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ALKALI ACTIVATION OF GRANULATED BLAST FURNACE SLAGS

VÁCLAVA TOMKOVÁ, SADANANDA SAHU, JÁN MAJLING, MIROSLAV TOMKO*

*Department of Ceramics, Glass and Cement, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava*** Research and Development Institute of Prefabrication, St. Vajnorská cesta 16, 832 44 Bratislava*

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Granulated blast furnace slags from VSŽ Košice was activated by using different alkalies such as NaOH, Na₂CO₃ and water glass. The influence of the slag fineness, curing conditions of the moulded specimens and the content of alkalies and silica module of water glass have been studied. Results show that curing conditions have great effect on the strength development. Slag activated in the presence of water glass had excellent mechanical properties, 28 days compressive strength up to 120 MPa was obtained.

INTRODUCTION

Table I

Chemical composition and fineness of the slags

Oxides	S _A [wt. %]	S _B [wt. %]	Fineness (Blaine) [m ² .kg ⁻¹]
CaO	41.74	43.15	S _{A1} = 265
SiO ₂	40.80	37.98	S _{A2} = 310
Al ₂ O ₃	6.12	7.84	S _{A3} = 425
Fe ₂ O ₃	0.84	1.85	S _{B1} = 340
MnO	0.69	0.51	S _{B2} = 495
MgO	8.42	8.46	S _{B3} = 540
Na ₂ O	0.18	0.11	
K ₂ O	0.33	0.19	
SO ₃	1.15	0.38	

MATERIALS

Granulated blast furnace slag is commonly used in building industries as admixture to portland cement, so as to save some amount of portland cement, that means saving a lot of fuel energy. Recently a lot of attention has been paid to activate the granulated blast furnace slag by chemical means to exploit its latent hydraulic properties. The hydraulic activity of slag depends upon its chemical composition as well as the content of glass phase [1]. The most common activators to produce cementitious materials from slag are ordinary portland cement, lime, gypsum, plaster of paris and anhydrite [2–7]. Recently A.J. Majumdar et al. have activated the slag in the presence of 12CaO.7Al₂O₃ and high alumina cement, which show superior properties and can be usable for special purposes [8,9]. The other approach which is gaining a lot of attention through out the world, in recent times, is the activation of slag by alkalies [10–16]. The alkalies mostly used as activators are NaOH, Na₂CO₃, Na₂SO₄ and water glass (sodium or potassium silicates) and in some cases additives such as portland cement, lime, silica fume and fly ash are used. There is a wide range of results on alkali activation of slags that have been reported [11–16]. The individual slags differ in their properties and suitability for alkali hydration.

Two different granulated blast furnace slags, S_A and S_B were used and each slag was ground to three different finenesses to produce samples S_{A1}, S_{A2}, S_{A3}, S_{B1}, S_{B2} and S_{B3}. The slag in both cases was glassy without significant presence of crystalline phases. The chemical compositions of the slags S_A, S_B and their finenesses are given in Table I.

This paper deals with hitherto not exploited blast furnace slag from East Slovakia Steel Works (VSŽ) Košice. It deals in particular with the influence of fineness of the slag and the amount of alkalies and silica module of the water glass on strength development.

The slag activity can be estimated according to different modules based on its chemical composition. The slag S_B is according to commonly use module of basicity $M_Z = (\text{CaO} + \text{MgO}) / (\text{Al}_2\text{O}_3 + \text{SiO}_2)$ more basic and should be therefore more active for hydration.

Table II

Compressive and tensile strengths of the specimens activated in the presence of NaOH

Slag	Curing condition	1 day		7 days		28 days	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
SA1	H	–	–	14.2	0.8	21.9	2.5
	P – H	4.0	0.1	5.5	0.2	9.8	1.4
SA2	H	–	–	21.5	1.4	26.0	2.4
	P – H	5.5	0.4	8.1	0.7	13.7	0.9
SA3	H	5.9	0.2	8.7	0.3	19.3	1.9
	P – H	9.1	0.3	9.9	0.1	17.0	0.7

