

SLAGS FROM STEEL PRODUCTION: PROPERTIES AND THEIR UTILIZATION

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During steel production a considerable amount of slags is produced. In addition to its usual processing, as recycling in device for steel production and preparation of aggregates, it is also possible to apply less common slag processing ways. Depending on cooling mode of the steel slags these may show some binding properties. Geopolymer type binders can be prepared from the slag using alkali activators or the hydraulic properties of the dicalciumsilicate present in the slag can be induced by water. The paper summarizes present state of material utilisation of the steel slags with focus on emphasize of the possible sources of the slag volume instability. The influence of process of slag cooling on its phase composition is documented. It was also found that slags from real sources show different parameters compared to samples obtained for laboratory examination.

Key words: steel slags, slag hydraulicity, chemical and phase composition of slags, slag stability

INTRODUCTION

A slag originates as a by-product which cannot be prevented either at blast furnace process either at steel production. Subject to a melting aggregate in which a slag was formed, slags can be classified into a blast furnace slag and steel slag which is further divided in a furnace slag (formed in arc furnace or oxygen converter, tandem furnace or in open-hearth furnace) and a ladle slag, which is produced within steel processing in secondary metallurgy.

Production of slags is generally considerable at steel and iron production. In the Czech Republic approximately two million tons of blast furnace slags and almost one million tons of steel slags are produced. Based on the total production of pig iron and steel it means that approximately 380 kg of blast furnace slag is produced per one ton of pig iron and 180 kg of slag is produced per one ton of steel [1]. Upon the stated facts the slag can be considered as a large-volume by-product for which a satisfactory material utilisation must be inevitably found.

The chemical as well as phase composition of steel slags is very variable due to different facilities in which they originate and due to variability of produced steel brands. The portion of crystalline phases and glass phase also depends on cooling speed of melted slag. The following minerals can be found in the steel slags: merwinite, olivine, dicalciumsilicate, tricalciumsilicate, dicalcium- ferrite, C_4AF , akermanite, gehlenite, cristo-

balite, CaO, periclase, sulphides and others. The steel slags are heterogenous system which is often shown by non-stoichiometric composition of present phases. Comprehensive overview dealing with the chemical and phase compositions of blast furnace slag and steel slag is presented in work [2].

The steel slags, furnace and ladle ones as well, harden and get setting after mixing with water in case they contain dicalciumsilicate in β modification ($\beta-C_2S$) or tricalciumsilicate (C_3S). With respect to $\beta-C_2S$ and C_3S higher presence of (tricalcium aluminate) C_3A and other calciumaluminates phases is not favourable, because they react with water too quickly but at the same time they do not provide sufficient mechanical properties.

With respect to phase composition the slags may show the so called latent hydraulic (pozzolana) properties in addition to the hydraulic properties. A quickly cooled granulated blast furnace slag (GBFS) is a typical example of the technogenous pozzolana [3]. Such a slag can be successfully activated in alkaline way and geopolymer type binders exceeding bonding systems based on Portland clinker can also be prepared. Also the quickly cooled steel slags with assumed of glass phase content show the latent hydraulicity. Glass forming ability of the steel slags is quite limited in comparison with GBFS due to the relatively high content of CaO and low amount of SiO_2 in steel slag. [2, 4, 5].

Application of the blast furnace slags is on an acceptable level. After milling the GBFS is added to Portland clinker at Portland cement production or it is added to concrete mixtures. The slowly cooled blast furnace slags is magnetically demetallised and after modification of granulometry the slag is marked as artificial dense aggregates (particle density is up to $3,0 \text{ Mg.m}^{-3}$),

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Table 1 Possibilities of steel slags utilisation [1]

