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MINIMIZATION OF THE CALCIUM OXIDE CONTENT IN THE STEEL SLAG, TO BE USED IN ROAD CONSTRUCTION

Irina VÎLCIU[1], Maria NICOLAE[2], Avram NICOLAE[3]

Zgurile de oțelărie sunt în principal zguri bazice care conțin o proporție mare de CaOlibe r şi MgOliber. Prin hidratare în stare solidă, acestea devin instabile volumetric, de aceea ele nu pot fi utilizate ca atare în construcția de drumuri. În această lucrare am analizat zgurilor de oțelărie în vederea minimizării oxidului de calciu pentru utilizarea acestora în construcția de drumuri.

The steel slag is mainly a basic slag that contains a great proportion of CaO_{free} and MgO_{free}. Through hydration in solid state, it becomes volumetric instable and that's why it can't be used as such in the road construction. In the present paper, we analysed the steel slag in order to reduce the CaO content, to make it fit for usage in this field.

Keywords: steel slag, volumetric instability, CaO_{free} melt

1. Introduction

The steel slag used for road construction comes from EAF/converter steel-making, and, in the same time, from the secondary steel-making, i.e. LF slag. In principal, the steel is made and refined under a strongly basic slag. This slag contains significant quantities of CaO_{free} and MgO_{free}, hydroscopic oxides [1]. In contact with water and/or atmosphere humidity, the calcium and magnesium oxides are transforming, by increasing their volume, into calcium hydroxide and, respectively, magnesium hydroxide, according to the reactions:

CaO_{free} hydration: $CaO_{free} + H_2O \rightarrow Ca(OH)_2$ (1)

MgO_{free} hydration: $MgO_{free} + H_2O \rightarrow Mg(OH)_2$ (2)

Following the disintegration: $\alpha \rightarrow \gamma$ C_2S transformed. (3)

The CaO_{free} comes from the undissolved CaO or from the dissociation of the tricalcium silicate in dicalcium silicate, according to the reaction:

$$3CaO \cdot SiO_2 \rightarrow 2CaO \cdot SiO_2 + CaO_{free} \quad (4)$$

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[1] Assist., Faculty „Managerial and Environment Engineering", University „Ecologica" of Bucharest, Romania; e-mail: irina_vilciu@yahoo.com

[2] Prof., Faculty "Science and Engineering of Materials", University POLITEHNICA of Bucharest, Romania; e-mail: nicolae_maria@yahoo.com

[3] Prof., Faculty "Science and Engineering of Materials", University POLITEHNICA of Bucharest, Romania

The quantity of free calcium oxide in the converter slag can reach approx. 20% [2].

The disintegration reaction of C_3S in C_2S can occur in parallel, reaction that increases the volumetric instability of the steel slag in solid state, but an important criterion for the materials used [3] for road construction is just the volumetric stability.

Therefore, the aim of the paper is to search the possibilities to reduce the free calcium and magnesium oxides contents. In this respect, we are going to analyse the various methods of treating the melted steel slag with siliceous sand.

For sake of comparison we mention that the slag obtained after the desulphurisation of the pig-iron is a typical blast-furnace slag (with low basicity), which requires, before being used for road construction, only a magnetic separation stage (to recover the iron metal). Then, it can be used without special issues.

Based on these considerations, we established the targets of the lab technological experiments:

- ✓ Reduction of the CaO_{free} content in the EAF/converter/LF slag down to a level where it is not able to produce further hydration effects during storing and, especially, after embedding in a road construction (target < 2%);
- ✓ Limitation of the beta-gamma structural transformation (with volume increasing) of the dicalcium silicate during cooling (at around 675 °C).

2. Results and Discussion

The realisation of the following flow sheet has been proposed:

a) Obtaining a liquid slag with a similar composition with the slag used in the steel shop;

b) Obtaining a control-sample of the slag cooled in normal conditions (similar to the conditions actually found in the real steel shop);

c) Casting the obtained slag in a cooling system similar to the one currently used in industry (slag pot), where we added some materials to modify the chemical and structural composition of the final slag.

A method of treating the steel slag with siliceous sand is the mixture of the solid slag with the siliceous sand [4]. But, the simple mixture of the two components doesn't actually change the chemical composition and structure of the slag.

That's why we considered that the steel slag must be firstly melted and then mixed with the siliceous sand. In this respect, two treating methods have been adopted:

1.treating the LF slag through mechanical means;

2.treating the slag in EAF with siliceous sand.

Both methods have been taken into consideration.

1.1. Treating the LF slag through mechanical means

To obtain a maximum homogenisation between the slag and the material found in the slag pot, we cast LF slag (the most friable slag) over a material with the highest potential of binding the CaO_{free} and transforming the dicalcium silicate (siliceous sand).

