

ALKALI-ACTIVATED COMPOSITES BASED ON SLAGS FROM IRON AND STEEL METALLURGY

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Slag as a secondary raw material from metallurgy is most often heaped in slag disposal areas without any profit. This paper deals with alkali activated slag from iron and steel production which can be used in the building industry. Products of alkali slag activation fulfil the role of inorganic binders.

Key words: steel slag, blast furnace slag, alkali activation, binder

Aktivno lužnati kompoziti dobiveni od troske željezne i čelične industrije. Kao sekundarna sirovina, troska od metalurškog procesa najčešće se odlaže na deponije bez ikakve financijske dobiti. Ovaj rad se bavi lužnato aktiviranom troskom iz proizvodnje željeza i čelika, koja kao anorgansko vezivo može biti korištena u građevinskoj industriji.

Ključne riječi: čelična troska, troska iz visoke peći, lužnata aktivacija, vezivo

INTRODUCTION

The world production of slag from iron and steel industries per year reaches almost 50 000 kt, whereas approximately 12 000 kt per year is produced in Europe [1]. Czech Republic ranks among the important producers of steel and pig iron in Europe (6,9 million ton of steel and 5,2 million ton of pig iron was produced in the year 2006 [2]) and thus approximately 1,2 million ton of steel slag and 1,9 million ton of blast furnace slag. Approximately 55 % of blast furnace slag production undergoes a granulation process and granulated blast furnace slag (GBFS) originates. A significant part of blast furnace slag is utilized for the production of aggregate. GBFS is commonly utilized in the cement industry for preparation of blended cement CEM II, CEM III and CEM V where cement clinker substitution by GBFS ranges from 6 to 95 wt % [3]. Steel slag is more variable in chemical composition in comparison with granulated blast furnace slag (see Table 1). From this point of view the utilization of steel slag for inorganic binder preparation is more complicated. Slag with a high content of iron (ladle slag) is returned to the blast or steel furnace in the form of agglomeration charge. Another part of steel slag is utilized for production of dense synthetic aggregate. The majority of ladle slag production is stored in slag disposal areas without any profit [4].

Table 1. Comparison of composition of GBFS and steel slag [5]

Slag origin	Composition / wt %					
	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	FeO+Fe ₂ O ₃
Blast furnace	35-38	34-38	6-9	10-14	0,5-2	0,5-1
EAF carbon steel	35-60	9-20	2-9	5-15	3-8	15-30
EAF alloy steel	39-45	24-32	3-8	8-15	0,4-2	1-6
Oxygen converter	30-55	8-20	1-6	5-15	2-8	10-35
Ladle	30-60	2-35	5-35	1-10	0-5	0,1-15

EAF - Electric arc furnace

SLAG ALKALI ACTIVATION

Induced cementitious properties of slag by suitable alkali activators allow effective usage of this secondary metallurgical product in the building industry as a valuable binding system which represents an alternative to cement binders. Apart from the value of slag for the building industry, raw materials and energy savings occur as well as CO₂ emission decreases even though the mortars range significantly increase [6].

The latent hydraulicity of slag as well as certain natural raw materials (tuffs and eruptive products) or antropogenous materials (slags, fly ashes, metakaoline and silica fume) is a property which is developed after alkali activation causes solidification and hardening of the material. For latent hydraulicity activation, soluble solutions of alkaline compounds - carbonates, aluminates and silicates can be used [7, 8].

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Davidovits clears up the theory of geopolymerization [9]. This process represents the controlled synthesis of phases, so-called geopolymers or polysialates, whose properties are similar to natural zeolites. From the polycondensation reaction, unordered systems containing SiO₂ and Al₂O₃ in high alkali environment can result. The chemical name polysialate represents the fact that the 3D sialate network is built up by chains of SiO₄ and AlO₄ tetrahedron linked up by shared oxygen atoms. The negative charge of Al in IV coordination is balanced by Na⁺, K⁺, Ca²⁺ ions which are linked in the structure [9]. With the growing content of CaO, the sequence of origination of new phases is changed during alkali activation as in the case of slag. Hydrated almost amorphous phases C-S-H (CaO-SiO₂-H₂O) which originate as a consequence of alkali activation significantly harden the resulting structure similarly as in the case of C-S-H Portland cement hydration products. The process of geopolymerization develops as a consequence.

