

HYDRAULIC PROPERTIES OF LADLE SLAGS

Received – Primljeno: 2015-08-14
Accepted – Prihvaćeno: 2016-01-05
Preliminary Note – Prethodno priopćenje

The article presents results of examining of hydraulic properties of ladle slags formed during production of steel. The studied ladle slags were subjected to different cooling mode from the molten state. Based on the ability of the slag react with the water was assessed their hydraulic activity. The hydraulic properties are caused by the presence of minerals dicalcium silicate, tricalcium aluminate, mayenite, brownmillerite and dicalcium ferite. The emergence of required hydrating phases in the ladle slags is conditioned by a sufficient CaO content and their cooling rate. The contact the slag with water during processing and their ageing has a negative effect. The experiment has shown that the phase transformation of the mineral dicalcium silicate which occurs during cooling of the ladle slags cause their volume instability.

Key words: steel slag, ladle slag, hydraulic properties, calorimetry

INTRODUCTION

A steel slag is a by-product from making steel. In the Czech Republic, approximately 0,7 mil tons of steel slags, ladle slag is about 15 % is created during the steel production. Based on this fact, it is necessary considering these slags as high volume waste product and therefore it is also necessary to look for an alternative use of these slags [1]. Steel slags are divided according to the type of aggregate in which they were created. Furnace slags are generated during steel production in a part of metallurgical process so called primarily metallurgy. Ladle slags are products from secondary metallurgy and these are formed in ladles. Furnace slags are used in production of artificial heavy aggregates and they are also recycled in aggregates where they were primarily formed. Ladle slags are mostly stored on landfills [2]. A chemical and phase composition of steel slags is highly variable because these slags are formed in various types of manufacturing steelmaking units. The chemical composition of slag is also affected by the type of the produced steel. The phase composition of the slag depends on its cooling rate. Hydraulic properties of the slags (the setting and hardening of the mixture after addition of water) are influenced by the phase composition, granulometry and cooling rate. The quantity of a crystalline and glass phase depends on the cooling rate. When the slags cool down very quickly, conditions for the formation of amorphous structure can be created there. Slow cooling of slags leads to the formation of a crystalline structure. Taking advantage of the hydraulic properties of the ladle slags is important due to the content of min-

erals such as β - C_2S , C_3S , C_3A , $C_{12}A_7$, C_2F , C_4AF , less important is the following mineral C_3MS_2 (C – CaO, S – SiO_2 , A – Al_2O_3 , F – Fe_2O_3 , below in text also M – MgO , H – H_2O , then C_2S is $2CaO \cdot SiO_2$). In the case of slow cooling of slags, the mineral γ - C_2S is formed there; this mineral is not hydraulic, therefore quickly cooled slags are preferable. There are retained a hydraulically active mineral β - C_2S and a glass phase that exhibit latent hydraulic properties in the rapidly cooled slags. It means that the excitation of slags hydraulicity can be achieved by adding an activator such as $Ca(OH)_2$ or water glass [3]. A glass phase formation cannot be ensured only by fast cooling of slags but there is also required a high proportion of basic glass forming silicon dioxide SiO_2 . Formation of hydraulically active mineral β - C_2S takes place at high temperatures and for its retention is necessary rapid cooling. Below to temperature 1 250 °C and under an equilibrium conditions the decomposition of hydraulically active mineral β - C_2S to hydraulically inactive form γ - C_2S occurs [2, 3].

EXPERIMENTAL METHOD

For this work, there were selected several ladle slags from different producers. These slags have different cooling regimes, granulometry, chemical compositions and phase compositions. The chemical composition in the Table 1 was determined by the X-ray fluorescence analysis.

From the chemical composition of the ladle slags is evident a high content of CaO and relatively a low content of SiO_2 . This composition is not ideal for an increased formation of the glass phase. The Table 1 contains the values of the basicity ratio C/S. All the mentioned ladle steel slags have a high content of CaO.

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Table 1 Chemical composition of ladle slags / wt. %

Slag	CaO	Al ₂ O ₃	SiO ₂	MgO	Fe ₂ O ₃	MnO	Na ₂ O	C/S
A	51	18	20	8	0,3	1,6	2,6	2,6
B	39	18	26	12	0,2	20	1,5	1,5
C	49	18	12	10	2	6	*	4,2
D	55	19	12	6	2	4,0	*	4,7
E	62	16	12	5	0,5	0,1	2,0	5,3
F	56	13	20	5	0,6	0,4	1,7	2,7
G	45	10	20	8	11	1,8	2,0	2,3

*not determined

References [4] indicate, that the satisfactory hydraulic properties have slags with a ratio C/S > 2,7.

