

M. KARBOWNICZEK* M. DZIARMAGOWSKI*, P. MIGAS*

THE CONVERTER SLAG REDUCTION PROCESS AT DIFFERENT WAYS OF REDUCER ADDING

PROCES REDUKCJI ŻUŻLA KONWERTOROWEGO PRZY RÓŻNYCH SPOSOBACH WPROWADZANIA REDUKTORA

Findings of laboratory tests of the converter slag reduction process in an electric arc furnace are presented in this paper. Slag premixed with carbon reducer was used for the tests, reducer was also injected in an air jet with a lance. Based on the tests performed it was found that injection of the reducer slowed down the reduction process due to poorer utilisation of the reducer. It was also found that the reduction process rate increased along with the growth in Al_2O_3 content in the phase reduced. At the same time its content in the resulting non-metallic phase increased. Therefore the mass of the Al_2O_3 added should be subject to its content in the converter slag.

W artykule przedstawiono wyniki badań procesu redukcji żużla konwertorowego w elektrycznym piecu łukowym, w warunkach laboratoryjnych. W czasie badań stosowano żużel wymieszany z reduktorem węglowym, a także wdmuchiwano reduktor przy pomocy lancy w strumieniu powietrza. Na podstawie przeprowadzonych badań stwierdzono, że wdmuchiwanie reduktora powoduje zmniejszenie szybkości procesu redukcji z powodu gorszego wykorzystania reduktora. Stwierdzono również, że szybkość procesu redukcji wzrasta wraz ze wzrostem zawartości Al_2O_3 w redukowanej fazie. Jednocześnie wzrasta również zawartość tego składnika w otrzytywanej fazie niemetalicznej. Z tego powodu masa wprowadzanego Al_2O_3 powinna być uzależniona od jego zawartości w żużlu konwertorowym.

1. Introduction

100% of blast furnace slag and up to 85% of steel-making slag are utilized in the world. It results from an excessive iron oxides content in steelmaking slag, which prevents its direct practical utilisation. The growing amount of steelmaking slag forces to look for new methods of its utilization. The reduction process mainly of iron oxides from converter slag in an electric arc furnace should fall within the developed new methods of slag utilization. Publications on this issue have been appearing in the world for many years [1-3]. However these publications are very scarce and presented findings and conclusions will not allow to use the process in the industrial practice.

Research on the converter slag reduction process in an electric arc furnace have been carried out also in Poland and its findings have been published [4-8]. The findings published so far have enabled to state that a non-metallic phase and a metallic phase are obtained as a result of the process. The non-metallic phase can be used as portland clinker or Ca-Mg fertilizer and the

metallic phase can be used as an input material in metallurgical processes. Reduction of converter slag of a specified chemical composition was tested after premixing the slag with graphite based carbon reducer. Findings of tests of some, selected chemical compositions of slag have not been sufficient to develop a consistent process practice where slag with variable chemical composition is used. So far also various ways of adding and the form and amount of the reducer have not been determined. Therefore it has been decided to continue research on the converter slag reduction process.

2. References on research on the converter slag utilization process

Findings of research on the utilization process by converter slag reduction were published for the first time in Japan in 1979. The tests were carried out in a 50 kg induction furnace and in an electric arc furnace of 200 kVA capacity. The reduction process was carried out at a temperature of 1800°C. The objective of the pro-

* FACULTY OF METALLURGY AND MATERIALS SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, AL. MICKIEWICZA 30, POLAND

cess was to obtain the non-metallic phase of a chemical composition similar to the Portland clinker composition. The obtained non-metallic phase was transferred to the furnace where carbon was oxidized with injected air. The chemical composition was controlled by addition of silica or lime. The resulting material was cooled down after the process. An adequate amount of gypsum was added to the obtained clinker and the resulting material was ground to get a suitable fraction. During the tests it was found that at the beginning of the process there was intensive foaming of the reduced slag which shortly ceased. One of the objectives of the tests performed was to determine how the reduction time after the end of foaming affected the chemical composition of the resulting non-metallic phase. Based on the performed tests it was found that in the process lasting 15 minutes the content of iron oxides, manganese oxides and phosphorus oxides was reduced and the reduction rate was respectively: 99,2%, 100% and 96,2% [1].

