MECHANICAL PROPERTIES OF ALKALI-ACIVATED BINDERS BASED ON COPPER SLAG

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Abstract

The paper describes the possibility of using copper slag, an industrial waste from smelting of copper as a basic component of hydraulic binders obtained by means of the alkaline activation. For the purpose, the aqueous sodium silicate and technical sodium metasilicate were used. Mortars, having undergone the activation process were cured under laboratory conditions (temp. 20±1°C and relative humidity approx. 60%) and were subjected to low pressure heat treatment at a temperature of 80°C. Research over the alkaline activation of slag proved that the desirable quality of alkali-activated binders is achievable just in case of using granulated copper slag, where 98% of the base mass constitutes of glassy phase, and water glass with the lowest value of silicate modulus ($M_k = 1.75$).

Streszczenie

W artykule przedstawiono możliwości wykorzystania odpadowego żużla pomiedziowego pochodzącego z hutnictwa miedzi jako podstawowego składnika spoiw hydraulicznych otrzymanych na drodze aktywacji alkalicznej. W procesie stosowano szkło wodne sodowe o zmiennym module krzemianowym oraz techniczny metakrzemian sodu. Zaprawy po procesie aktywacji dojrzewały w warunkach laboratoryjnych (temp. 20±1°C i wilgotność względna ok. 60%) oraz były poddane niskociśnieniowej obróbce cieplnej w temperaturze 80°C. Badania nad aktywacją alkaliczną żużla dowiodły, że możliwe jest uzyskanie pożądanej jakości spoiw aktywowanych alkalicznie tylko w przypadku stosowania granulowanego żużla pomiedziowego, w którym 98% masy zasadniczej stanowi faza szklista oraz przy użyciu szkła wodnego o najniższym module krzemianowym ($M_k = 1.75$).

Keywords: Alkaline activation; Alkali activated binders; Copper slag; Silicate module; Water glass.

1. INTRODUCTION

Alkaline activations is a process with a long history of practice. Hence, fly ash from power industry as well as granulated blast furnace slag from iron industry are mainly being used. The use of alkaline activation brings many economic and environmental benefits, such as reduction of CO_2 emissions resulting from the reduction of cement clinker production, industrial waste management and saving of energy and natural resources. Until today, the most attention was paid to the activation of alkaline granulated blast furnace slag [1-4], while very limited number of works have been devoted to the activation of the alkaline copper slag. This by-product of the steel industry was the subject of many studies aiming at its application as an aggregate in the composition of concrete and mortar [5-8] and as a component of common cements [9-14]. The tests performed on the cements with copper slag confirmed, that this waste is characterized by a high content of acidic oxides, such as Fe_2O_3 and SiO_2 but also

Al_2O_3 in case of Polish slag (Table 1), which can react with calcium hydroxide of the hydrated cement silicate phases (pozzolanic activity) [12, 13]. Some researchers accounted [14] the copper slag in the relation with cement to behave passively, however, its small addition to cement shows an advantageous effect of increasing the stability of the cement matrix in various corrosive environments. World's production of copper slag exceeds several tens of million tonnes (approx. 25 million) per year [14, 15], and its composition, depending on the region of mining copper ore can be variable, especially in terms of the content of major oxides such as Fe_2O_3, SiO_2 and Al_2O_3. These differences are built not only upon on the mineral composition of ore, but also on the manufacturing technology and the type of furnace. The chemical composition of copper slag from different parts of the world are shown in Table 1.

