U.P.B. Sci. Bull., Series B, Vol. 69, No. 2, 2007 ISSN 1454-2331

X-RAY DIFFRACTION ANALYSIS OF STEEL SLAG AND BLAST FURNACE SLAG VIEWING THEIR USE FOR ROAD CONSTRUCTION

Maria NICOLAE[1], Irina VÎLCIU[2], Florian ZĂMAN[3]

Dezvoltarea siderurgiei impune rezolvarea problemelor de protecţie a mediului înconjurător şi utilizarea deşeurilor de producţie urmărindu-se astfel obţinerea unei economii de resurse minerale şi energetice. Zgura reprezintă principalul deşeu rezultat de la elaborarea metalului şi reprezintă o materie primă valoroasă pentru multe ramuri ale industriei. Zgura de oţel este un produs de valoare pentru construcţia de drumuri, înlocuind cu succes materialele naturale. Analiza prin difracţie de raze X dă o mai profundă înţelegere a comportării unor asemenea zguri ca material de construcţie.

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, blast furnace slag, recycling, road construction.

1. Introduction

The steel slag shows good technical and ecological properties, thus being used for the manufacturing of aggregates required by road construction. The reuse of furnace and 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 hydratation 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

---

[1] Prof., Faculty “Science and Engineering of Materials”, University “Politechnics” of Bucharest, Romania;

[2] Eng., Faculty “Science and Engineering of Materials”, University “Politechnics” of Bucharest, Romania;

[3] Eng., Metallurgical Research Institute (ICEM SA), Bucharest, Romania.

possible by improving the volumetric stability. Insufficient volumetric stability results from the presence of free CaO and occasionally, MgO in the slag.

2. Quantitative evaluation on short and average term of steel and blast furnace 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 2008 (short term) complying with the restructuring strategy of steel industry will amount to 8,6 mil. t/year;
- 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;
- desulphurized iron: 2,5 mil. t in 2008 and 4 mil. t in 2015;
- 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.

Under conditions presented above, Table 1 and Fig.1 present the quantitative evaluation of steel slags.

Table 1

Quantitative evaluation of steel and blast furnace slags from Romania [2]

Slag type	2006		2008		2015	
	Production, (steel/iron) mil. t/year	Generated slag mil. t/year	Production, (steel/iron) mil. t/year	Generated slag mil. t/year	Production, (steel/iron) mil. t/year	Generated slag mil. t/year
Slag from iron desulphurization	1	0,200	2,500	0,500	3,000	0,600
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

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.

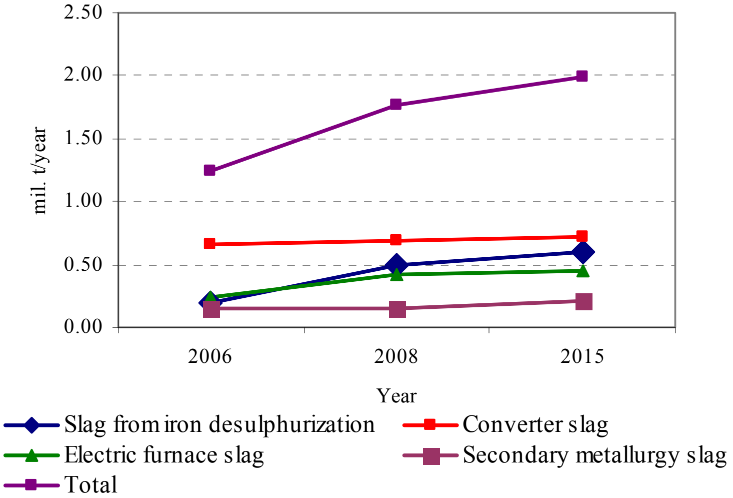

Fig. 1. Quantitative evaluation of steel slag and blast furnace slag from Romania [2].