Information about erection of a slag processing plant planned by the Belgian CBR group was realised in 1984. Preliminary tests showed that it was possible to obtain clinker in an electric arc furnace from the mixture of converter slag and alumina carriers added in order to lower the slag melting temperature. Addition of aluminium oxide to the charge caused an increase in Al_2O_3 content in the converter slag from 0,9% to 5,5–6,2% in the resulting Portland clinker. The content was higher than the acceptable limit but it would not cause deterioration of the clinker properties [2].

Tests of utilization of converter slag by reduction with graphite reducer were carried out in an induction furnace in China in 2003. The reduction process was carried out at temperatures of 1650 and 1800°C, they used slag premixed with reducer. It was found that as a result of the process iron and manganese could be reduced virtually in whole. The phosphorus content after reduction decreased by 95,5%, only 62,7% of which was reduced to the non-metallic phase and the balance constituted evaporation losses [3].

It is a drawback of the abovementioned methods of converter slag processing that the process is aimed mainly at production of Portland clinker. With fluctuating chemical composition of slag it is not always possible to obtain the desired chemical composition and clinker characteristics. Therefore it is often necessary to correct the chemical composition of the obtained phase, which makes stable performance of the utilization process more difficult. Moreover, it is required to refine process engineering parameters, such as the type and amount of the reducer, method of its addition, type and amount of materials for correction of chemical composition, temperature and time of the process. The method of utilization of the resulting metallic phase is a separate issue.

Laboratory tests were carried out in Poland to determine the scope of corrections of chemical composition of the resulting non-metallic phase intended for Portland clinker as well as the conditions of the reduction process when utilizing it as a Ca-Mg fertilizer [6-7].

Based on the tests performed it was found that the resulting non-metallic phase could be utilized as portland clinker after adding lime to the charge in the amount of about 1-2% of the mass of converter slag in order to achieve changes in the mineralogical composition consisting in an increase in the share of 3CaOSiO_2 and a decrease in the share of 2CaOSiO_2 [6]. If the non-metallic phase was intended to be utilized as a Ca-Mg fertilizer it was necessary to obtain the total degree of slag reduction exceeding 21% [7].

A carbon or graphite lining of the furnace crucible had been used in all experiments carried out in the world so far. No other kind of lining had ever been mentioned. Therefore it was decided to perform experimental heats in a crucible made of a refractory material based on Al_2O_3 . Use of a crucible like this enables to control the scope of reduction, making the process independent of reducing effect of the crucible lining graphite.

3. Research methodology

The converter slag reduction process was tested in a single electrode electric arc furnace. The furnace was supplied by a 75 kVA transformer, at a supply voltage of 380 V. The transformer enabled to obtain an electric arc current intensity up to 1200 A, at a voltage of 40 V. The facility was equipped in an automated system for control of current parameters, keeping the set length of the electric arc and current intensity at a constant level during the process. A 50 mm diameter graphite electrode was used. The metallurgical process was carried out in a graphite crucible of the external height of 400 mm and the external diameter of 310 mm. The inside of the crucible was lined with a refractory material consisting mainly of Al_2O_3 . The internal height of the crucible was 205 mm and the internal diameter 180 mm.