The chemical compositions of the raw materials used to form the LF slag are presented in Table 1.

Table 1

The chemical composition of the constituents used to make the LF slag

Composition, %	Alumina	Lime	Sand	Magnesite	Blast furnace slag
CaO		96.88	0.7	7.02	45
SiO_2	0.07	0.36	98	1.19	35
Fe_2O_3	0.13	0.11	0.5	7.26	
MnO					0.5
FeO					0.5
Al_2O_3	99.74	0.05	0.3	0.43	10
MgO		1.21		83.85	5
S		0.05			0.4

The heats of this batch were made according to the recipe presented in Table 2.

Table 2

Recipe for making the LF slag

Alumina, g	Lime, g	Sand, g	Magnesite, g	Blast furnace slag, g	Total, g
60	110	30	20	20	240

The data obtained as a result of these experiments are presented in Table 3. The chemical compositions of the LF slag, before treatment, were calculated according to the material balance sheet and, similarly, in case of the LF slag treated with siliceous sand.

The theoretical and experimental chemical compositions were transformed in the $[(CaO + MgO) – SiO_2 - Al_2O_3]$ system, in order to analyse the limitation of the possibility to obtain dicalcium silicate during the slag cooling process.

Fig. 1 presents the influence of the casting height in the slag pot on the reduction of the CaO and CaO_{free} contents in the slag treated with cu siliceous sand.

Fig. 2 presents the reduction of the CaO_{free} content after treating the slag.

Table 3

Experimental data: determination of the casting height for the heats: 1, 2, 3

The chemical composition of the untreated liquid slag, %	The theoretical heat	The experimental heats			The chemical composition of the treated liquid slag, %	The theoretical heat	The experimental heats		
		1	2	3			1	2	3
CaO	54.49	57.21	56.12	55.58	CaO	50.63	53.16	52.15	51.64
SiO_2	14.45	13.37	14.01	13.87	SiO_2	20.42	19.40	19.80	20.21
Fe_2O_3	0.75	0.77	0.74	0.69	Fe_2O_3	0.73	0.77	0.67	0.72
MnO	0.04	0.20	0.22	0.21	MnO	-	0.20	0.22	0.21
FeO	0.04	0.12	0.11	0.10	FeO	-	0.12	0.11	0.10
Al_2O_3	24.86	22.88	22.38	23.87	Al_2O_3	23.11	21.26	20.80	22.19
MgO	6.96	6.61	6.75	7.03	MgO	6.48	6.16	6.29	6.55
CaO_{free}	-	8.00	7.80	7.20	CaO_{free}	-	4.50	4.70	3.60
IB	3.77	4.17	4.00	4.01	IB	2.48	2.74	2.63	2.56
CaO + MgO	61.45	63.82	62.87	62.61	CaO + MgO	57.12	59.32	58.44	58.19
The slag composition in ternary system, %									
CaO + MgO	60.98	63.55	63.34	62.39	CaO + MgO	56.68	59.07	58.87	57.99
SiO_2	14.34	13.67	14.12	13.82	SiO_2	20.26	19.31	19.95	20.14
Al_2O_3	24.68	22.78	22.54	23.79	Al_2O_3	22.94	21.17	20.95	22.11
Quantity of slag in the slag pot, g		30	30	30					
The falling height		60	40	20					

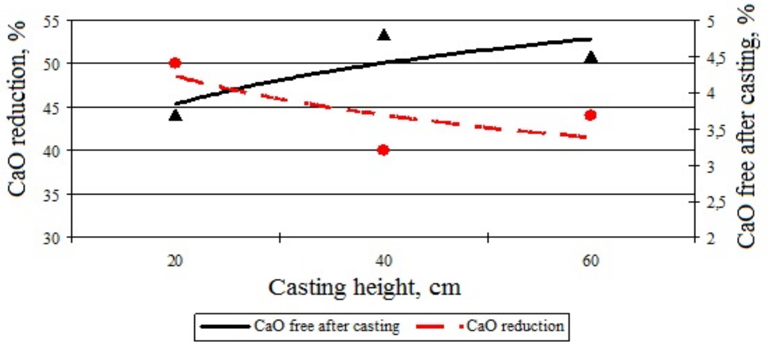

Fig. 1. The influence of the LF slag casting height on the CaO_{free} content, after treating with siliceous sand