The most spectacular increase will be that of slag resulting from iron desulphurization, due to the large scale expansion of this technology in the steelworks with converters (0,2 mil. t in 2005 and 0,6 mil. t in 2015).

3. Steel slag and furnace 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/cm^3. 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 errosion. By providing a granulometric distribution determined by technical regulations, one can observe that the manufactured mineral materials mixtures have to resist to repeated frost-defrost cycles.

Steel slags contains 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].

Table 2

Chemical compositions for steel slag and blast furnace slag

Constituent %	Slag from iron desulphurization	Converter slag	Secondary metallurgy slag (LF)	Electric furnace slag – EAF (average)
CaO	34,16	40,10	49,56	40,78
SiO_2	20,66	17,80	14,73	17,81
FeO	0,32	12,92	0,44	9,25
Fe_2O_3	0,06	6,58	0,22	3,97
Fe_{tot}	0,46	21,18	0,68	12,51
Fe_{met}	22,69	6,55	0,17	2,56
MnO	0,05	6,52	0,39	9,79
MgO	9,44	6.32	7,88	8,53
P_2O_5	0,01	1.13	0,20	0,74
S	1,47	0,46	0,80	0,30
Cr_2O_3	0,00	0,00	0,00	1,42
Al_2O_3	10,13	2,04	25,55	4,23
C	1,01	0,45	0,07	0,64
CaO_{liber}		3.90		

Table 3

Main characteristics of steel and blast furnace slags

Characteristics	Slags	Crushed aggregates	Pit ballast aggregates
Apparent density, kg/m^3	3300-3500	2500-2700	2600
Water absorbtion, 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
Polising factor (PSV), %	58-61	48	45

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 50^0C. The slag furtherly desintegrated/attrited under the influence of atmospheric factors cause its decay due to the carbonation of the hydrated lime.

4. Results on X-ray diffraction 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; annodic current 34 mA;
- radiation used CoKα;
- angular frequency $\omega=1/2^0$ min.

The phases identified from the viewpoint of qualitative and quantitative estimation and their specific diffractometric parameters (diffraction angles, interplanar distances, Miller indices of crystalographic 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 sample have been codified as follows:

- code D – slag resulting from iron desulphurization;
- 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.

After analyzing the results obtained, one can state following:

- Slag code D contains, besides the constituents which are specific to the reactions within the desulphurization installation (calcium silicate $Ca_3Si_2O_7$, CaC_2, MgO), also Fe_2O_3, their quantitative ratio being 18,7%. In addition was also put in evidence but also Fe as chemical element, in a higher proportion (21,0%);
- 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 aluminium 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.

Table 4

Phases identified in iron and steel slags

Test code	Identified phases	Proportion of phase [%]	Miller index of planes crystallographic (hkl)	Crystallographic system
D	$Ca_3Si_2O_7$ rankinite	40,3	(202); (112); (221); (121); (320); (124); (115);	M
	CaC_2	7,7	(101); (110); (111);	T
	Fe_2O_3	18,7	(112); (101); (202); (123); (224); (202); (134); (231);	R
	Feα	21,0	(110); (200); (211); (220);	C.V.C.
	MgO	12,3	(111); (200); (220); (400);	C.C.
OLD	$2CaO\cdot Al_2O_3.SiO_2$ 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
	$CaO\cdot Al_2O_3.2SiO_2$ 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	$2CaO\cdot Al_2O_3.SiO_2$ gehlenite	14,7	(111); (211); (212); (400); (410); (600);	T
	γ Ca_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

The main features of X-ray diffraction patterns of the investigated samples are emphasized in Figs. 2-6.

