

^{1,3} Irina VÎLCIU, ² Maria NICOLAE, ³ Manuela-Daniela STOICA

DIFFRACTOMETRIC ANALYSE OF STEEL SLAGS VIEWING THEIR USE FOR ROAD CONSTRUCTION

^{1,3} ECOLOGICAL UNIVERSITY OF BUCHAREST, ROMANIA

² POLITEHNICA UNIVERSITY BUCHAREST, ROMANIA

ABSTRACT: The development of steel industry must provide solutions for environmental protection issues and using of production wastes, thus, aiming mineral resources and energy savings. The slag is the main waste type resulting from metal making and represents a valuable raw material for many industries. Steel slag is a product of much importance for road construction, successfully substituting natural materials. The X-ray diffraction analysis carried out in this paper gives a deeper insight in the mineralogical constitution and behavior of such slags when used for road construction purposes.

KEYWORDS: steel slag, recycling, road construction

❖ INTRODUCTION

The steel slag shows good technical and ecological properties, thus being used for the manufacturing of aggregates required by road construction. The reuse steel making slags for road construction must comply with an essential requirement, namely their volumetric stability. This is a condition to be met especially by steel slag, its composition having free calcium and magnesium oxides. The hydration of these oxides increases its volume, possibly causing important damages [1]. Therefore, these slags need a so-called “ageing” time (6 to 12 months) in order to be reused without creating any problems. The increasing use of the converter slag in application fields which demand high qualities is possible by improving the volumetric stability. Insufficient volumetric stability results from the presence of free CaO and occasionally, MgO in the slag.

❖ QUANTITATIVE EVALUATION ON SHORT AND AVERAGE TERM OF STEEL SLAGS FROM ROMANIA

In order to perform a quantitative evaluation of slags from Romania, the following presumptions were made:

- ❖ Converter and electric steel production in 2015 (average term): 5% increase for converter steel production and 10% increase for electric steel production means 9,173 mil. t/year;
- ❖ Steel treated by secondary metallurgy LF type: 7,5 mil. t in 2008 and 8 mil. t in 2015;
- ❖ There is no forecast concerning any progress within the specific slag share in steel industry.

Table 1. Quantitative evaluation of steel slags from Romania [2]

Slag type	2006		2008		2015	
	Production, (steel) mil. t/year	Generated slag mil. t/year	Production, (steel) mil. t/year	Generated slag mil. t/year	Production, (steel) mil. t/year	Generated slag mil. t/year
Converter slag	5,5	0,660	5,745	0,689	6,032	0,724
Electric furnace slag	1,65	0,240	2,855	0,414	3,141	0,455
Secondary metallurgy slag (LF)	5,25	0,150	6,000	0,156	8,000	0,208
Total	Total	1,250	Total	1,759	Total	1,987

Under conditions presented above, Table 1 and Fig.1 present the quantitative evaluation of steel slags. Based on the presented evaluation, one considers that on short term the generated total slag amount will increase up to approximately 1,75 mil. t and on average term even to 1,9 mil. t.

❖ STEEL SLAG CHARACTERIZATION

The chemical compositions and main performances of analyzed slags as compared with those of crushed stone and pit ballast products most frequently used for road construction are shown in Table 2 and 3.

Steel slag is a dense rock having a raw density > 3,2 g/cm³. Thus, steel slag is successfully used for road construction (e.g. for portant layers or asphalt layers submitted to high loads). Steel slags are resistant to erosion. By providing a granulation distribution determined by technical regulations, one can observe that the manufactured mineral materials mixtures have to resist to repeated frost-defrost cycles.

Steel slags contain pores, which provide a durable adherence if they are used as mineral material for wear resistant layers. Thus, steel slags are recommended to be used in wear resistant asphalt layers as chippings. The high values of polishing strength are tied to the low shock attrition value (less than 18% of the weight), which is concomitantly the precondition of manufacturing asphalt layers having the capability to reduce the level of traffic noise.

Due to the metallurgical technology, steel slags contain only low amounts of CaO not chemically bound and/or free magnesium oxides. Because these mineral constituents retain water by increasing their volume, for road construction one must check the volumetric constancy [3].

The portant capacity values required by standards for the manufacturing of frost-resistant layers and portant layers consisting in ballast were easily reached and frequently, outstripped due to the 100% crushed stone content, the compact shape of the grains and the harsh surface of steel slag.

These favorable properties give a high deformation resistance to portant asphalt, asphalt binder and wear resistant asphalt layers after placing and compacting.

