2.2.2. COMPOSITION OF CEMENTS

The three series of blended cements were produced using Portland cement clinker, slags and gypsum. The dosages of slag correspond to the contents indicated in EN 197-1 standard for common cements. Therefore, in each series the contents of slag was 5% (slag as secondary component in the standard CEM I type common cement), 10% (so-called CEM II/A standard material), 20% (the limit of slag dosage between CEM II/A and CEM II/B), 30% (corresponding to CEM II/B) and 50% (CEM III - slag cement) respectively. In such a way all the categories of common cements produced with slag additive only were taken into account.

One should underline that the slags cements produced using an old, weathered slag exhibit relatively good grindability. The target for specific surface area of prepared cements was  $3800 \text{ cm}^2/\text{g}$ , as it was found for the reference material after 30 minutes grinding in the laboratory mill.

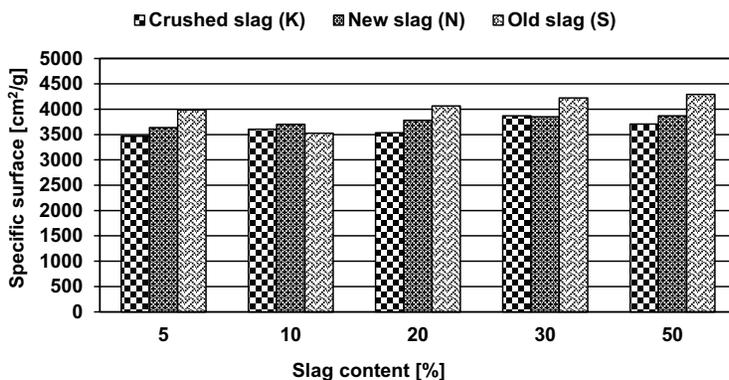


Figure 1. Specific surface of slag cement - blends (standard deviation -  $245 \text{ cm}^2/\text{g}$ )

Subsequently, the mixtures were ground 30 minutes in this mill too - slag cements produced with “old” slag in most cases exhibited slightly higher specific surface (see Figure 1); a better grindability of cements with slag was thus proved. This is in accordance with the data reported previously [32].

## 2.3. RESULTS AND DISCUSSION

### 2.3.1. STANDARD PROPERTIES OF CEMENT - SLAG BLENDS

The cements with granulated blast furnace slag as the main component meet the EN 197-1 standard requirements for initial setting time and soundness ( Le Chatelier expansion test).

The addition of granulated blast furnace slag as a component of cement influences the mechanical properties (Figs 1 - 3). Obviously, the strength decreases with the percentage of slag. However, the early strength seems to be a little higher when the slag additive is used and the elder material gives an increase of strength, particularly at lower slag content. This trend alters with time and slag substitution in such a way that after 28 days the materials with older additive reveal lower strength.

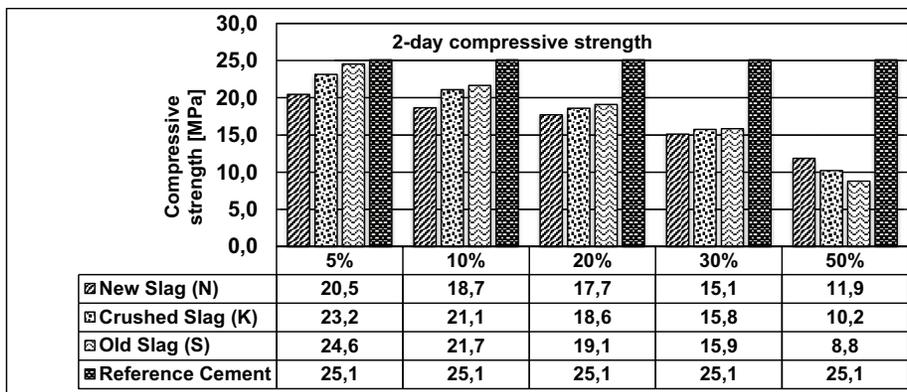


Fig. 2. Compressive strength of mortars after 2-day maturing as a function of the type and percentage of slag