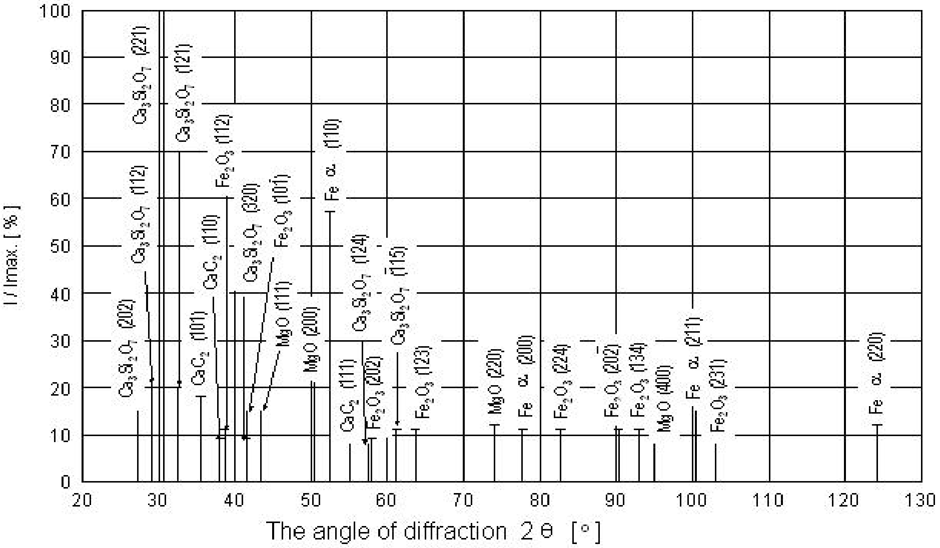

Fig. 2. Relative intensity of the diffraction lines function of the diffraction angle for sample code D.

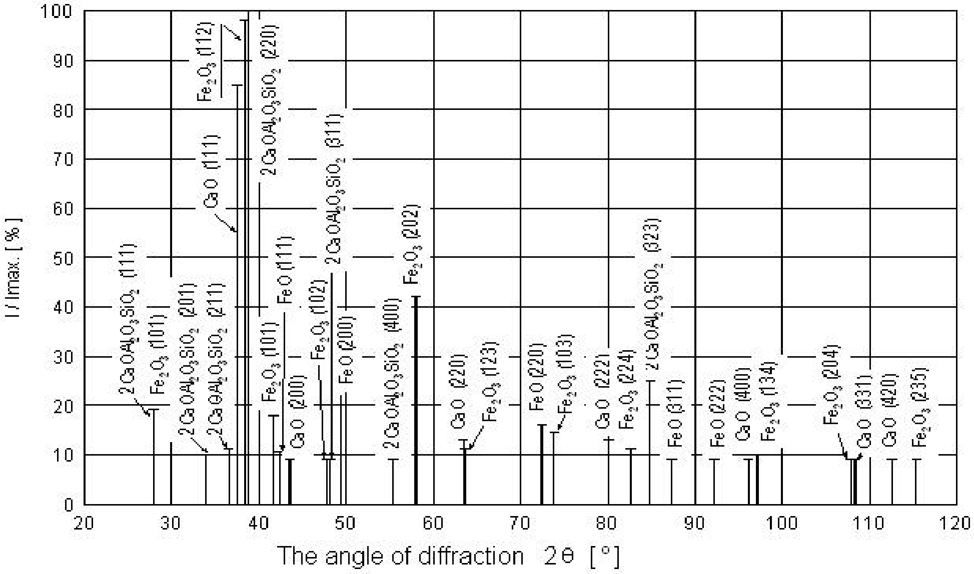

Fig. 3. Relative intensity of the diffraction lines function of the diffraction angle for sample code OLD.