Slag	Application area	Processing requirements	Marking of product	Utilisation	Benefits
Steel furnace slag	Metallurgy	Demetallised slag with high FeO, content without requirement for cooling mode	Recyclate	Slag is a part of batch mixture in sintering plant and blast furnace	Saving of natural raw material resources
		Demetallised slag with high content of CaO, MgO, Al ₂ O ₃ , without requirement for cooling mode	Recyclate	Slag is dosed in furnace aggregate in which it was formed	Saving of natural raw material resources, reduction of energy intensity at primary slag formation
	Civil engineering	Slowly cooled demetallised slag with modified grain size, the slag must show low content of free CaO and MgO	Artificial heavy weight slag aggregates	Aggregates as a solidifying base, also can be used in asphalt mixtures and as aggregates for hydraulic engineering	Saving of natural raw material resources
		Quickly cooled slag, must be stabilised β -C ₂ S	-	Alternative binder system - component for cements, the utilisation way is not included in European standards system	Saving of natural raw material resources
		Quickly cooled slag, content of glass phase must be supported	-	A slag suitable for binders activated in alkaline way (geopolymer), the utilisation way is not included in European Standards System	Saving of natural raw material resources
Steel and ladle slags	Metallurgy	Demetallised slag with high content of CaO, MgO, Al ₂ O ₃ , without requirement for cooling mode	Recyclate	Slag is dosed in furnace aggregate in which it was formed	Saving of natural raw material resources, reduction of energy intensity at primary slag formation

which can be used even for more sophisticated applications [3].

Contrary to blast furnace slags, utilization of steel slags is more limited. Its recycling in melting aggregates of metallurgical factory is the simplest one. Iron which is present in form of oxides is thus reused. Also civil engineering represents interesting field for application of the furnace steel slags [6]. From the slags the heavy weight aggregates (particle density is above 3,0 Mg.m⁻³) are prepared. The utilisation of the stated aggregates is limited by its possible volume instability [7]. At present, ladle slags utilisation is not realised due to its inclination to disintegrate.

Possibilities of steel slags utilisation are shown in the Table 1.

EXPERIMENTAL METHODS

The slags under investigation were taken from metallurgical factories directly in liquid state from the units in which they were formed (samples Aq, As, Bq, Bs, Cq, Cs, Fq), or in solid state after cooling from the place of its processing (samples Fsa, Fsb, Fsc and G) or were taken from the place of its long-term stock-pile (samples D, E, H). The samples Aq, Bq, Cq and Fq were taken from ladle in liquid state and immediately cooled in water bath after sampling. Cooling of slags As, Bs and Cs was slow. Three pairs of slags are presented, which were taken from one melt of steel (Aq-As, Bq-Bs and Cq-Cs) with which a different cooling mode was subsequently applied. Solid samples of slags were taken from several spots with emphasis on provision of a representative sample. Each sampled slag amount was within 2 – 5 kg.

Chemical compositions of the slags were assessed using X-ray fluorescence method by ARL 8680s equipment.

The X-ray diffraction patterns of slags were recorded under CoK α irradiation ($\lambda = 1,78897 \text{ \AA}$, $U = 35 \text{ kV}$, $I = 25 \text{ mA}$) using the Bruker D8 Advance diffractometer equipped with fast position sensitive detector VANTEC 1. The measurements were carried out in the reflection mode. Phase composition was evaluated using the PDF 2 Release 2004 database (International Centre for Diffraction Data).

A shortened record of chemical compounds is used in the work when C means CaO, S – SiO₂, A – Al₂O₃, then C₂S is 2CaO·SiO₂, etc.

RESULTS AND DISCUSSION

Chemical composition of slags is stated in the Table 2, phase composition in the Table 3.

The selection of the analysed slags does not directly correspond with frequency of its production, but accents the diversity of its chemical and phase compositions and further it adverts to the change of slag parameters during its processing. The ladle slag was the most numerously represented one from the set of presented slags. Its low rate of material utilisation is the reason of the increased interest in this slag.

In case of analyzed steel slags the basicity value was lower than 1,5 for slags F type and C type. Other steel slags (furnace and ladle ones) have basicity value higher than 1,5. The ladle slags with higher content of SiO₂ originate due to intended addition of slag-making wolastonite admixture.