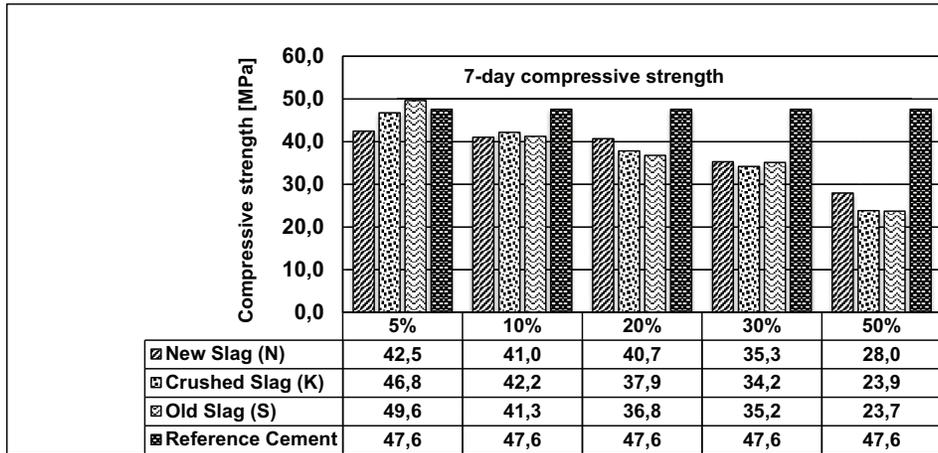


Fig. 3. Compressive strength of mortars after 7-day maturing as a function of the type and percentage of slag

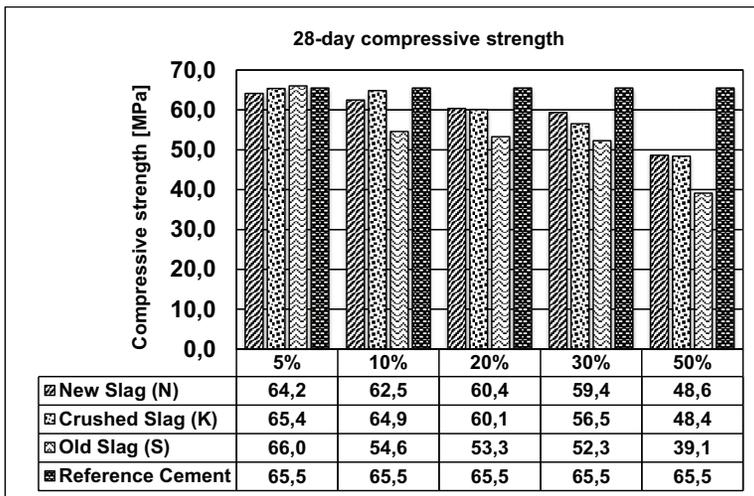


Fig. 4. Compressive strength of mortars after 28-day maturing as a function of the type and percentage of slag

Both the tested slag from the storage yard or the material from the current production acts as a substitute of Portland cement clinker when replacing up to 5% of clinker in cement. These cements comply with the requirements of the relevant standards for reference CEM I material. Introducing up

to 50% of slag it is possible to produce the binder complying with the requirements of the standards for CEM III/A, at least class 32,5 and, at lower substitution, the slag Portland cement CEM II/(A,B)-S class 42,5 and/or 32,5. To obtain the strength class of 42,5, the cement with the old slag (S) would have to be ground to higher surfaces.

### Statistical approach

The analysis was carried out using the statistical method ANOVA [37]; the summarizing results are presented in Table 2. The analysis has been carried out to determine whether there is a relationship between the content of slag and the strength of the cement tested at given time of maturing. A zero hypothesis  $H_0$  was put forward that there are no differences between the results of strength tests after 2, 7 and 28 days maturing respectively, between the samples containing the same amount of slag, regardless of its origin. At the significance level 0.05 at which the analysis was carried out, a close convergence of results for the 2- and 7-day strength was found. Summarizing, the statistical analysis of variance of cement strength shows that there are no differences, as the early strength is concerned (2-day and 7-day curing), between the series of cement containing the same quantity of slag but of different origin. However, samples after standard 28-day maturing show well visible diversity in compressive strength regarding their composition and slag "age".