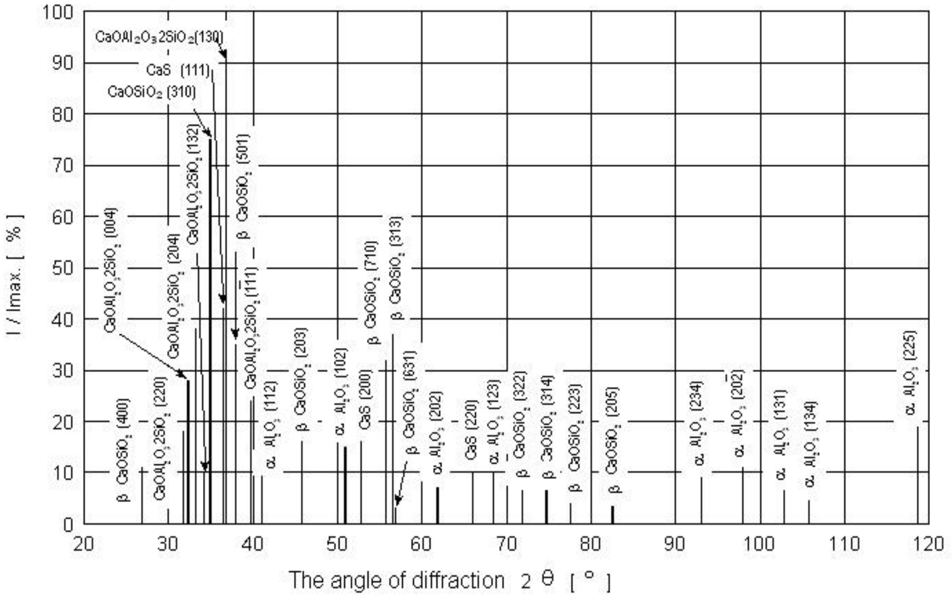

Fig. 4. Relative intensity of the diffraction lines function of the diffraction angle for sample code LF.

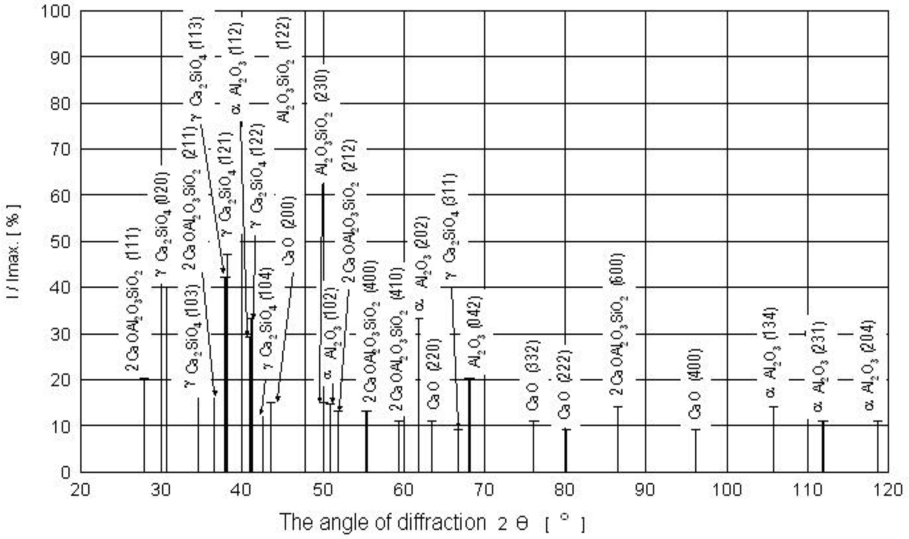

Fig. 5. Relative intensity of the diffraction lines function of the diffraction angle for sample code TC.