Due to its chemical and mineralogical composition, the slag desintegrates in free atmosphere (in stockpiles) under the action of atmospheric factors, reaching a quasistatic state after cca. 6 months [4]. This duration can be diminished by watering the fresh slag, the temperature of water ranging from 40 to 50°C. The slag further desintegrated/attrited under the influence of atmospheric factors cause its decay due to the carbonation of the hydrated lime.

❖ DIFFRACTOMETRIC ANALYSIS

In order to identify the structural constituents in slags, we have performed phase-analyses on diffractometer DRON 2.0. The working parameters used were:

- ❖ 30 kV tension; anodic current 34 mA;
- ❖ radiation used CoK α ;
- ❖ angular frequency $\omega=1/2^0$ min.

The phases identified from the viewpoint of qualitative and quantitative estimation and their specific diffraction parameters (diffraction angles, interplanar distances, Miller indices of crystallographic planes) are presented in Table 4.

Four slag specimens sampled from different zones of the integrated process line and a specimen from the electric furnace process line have been examined. The samples have been codified as follows:

- ❖ Code OLD - slag removed after LD converter steelmaking process;
- ❖ Code LF - slag resulting from treatment on LF installation;
- ❖ Code TC - slag resulting after stirring in the casting ladle;
- ❖ Code OE - slag removed after electric furnace steelmaking process.

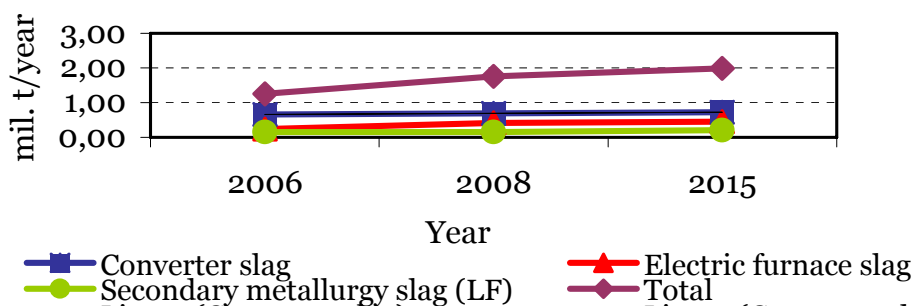


Fig. 1. Quantitative evaluation of steel slag from Romania [2]

Table 2. Chemical compositions for steel slag

Constituent %	Converter slag	Secondary metallurgy slag (LF)	Electric furnace slag - EAF (average)
CaO	40,10	49,56	40,78
SiO ₂	17,80	14,73	17,81
FeO	12,92	0,44	9,25
Fe ₂ O ₃	6,58	0,22	3,97
Fe _{tot}	21,18	0,68	12,51
Fe _{met}	6,55	0,17	2,56
MnO	6,52	0,39	9,79
MgO	6,32	7,88	8,53
P ₂ O ₅	1,13	0,20	0,74
S	0,46	0,80	0,30
Cr ₂ O ₃	0,00	0,00	1,42
Al ₂ O ₃	2,04	25,55	4,23
C	0,45	0,07	0,64
CaO _{liber}	3,90		

Table 3. Main characteristics of steel slags

Characteristics	Slags	Crushed aggregates	Pit ballast aggregates
Apparent density, kg/m ³	3300-3500	2500-2700	2600
Water absorption, mass %	0,7-1,0	<0,5	<0,5
Grain shape - shape factor, %	<10	<10	<10
Crushing degree, mass%	13-17	17	21
Los Angeles test machine, wear %	18-22	12	21
Compression strength, N/mm ²	320-350	260	250
Frost-thaw resistance, mass% - frost cleftness factor	<0,5	<0,5	<1
Bitum adhesivity, %	>90	>80	>80
Polishing factor (PSV), %	58-61	48	45