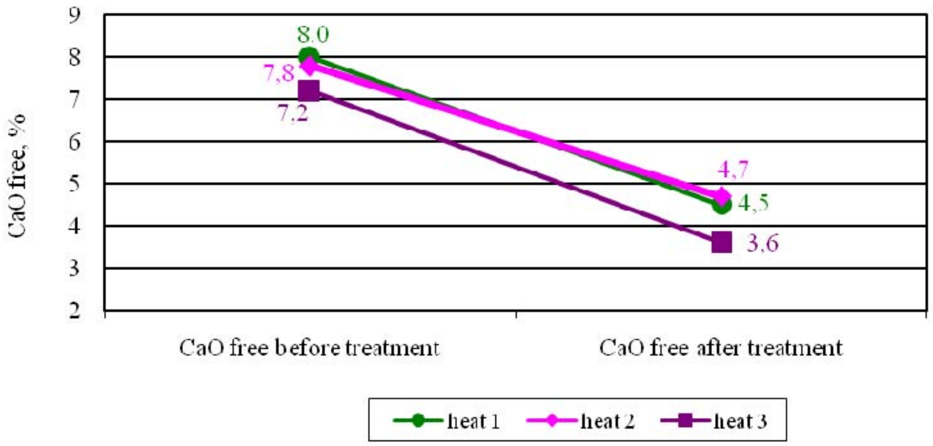

Fig. 2. The CaO_{free} content reduction

The data obtained from the experiments made by using various casting heights showed that:

- smaller casting heights determines lower CaO_{free} contents and, therefore, further reductions during the casting;
- we realised 40-50% reduction of the CaO_{free} content;
- after casting, the average content of CaO_{free} was 4.27 %.

Although these experiment were intendent to establish an influence of the casting height on the reduction of the CaO_{free} content, we saw that, actually, the increasing of the casting height didn't encourage the mixture between the LF slag and the siliceous sand (in fact, we found significant quantities of siliceous sand in the slag pot after casting). An explanation can be the fact that a great casting height, especially in case of small slag quantities (low flow rate of the cast slag), has rather a strong influence on the slag cooling in the casting jet than an influence on the mechanical mixture between the slag and the siliceous sand.

For this reason, at the next experimental heats we added siliceous sand in the crucible where we prepared the slag, immediately after sampling the slag, right before casting in the slag pot.

The fact that the LF slag didn't completely reat with the siliceous sand, in case of these experimental heats, can be also seen in the evolution of the LF slag composition before and after treating, presented in the [(CaO + MgO) – SiO_2 - Al_2O_3] ternary diagram (Fig.3).

The data presented in this ternary diagram showed that the treatment with siliceous sand of the LF slag led to the migration of the slag from the C_3S compounds area only towards the limit of the C_2S – CS area, so we were expecting to still have much friable slag and a significant content of $CaO_{free.}$

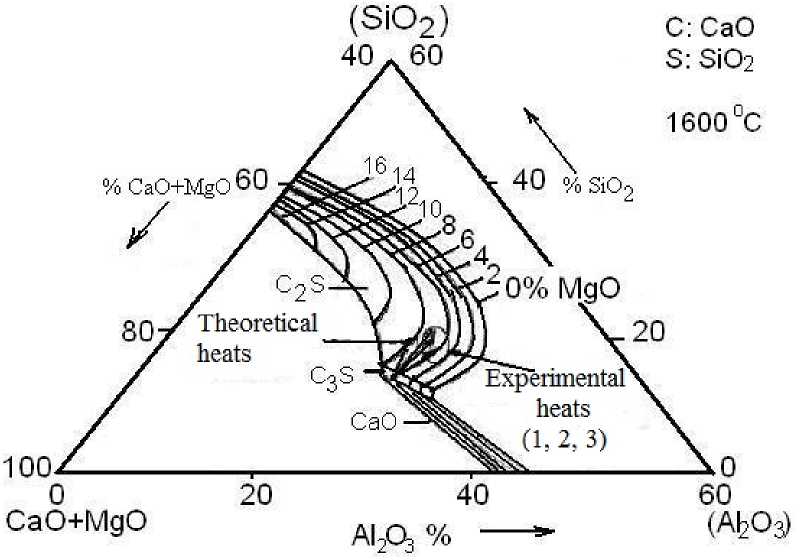

Fig. 3. Experimental heats for establishing the casting height (LF slag + siliceous sand)

1.2. Treating the slag in the EAF with siliceous sand

1.2.1. Experimental researchs regarding the treating of the LF liquid slag

The purpose of these experiments was to treat the LF slag with siliceous sand for obtaining, after casting, a slag with low CaO_{free} content and limited compounds of C_3S/C_2S type.

The experiments were carried out in the same conditions as in case of the previous batch (raw materials for making the LF slag, siliceous sand for the admixture), and the siliceous sand was added in the melting crucible after sampling the slag. The casting was performed from 20cm height. The data obtained from this set of experiments are presented in Table 4.

The chemical compositions of the LF slag, before treatment, were calculated according to the material balance sheets, similarly as we did in case of the LF slag treated with siliceous sand [4].

The theoretical and experimental chemical compositions were transformed in the [(CaO + MgO) – SiO_2 - Al_2O_3] system, to be able to analyse the slag constituents after cooling and to see whether we succeeded to limit the formation of the dicalcium silicate.