H = Humid atmosphere

P – H = Preheat treated and the humid atmosphere

Table III

Compressive and tensile strengths of the specimens activated by Na₂CO₃

Slag	Curing condition	1 day		7 days		28 days	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
SA1	H	1.5	0.3	5.3	0.2	7.8	0.2
	P – H	20.3	1.2	21.7	0.7	26.3	2.0
SA2	H	2.3	0.2	7.6	0.4	12.2	0.3
	P – H	27.8	2.0	30.5	2.1	35.8	2.1
SA3	H	14.7	1.1	26.8	2.2	31.5	0.7
	P – H	33.2	1.1	35.8	2.0	42.2	1.2
	W	12.4	1.1	29.5	1.8	39.4	2.2
	P – W	29.0	0.5	29.4	1.4	37.7	3.7

W = Under water

P – W = Preheat treated and then under water

Pure chemicals of NaOH, Na₂CO₃ and water glass (sodium silicate) were used as activators.

EXPERIMENTAL

In the first series of experiments slags SA₁, SA₂, SA₃ were activated by NaOH and Na₂CO₃. The dosages of alkalis were applied in such a way as to keep the Na₂O content at 3 wt. % of the slag (Table II and III). The activation by the NaOH solution was applied also in the case of the slag SB, at concentrations of Na₂O from 3.0 to 4.5 wt. % (Table IV).

In the second series the solutions of water glass were used for the activation. Their silicate modules $M_S = \text{SiO}_2/\text{Na}_2\text{O}$ (molar ratio) was adjusted from its original value $M_S = 3.3$ by addition of 50% solution of NaOH in the range of M_S from 1.35 to 2.00.

Small scale test specimen of the size 1×1×3 cm were prepared in the form of paste with water to solid ratio 0.3. The specimens were left in humid atmosphere for 24 hours and after that they were demoulded. Some of the demoulded specimens were kept in humid atmosphere, some under water for further hydration. Some of the samples were heat treated at

80°C for four hours in humid atmosphere and again divided into two groups, one group kept in humid atmosphere and another under water, for further hydration.

For three values of M_S activator and for the three different Na_2O contents at constant water to solid ratio approximately 0.3 the result obtained on small specimens were also verified on larger size specimens (4×4×16cm) (Table VIII). All other parameters for testing were followed according to ČSN except keeping the slag to sand ratio at 1:2, grob fraction of sand was not used.

In case of small as well as of larger size specimens the deviation of individual strengths values did not exceed 8% from the mean value.

RESULTS AND DISCUSSION

Influence of NaOH and Na_2CO_3

When NaOH is used as an activator the compressive and tensile strengths of the hydrated specimens of the both slags were low (Table II, IV). Increase the fineness of slag and amount of Na_2O have no significant effect in increasing the strengths.

When the activator solution of Na_2CO_3 was used the compressive strengths were approximately doubled; 42 MPa after 28 days at the slag S_A with highest value of specific surface (Table III).

Preliminary heat treatment was not advantageous in the case of the slag S_A with NaOH activator and has no influence in the case of slag S_B . In the case when Na_2CO_3 is used as activator preliminary heat treatment exhibit pronounced increase in strength in comparison to specimens cured only in humid atmosphere. Specimens heat treated and stored under water has no significant difference in strength deve-

lopment in comparison to specimens stored in water without heat treatment.

Influence of the water glass

Table V shows the influence of the silicate modules and the amount of the water glass on the compressive strengths of slag specimens which were kept for 28 days in humid atmosphere. At 3% of Na_2O content the strengths increase with increasing of silicate modules from 1.35 till to $M_S=3.3$ (at the original water glass) At 4.5 wt.% of Na_2O the tendency is to the contrary; from the modules 15 the strengths is continuously decreasing with the increase of this modules. The last sensitive to the preservation of M_S in its influence is the activator with 3.7 wt.% Na_2O .

The individual samples were tested for the setting rate: The slowest setting was shown by mixtures activated by the original water glass ($M_S = 3.3$), adjusted activators with lower M_S shortened the setting time (until the setting time only 1.5–2 hours in average).