Table 4. Phases identified in iron and steel slags

Test code	Identified phases	Proportion of phase [%]	Miller index of planes crystallographic (hkl)	Crystallographic system
OLD	$2CaO \cdot Al_2O_3 \cdot SiO_2$ gehlenite	28,3	(111); (201); (211); (220); (311); (400); (323);	T
	Fe_2O_3	39,0	(101); (112); (101); (102); (202); (123); (103); (224); (134); (204); (235);	R
	CaO	22,5	(111); (200); (220); (222); (331); (400); (420);	C.F.C
	FeO	10,2	(111); (200); (220); (311); (222);	C.F.C
LF	$\beta CaO \cdot SiO_2$ wollastonite	38,0	(400); (310); (501); (203); (710); (313); (631); (322); (314); (223); (205);	Tr
	$CaO \cdot Al_2O_3 \cdot 2SiO_2$ anorthite	36,1	(220); (004); (204); (132); (130); (111);	Tr
	CaS	11,3	(111); (200); (220);	C.C.
	αAl_2O_3	14,6	(112); (102); (202); (123); (234); (202); (131); (134); (225);	H
TC	$2CaO \cdot Al_2O_3 \cdot SiO_2$ gehlenite	14,7	(111); (211); (212); (400); (410); (600);	T
	γCa_2SiO_4	33,9	(020); (103); (113); (121); (104); (311);	O
	αAl_2O_3	19,0	(112); (102); (202); (134); (231); (204);	H
	CaO	9,4	(200); (220); (332); (222); (400);	C.F.C
	$Al_2O_3 \cdot SiO_2$	23,0	(122); (230); (042);	O
OE	MnO_2	8,0	(111); (200); (301);	T
	MnO	13,9	(111); (200); (220);	C.F.C.
	Fe_2SiO_4	52,5	(002); (130); (022); (112); (230); (150); (113); (241); (152); (311); (321); (224); (400); (314); (174);	O
	Fe_7SiO_{10}	25,6	(311); (411); (112); (312); (131); (114); (121); (604);	M

- After analyzing the results obtained, one can state following:
- ❖ Slag code OLD contains iron oxides as FeO (10,2% quantitative ratio), but also Fe_2O_3 in a higher proportion, 39%;
 - ❖ Slag code TC, besides CaO, Al_2O_3 and simple or complex calcium and aluminum silicates *does not contain iron oxides*;
 - ❖ Slag code OE contains manganese oxides MnO_2 , MnO and iron silicates of Fe_2SiO_4 , Fe_7SiO_{10} types;
 - ❖ Slag code LF contains Ca, Si and Al oxides.

The graphic of diffractogramms is emphasized in Figures 2-5.

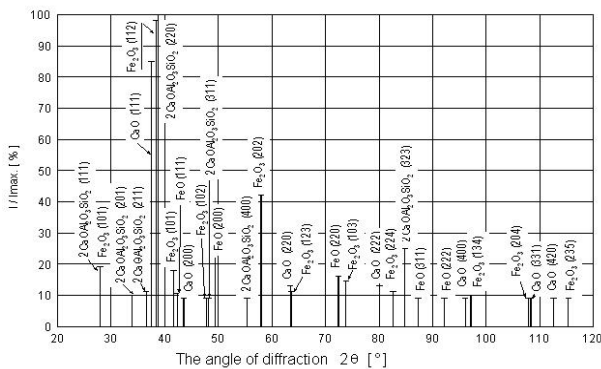


Fig. 2. Relative intensity of the diffraction lines function of the diffraction angle for sample code OLD.

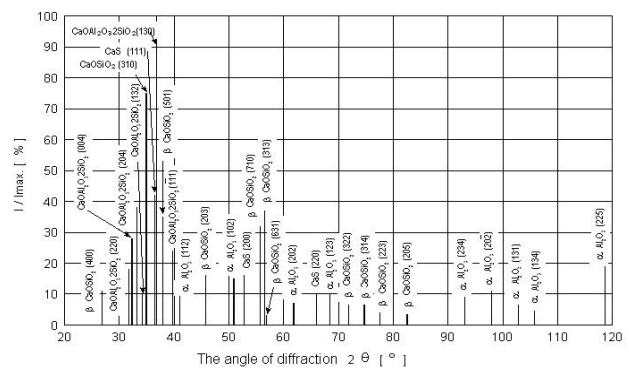


Fig. 3. Relative intensity of the diffraction lines function of the diffraction angle for sample code LF.

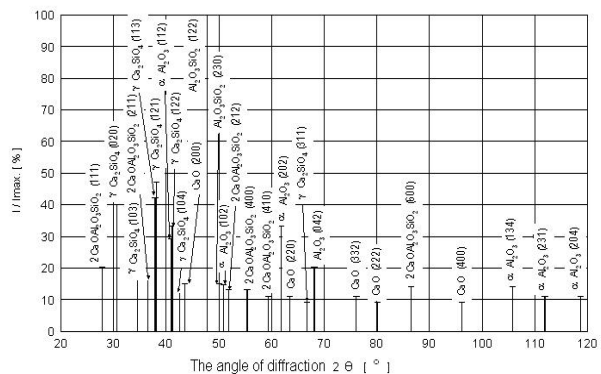


Fig. 4. Relative intensity of the diffraction lines function of the diffraction angle for sample code TC.