The necessary condition for latent hydraulicity of slag is the occurrence of an amorphous glassy phase. The presence of an activator causes the interruption of Si-O, Al-O and Ca-O bonds.

EXPERIMENTAL PART

The aim of this paper is to document iron and steel slag binding competence during the preparation of dense and lightweight (porous) materials.

Basic raw materials chosen for alkali activation experiments are characterized in Table 2. This table shows main components in GBFS, power plant fly ash and four types of ladle steel slag (marked as A, B, C, D) obtained from ArcelorMittal Ostrava, a.s. Ladle slag with very different chemical composition in main substances (CaO, SiO₂ and Al₂O₃) were chosen. With respect to ceramic convenience, the oxides are indicated by abbreviations C, S, A e.g. C₂AS=2CaO·Al₂O₃·SiO₂.

The sums of C+S+A content reach values in the range 77 ~ 97 % in all studied raw materials - such high amounts of C, S, A as allowed when considering studied materials as ternary systems. From this point of view the measured amount of C, S and A was recalculated to 100 % (Table. 2). The composition of the studied materials is graphically presented in Figure 1. On the basis of the simplified content the raw material composition is illustrated in constitution ternary diagram C-S-A (Figure 1) Š10Č. So expressed raw material composition enables the determination of a potential equilibrium phase association for individual slag (equilibrium composition of totally recrystallized systems). The data is summarized in Table 2. For comparison of the phase composition of studied materials obtained with the help of X-ray powder diffraction (XRPD), analysis performed on diffractometer INEL is also shown in Table 2.

Table 2. Chemical and phase composition of used raw material and composition calculated on macrocomponents

	GBFS	Slag A	Slag B	Slag C	Slag D	Fly ash
/ wt %						
CaO	37,65	37,52	46,10	51,84	57,74	3,40
SiO ₂	38,07	31,93	23,80	17,30	3,50	50,39
Al ₂ O ₃	5,87	7,24	11,80	18,85	35,76	27,85
MgO	10,61	7,10	11,40	7,44	2,10	3,00
FeO/Fe ₂ O ₃	0,28	8,16	1,38	3,88	0,66	7,90
ΣC+S+A	81,59	76,69	81,70	87,99	97,00	81,60
C	46,15	48,92	56,43	58,92	59,53	4,16
S	46,66	41,64	29,13	19,66	3,61	61,72
A	7,19	9,44	14,44	21,88	36,86	34,12
Equilibrium phase assoc.	CS-C ₂ A S-CAS ₂	C ₃ S ₂ -CS -C ₂ AS	C ₂ S-CA -C ₂ AS	C ₂ S-C ₃ A-C ₁₂ A ₇	C ₂ S-C ₃ A-C ₁₂ A ₇	A ₃ S ₂ - S-CAS ₂
Phase composition. XRPD	glass, (meli-lite CAS ₂)	glass, C ₃ S ₂ , CS, C ₂ AS	glass, C ₃ A, β-C ₂ S, γ-C ₂ S	β-C ₂ S, γ-C ₂ S, C ₃ A, (glass)	C ₃ A, γ-C ₂ S, (β-C ₂ S)	glass, A ₃ S ₂ , β-cristo-ba-lite β-quartz

During the selection of raw materials (mentioned in Table 2) for experiments, the main emphasis was placed on their glassy character which is assured mainly by their quick cooling. The high amount of glassy phase is a necessary condition for the successful alkali activation process and optimal phase composition for the development of hydrated systems. Comparing the amounts of the main components (C, S, A) in studied materials (Table 2), it is evident that initial phase composition will be different to what was also approved by XRPD and the course of the hydration process will be different for each given raw material. Differences in the hydration processes cause changes in phase composition, microstructure and functional parameters of hardened binders.