On the basis of these experiments the water glass effect was more extensively investigated for specimens containing 3.7 wt.% Na_2O . The boundary possibilities were tested, e.g. for $M_S = 1.35$ and 2.00 two regimes for samples treatment were adapted, humid storage and water storage. The results of the strength experiments are shown in Tables VI and VII.

When we compare the development in strengths of S_{B1} (Table VI and VII), up to 7 days the strengths are higher in the case where the silica module of water glass is 2.00. This is equally valid for the strengths at 28 days. Whereas S_{B2} does not show any large difference in strength development with respect to change in silica module. The results of S_{B3} are not quite representative. Because of the high fineness of the slag

Table IV

Compressive and tensile strengths of the specimens activated by NaOH Slag S_{B1} , 28 days

Curing condition	Na_2O content [wt. %]					
	3.00		3.70		4.50	
	Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
	[MPa]					
H	13.2	8.2	16.8	8.1	15.4	8.0
P - H	14.9	6.8	17.8	7.4	19.9	9.5
W	11.6	6.8	12.6	5.9	16.6	6.0
P - W	13.7	6.3	18.5	5.8	20.8	6.1

Table V

28-days compressive strengths of the slag S_{B1} prepared from water glass having $M_S = 1.35-2.00$ and 3.3 (Humid atmosphere)

M_S	3.0% Na_2O	3.7% Na_2O	4.5% Na_2O
	[MPa]		
1.35	52.8	79.0	96.6
1.50	58.4	94.8	121.3
1.60	62.8	92.6	120.8
1.70	76.9	106.6	113.6
1.80	87.6	99.6	101.4
1.90	87.9	111.3	100.5
2.00	92.6	109.0	98.9
3.30	104.1	96.5	93.0

Table VI

Compressive and tensile strengths of the specimens prepared with water glass of $M_S = 1.35$

Slag	Curing condition	3 days		7 days		28 days	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
SB ₁	H	35.8	8.5	43.8	8.8	79.2	9.0
	W	33.8	3.6	51.9	5.2	65.9	8.8
SB ₂	H	69.0	8.5	93.4	7.8	122.7	9.3
	W	84.4	5.3	95.2	9.4	95.8	6.3
SB ₃	H	58.5	5.3	61.2	6.5	91.5	7.9
	W	53.0	4.7	63.0	6.2	81.2	2.8

Table VII

Compressive and tensile strengths of the specimens prepared with water glass of $M_S=2.0$

Slag	Curing condition	3 days		7 days		28 days	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
SB ₁	H	53.2	10.4	68.6	9.4	109.0	9.0
	W	50.2	4.7	71.1	6.6	95.6	5.6
SB ₂	H	65.6	9.7	79.4	7.9	122.2	9.2
	W	67.7	5.6	95.2	5.5	109.6	10.4
SB ₃	H	62.7	6.8	75.0	7.4	94.4	6.3
	W	40.4	3.3	65.6	6.5	62.6	5.6

difficulties were encountered in preparing homogeneous pastes. The specimen preparation needs some modification and at proper mixing technology, the strength values are expected to be increased.

The highest bulk densities were achieved for samples activated by the solution with $M_S=1.35$, what indirectly indicate the lowest porosity of the samples.

By the observation of fresh fracture surfaces of samples after 28 days of hardening using SEM it was ascertained that there were not present any crystalline phases characteristic for hydrated portland cements; from newly created phases C-S-H phases are most distinctly to be seen.

Table VIII shows the results of the samples SB₁ prepared with sand keeping the slag to sand ratio 1:2. The results are comparable with that of the samples prepared without sand. Tables V and VIII contain the strength results of samples prepared using further untreated water glass (modules $M_S=3.3$). High

Table VIII

Compressive and tensile strengths of mortars activated with water glass. Slag SB₁, slag : sand = 1 : 2

M_S	Curing cond.	3.0%Na ₂ O		3.7%Na ₂ O		4.5%Na ₂ O	
		Comp.	Tens.	Comp.	Tens.	Comp.	Tens.
		[MPa]					
1.35	H	–	–	82	9.2	96	6.8
	W	–	–	71	9.0	105	7.7
2.00	H	–	–	80	5.6	80	5.0
	W	–	–	74	5.3	82	5.7
3.30	H	112	7.8	115	6.9	102	6.1
	W	60	7.2	63	5.8	55	3.8

strength values were obtained at storage in the humid atmosphere; water storage has negative influence (the strength reduction up to approx. 50%). The pastes with the activator of $M_S=3.3$ were difficult to mix, such an activator is therefore not suitable for the common use.