Three series of test heats were performed, 3000 g of converter slag and carbon reducer were used as the charge. The chemical composition of the converter slag is presented in the table 1. The carbon reducer contained 93% C, 0,7% S, 5% ash and 2,5% volatiles and 1,5% moisture. The reducer grain size ranged within 0÷3 mm, 150 g of reducer was used which constituted 5% of the slag mass. The course of the test heats included: adding and melting of the slag, reduction process after melting and casting the resulting non-metallic and metallic phases to a special metal mould. After solidification both phases were separated and weighted. The mass of the

obtained non-metallic phase ranged within 2000÷2200 g and the metallic phase within 480÷580 g. A sample was taken from the non-metallic phase to analyse chemical composition. The slag was melted by adding its small portions into the area of electric arc influence. The whole process of slag melting took 4 minutes. Reduction times after melting of the slag in the series I and III were respectively 3, 6, 9, 12 and 15 minutes and in the series II respectively 3, 6, 9 minutes.

Ground converter slag blended with the carbon reducer was used in the first series. In the second series the reducer was injected with a specifically designed lance, the tip of which was immersed in liquid slag. Air was used as the carrier and the injection time of a 150 g portion was 2 minutes. Significant wear out of the crucible refractory lining was observed in both series, which manifested in passing of Al_2O_3 to the slag. The chemical composition of the resulting non-metallic phase was characterised by a high Al_2O_3 content, exceeding the acceptable limit in clinker by more than twice. In the third series current parameters were changed, which caused less intensive passing of Al_2O_3 to the slag. Again the reducer mixed with the slag before the reduction process was used.

4. Assessment of the chemical composition of the resulting non-metallic phase

The basic condition of utilization of the non-metallic phase as Portland clinker is to obtain its chemical composition similar to the chemical composition of clinker. The Portland clinker chemical composition ranges within the following limits: 63÷67% CaO, 21÷24% SiO_2 , 4÷7% Al_2O_3 , 2÷4% FeO, max. 5% MgO, max. 1,5% SO_3 . The resulting non-metallic phase must not disintegrate autogenously, which occurs as a result of transformation of the $\beta 2CaOSiO_2$ form into the γ form. As a result of the transformation the volume increases and the non-metallic phase loses its hydraulic binding properties.

Possibilities of stabilization of the $\beta 2CaOSiO_2$ variety have been researched for many years. It has been found that stabilization of the $\beta 2CaOSiO_2$ variety depends on the chemical composition of the resulting phase and conditions of its cooling. A non-metallic phase not disintegrating autogenously can be obtained if the P_2O_5 content exceeds 0,3% molar concentration. If the P_2O_5 content is lower it is necessary to cool down the resulting phase quickly [1, 5, 9].

TABLE
Test results of the chemical content of the resulting non-metallic phase for series I, II, III

Lp.	Series	Time, min.	Chemical content, %							
			CaO	SiO_2	MgO	FeO	MnO	P_2O_5	Al_2O_3	S
1	Converter slag		41,53	14,36	4,35	28,28	3,95	0,86	4,06	0,14
2	I	3	50,79	18,64	5,20	5,64	4,44	1,04	9,23	0,23
3		6	47,04	16,06	5,69	4,51	4,10	0,72	18,21	0,21
4		9	47,15	16,17	5,99	3,52	3,71	0,41	20,11	0,22
5		12	47,63	17,16	5,27	3,50	4,10	0,44	18,99	0,17
6		15	49,34	19,82	4,51	1,26	2,30	0,01	21,02	0,16
7	II	3	44,30	15,12	4,82	10,07	4,19	0,89	15,75	0,13
8		6	44,65	14,94	5,16	8,45	4,28	0,88	17,36	0,13
9		9	44,03	14,29	5,22	8,50	4,06	0,70	18,88	0,13
10	III	3	45,39	16,93	4,29	14,89	4,60	1,01	4,60	0,14
11		6	44,41	16,79	5,24	13,52	4,46	1,00	6,85	0,13
12		9	47,88	17,98	5,17	7,45	4,55	1,03	10,67	0,13
13		12	49,73	18,53	5,05	5,11	4,27	0,97	12,38	0,13
14		15	48,65	18,82	5,56	4,68	3,70	0,54	13,33	0,15

Findings of tests of chemical composition of the non-metallic phases obtained at different reduction times and different ways of adding of the reducer are presented in Table.