Table 2. Comparison of variances analysis for cement compressive strength

	$F_{\text{calc}}$	$F_{\text{tab}=0,05}$	$F_{\text{tab}=0,025}$	$F_{\text{tab}=0,01}$	$F_{\text{tab}=0,1}$
2 days of hardening	0,64	3,18	6,42	4,86	2,36
7 days of hardening	0,03				
28 days of hardening	<b>7,29</b>				

### Calorimetric studies

Calorimetric data (Table 3) indicate generally the active participation of slag in the hydration process. Slag grains act as the nuclei of hydration products and subsequently they participate in the pozzolanic reaction. 5% of the additive acts as a cement substitute; with increasing content in the binder, the effect of "diluting" the active material with the less active one is clearly visible. The effects are weaker with the age of additive. The introduction of slag in the amount of up to 50% allows to decrease the total heat evolved by the slag cement pastes: by 27% for the new slag, 35% for the crushed slag and 36% for the old one as compared to the reference cement with no additive. Simultaneously, an increase of the heat emitted per 1g of clinker + gypsum in the samples is observed.

Table 3. The total heat evolved values for blended cements after 24h and 40h hydration

No	Heat evolved after 24h and 40h in hydrated slag cement pastes, in kJ/kg						
	Slag content [%]	new		crushed		Old	
		24h	40h	24h	40h	24h	40h
1	0	257	315	257	315	257	315
2	5	245/258*	299/315	246/259	304/320	245/258	296/312
3	10	254/282	306/340	251/279	306/340	234/260	280/311
4	20	239/299	286/358	218/273	276/345	206/258	255/319
5	30	211/301	262/374	196/280	260/371	198/283	259/370
6	50	181/362	226/452	148/296	205/410	146/292	199/398

\* values calculated per 1g of "neat" cement

Summary of phase assemblage examination (XRD - DTA/TG/DTG results)

The XRD results (example set of XRD patterns, Fig. 4) suggest that the change in the percentage of slag up to 50% in the binder does not significantly affect the nature of the phase assemblage in cement pastes. The type of slag in cement pastes does not significantly affect the phase assemblage as well. The hydration products detected are as follows: calcium hydroxide - portlandite (P), calcium silicate hydrate (C-S-H) and calcium sulfoaluminate - ettringite (E). The C-S-H phase can be easily observed as a shoulder in the range 28-35 °2θ. The peaks coming from cement phases are significantly reduced, particularly with the increasing granulated blast-furnace slag percentage up to 50%. This is due to the progress of hydration with time and transformation of this phases into hydration products.

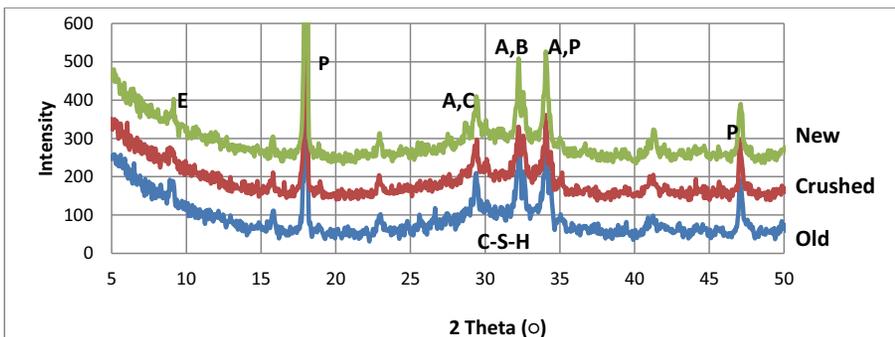


Fig. 5. XRD patterns of 7-day matured pastes produced with 50% slag additive; E - ettringite, P - portlandite, A - alite, B - belite, C-S-H "shoulder" attributed to calcium silicate hydrate phase

The results of DTA measurements are typical for the hydrated cement pastes and match with the XRD data. The peaks corresponding to the dehydration of C-S-H, ettringite and gypsum are visible on the DTA curves of all samples in the range up to 200°C. They become more sharp in the case of samples hydrated for at least 7 days and after 28-day hydration. Subsequently, the peak attributed to the

calcium hydroxide dehydration appears in the range up to 500°C and the peak attributed to the decarbonation - above 800°C. The calcium hydroxide and carbonate contents based from TG data are presented in Table 4.

Table 4. Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> content based on the results of DTA/TG/DTG measurements

Time	Reference cement			Cement with 50% New slag			Cement with 50% Old slag		
	2 days	7 days	28 days	2 days	7 days	28 days	2 days	7 days	28 days
% Ca(OH) <sub>2</sub>	18.3	24.6	29.5	11.3	15.4	18.1	9.8	12.9	16.8
% CaCO <sub>3</sub>	2.5	3.2	5.4	4.7	2.6	6.0	5.8	4.6	7.8

The lowered content of Ca(OH)<sub>2</sub> in the mixtures with growing slag content, due to the pozzolanic reaction of aluminosilicate glass is observed. The differences are not significant as in the case of typical pozzolans since these slags contain CaO. Ca(OH)<sub>2</sub> in the pastes is rising with time of hydration; it means that the pozzolanic reaction up to 28-day maturing is not so advanced.