Table 2 Chemical composition of slag

Slag	Fe _{metal}	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe _{total}	Basicity
	/ wt%								
Aq	---		1,1	18,6	11,3	53,9	14,0	0,8	2,3
As									
Bq									
Bs			2,8	24,1	2,4	62,7	6,8	2,0	2,6
Cq									
Cs			1,8	24,1	16,9	34,4	21,5	1,25	1,4
D	0,4	16,1	8,2	16,3	6,2	47,0	5,0	18,6	2,3
E	0,5	16,0	12,6	14,7	4,1	40,7	10,9	21,6	2,7
Fq	0,5	1,8	0,6	37,9	7,0	38,7	12,8	2,2	1,0
Fsa	0,5	12,0	7,6	27,8	4,3	36,9	10,3	15,1	1,5
Fsb	0,6	10,2	8,3	27,8	4,5	37,7	10,2	14,2	1,5
Fsc	0,4	11,6	7,1	28,0	4,2	36,2	11,8	14,2	1,5
G	0,6	21,8	12,4	12,8	2,0	38,9	11,0	26,0	3,4
H	0,8	21,6	12,7	18,7	5,3	28,7	11,4	26,3	1,7

Low iron content is typical for ladle slags according to references information [4]. Considering the metallurgical processes running in secondary metallurgy, the ladle slag contains iron in low amount. The knowledge that this fact was confirmed only in case of slags taken in liquid state is important finding of this work. The sample taken consequently in this way contains only

slag. Other samples of ladle slag which were taken in particular nodal points of the subsequent processing or its final storage contain iron. Once the steel is cast the ladle together with rest of uncast steel with slag is transported to the place of its processing where the slag is frequently cooled with water. Part of the iron present in the steel is being oxidised at this moment and phases with content of iron become part of the slag. The given opinion is well confirmed by analysis of F type samples, which is slag from the same melt taken in various nodal points of its formation or processing. The sample Fq was taken from casting ladle and shows a low iron content (Fe_{total} 2 wt%). The sample Fsa presents the same slag which was taken after its cooling. Here the slag contains even 15 wt% of total iron. Similar content of iron (Fe_{total} 14 wt%) is shown by samples Fsb and Fsc that were taken after granulometric separation of the same slag to grain size 0 – 8 mm resp. 6 – 64 mm. Also slags D and E taken from ladle slag stock-pile contain approximately 20 wt% of the total iron. Similarly like the sample Fq, also samples Aq, As, Bq, Bs, Cq and Cs, that were also taken in liquid state directly from the casting ladle show the low content of iron (Fe_{total} do 2 wt%).

The iron in slags almost does not occur in fundamental form but it is part of other phases. The funda-

Table 3 Phase composition of slag

q.c. quickly cooled s.c. slowly cooled BOF slag slag from Basic oxygen converter S-M slag slag from Open hearth furnace	Aq	As	Bq	Bs	Cq	Cs	D	E	Fq	Fsa	Fsb	Fsc	G	H
	Ladle slag q.c.	Ladle slag s.c.	Ladle slag q.c.	Ladle slag s.c.	Ladle slag q.c.	Ladle slag s.c.	Slag landfill	Slag landfill	Ladle slag q.c.	Industrial cooled slag	Grinding slag 0- 8 mm	Grinding sl. 6- 64 mm	BOF slag	S-M slag
Phase														
CFS Ca ₆ O ₅ xSi ₂ O ₁₀ xFe _x	+		+											
Mayenite (Ma) Ca ₁₂ Al ₁₄ O ₃₃	+	+	+				+							
Dicalcium silicate β-C ₂ S	+	+	+	+				+			+	+	+	+
Dicalcium silicate γ-C ₂ S	+	+	+	+				+						
Periclase (P) MgO	+	+	+	+				+						
Fluorspar CaF ₂				+										
Gehlenite Ca ₂ Al ₂ SiO ₇						+								
Bredigite (B) Ca ₁₄ Mg ₂ (SiO ₄) ₈								+						
Diopside (D) Ca(Mg,Al)(Si,Al) ₂ O ₆										+	+	+		
Wüstite FeO											+	+	+	
Fe ₃ O ₄														
Fe														
Merwinite (M) Ca ₃ Mg(SiO ₄) ₂						+		+						
Akermanite (A) Ca ₂ Mg(Si ₂ O ₇)										+	+	+		
Melilite (akermanite + gehlenite solution)														
Tricalcium silicate C ₃ S				+										
Brownmillerite C ₃ AF													+	+
Enstatite (E) Mg ₂ Si ₂ O								+						
CaO													+	
RO phase (FeO) _x (MgO) _y						+					+	+		+
RO phase (FeO) _x (MnO) _y						+								
Quartz SiO ₂							+				+	+		
Portlandite (P) Ca(OH) ₂														+
Monticellite CaMgSiO ₄														+
Mg ₆ Al ₂ (CO ₃) ₂ (OH) ₁₆ ·4H ₂ O											+	+		