Table 4

Experimental data: LF slag + siliceous sand (heats: 4, 5, 6)

The chemical composition of the untreated slag, %	The theoretical heat	The experimental heats			The chemical composition of the treated slag, %	The theoretical heat	The experimental heats		
		4	5	6			4	5	6
CaO	52.49	51.44	55.11	54.06	CaO	43.58	45.75	44.88	45.75
SiO_2	15.45	15.91	14.21	14.98	SiO_2	29.60	28.12	28.71	29.90
Fe_2O_3	0.75	0.77	0.73	0.71	Fe_2O_3	0.71	0.74	0.65	0.69
MnO	0.04	0.18	0.28	0.23	MnO	-	0.20	0.22	0.21
FeO	0.04	0.12	0.15	0.13	FeO	-	0.12	0.11	0.10
Al_2O_3	24.86	24.12	23.37	22.38	Al_2O_3	20.65	19.00	18.59	19.83
MgO	6.96	7.52	6.82	7.31	MgO	5.82	5.53	5.64	5.88
CaO_{free}	-	7.43	7.30	7.70	CaO_{free}	-	1.20	1.70	1.50
IB	3.40	3.23	3.88	3.61	IB	1.47	1.63	1.56	1.53
CaO + MgO	59.45	58.95	61.93	61.37	CaO + MgO	49.39	51.28	50.53	51.63
The slag composition in ternary system, %									
CaO + MgO	59.59	59.56	62.23	62.16	CaO + MgO	49.51	51.81	50.77	52.29
SiO_2	15.49	16.08	14.28	15.18	SiO_2	29.67	28.41	28.85	30.28
Al_2O_3	24.92	24.37	23.49	22.67	Al_2O_3	20.70	19.20	18.68	20.08
Quantity of siliceous sand added in the heat, g	-	30	30	30					

The influence of the liquid slag treated with siliceous sand on the decreasing of the CaO_{free} content and basicity ratio (IB) is presented in Fig. 4 and Fig. 5, respectively.

The evolution of the LF slag before and after treatment is presented in the [(CaO + MgO) – SiO_2 - Al_2O_3] ternary diagram (Fig. 6).