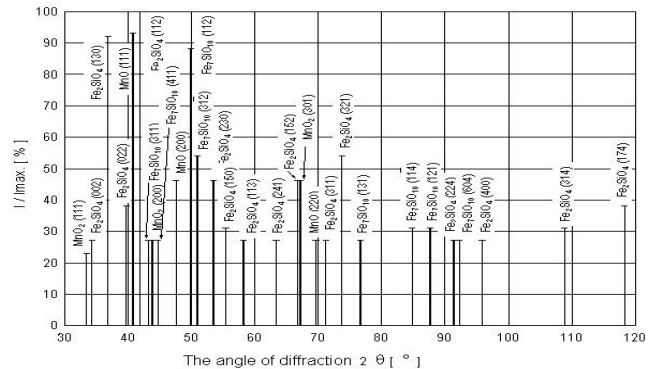


Fig. 5. Relative intensity of the diffraction lines function of the diffraction angle for sample code OE.

❖ DISCUSSION

The LF slag comprises mainly CaO. During the cooling process, can be emphasized a beta-gamma structural transformation of dicalcic silicate. Furthermore, it results a pulverized material by the reaction of calcium oxide with carbon dioxide, in the presence of atmospheric humidity (CaO - 50-60%, MgO - 5%, SiO₂ - 5-10% and Al₂O₃ - 5-10%).

After analyzing the converter slag in the CaO-FeO_n-SiO₂ system one can understand how it is possible to avoid this phenomenon (Figure7).

Similarly, the converter slag is deficiently as concerns its volumetric stability. The volumetric stability is influenced especially by the free CaO content. During the free air deposition, over time, due to the atmospheric humidity and rain, the major part of free lime is transformed into calcium hydroxide. This reaction is accompanied by a volume increase of almost 100% and an attrition of the slag aggregate structure. This is disadvantageous because of the amount of dust generated that creates dysfunctions.

The primary converter slag belongs rather to the FeO_n-SiO₂ system. The higher is the lime amount, the closer to the final slag, which can be observed in the saturation zone in 2CaOSiO₂, 3CaOSiO₂ and CaO. Therefore, the converter slag contains important amounts of free CaO, which influence the volumetric stability of the solid slag through hydration phenomena. In order to avoid this phenomenon, after the final slag has fulfilled its function in the converter, it is preferred to treat it and to let it migrate into the unsaturated slag zone in CaO and C₂S (eventually by increasing SiO₂ amount).

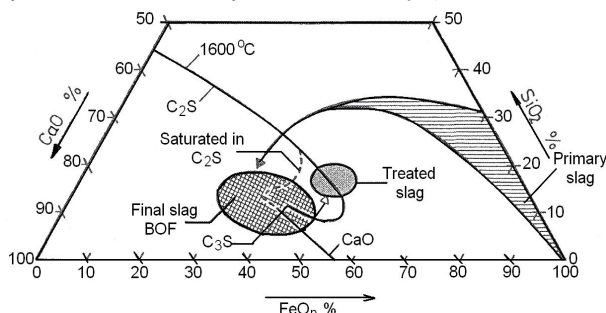


Fig.7. Converter slag location in the system CaO-FeO_n-SiO₂

❖ CONCLUSIONS

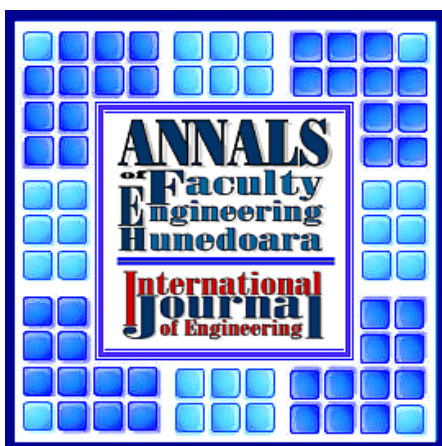
Due to its raw density, the steel slag is considered a dense rock successfully used in road construction for portant layers or asphalt layers submitted to high loads.

During the cooling of the LF slag, besides the beta-gamma structural transformation of dicalcic silicate, the calcium oxide reacts with carbon dioxide and in humid atmosphere one can obtain a pulverous material (CaO - 50-60%, MgO - 5%, SiO₂ - 5-10% and Al₂O₃ - 5-10%).

The converter slag is volumetrically instable, being influenced by the free CaO content, thus, requiring a free air deposition and due to the atmospheric humidity, the major part of the free lime is transformed into calcium hydroxide.

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