mental iron is magnetically separated from the slags. Chemical analysis is generally performed for slags taken from casting ladle before casting of the steel. The analyses almost do not show the total iron which is at variance with really occurring ladle slags.

C₂S in modifications β and γ are the most often occurring phases in monitored steel slags, next phases are akermanite, periclase, mayenite, RO phases and others. Phase composition of steel slags is relatively various and out-of-balance and on that ground the precise quantitative analysis of samples by X-ray diffraction method is practically impossible. From the registered diffraction patterns only higher and lower occurrence rates of particular phases can be assessed. The quickly cooled slags (Aq, Bq) show higher amount of β-C₂S than slags As, Bs, which contain predominantly β-C₂S (Figure 1).

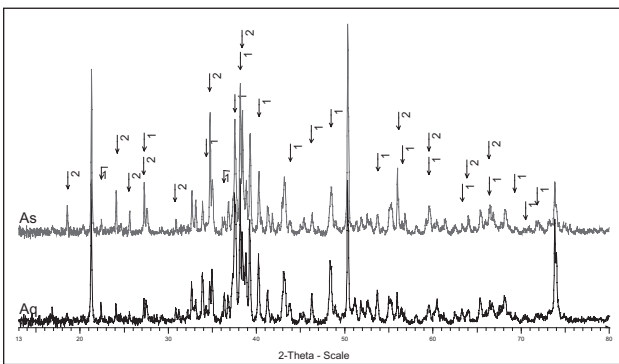


Figure 1 XRD pattern of slags Aq and As; 1- β-C₂S, 2 - γ-C₂S

The β-C₂S content is also important due to its direct hydraulicity. Slag with sufficient content of this phase can be used for preparation of alternative binder systems. The C₂S phase is also important due to monitoring of volume stability of ladle slags. Transformation of β-C₂S → γ-C₂S running during cooling of slags is one of the causes of ladle slag disintegration. Change of modification is connected with change of density within 3,29 → 2,97 Mg.m⁻³. Under balanced conditions of the cooling the β-C₂S is stable in thermal interval from 680 - 630 to 500 °C. At temperature lower than 500 °C the β-C₂S is stable. If the slag is cooled quickly, the transformation does not occur [8, 9].