All used raw materials were milled to achieve the specific surface area of 320 ± 20 m²/kg according to the žBlaine' method. Sodium metasilicate solutions (water glass) from different commercial sources were used for alkali activation. After the initial measurement of density and silicate module M_s (equation 1), the activator quality was subsequently changed using NaOH solution (50 %) to reach M_s in the range 1,35 – 2,00.

$$M_s = \frac{n_{SiO_2}}{n_{Na_2O}} \quad (1)$$

The modified water glass solution with the required amount of Na₂O was added to the prepared mixtures. For dense materials the content of Na₂O reached 3,1 – 5,0 wt% and the water ratio (solid to liquid ratio) was set to give the value 0,33±0,02. In the case of lightweight materials, the optimization of the alkali activator amount was one of the goals of the presented work.

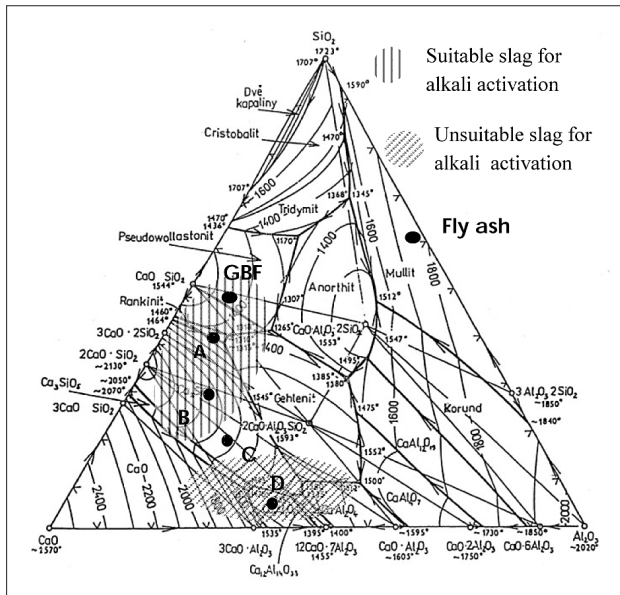


Figure 1. Occurrence range of used slags marked in equilibrium phase diagram CaO – Al₂O₃ – SiO₂

Preparation and characteristic of dense samples

In the case of dense samples, initial substances (given latent hydraulic material, alkali activator and water) were homogenized and cast into laboratory moulds (mould dimensions are 20×20×20 mm). The hydration of samples proceeded in a moist environment (relative humidity 99 % and laboratory temperature) until a strength test was performed. The strength test was realized after 2, 7, 28 and 50 days. In the same time intervals the bulk densities (without drying) were measured.

The measured values of strength for a single alkali activated ladle slag (A, B, C, D) and these alkali activated ladle slags in combination with GBFS and fly ash are shown in Table 3. The combination of ladle slag with GBFS and fly ash were prepared with the aim to change chemical composition of initial mixtures resulting in the different hardening processes and different strengths of prepared samples.

Excellent strength values after 28 days hydration show samples prepared from GBFS and water glass in a broad range of quality and dosage. Strength values of 70 MPa reached samples using water glass with 3,1 wt% of Na₂O and M_s=2,0 after 28 days of hydration. By increasing the dosage of Na₂O up to 5,0 wt %, the strength values reached 115 MPa. Using the water glass with M_s = 1,35 and 5,0 wt% of Na₂O, the prepared samples reached a compressive strength of 90 MPa, with prolonged setting time. The achieved values of compressive strength exceeded the strength of samples prepared from ordinary Portland cement CEMI 42,5R (Figure 2).

The samples prepared only from GBFS and the mixtures of GBFS with fly ash showed also excellent strength values (Figure 3) if water glass with 3,5 wt % of Na₂O and M_s = 2,0 was used.

Table 3. Compressive strength values of prepared samples using water glass with 4,5 wt % of Na₂O and M_s = 2,0

Ladle slag	Mixture composition / %			Compressive strength / MPa			
	Slag	GBFS	Fly ash	2 days	7 days	28 days	50 days
A	100	0	0	20,8	41,3	51,3	68,0
	50	50	0	33,8	47,5	55,0	76,0
	50	25	25	25,4	46,3	54,9	77,3
B	100	0	0	27,6	54,2	73,4	76,0
	50	50	0	29,6	45,8	60,0	72,3
	50	25	25	16,8	46,2	53,4	57,1
C	100	0	0	21,3	33,0	41,3	45,7
	50	50	0	23,8	37,5	45,0	51,2
	50	25	25	8,8	20,0	27,5	34,6
D	100	0	0	-	17,8	20,0	27,8
	50	50	0	12,6	28,4	36,3	47,7
	50	25	25	10,5	15,9	24,7	33,6