Table 1.
Chemical composition of copper slag from different sources by mass (%) [10]

No.	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	SO_3	Country
1.	44.78	40.97	5.24	1.16	3.78	1.06	Iran
2.	44.80	24.70	10.9	1.70	15.6	0.28	USA
3.	49.50	34.51	2.20	1.48	6.55	1.20	Canada
4.	45.30	36.00	9.30	3.24	3.45	0.49	Australia
5.	62.0	26.00	2.50	3.70	-	-	Brazil
6.	52.0	35.50	2.11	1.06	5.90	0.14	Japan
7.	60.00	30.07	0.6	0.75	3.97	0.32	Spain
8.	53.72	34.30	7.91	0.94	3.83	3.02	Taiwan
9.	36.00	31.00	4.00	-	6.00	-	Malaysia
10	41.53	37.13	-	-	-	0.11	Chile
11.	39.65	31.94	3.95	2.82	2.40	-	Turkey
12.	7-21	37-41	8-30	1,5-8	5-16	-	Poland

Hereby paper presents the properties of alkali-activated binders from ground, granulated and lump copper slag deriving from Polish copper smelters. To execute the process of alkaline activation, the sodium water glass was used with variable molar ratio SiO_2/Na_2O (variable silicate module M_k). Slag mortars achieved by alkaline activation method were subjected to accelerated curing (low pressure infusion), and the obtained strength results were compared with results of mortars maturing in the laboratory. It should be emphasized that the alkaline activation of alumina silicate materials containing a small amount of calcium compounds in its composition, requires the selection of an appropriate alkaline activator. Previously conducted studies on the activation of alkaline copper slag have shown, that due to the

chemical reactions between the ground copper slag and an alkaline activator (NaOH or sodium water glass) there are formed low alkali hydrosilicates type CSH, low alkali hydrated aluminates and aluminosilicates type hydroglossular, calcite, magnesium hydrosilicates, mixed sodium-potassium compounds as well as alkaline hydrated aluminosilicates of hydronefeline type, analcime and natrolite [16]. The resulting products in the form of hydrates, significantly differ from the products of the hydration of CaO- rich conventional common cements. Along with the decreasing content of CaO, the amount generated by the hydration of CSH and CAH phases decreases, though, a higher content of phase-like zeolites. Choosing the appropriate type and amount of activator is a complex task and depends mainly on the chemical composition and the proper surface area of the slag. Dissolution of alumina and silica is faster the higher the pH of the system and dependent on the quality and content of the activator [2, 4, 17].

2. CHARACTERISTIC OF BINDER COMPONENTS AND TEST METHODOLOGY

2.1. Composition of binder

a) Copper slag

The study used the two types of copper slag waste: air cooled slag and granulated slag. The chemical composition of both types of slag are shown in Table 2. The chemical composition of slags, and slag mortars mechanical properties were determined according to the procedure set out in the European Standard EN 196 on methods of testing cement [20, 21].

Lump shaft slag is obtained in the process of melting briquetted copper concentrate in a shaft furnace. Thus, the slag obtained in the process, considering its low content of Cu, is the final waste of the melting procedure. In a liquid phase and a temperature of about 1200°C, it is transported to a storage location - a heap, wherein, after pouring a process of solidification and gradual cooling under atmospheric conditions follows [18, 19]. Slow cooling of the slag leads to a significant extent of the crystallization of its structure, as seen in the diffraction pattern (Fig. 1a).

In contrast, granulated copper slagis formed by the rapid cooling using water (granulation process) received during copper removal phase in an electric furnace. Glassy phase is the dominant component of this type of slag, illustrated in the diffraction in Fig. 1b.

Determination of mineral composition of granulated and lump slag was performed by X-ray diffractometer