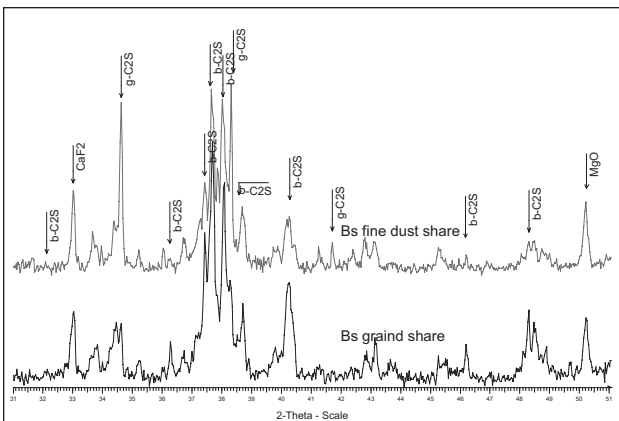


Figure 2 Representation of β-C₂S a β-C₂S in piece and dust slags

Samples of quickly cooled slags were characterised with presence of bigger aggregates of β-C₂S compared to slowly cooled slags that disintegrated in dust share. As an example the comparison of diffraction patterns of fine dust portion and coarse-grained portion are shown in Figure 2. The shares were separated from the slag Bs. The differences in phase composition are demonstrated by higher intensities of diffractions γ-C₂S in the fine dust share and on the contrary the β-C₂S shows higher intensities in case of coarse grained share.

Other reason for volume instability is the presence of free CaO and/or MgO. By hydration of these components relevant hydroxides are formed which are able of further carbonisation, more detail can be found in the work [1], [9].

The presented slags mostly show crystalline character. Quick cooling of melted slags was performed with aim to ensure its amorphous glass character. This was successful only in case of two ladle slag samples. The slag Fq includes a high share of glass forming SiO₂ (38 wt%) and basicity is 1,0. Other sample with amorphous structure is the slag Cq, where content of SiO₂ (24 wt%) is lower in comparison with the slag Fq, but also contains a lower share of alkaline components, the basicity reaches the value 1,4.

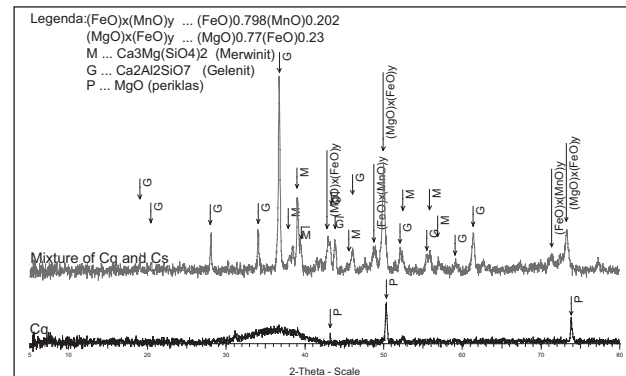


Figure 3 XRD pattern of slags Cq and mixture of Cq and Cs

The fact the x-ray diffraction with other slags did not mean presence of glassy phase does not exclude its factual presence. The diffraction pattern on Figure 3 is the proof. The X-ray record of mixture of slags Cq and Cs (60:40 wt%) did not noticed content of glass while the record of glassy phase has typical XRD course for amorphous materials.

From the Table 2 it is also obvious that industrial slag processing within the metallurgical factory forms its phase composition differently from composition of slags taken from melting units. While the slag Fq taken from the casting ladle shows amorphous structure, the same slag taken from different nodal points of its further processing (samples Fsa, Fsb and Fsc) shows crystalline character. Cooling speed that in industrial conditions in respect of slag volume (approximately 10 tons) took place notably more slowly than in case of incomparably smaller laboratory sample (approx. 5 kg) is the reason. At the same time the phase composition of the

slag in various processing nodal points is unchanged as assumed.

CONCLUSIONS

Origination of the slags during the steel production is inevitable and cannot be prevented. Utilisation of the slags is limited by its chemical and phase composition. In case of slag recycling in melting plants for steel production the present iron is being used and eventually other components CaO, MgO and Al_2O_3 as well. In the mentioned case the chemical composition of the slags is decisive. On the contrary the phase composition of slags is decisive at its processing for aggregates or at utilisation of slag binder properties.

To find an optimal way for utilisation of steel slags it is necessary to monitor parameters of the slags during its processing. Owing to processes to which the slag is exposed to in this phase, its chemical and phase composition may change what is essential fact for slag utilisation.

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Note: The responsible translator for English language is the lectures from TU Ostrava, Czech Republic