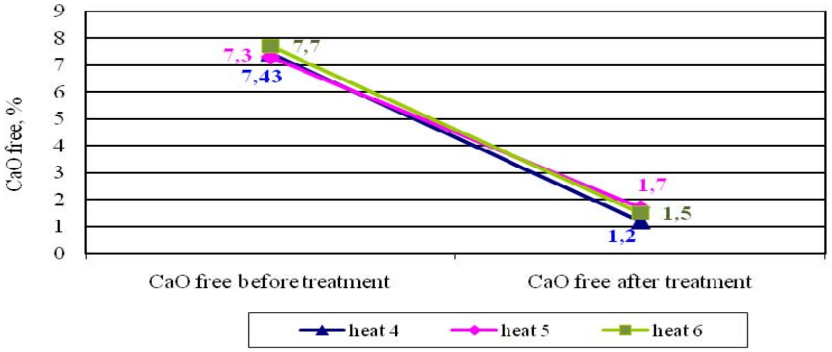

Fig. 4. The CaO_{free} content reduction

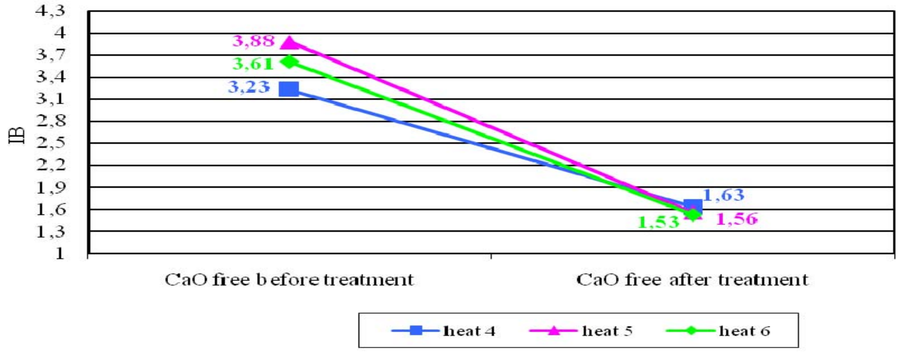

Fig. 5. The reduction of IB

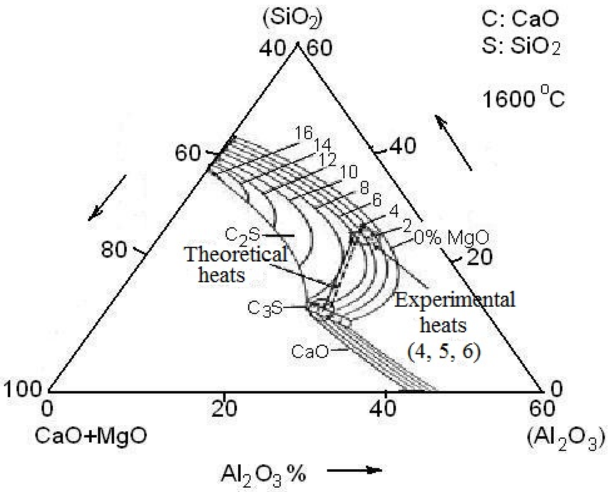

Fig. 6. Experimental heats LF slag + siliceous sand

The data obtained from the experiments carried out on this batch showed that:

- the reduction of CaO_{free} was 80%;
- the basicity ratio dropped to 1.57;
- the average CaO_{free} content after casting was 1.47 %, within the target of max. 2%;
- the treatment with siliceous sand of the LF slag led to the migration of the slag from the C_3S compounds area to the CS area limit, so we were expecting to have a lower CaO_{free} content.

If we plot on a ternary diagram the results of the first batch experiments (casting the LF slag in a slag pot with siliceous sand) and the second batch experiments (LF slag mixed with siliceous sand in the melting crucible), we can better put in vidence the influence of the thermal factor on the chances to obtain a slag closer to the CS area (Fig. 7).

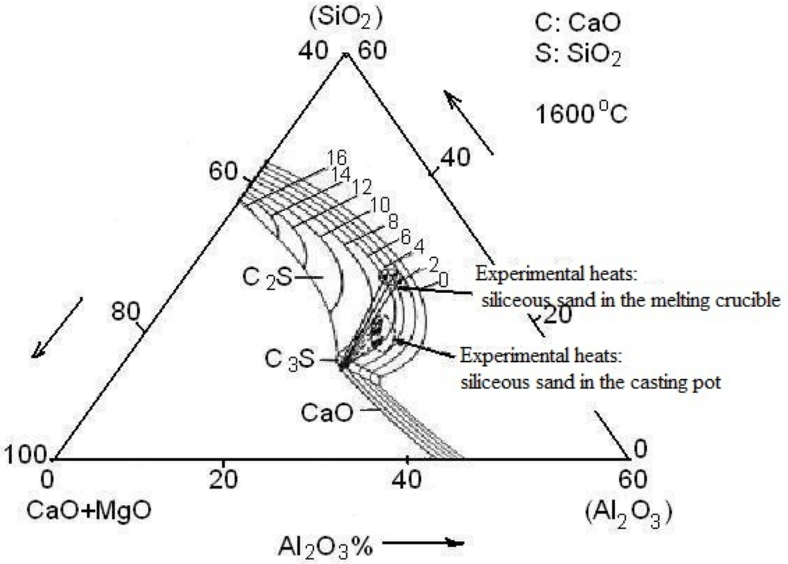

Fig. 7. Experimental heats: LF slag + siliceous sand (batch with siliceous sand in the casting pot/melting crucible)

1.2.2. Experimental researches regarding the treating of the liquid slag in the EAF

The purpose of the experiments carried out in this stage was the treatment of the EAF slag with siliceous sand for obtaining, after casting, a slag with low CaO_{free} content and limited compounds of C_3S/C_2S type.

The experiments were performed in the same conditions as the previous batch. The raw materials we have used were EAF slag and siliceous sand admixture. The siliceous sand was added in the melting crucible, after sampling the slag. The casting was performed from the same height, 20 cm. The data obtained from this set of experiments are presented in Table 5.

Also in this case, the chemical compositions of the EAF melt slag, before treatment, were calculated according to the material balance sheets and, similarly, for the EAF slag treated with siliceous sand. The theoretical and experimental chemical compositions were transformed in the CaO – SiO_2 - FeO_n system, to be able to analyse the slag constituents after cooling and to see whether we succeeded to limit the formation of the dicalcium silicate.

The influence of the EAF liquid slag treatment with siliceous sand on the reduction of the CaO_{free} content and basicity ration (IB) is presented in Fig. 8 and 9, respectively.