The phase composition was determined by using the X-ray diffraction analysis. This analysis was performed on the X-ray diffractometer Bruker D8 Advance type (theta/2theta). As an X-ray source a cobalt lamp was used. The software Diffrac.eva a COD crystallographic databases was used to determine the position of diffraction on the registered diffraction patterns.

The content of the glass phase is in the range between 12 and 32 wt. %, see Table 2. The phase composition of the ladle slags is extremely diverse and the formation of minerals depends on the chemical composition of the slag and solidification conditions in which it often gives rise to the formation of unbalanced states [3]. A ladle slag usually contains dicalcium silicate, merwinite, periklase, brownmillerite, akermanite, anorthite, mellilite and other minerals, given in the Table 2.

Table 2 Phase composition of ladle slags

Slag	Phase composition
A	Crystallinity 68%; b - dicalcium silicate 29%; g - dicalcium silicate 16%; akermanite 11%; anorthite 5%; periklase 4%; tricalcium aluminate 3%
B	Crystallinity 80%; merwinite 53%; Gehlenite 17%; Al ₂ O ₃ MgO 10%
C	Crystallinity 75%; merwinite 33%; b - dicalcium silicate 24; g - dicalcium silicate 8%; brownmillerite 5%; lime 3%; periklase 2%
D	Crystallinity 80%; merwinite 34%; b - dicalcium silicate 21%; monticellite 14%; brownmillerite 4%; CaFe ₄ O ₆ 3%; akermanite 3%
E	Crystallinity 87 %; anorthite 19%; mayenite 17%; b - dicalcium silicate 16%; brownmillerite 12%; periklase 8%; mellilite 7%; fluorite 7%; g - dicalcium silicate 7%
F	Crystallinity 88 %; g - dicalcium silicate 30%; augite 16%; merwinite 14%; diopside 10%; b - dicalcium silicate 6%; mayenite 5%; periklase 4%; lime 3%
G	Crystallinity 74%; g-dicalcium silicate 26%; tremolite 13%; merwinite 11%; hydrogarnet 9%; mayenite 6%; brownmillerite 4%; halloysite 4%; portlandite 1%

b(g) - C₂S - dicalcium silicate, C₂MS₂ - akermanite, CAS₂ - anorthite; M - periklase, C₃A - tricalcium aluminate, C₃MS₂ - merwinite, C₂AS - gehlenite, AM - spinel, C₄AF - brownmillerite, C - lime, CMS monticellite, (Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆ - augite, C₁₂A₇ - mayenite, solid solution of C₂AS and C₂MS₂ - mellilite, CMS₂ - diopside, Ca₂Mg₃Si₈O₂₂(OH)₂ - termolite, Al_{2,85}Ca₃H_{9,6}O₁₂ - hydrogarnet, Al₂Si₂O₃(OH)₄ - halloysite, Ca(OH)₂ - portlandite

Slags A to D were taken in liquid state from the ladle. Slags E and F were taken from slag yards as “fresh” slags because they were taken immediately after pouring out from ladle. The sample of E was represented by

a coarse grained proportion (grain size > 100 mm) and the sample F was represented by a fine grained proportion (grain size < 3 mm). The sample G was a matured slag (few weeks old), the slags was removed from slag yards. This sample came into contact with water before its sampling. Other slags were not in contact with water before their sampling.

The hydraulic properties were studied of the above mentioned slags after their excitation by water. Before the preparation of mixtures, the slags were milled up to fineness (300 (15 %) m²·kg⁻¹ Blain) in order to increase their surface area; that is their higher reactivity. Thus prepared raw materials were moistened by water. The quantity of water was added with respect to perfect of activated mixture into the metal mould of size 20 × 20 × 20 mm. Water ratio was determined according to DIN EN 206-1 and its value ranged from 0,3 (10 %). This way prepared samples were stored in the hydration box (room temperature and relative humidity 99 %) and after 2, 7 and 28 days the determination of compressive strength according to DIN EN 12390-3 was performed. Slags activated by water are marked by index *h*, i.e. A_h to G_h.

Table 3, there are presented achieved values of the compressive strength after 2, 7 and 28 days of the hydration. These ladle slags were activated by water. Disintegration of any samples was not observed during hydration process.