The (de)carbonation is clearly visible particularly in the case of old slag (S) higher percentage; one should remember that the sample of old slag contains initially 4,4% CaCO<sub>3</sub>. Calcium carbonate content is rising only slightly with time of hydration - and is around two times higher than in the reference paste or even in the sample with the new, less carbonated slag.

Microstructure observations – SEM/EDS and BSE/EDS

Microstructure observation of cement pastes shows that there are different types of C-S-H product present, from the needle-like forms, plates and compacted mass, well adjacent to the slag grains. Some selected samples containing 50% slag were examined as polished section in the back scattered electron mode. The uptake of magnesium and aluminum from slag into the C-S-H structure was found; an example is shown as Fig.5.

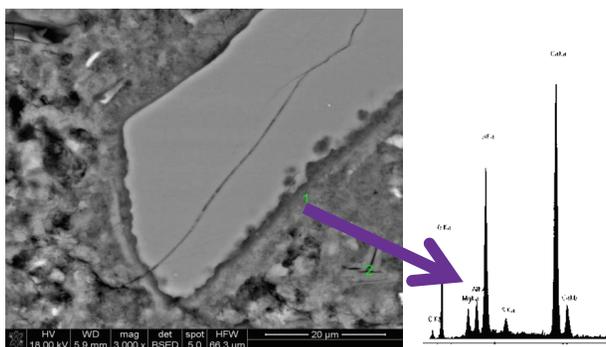


Fig. 6. BSE-EDS. Cement paste with 50% fresh slag (slag N), 28-day hydration. Slag grain surrounded by hydration products. The incrustation of C-S-H formed near the slag grain boundary with aluminum and magnesium from slag is visible

### 3. SUMMARY

The role of calcium carbonate as a hydration kinetics and strength modifying agent in the older slag containing materials could be proved. It seems that a higher calcium carbonate content is responsible for relatively good activity of the old slag in the heat evolution process. The strength reduction which, at later age, is not proportional to the lowered clinker ratio but much lower, can be related to the increasing carbonate content too. It seems that the layer of hydration products formed at early age with calcium carbonate and other weathering products nuclei leads to the retarding effect at later age by slower diffusion from the slag grains, particularly at lower active vitreous component content. This layer is compact and very well adjacent to the slag grain.

The effect of calcium carbonate grains acting as hydration accelerating nuclei or improving the structure was indicated in many reports [38-41].

### 4. CONCLUSIONS

1. Blast furnace slags from one source, regardless of the age of storage, can be the active supplementary cementing materials, complying with the standard requirements relating to the initial setting time and soundness.
2. Replacing the clinker in cement with relevant percentage of each among the tested slag, from the storage yards or from the current production it is possible to obtain the binder complying with the requirements of the standards for CEM I 42,5 R, CEM II/(A/ B)-S class 42,5 and/or 32,5 or CEM III /A respectively.
3. The vitreous phase content and the percentage of products formed as a result of slag weathering, particularly the calcium carbonate, affect the hydration process and the properties of cements with slag.
4. Analysis of the heat evolution during hydration of cements shows that the 5% substitution of clinker by slag almost does not affect the amount of heat released. The introduction of slag in the amount of up to 50% allows to decrease the total heat evolved by the slag cement pastes but the heat reduction is not proportional to the lowering of clinker ratio in cement, comparing

to the reference cement with no additive. An increase in the heat emitted per 1g of “neat” cement (clinker + gypsum) is observed; an active participation of slag components in setting and hardening is thus proved.

5. The hydration products detected in slag cement pastes are as follows: calcium hydroxide - portlandite (P), calcium silicate hydrate (C-S-H) and calcium sulfoaluminate - ettringite (E); calcium carbonate is the product of carbonation. The XRD results match well with the thermoanalytical data.