Table 5

Experimental data: EAF slag + siliceous sand (heats: 7, 8, 9)

The chemical composition of the untreated slag, %	The theoretical heat	The experimental heats			The chemical composition of the treated slag, %	The theoretical heat	The experimental heats		
		7	8	9			7	8	9
CaO	40.78	41.18	40.37	39.96	CaO	36.30	36.67	35.94	35.58
SiO_2	17.81	18.17	16.92	17.99	SiO_2	26.72	27.04	25.93	26.88
Fe_2O_3	3.97	3.97	3.89	3.57	Fe_2O_3	3.53	3.53	3.46	3.18
MnO	9.79	9.99	9.59	9.89	MnO	8.70	8.88	8.53	8.79
FeO	9.25	9.44	9.07	9.34	FeO	8.22	8.39	8.06	8.31
Al_2O_3	4.23	4.19	4.19	3.89	Al_2O_3	3.76	3.72	3.72	3.46
MgO	8.53	8.70	8.44	9.04	MgO	7.58	7.73	7.51	8.04
CaO_{free}		7.20	7.35	7.56	CaO_{free}		1.20	1.30	1.45
IB	2.29	2.27	2.39	2.22	IB	1.36	1.36	1.39	1.32
The slag composition in ternary system, %									
CaO	49.98	49.78	50.57	49.49	CaO	43.49	43.39	43.88	43.01
SiO_2	21.83	21.95	21.19	22.27	SiO_2	32.01	32.00	31.65	32.49
FeO_n (FeO+ Fe_2O_3+ MnO)	28.20	28.27	28.24	28.24	FeO_n (FeO+ Fe_2O_3+ MnO)	24.50	24.61	24.47	24.50
Quantity of siliceous sand added in the heat, g		30	30	30					

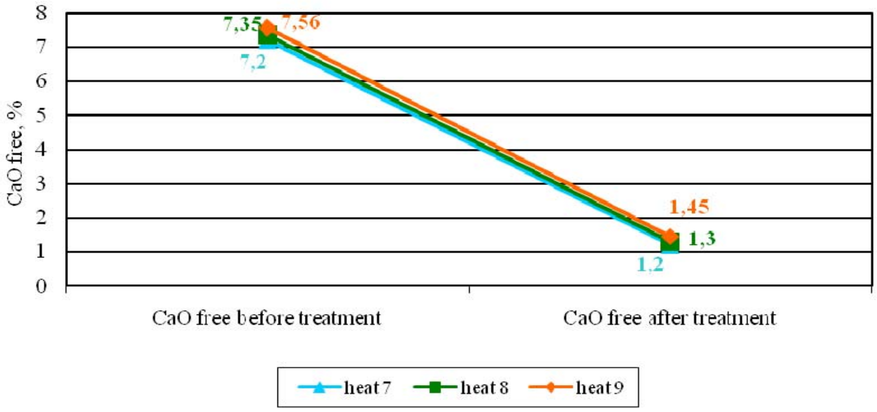

Fig. 8. The CaO_{free} content reduction

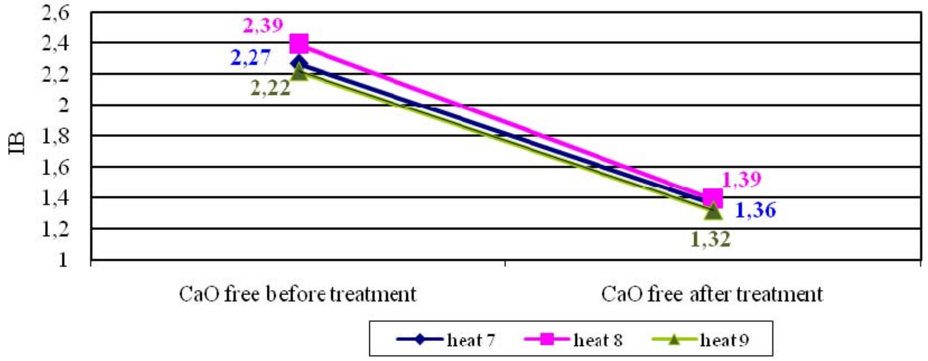

Fig. 9 The reduction of IB

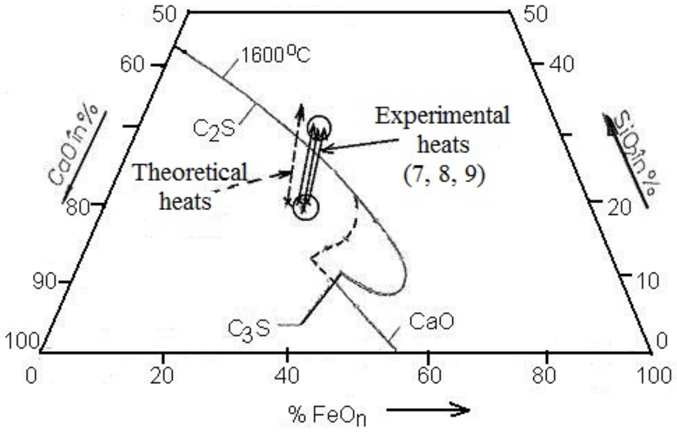

Fig. 10. Experimental heats: EAF slag + siliceous sand

The evolution of the EAF slag composition, before and after treatment, is presented in the ($CaO - SiO_2$ - FeO_n) ternary diagram (Fig. 10).