Table 3 Compressive strength of the prepared samples / MPa

Hydrated mixture	A _h	B _h	C _h	D _h	E _h	F _h	G _h
2 day	26,0	2,2	5,7	2,7	3,7	8,4	2,9
7 days	29,2	2,2	9,6	5,5	6,7	9,0	3,1
28 days	30,0	2,4	12,4	11,0	12,0	12,4	3,2

In order to assess the reactivity of slags, the calorimetric analysis was used. The isothermal titration calorimeter TAM Air was used for these measurements. This device monitors the heat flow in the sample which is placed in a glass ampoule with an injection system that ensures the application of water to the powder mixture. The hydration process was monitored in time dependence. The advantage of this device is the possibility of monitoring the progress of hydration reactions immediately after addition of the reactant (water) into the slag sample. Based on this experiment it is possible to evaluate the relation between hydration heat development and hydraulic properties of the tested material.

The Table 4 presents the hydration heat of samples which was measured on a calorimeter TAM Air for 24 hours of hydration.

The Figure 1 presents the calorimetric records of ladle slags heat of the hydration during 24 hours.

Table 4 Heat of hydration of ladle slags after 24 hours

Heat of hydration /J·g ⁻¹	Slag						
	A	B	C	D	E	F	G
	159	4	103	139	111	172	10

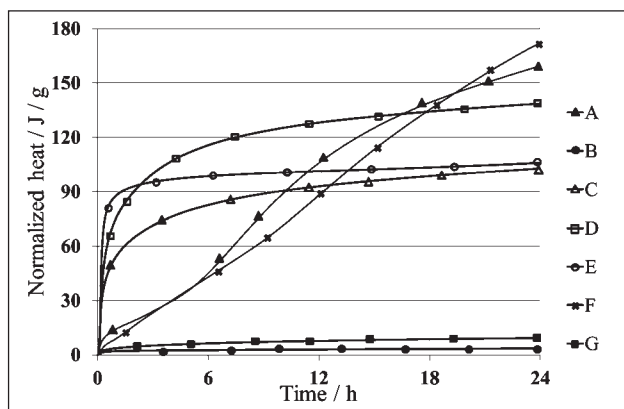


Figure 1 Calorimetric analysis of ladle slags

RESULTS AND DISCUSSION

Selected ladle slags are multiple representatives characterizing variable chemical and phase composition of these products. In the

The hydration of ladle slags with a content of hydraulically active mineral and the glass phase is taking place after adding water, without having to supply an alkali activator. Hydrating abilities are influenced by the phase composition. Samples B_h and G_h do not have a high compressive strength, while the other samples have a good compressive strength about 10 MPa after 28 days of hydration. Samples for which compressive strength values are higher than 10 MPa contain mineral dicalcium silicate in the modification b. This mineral occurs in Portland clinker and thanks to its hydration there are the so-called C - S - H phases formed. These phases are bearers of the strength in the hydrated cement.

The highest values of the compressive strength were achieved with a mixture A_h . The slag for the preparation of this mixture contains the highest amount of mineral b - C_2S . Furthermore, this slag also contains minerals like tricalcium aluminate and akermanite which also contributes to the increased strength values. It is interesting to compare the compressive strength of mixtures made up of slags E and F. Mixtures containing the slag E and F have approximately the same compressive strength. Both slags come from one melting process. The slag E was of a lumpy character and the slag F was a breakdown product from these slags. The disintegration of the slag F into the fine grained fraction has occurred during its cooling as a result of transformation b - $C_2S @ g - C_2S$ [2,5]. The content of the hydraulically inactive mineral g - C_2S in the slag F is 35 %, while in the case of the lumpy slag E is 6 %. The content of hydraulically active phase b - C_2S is 7 % (slag F) and 17 % (slag E). The fact that the mixture prepared from slag F containing less b - C_2S but exhibits similar compressive strength characteristic as a mixture prepared from the slag E with a higher content b - C_2S is given by the presence of this phase and minerals like mayenite and merwinite in combination. The mineral mayenite is hydraulically active. This mineral can be found in the aluminous cement and it is typical for its fast reaction with water. Merwinite is regarded as a

low hydraulically active mineral [4,6]. The difference between the slag E and F can be observed not only in their mineralogical composition but in the chemical composition as well. Both slags come from the same melting process and from the same ladle. The diversity in their composition confirms the strong heterogeneity of these slags and imbalances in their solidification.

The hardening of the hydrated slags is also involved in the presence of the amorphous phase, especially in the case of slags containing free CaO [7]. Calcium hydroxide is the activator of the latent hydraulicity for the amorphous phase [8].

The compressive strength of samples prepared from the slags C and D were secured primarily by the presence of b - C_2S phase and also the brownmillerite and merwinite phases. Although, the b - C_2S phase can be considered to be the most important for ensuring the strength of products with water activated ladle slags.