Table 2.
Chemical composition and glass phase content of copper slag

Sample	Chemical composition, [%]								Glassy phase content, [%]
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Cl^-	Suma	
Lump slag	42.76	17.38	15.56	11.88	7.29	0.12	0.015	95.01	4.75
Granulated slag	35.24	18.57	12.31	21.27	7.77	0.16	0.002	95.32	98
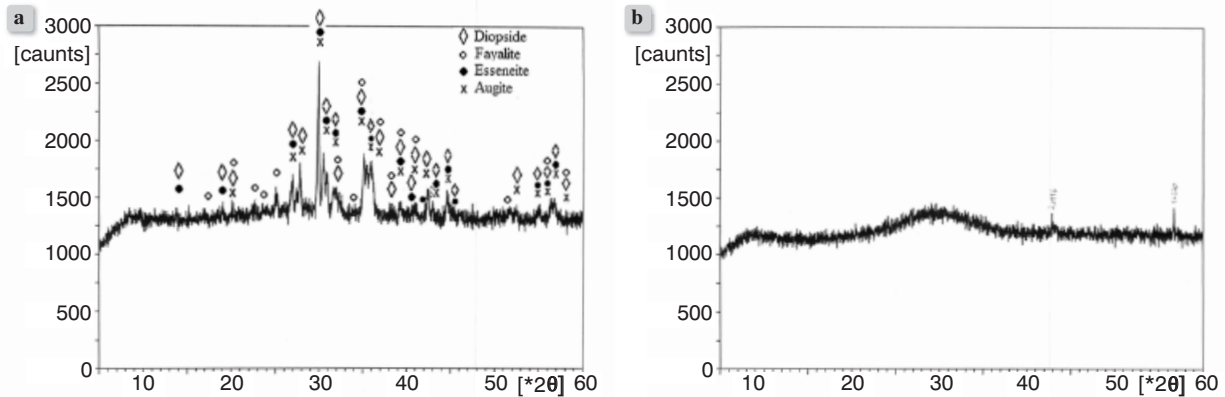
Figure 1.
XRD of copper slag (a) lump; (b) granulated

XRD, including a vitreous phase content, determined using microscopic method described in the Polish standard [22].

b) Alkaline activator – sodium water glass

Alkaline activation was performed using two types of activators: liquid sodium water glass (4 types), and technical sodium metasilicate in the granule form. Sodium water glass differed in terms of silicate modulus value, i.e. the molar ratio SiO_2/Na_2O. Sodium silicate is the only common water-soluble silicate. The characteristics of the individual activators are shown in Table 3.

Table 3.
Characteristics of sodium water glass samples applied in tests (producers data)

Type of activator		Content of Na_2O+SiO_2, [%]	Silicate modulus M_k	Density in 20°C [g/cm³]
I	Liquid water glass	44.0	1.75	1.54
II		44.0	2.00	1.52
III		41.6	2.50	1.46
IV		39.5	3.00	1.42
V	Sodium metasilicate – granules	54.2	1.00	-

3. TESTS METHODOLOGY

The samples of lump and granulated slag were grounded in a ball mill for the two specific surface areas by Blaine: 3500 cm²/g and 4000 cm²/g. Thereafter, the mortars consisting of: 450 g of copper slag, 1350 g of standard sand and 180 ml solution of water and an alkali activator. The value of water-binder ratio w/s = 0.4 was adopted. The amount of the activator relative to the slag mass was 7% (in the case of granulated slag) and 10% by weight (both types of slag) corresponding to the content of solid sodium silicate in the water glass. The molded rectangular samples of mortar with dimensions 40 x 40 x 160 mm, after the initial maturation (24 hours, relative humidity > 90%, temperature 20°C), were subjected to curing process:

a) In laboratory conditions for 7, 28 and 90 days at temperature of 20±1°C and relative humidity approx. 60%;

b) Accelerated (low pressure infusion process). The mortars were cured for 3 and 6 hours at temperature of 80°C and relative humidity over 90%. The diagram of complete, accelerated infusion process depicts Fig. 2a and 2b.
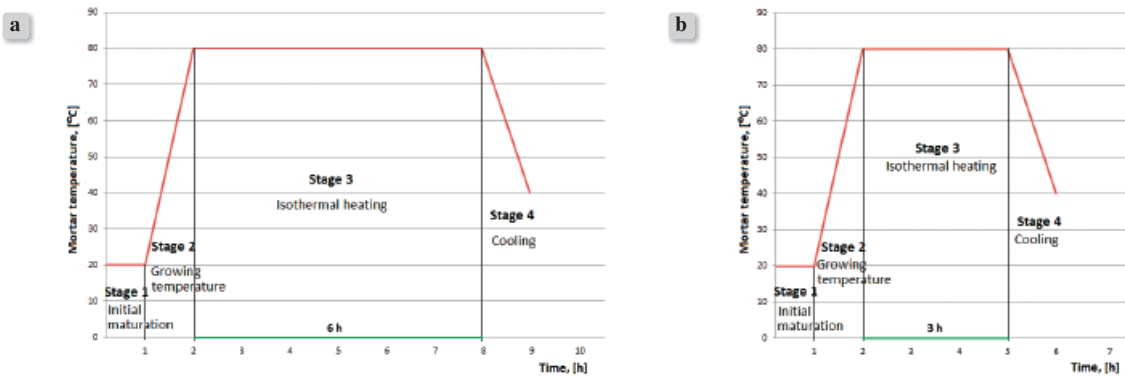
Figure 2.
The diagram of slag mortar infusion (a) in cycle 6h; (b) in cycle 3h