It follows from the dissociation pressure of oxides comprising slag that under test conditions the following

oxides should be reduced: iron oxide, manganese oxide, phosphorus oxide and within a limited scope silicon oxide and aluminium oxide. The other components should not be reduced. It is confirmed by test results of chemical composition of the resulting non-metallic phase. As follows from the data in Table, the contents of CaO,

SiO₂ and MgO increased after the reduction process, in each case. As the slag mass after the reduction process decreased (which follows from a loss of components reduced), if the mass of a component remained the same its percentage share increased. In each case the Al₂O₃ content increased, which resulted from its passing from the crucible refractory lining to the non-metallic phase.

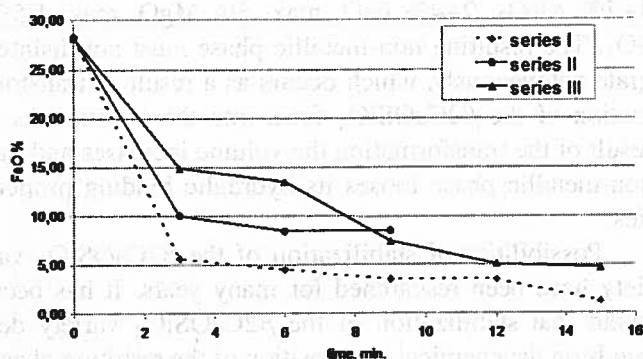


Fig. 1. FeO content in the non-metallic phase after the reduction process

The diagram of FeO content in the resulting non-metallic phase is presented in Fig. 1. As follows from the curves the most favourable conditions for reduction were achieved for the series I. Only after 3 minutes of reduction the FeO content decreased from 28,28% to 5%. An increase in the reduction time up to 12 minutes practically would not cause any further reduction. Only increase in the reduction time up to 15 minutes caused decrease in the FeO level in the non-metallic phase up to ca. 1%. After 9 minutes of reduction in the series II the FeO content in the non-metallic phase was 8,50%, i.e. over twice as much as in the series I. At the same time it was found that higher contents of manganese and phosphorus oxides had been obtained in this series than in the series I. It was most likely caused by much lower rate of reducer utilization as the reducer partially oxidised during injection in the air jet. Therefore tests with longer reduction times were not continued any more. It was decided however to carry out the III series of heats, where slag was mixed with the reducer, but current parameters were changed to restrict passing of Al₂O₃ from the refractory lining. At lower Al₂O₃ contents the course of FeO reduction process was different in nature. The resulting content of iron oxide decreased more slowly than in the series I. Only after 12 minutes of reduction the FeO content was about 5%. The obtained findings indicate that both the method of feeding the reducer and the chemical composition of the liquid reduced phase have significant effect on the rate of iron oxide reduction.

The diagram of MnO content in the resulting non-metallic phase is presented in Fig. 2. As follows

from the curves in the diagram the course of the reduction process was similar for all the series. In series I and III the reduction process lasting up to 12 minutes caused little changes in the MnO content. Only increase of the reduction time to 15 minutes caused decrease in the MnO content. However influence of physico-chemical characteristics of the reduced phase is clearly visible. Lower MnO content in the non-metallic phase was obtained in the series I than in the series III, which was caused by a higher Al₂O₃ content. It follows from the above that reduction of the manganese oxide starts only after the end of reduction of the iron oxide. From the standpoint of the reduction scope it is better to mix the reducer with the slag before the process than injecting it to the liquid reduced phase. Also a higher content of Al₂O₃ is more favourable to the course of reduction. The forming fusible calcium – aluminium eutectic mixtures cause decrease in viscosity and surface tension of the reduced phase.