The studied ladle slags which after adding water have sufficient strength are in accordance with condition $C/S > 2,7$. The low ratio C/S shows the slag B which is hydraulically inactive. The slag G has a satisfactory C/S ratio but its hydraulicity is low because its hydration was partly carried out before sampling. The slag G shown in the Table 2 contains a phase like tremolite, hydrogarnet and portlandite and these are typical for their water content. Other hydrated phases may be amorphous and therefore these are unidentifiable by the XRD analysis. Other slags did not contain the crystalline phase with comprising water in its structure.

In the Table 4 there are showed very low levels of hydration heat of samples B and G. The slag B does not contain a phase which would be involved in the hydration process (Table 2). This finding is confirmed by the fact that the samples prepared from the slag B did not show satisfactory compressive strength parameters after the hydration. A low development of hydration heat was recorded for the sample G as well. The slag G came in the course of its processing into contact with water before its sampling. Thus, it is probable that the partial hydration reaction could take place before the slag sampling.

Other samples of slags react with water to emit significantly more heat (during 24 hours more than $100 J \cdot g^{-1}$). The heat source in the first „wave“ are minerals of calcium aluminate group, like mayenite and tricalcium aluminate and other mineral brownmillerite. In the next period of time there is a hydration of other minerals like merwinite, akermanite, C_2S , CaO and MgO.

The hydraulic properties of ladle slags are incommensurable in comparison with Portland cement. In spite of that fact, there can be seen applications where the binding ability of the ladle slags can be used with success.

CONCLUSIONS

From gained information it can be concluded that a steel ladle slag has hydraulic properties. The hydraulic

properties are caused by the presence of phases β - C_2S (dicalcium silicate), C_3A (tricalcium aluminate), $C_{12}A_7$ (mayenite), C_4AF (brownmillerite) and C_2F (dicalcium ferite). The presence of hydraulic phases allows the slags to react with water, whereby the mixture is setting and hardening. This means that the slag has binding properties. Less significant may be further considered mineral C_3MS_2 (merwinite) which provides insignificant hardening of mass after reacting with water.

The most important phase for binding properties is β - C_2S . With the increasing content of this phase, a higher compressive strength in the hydrated ladle slags is ensured. The experiment has shown that the transformation of β - C_2S @ g - C_2S which occurs during cooling of the ladle slags cause their volume instability.

The emergence of required hydrating phases in the ladle slags is conditioned by a sufficient CaO content. Very good hydraulic properties were measured for ladle slags having the ratio CaO/SiO_2 higher than the value of 2,6. Hydraulic properties have only a timely sampled ladle slag, i.e. before its possible reaction with water in the slag yard. In practice, ladle slags cooling takes place outside with the support of the water spray.

Acknowledgements

This paper was created in the Project No. LO1203 „Regional Materials Science and Technology Centre -

Feasibility Program“ funded by Ministry of Education, Youth and Sports of the Czech Republic and in the projects No. SP2015/86 “Reduction of the energy demands of the material production processes” and No. SP2015/125 Thermal waste treatment and environmental protection.

REFERENCES

- [1] J. Vlček, J. Fiedor, Průmyslové odpady Strusky z výroby železa a oceli, ECOFER, Ostrava, 2015, pp. 48-86.
- [2] J. Hlaváč, Základy technologie silikátů, SNTL, Praha, 1988, pp. 445-464.
- [3] W. Kurdowski, Chemia cementu, Wydawnictwo naukowe, Warszawa, 1991, pp. 300-449.
- [4] L. Muhmood, S. Vitta, D. Venkateswaran, Cementitious and pozzolanic of electric arc furnace steel slags, Cement and Concrete Research 39 (2009) 2, 102 – 109.
- [5] S. Caijun, Characteristics and cementitious properties of ladle slag fines from steel production, Cement and Concrete Research 32 (2002) 3, 459-462.
- [6] D. Adolfsson, R. Robinson, F. Engström, B. Björkman, Influence of mineralogy on the hydraulic properties of ladle slag, Cement and Concrete Research 41 (2011) 8, 865-871.
- [7] C. Shi, P. Krivenko, D. Roy, Alkali-Activated Cement and Concretes, Taylor & Francis, London, 2006, pp.35-48.
- [8] L. Svoboda, Stavební hmoty, JAGA GROUP, Bratislava, 2007, pp. 42 – 108.

Note: The responsible for English language is Barbora Malkova, Ostrava, Czech Republic