4. TESTS RESULTS AND THEIR INTERPRETATION

Granulated and lump copper slag used in the study contain mainly silicon oxide and oxides of iron, calcium and aluminum. Granulated slag has almost a 10% of calcium oxide and approx. 7% less of silicon oxide compared to lump slag (Table 2). Applied alkaline activators in the form of sodium water glass and technical sodium metasilicate showed variable value of silicate modulus M_k (SiO_2/Na_2O). Activators were identified with symbols I, II, III, IV, V and the value of M_k module for each of them was successively 1.75, 2.00, 2.50, 3.00 and 1.00 (Table 3).

The lump slag revealed the presence of crystalline phases. These are mainly pyroxenes – augite $Ca(Mg,Fe^{+3},Al)(Si,Al)_2O_6$, diopside $Ca(Mg,Al.)(Si,Al)_2O_6$ and esseneite $(Ca,Na)(Fe,Mn,Zn)Si_2O_6$ (Fig. 1a). The occurrence of fayalite Fe_2SiO_4. a silicate belonging to the olivine group was also noted. The granulated copper slag diffraction pattern (Fig. 1b) shows no peaks suggesting the existence of crystalline phases inside. Microscopic examination proved that the granulated slag within approx. 98% consists of a glassy phase, whereas the lump slag contains only 4.75%.

Compressive strength of mortars with alkali-activated copper slag were determined in two variants: for the slag proper surface areas of 3500 cm^2/g and 4000 cm^2/g, illustrated in the diagrams in Fig. 3÷6. Lump slag mortars had very low compressive strength (the highest surface area development and after 90 days of setting, the compressive strength reached only 1.88 MPa). There was also no strength increasing trend observed in longer setting periods. The lack of strength is caused primarily by the poor content of glassy phase (4.75%), a critical component of the active slag.

The compressive strength of mortars produced with activated binders on granulated copper slag appeared to be incomparably higher than those obtained with binders based on lump slag (when using activator I with the lowest silicate modulus $M_k = 1.75$ and with the specific surface area of 4000 cm^2/g, compressive strengths after 90 days were nearly 28 times higher than the strength obtained for the mortars with lump slag). It should be noted that the granulated copper slag was almost completely vitrified (98%). The high-
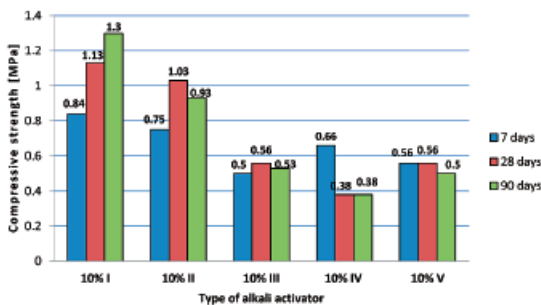

Figure 3.
Compressive strength of copper lump slag mortars with the addition of 10% of activators (slag proper surface 3500 cm^2/g)
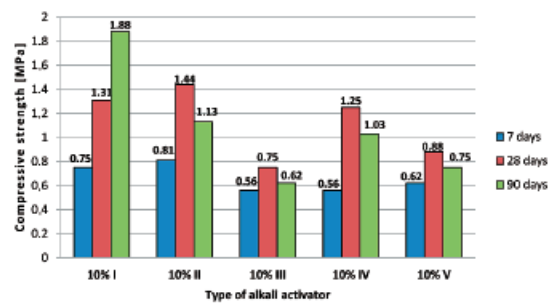