The data obtained from the experiments performed on this batch showed that:

- the reduction of CaO_{free} was 82%;
- the basicity ratio dropped to 1.36;
- the average CaO_{free} content after casting was 1.32 %, within the target of max. 2%;
- the treatment with siliceous sand of the EAF slag led to the migration of the slag from the C_2S compounds area to the CS area, so we were expecting to have a lower CaO_{free} content.

1.2.3. Experimental researches regarding the treatment of the converter liquid slag

The purpose of the experiments performed in this stage was the treatment of the converter slag with siliceous sand for obtaining, after casting, a slag with low CaO_{free} content and limited compounds of C_3S/C_2S type.

The experiments were carried out in similar conditions as the previous batch. As raw materials, we used converter slag and siliceous sand admixture. The siliceous sand was added in the melting crucible, after sampling the slag. The casting height was 30 cm. The data obtained from this experiment batch are presented in Table 6.

As in the previous case, the chemical compositions of the converter slag, before treatment, were calculated according to the material balance sheets and, similarly, in case of the converter slag treated with siliceous sand. The theoretical and experimental chemical compositions were transformed in the [CaO–SiO_2–FeO_n] system, to be able to analyse the constituents of the slag after cooling and to see if we succeeded to limit the formation of the dicalcium silicate.

The influence of the converter liquid slag treatment with siliceous sand on the reduction of the CaO_{free} content and basicity ration (IB) is presented in Fig. 11 and 12, respectively.

The evolution of the converter slag composition, before and after treatment, is presented in the [$CaO - SiO_2$ - FeO_n] ternary diagram (Fig. 13).

Table 6

Experimental data: converter slag + siliceous sand (heats: 10, 11, 12)

The chemical composition of the untreated slag, %	The theoretical heat	The experimental heats			The chemical composition of the treated slag, %	The theoretical heat	The experimental heats		
		10	11	12			10	11	12
CaO	42.52	42.95	42.09	41.67	CaO	37.85	38.23	37.47	37.10
SiO_2	18.54	18.91	17.61	18.73	SiO_2	27.37	27.70	26.54	27.53
Fe_2O_3	6.50	6.50	6.37	5.85	Fe_2O_3	5.78	5.78	5.66	5.20
MnO	6.55	6.68	6.42	6.62	MnO	5.82	5.94	5.71	5.88
FeO	13.95	14.23	13.67	14.09	FeO	12.40	12.65	12.15	12.53
Al_2O_3	2.5	2.48	2.48	2.30	Al_2O_3	2.22	2.20	2.20	2.05
MgO	8	8.16	7.92	8.48	MgO	7.11	7.25	7.04	7.54
CaO_{free}		6.55	6.35	6.46	CaO_{free}		1.80	1.50	1.55
IB	2.29	2.27	2.39	2.23	IB	1.38	1.38	1.41	1.35
The slag composition in ternary system, %									
CaO	48.29	48.11	48.85	47.92	CaO	42.42	42.34	42.81	42.04
SiO_2	21.05	21.18	20.44	21.54	SiO_2	30.67	30.68	30.32	31.20
FeO_n (FeO+ Fe_2O_3+ MnO)	30.66	30.71	30.71	30.54	FeO_n (FeO+ Fe_2O_3+ MnO)	26.90	26.99	26.87	26.76
Quantity of siliceous sand added in the heat, g		30	30	30					