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## LIST OF FIGURES AND TABLES:

Fig. 1. Specific surface of slag cement - blends (Standard deviation - 245cm<sup>2</sup>/g )

Rys. 1. Powierzchnia właściwa cementów z dodatkiem żużla (odchylenie standardowe - 245cm<sup>2</sup>/g )

Fig. 2. Compressive strength of mortars after 2-day maturing as a function of the type and percentage of slag

Rys. 2. Wytrzymałość na ściskanie po 2 dniach twardnienia w funkcji rodzaju i zawartości żużla

Fig. 3. Compressive strength of mortars after 7-day maturing as a function of the type and percentage of slag

Rys. 3. Wytrzymałość na ściskanie po 7 dniach twardnienia w funkcji rodzaju i zawartości żużla

Fig. 4. Compressive strength of mortars after 28-day maturing as a function of the type and percentage of slag

Rys. 4. Wytrzymałość na ściskanie po 28 dniach twardnienia w funkcji rodzaju i zawartości żużla

Fig. 5. XRD patterns of 7-day matured pastes produced with 50% slag additive; E - ettringite, P - portlandite, A - alite, B - belite, C-S-H "shoulder" attributed to calcium silicate hydrate phase

Rys. 5. Zestawienie dyfraktogramów zaczynów z dodatkiem 50% żużła; E - ettringit, P - portlandyt, A - alit, B - belit, "garb" przypisywany uwodnionym krzemianom wapnia, tzw. fazie C-S-H

Fig. 6. BSE-EDS. Cement paste with 50% fresh slag (slag N), 28-day hydration. Slag grain surrounded by hydration products. The incrustation of C-S-H formed near the slag grain boundary with aluminum and magnesium from slag is visible

Rys. 6. BSE-EDS. Zaczyny z udziałem 50% żużła po 28 dniach hydratacji. Ziarno żużła z otoczką produktów hydratacji. Produkt C-S-H z pobliżu granicy ziarna żużła z wbudowanym glinem i magnezem uwolnionym z żużła

Tab. 1. Chemical composition of cements

Tab. 1. Skład chemiczny cementów

Tab. 2. Comparison of variance analysis data for cement compressive strength

Tab. 2. Porównanie wariancji wytrzymałości na ściskanie

Tab. 3. The total heat evolved values for blended cements after 24h and 40h hydration

Tab. 3. Ciepło wydzielone po 24h i 40h hydratacji zaczynów

Tab. 4. The results of DTA/TG/DTG measurements

Tab. 4. Zawartości wodorotlenku i węgla wapnia na podstawie wyników pomiarów DTA/TG/DTG

## ZASTOSOWANIE ŻUŻLI O DŁUGIM CZASIE SKŁADOWANIA JAKO SKŁADNIKÓW CEMENTÓW POWSZECHNEGO UŻYTKU

*Słowa kluczowe: dodatki mineralne do cementu; żużel o długim czasie składowania; wietrzenie żużła; wytrzymałość na ściskanie; ciepło hydratacji; mikrostruktura*

### STRESZCZENIE:

Praca dotyczy właściwości cementów zawierających granulowane żużle wielkopiecowe o różnym czasie składowania, z jednego źródła (huty żelaza). Porównano właściwości materiału z żużlem pochodzącym sprzed 20 lat, żużlem składowanym około 2 lat i żużlem z bieżącej produkcji. Cementy wyprodukowano poprzez przemiał klinkieru cementu portlandzkiego z gipsem; udział żużła stanowił od 5% do 50% masy spoiwa. Otrzymane cementy poddano badaniom

standardowym; przeprowadzono również ocenę kinetyki i produktów hydratacji. Ustalono w pierwszej kolejności, że wprowadzenie żużla składowanego przez długi czas w charakterze składnika cementów powszechnego użytku wpływa na właściwości cementów w taki sposób, że wytrzymałości wczesne nie ulegają znaczącym zmianom, natomiast wytrzymałość po 28 dniach twardnienia zmniejsza się. Zredukowanie wytrzymałości jest wyraźniejsze w przypadku żużla o długim czasie składowania i przy większym jego udziale. Jest to powiązane ze zmniejszeniem zawartości fazy szklistej w żużlu i obniżeniem aktywności w następstwie procesów wietrzenia. Jednakże i tak przy odpowiednich udziałach żużla w granicy do 50% jest możliwe otrzymanie cementów powszechnego użytku typu CEM III/A lub CEM II/(A,B)-S spełniających wymagania normy EN 197-1 klasy przynajmniej 32,5. Należy podkreślić, że rolę modyfikującą pozytywnie właściwości cementów takie, jak mielność oraz generalnie proces wiązania i twardnienia wydaje się pełnić węglan wapnia tworzący się jako produkt wietrzenia żużli.

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