Figure 4.
Compressive strength of copper lump slag mortars with the addition of 10% of activators (slag proper surface 4000 cm^2/g)
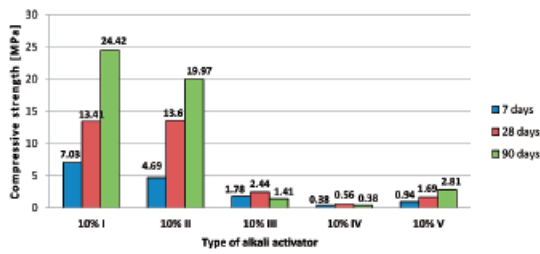
Figure 5.
Compressive strength of granulated copper slag mortars with the addition of 10% of activators (slag proper surface 3500 cm^2/g)
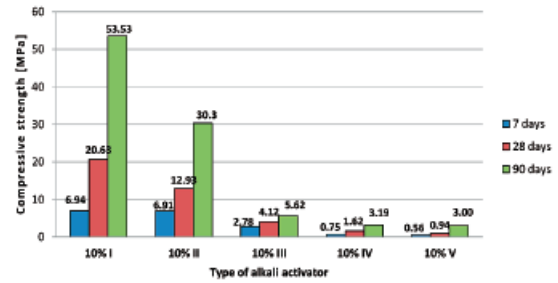

Figure 6.
Compressive strength of granulated copper slag mortars with the addition of 10% of activators (slag proper surface 4000 cm^2/g)

est strengths were gained using water glass with symbols I and II, which corresponded to the silicate modulus values 1.75 and 2.00 respectively. Noteworthy was also the positive impact of the increased development of the granulated slag surface area for the strength of mortars with their addition (Fig. 5 and 6). The compressive strength of mortars increased after a long period of curing, in particular, when an activator with the lowest molar ratio of SiO_2/Na_2O equals to 1.75 (compressive strength after 28 days – 20.63 MPa, after 90 days – 53.53 MPa) was applied. Since only two of the five used alkaline activators generated positive results, further research was continued only with these two. The use of several types of liquid alkali activator with different modulus values SiO_2/Na_2O allowed to reach the conclusion that the lower the value, the greater is the alkalinity of solutions reacting with slag, which leads to a greater activation effect.

Fig. 7 illustrates the compressive strength of mortars made with activated binder with granulated copper slag and subjected to a low-pressure heat treatment at the temperature of 80°C according to a 3 and 6-hours cycle (Fig. 2). It was decided not to perform the tests on lump slag due to the low strengths in the course of setting in laboratory conditions (low activity of the slag).
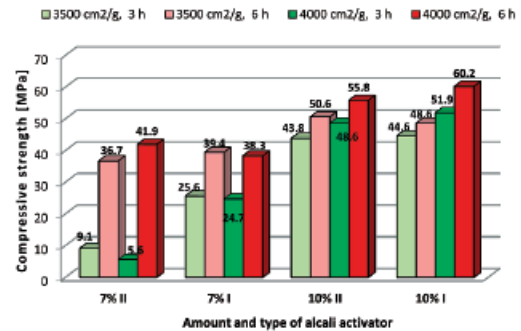

Figure 7.
Compressive strength of mortars with 7 and 10% of activator addition (I and II) subjected to infusion process in 3 and 6-hour cycles

Analysis of the results obtained for mortars exposed to heat-treatment confirmed, that as in the case of mortars aged in the laboratory conditions (Table 4), the type and amount of activator used and the size of the slag proper surface area development is the key element of strength growth. Using the method of the low pressure infusion allowed obtaining a much higher compressive strength than in mortars cured naturally (Table 4).