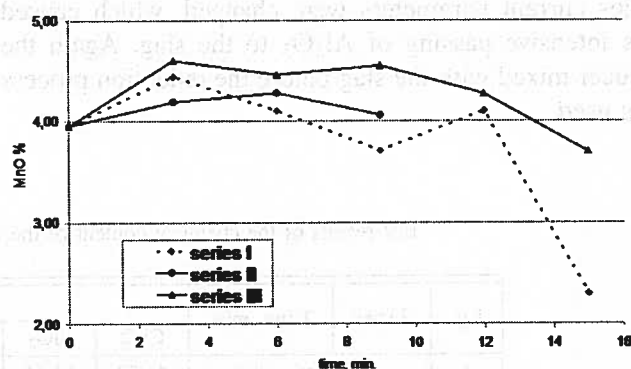


Fig. 2. MnO content in the non-metallic phase after the reduction process

The diagram of P₂O₅ content in the resulting non-metallic phase is presented in Fig. 3. As follows from the curves in the diagram series III, if the reducer was mixed with converter slag before the reduction and if the Al₂O₃ contents were lower, the reduction process lasting up to 12 minutes caused little changes of P₂O₅ content. Only at the reduction time of 15 minutes P₂O₅ content decreased. The fastest reduction process was observed in the series I, that is when the reducer was mixed with the converter slag before the process and at higher Al₂O₃ contents. Injection of the reducer as compared to premixing caused less favourable conditions for the P₂O₅ reduction process. It is most likely caused by partial oxidation of the reducer injected in an air jet. Therefore at injecting the reducer and extending the process time one should use higher amounts of the reducer than in the case of mixing it with the slag before the process. Findings of the tests confirm the effect of the phosphorus oxide on stabilization of β2CaOSiO₂ variety. Only in the series I

after 15 minutes of reduction autogenously disintegrating non-metallic phase was obtained where resulting P_2O_5 content was 0,01% that is it was much lower than the limiting stabilizing value.

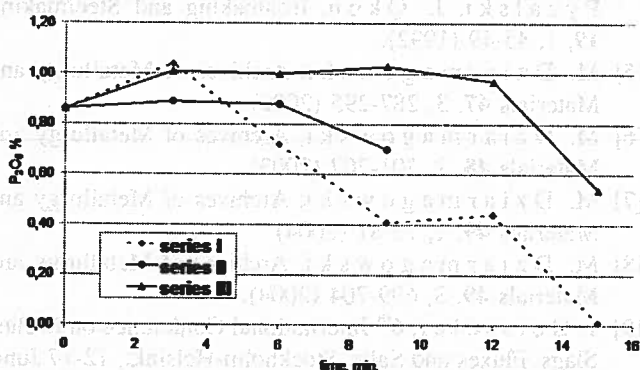


Fig. 3. P_2O_5 content in the non-metallic phase after the reduction process

The diagram of Al_2O_3 content in the resulting non-metallic phase is presented in Fig. 4. As follows from the curves in the diagram in all series passing of aluminium oxide from the crucible refractory lining is observed. In series I and II the process is similar, the highest increase in Al_2O_3 content is observed before 3 and 6 minutes. Later the content increase is lower. Much lower wear out of the crucible refractory lining and a lower increase of Al_2O_3 in the reduced phase was obtained after reduction of current parameters.

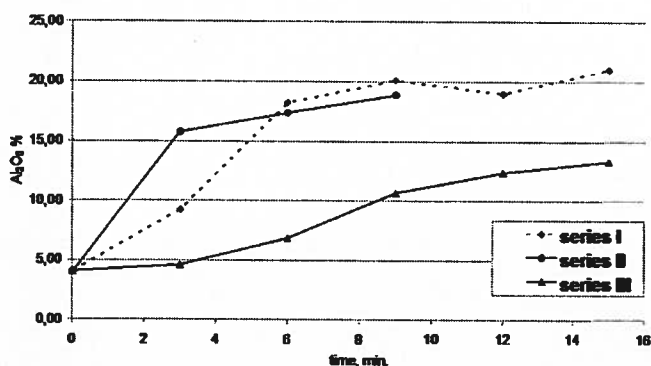


Fig. 4. Al_2O_3 content in the non-metallic phase after the reduction process

The autogenously disintegrating non-metallic phase was obtained only in series I after 15 minutes of the reduction process. It was caused by very low phosphorus content of 0,01% and low contents of FeO and MnO, which being respectively 1,26% and 2,30% were lower than the contents of these components in the series II and III.