CONCLUSIONS

The obtained results show that the granulated blast furnace slag from VSŽ Košice is suitable for alkali activation and in the preparation of high strength concrete. The experimental conditions are defined at which best strength values are attained. The results show that solutions of NaOH and Na_2CO_3 are not suitable activators for this kind of slag. Highest compressive strength with good workability of mixes and their appropriate setting time can be achieved by using water glass of silica module in the range of $M_S=1.7-2.0$ and Na_2O content approx. 3.5 wt.% to the slag. Slag having high fineness ($>500\text{ m}^2\cdot\text{kg}^{-1}$) create problem in the workability of the paste and needs special way of its homogenization.

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AKTIVÁCIA GRANULOVANEJ VYSOKOPECNEJ TROSKY ALKÁLIAMI

VÁCLAVA TOMKOVÁ, SADANANDA SAHU, JÁN MAJLING, MIROSLAV TOMKO*

*Katedra keramiky, skla a cementu,
Chemickotechnologická fakulta STU,
Radlinského 9, 812 37 Bratislava*

** Výskumný a vývojový ústav prefabrikácie,
St. Vajnorská cesta 16, 832 44 Bratislava*

Príspevok zhrňa výsledky prác, zameraných na zistenie možnosti prípravy bezcementových betónov na báze granulovanej vysokopecnej trosky z VSŽ Košice. Príprava tzv. troskoalkalických betónov spočíva vo využití latentnej hydraulicity trosiek – v ich aktivovaní rôznymi alkalickými roztokmi. Vhodnosť trosky pre tento spôsob spracovania nie je možné posúdiť z jej chemického alebo mineralogického zloženia, ale vyžaduje si to experimentálne odskúšanie a vymedzenie hlavných parametrov zložení zmesi a spôsobu ich spracovania.

Bola použitá troska z VSŽ Košice z bežnej produkcie v dvoch kvalitách, pričom v oboch prípadoch ide o trosku slabo zásaditú a prevážne sklovitú, smalým podielom kryštalických fáz. Trosky boli zomleté na odstupňovanú jemnosť (vyjadrené veľkosťou špecifického povrchu podľa Blaina – tab. I). Ako alkalické aktivátory sa použili: NaOH, Na_2CO_3 a roztok vodného skla, pričom obsahy Na_2O sa volili v rozmedzí od 3,0 po 4,5% vzhľadom k troske a roztoky vodného skla v rôznej kvalite ($M_S=SiO_2/Na_2O$ od 1,35 po 3,30).

Prípravili sa skúšobné vzorky troskoalkalických kaší a mált (ako plnivo sa použili 2 frakcie normových pieskov) a volili sa 4 rôzne režimy spracovania vzoriek: uloženie vo vlhkej atmosfére alebo vo vode a buď s predbežným preteplovaním vzoriek alebo bez neho. Skúšali sa pevnosti vzoriek v ohybe a v tlaku, doba tuhnutia zmesi a sledovala sa morfológia vybraných vzoriek.

Získané výsledky ukázali, že granulovaná vysokopecná troska z VSŽ Košice je použiteľná pre prípravu betónov formou alkalického aktivácie. Roztoky NaOH a Na_2CO_3 nie sú pre tento druh trosky vhodnými aktivátormi. Najvyššie hodnoty tlakových pevností (na úrovni 90 až 120 MPa) pri súčasne vhodných parametroch spracovateľnosti zmesi a priebehu ich tuhnutia možno dosiahnuť použitím vhodného roztoku vodného skla. Jemnejšie zomleté vzorky trosky vykazovali lepšie pevnosti, ale z dôvodov spracovateľnosti zmesi hornou hranicou je veľkosť špecifického povrchu trosky na úrovni $500\text{ m}^2\cdot\text{kg}^{-1}$.