Table 4.
Strength of granulated copper slag mortars cured in the laboratory and subjected to 3 and 6-hour cycle processes of low pressure infusion

Slag type	Blaine surface [cm^2/g]	Type of activator	Content of activator [%]	Curing in laboratory conditions			Accelerated curing (low pressure infusion)	
				Compressive strength, [MPa]				
				7 days	28 days	90 days	3h	6h
Granulated copper slag	3500	I	7	1.78	3.19	3.56	25.6	39.4
			10	7.03	13.41	24.42	44.6	48.6
		II	7	1.88	2.48	2.81	9.1	36.7
			10	4.69	13.6	19.97	43.8	50.6
	4000	I	7	2.06	3.38	3.94	24.7	38.3
			10	6.94	20.63	53.53	51.9	60.2
		II	7	2.1	2.81	3.00	10.6	41.9
			10	6.91	12.93	30.30	48.6	55.8

In case the water glass is used in an amount of 7%, strength results are significantly lower. Higher amount of activator (10%) substantially increases them. Moreover, the increase in the development of the slag specific surface area proved advantageous effect on strength, particularly, when used with a larger amount of the activator. For 7% of added water glass you cannot define a positive impact of the larger surface area on the strength level. The process of infusion prolonged from 3 h to 6 h results in a clear increase in strength of the samples with 7% addition of the activator. Alkaline activated binders with 10% content of both types of water glass achieve a similar level of compressive strength.

Fig. 8 and 9 compare the results of the compressive strength of mortars immediately after infusion and subsequently 7 days form the process inception.
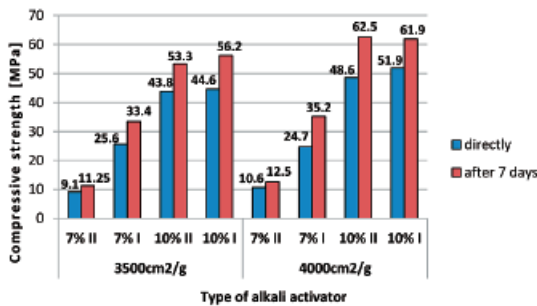

Figure 8.
Summary of mortars strength results after 3 h directly after curing and after 7 days from the infusion process
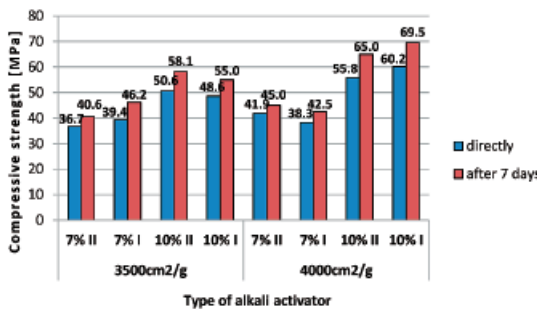

Figure 9.
Summary of mortars strength results after 6h directly after curing and after 7 days from the infusion process

The tests proved compressive strength increase after 7 days of curing after the heat treatment process. The samples subjected to six hours of curing showed the increase from 7.4% to

16.5%, yet, for the mortars subjected to 3 hours of accelerated curing, strength growths were higher and ranged from 19% to 42.5%.

5. CONCLUSIONS

Carried study allow to draw the following conclusions:

1. On the basis of granulated copper blast furnace slag binders with alkaline activation can be produced. A glassy phase (98% by weight) is a major component in this type of copper slag. The presence of the glassy phase slag plays a key role, since it represents the active ingredient. Lump slag was characterized by a structure mostly crystallized, which resulted in its low reactivity in the present method of activation.

2. The level of compressive strength of mortars prepared with slag alkaline binder (granulated cooper slag) is decisively influenced by the amount and type of activator used and the slag grinding degree (specific surface area). The level of achieved compressive strength was from 2.5 MPa to almost 21.0 MPa after 28 days of curing in laboratory conditions with an upward trend during a longer period of time (up to 90 days).

3. Mortars subjected to accelerated curing by infusion (80°C) showed a significant increase in compressive strength as compared to the mortar cured under natural conditions (T = 20±1°C, RH = 60%), especially with less activator (7%). The level of obtained compressive strength was from over 9 to more than 60 MPa. A significant increase in strength during the 7 days of infusion (compressive strength of 12.5 MPa to over 69.5 MPa) was also observed.

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