The highest values of compressive strength were achieved in the samples containing GBFS. The main reason for the high values of compressive strength of these samples is the significant amount of SiO₂ which assured a high content of amorphous glassy phase. Glassy slag is an optimal starting material for alkali activation and together with sufficient amounts of CaO in this slag is responsible for the C-S-H phase formation which guarantees high initial strength values.

Ladle slag A shows similar properties to GBFS – high amount of glassy phase, CaO, SiO₂ and Al₂O₃ which assure origination of suitable hydration products. The chemical composition of slag B showed a sufficient amount of SiO₂ and low amount of Al₂O₃. Overall the hydration process of slag B probably consists of alkali activation of a glassy phase together with direct hydration of β-C₂S with water. Slag A and B in mixtures with GBFS or fly ash show also favourable mechanical properties (see Table 3). Two areas representing suitable and unsuitable phase compositions of raw materials for alkali activation are depicted on ternary diagram presented in Figure 1. Both slag A and B lie in the area des-

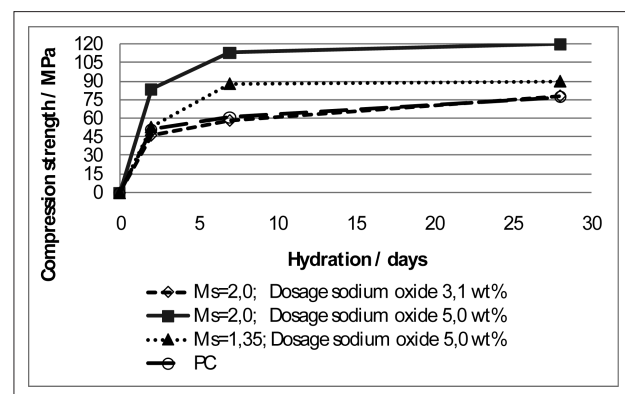


Figure 2. Compressive strength of alkali activated granulated blast furnace slag and CEMI/42,5 R

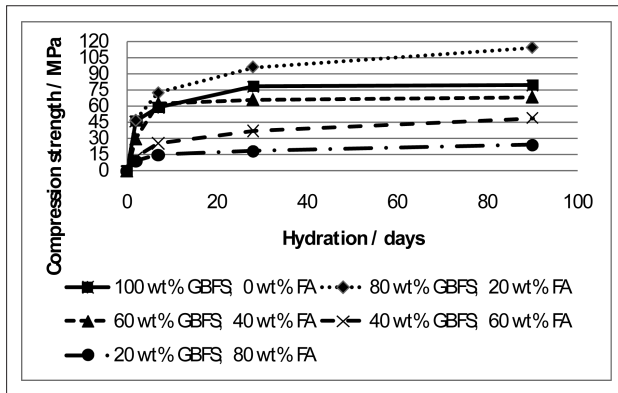


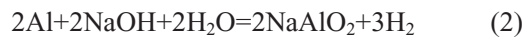
Figure 3. Compressive strength of alkali activated mixtures granulated blast furnace slag (GBFS) and fly ash (FA)

ignated as the area with suitable slag composition for alkali activation and thus suitable for alternative inorganic binder preparation.

On the other hand slag C and D lie in the area designated as an area with unsuitable slag composition for alkali activation. The amount of SiO₂ is lower for this slag which is not favourable for the formation of a glassy phase. For this reason slag D doesn't contain a glassy phase, also CaO and Al₂O₃ content is high and the main crystalline phases are calciumaluminates (C₃A, C₁₂A₇). Mixtures containing these slags (C and D) harden more rapidly but resulting values of compressive strength are lower. This trend is evident for slag D which has a negative influence on compressive strength values in its mixtures with GBFS.