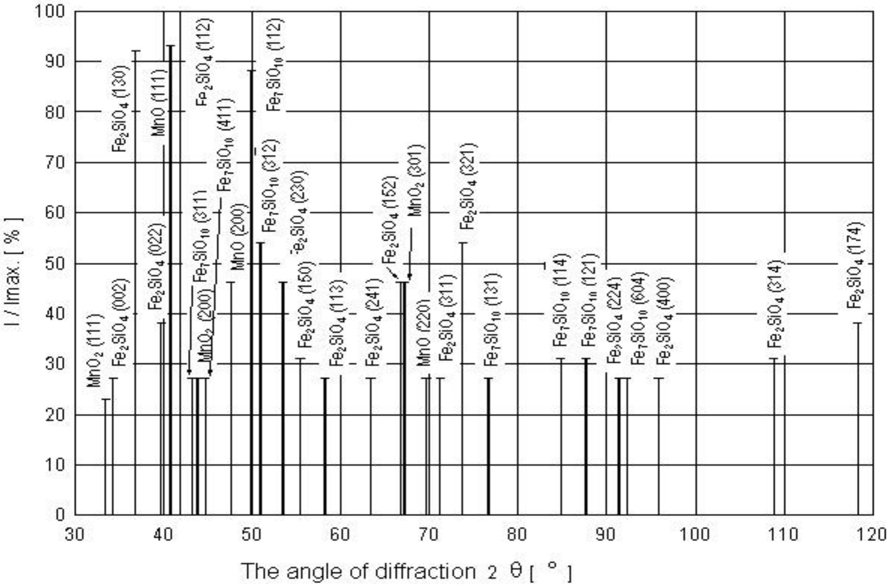

Fig. 6. Relative intensity of the diffraction lines function of the diffraction angle for sample code OE.

5. 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 pulverulent material by the reaction of calcium oxide with carbon dioxide, in the presence of atmospheric humidity (CaO – 50-60%, MgO – 5%, SiO_2 – 5-10% and Al_2O_3 – 5-10%).

After analyzing the converter slag in the CaO-FeO_n–SiO_2 system one can understand how it is possible to avoid this phenomenon (Fig. 7).

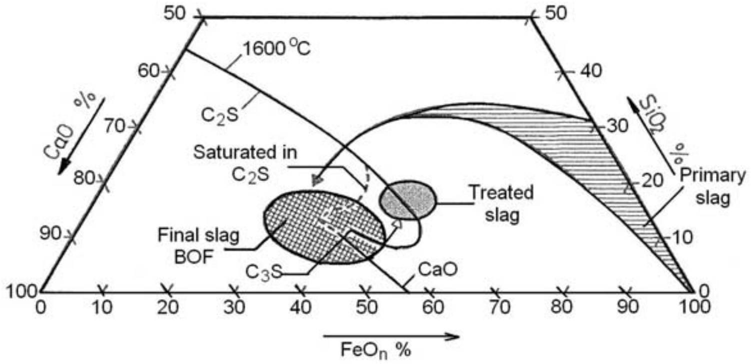

Fig.7. Converter slag location in the system CaO-FeO_n-SiO_2.

Similarily, the converter slag is defficientli as concerns its volumic stability. The volumic 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 hidroxide. 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 disfunctions.

The primary converter slag belongs rather to the FeO_n–SiO_2 system. The higher is the lime amount, the closer to the final slag, which can be observed in the saturation zone in $2CaOSiO_2$, $3CaOSiO_2$ and CaO. Therefore, the converter slag contains important amounts of free CaO, which influence the volumic 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 C_2S (eventually by increasing SiO_2 amount).

6. 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 humide atmosphere one can obtain a pulverulent material (CaO – 50-60%, MgO – 5%, SiO_2 – 5-10% and Al_2O_3 – 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 hidroxide.

REFERENCES

[1]. *Aşmin B., Smirnov L., ş. a.*, Prelucrarea zgurelor metalurgice - Sinteză Informstal, nr. 20, 1988;

[2]. *Nicolae M., Nicolae A., ş.a.*, Dezvoltarea durabilă în siderurgie prin valorificarea materialelor secundare, Editura PRINTECH, Bucureşti 2004;

[3]. *Kuehn M., Drissen P.*, Future development of minimising the residues in EAF steelmaking, Forschungsgemeinshchaft eisenhüttenschlachen E.V., Duisburg, Germany;

[4]. *** Integrated Pollution Prevention and Control (IPPC), Best Available Technicques Reference Document on the Production of Iron and Steel, December 2001;