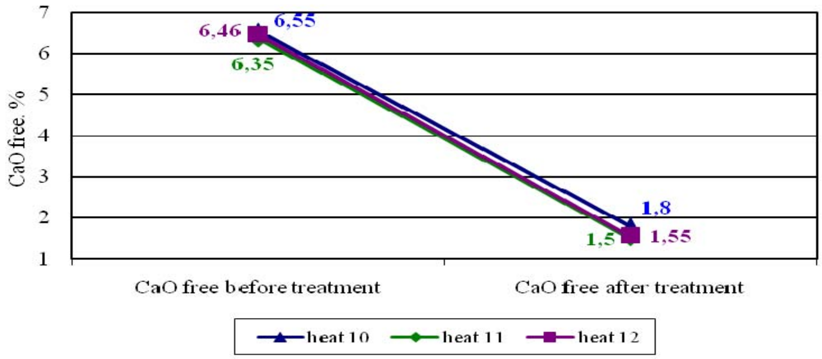

Fig. 11. The CaO_{free} content reduction

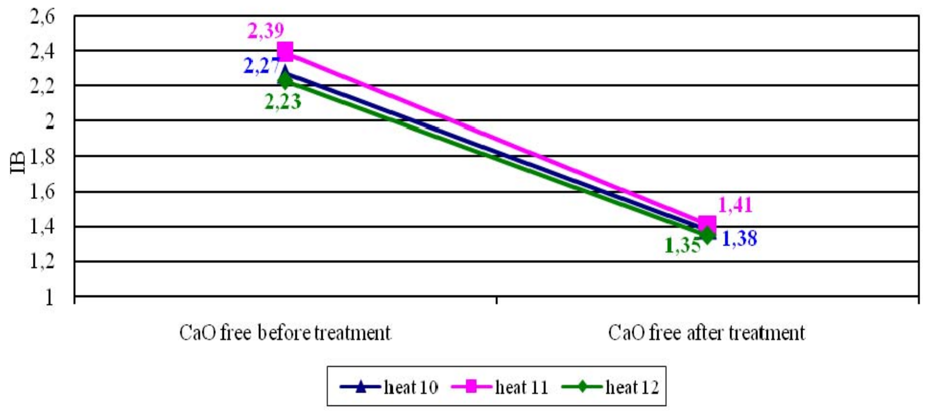

Fig. 12. The reduction of IB

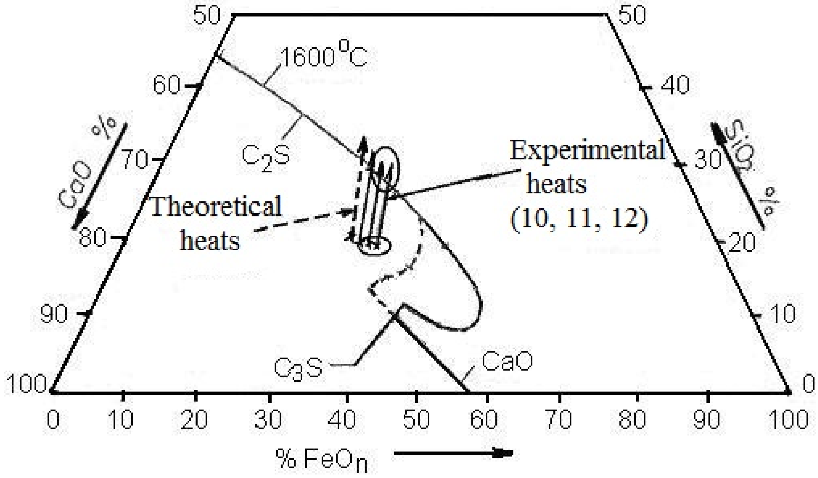

Fig. 13. Experimental heats: converter slag + siliceous sand

The data obtained from the experiments performed on this batch showed that:

- the reduction of CaO_{free} was 75%;
- the basicity ratio dropped to 1.38;
- the average CaO_{free} content after casting was 1.62 %, within the target of max. 2%;
- the treatment with siliceous sand of the converter slag led to the migration of the slag from the C_2S compounds area to the CS area, so we were expecting to have a lower CaO_{free} content.

2. Conclusions

To minimise the CaO_{free} content in the metallurgical slag, we have proposed and performed laboratory according to experiments on synthetic slag, proposing two methods:

1. treating the LF slag through mechanical means, and
2. treating the LF slag in EAF with siliceous sand.

In the first case, after experiments, we found that: a lower casting height leads to a lower CaO_{free} content and, therefore, to its greater reduction during the casting. We obtained a reduction of the CaO_{free} content with 40-50%, the average CaO_{free} content after casting being 4.27%.

According to our experiments, we saw that, actually, the increasing of the casting height didn't encourage the mixture of the LF slag with the siliceous sand (we found significant quantities of siliceous sand in the slag pot after casting).

A greater casting height, especially in case of small slag quantities (low flow rate of the cast slag) has rather a strong influence on the cooling of the slag in the casting jet that an influence on the mechanical mixture of the slag with the siliceous sand.

For this reason, in case of the second method experimental heats, we added the siliceous sand in the slag crucible immediately after sampling the slag, and then we cast in the slag pot.

The fact that the slag didn't integrally react with the siliceous sand in the case of these experimental heats can be also seen in the evolution of the LF slag composition before and after treatment, when the contents of the slag after treatment didn't drop significantly.

After applying the second experiment al method, we obtained the fallowing results:

- in case of LF slag, we obtained a CaO_{free} content reduction of 80%, an average dropping of the basicity ration down to 1.57%, the average CaO_{free} content after casting being 1.47%;

- in case of EAF slag, we obtained a CaO_{free} content reduction of 82%, an average dropping of the basicity ration down to 1.36, the average CaO_{free} content after casting being 1.32 %;

- in case of the converter slag, we obtained a CaO_{free} content reduction of 75 %, an average dropping of the basicity ration down to 1.38, the average CaO_{free} content after casting being 1.62 %.

Through the experiments made in the laboratory, we obtained significant reductions of the calcium oxide (approx. 80%), which means that these types of slag are fitted to be used in the road construction field.

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