Preparation and characteristic of lightweight samples

On the basis of the previously mentioned results, the presumption that GBFS could be a suitable component for preparation of lightweight materials, similar to porous concrete, can be made. The porous structure is acquired by the addition of Al powder which in an alkali medium undergoes a chemical reaction (2) during which hydrogen is released and a lightened porous structure originates. The character of the porous structure is dependent on the hydrogen evolution rate [11].



In this part of research we focused on the determination of the optimal amount of Al powder and amount of alkali activator (water glass).

Prepared mixtures of selected substances were homogenized by milling. The Al powder was added to the homogenized mixtures just before forming, which avoids the development of hydrogen too early. The prepared homogenized mixtures were cast into tubular moulds. Hydration of samples proceeded in a moist environment (relative humidity 99 % and laboratory temperature) until the strength test was performed. After 28 days of hydration, compressive strengths and bulk den-

sities were determined. The composition of prepared samples and measured parameters are shown in Table 4.

The alkali activator increases pH values of prepared mixtures and is responsible for the disruption of disordered structures of latent hydraulic materials. The hydration products are calciumsilicate hydrates (C-S-H phases) and zeolites.

Present experience with the preparation of lightweight materials clearly shows that the main problem is one of proper timing of the addition of both the Al powder as well as of the alkali activator. The reaction (2) is probably the fastest one which occurs during the lightweight samples preparation and must follow the appropriate stage of other processes.

The lower amount of Na₂O (3,5 and 4,0 wt %) and currently higher amount of Al powder (0,26 and 0,35 wt %) in the mixtures cause hydrogen evolution whereas the creation of suitable hydration products during alkali activation doesn't occur. This causes the formation of big non-uniformly distributed pores, which are responsible for the fragmentation of prepared samples. A high amount of Na₂O and also an increasing amount of Al powder causes the bulk densities and compressive strength values to decrease as is shown in Table 4.

Table 4. Compressive strength and bulk density values of prepared samples

Lightweight samples	Na ₂ O / wt %	Compressive strength after 28 days of hydration / MPa				Bulk density after 28 days / kg/m ³			
		Al /wt .%				Al /wt .%			
		0,13	0,19	0,26	0,35	0,13	0,19	0,26	0,35
E	3,5	5,1	2,1	-	-	867	708	-	-
F	4,0	2,8	3,0	-	-	849	732	-	-
G	4,5	3,5	3,2	2,7	2,1	1030	885	802	793
H	5,0	2,8	2,5	2,0	2,0	835	731	564	634
I	5,5	2,4	2,0	1,8	1,9	696	551	520	534

CONCLUSION

This paper summarizes the experimental results obtained for the alkali activated technogenous puzzolana-granulated blast furnace slag, steel slag and fly ash from power plants. The prepared materials, both dense and lightweight, displayed good product manufacturing qualities while their preparation is economically acceptable as well as being environmentally friendly.

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REFERENCES

- [1] S. Kourounis, et al., *Cement and Concrete Research*, 37 (2007), 815 – 822.
- [2] International Steel and Iron Institute, [on line] Search statistics archive org Available from <http://www.worldsteel.org>
- [3] CSN EN 197 - 1 Cement - Part 1: Composition, Specifications and Conformity Criteria for Common Cements. Praha: Český normalizační institut, 2001.
- [4] B. Gajdzik, *Metalurgija*, 48, (2009) 1, 63 – 67.
- [5] C. Shi, P. Krivenko, D. Roy, *Alkali-Activated Cement and Concretes*, Taylor & Francis, London, 2006, 100 – 101.
- [6] V. Tomková, J. Vlček, et al., 11th Conference on Environment and Mineral Processing, VŠB-TU, Ostrava, 2007, 61-64.
- [7] V. Gluchovskij, A. Pachomov, *Šlakošočoločnyje cementy i betony*, Budivelnik, 1978, Kijev.
- [8] J. Brandštetr, *Stavivo*, 62 (1984), 110 – 114.
- [9] J. Davidovits, *Journal of Thermal Analysis*, 37 (1991), 1633 – 1656.
- [10] E. F. Osborn, *Phase Equilibria Diagrams*. Am. Ceramics Society, 1960.
- [11] R. Drochytka, *Pórobeton*, VUTIUM, Brno, 1999.

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