Findings of the tests allow to confirm the thesis that it is possible to obtain as a result of the reduction pro-

cess a non-metallic phase, which does not disintegrate autogenously and the chemical composition of which is similar to the chemical composition of portland clinker. However too low CaO content and too high Al_2O_3 content are noticeable in the chemical composition of the resulting phase. The rate of the reduction process can be increased by use of Al_2O_3 carriers. However it causes an increase in the content of this component in the resulting non-metallic phase. Therefore lowering of the melting temperature of the system by intentional addition of Al_2O_3 is possible only if the content of this component in the converter slag is low.

The chemical composition of the autogenously disintegrating non-metallic phase generally met the conditions for the chemical composition of Ca-Mg fertilizer [4]. Only relatively a high Al_2O_3 content would require additional approval. If the slag reduction method is to be used for obtaining Ca-Mg fertilizer on an industrial scale it would be necessary to determine the acceptable content of this component beforehand. Intentional addition of Al_2O_3 carriers to the process allows to lower the melting temperature of the non-metallic phase which results in lower viscosity and increased reduction rate and thus reduction of the production costs. As obtaining of the autogenously disintegrating non-metallic phase requires much longer process time than the phase intended to use as clinker, the process time is essential.

5. Summary

The growing amount of steelmaking slag forces to look for new methods of its utilization. Slag reduction in an electric arc furnace is one of the new methods. However research carried out so far does not allow to use this process on an industrial scale. Therefore research on the process is continued.

As a result of laboratory tests it has been confirmed that the converter slag reduction process could result in obtaining a non-metallic and metallic phase. The chemical composition of the non-metallic phase is similar to the chemical composition of the Portland clinker. If the process time is extended, it is possible to obtain an autogenously disintegrating non-metallic phase of chemical composition corresponding to the composition of Ca-Mg fertilizer. Based on the findings obtained it has been found that if the reducer is premixed with the slag before starting the process it is more efficiently utilized than if it is injected during the process. Addition of Al_2O_3 during the process enables to create fusible Ca-Al eutectics causing decline in melting temperature, decrease in viscosity and surface tension. Under this conditions the reduction rate is higher. However the Al_2O_3 content in the resulting non-metallic phase increases. Adding too

much of it may cause exceeding of its acceptable limit in clinker. Therefore the amount of Al_2O_3 added should be subject to its content in the converter slag. In the case of high aluminium oxide contents in the reduced slag it must not be a component of the refractory lining. Obtaining of a non-metallic phase intended for Ca-Mg fertilizer requires a longer process time than of a phase intended for Portland clinker. The process time can be shortened by addition of Al_2O_3 carriers to the reduced slag. It require however earlier determination of the acceptable Al_2O_3 content in the Ca-Mg fertilizer.

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REFERENCES

[1] S. Kubodera, T. Koyama, R. Ando, R. Kondō, Transactions of the Iron and Steel Institute of Japan **19**, 7, 419-427 (1979).

[2] J. Piret, A. Dralants, Stahl und Eisen **104**, 16, 774-778 (1984).
[3] G. A. Li, F. Zhang, L. Zhang, Z. T. Sui, Journals of Materials and Metallurgy **2**, 3, 167-172 (2003).
[4] M. Dziarmagowski, M. Karbowniczek, M. Pyzalski, J. Okon, Ironmaking and Steelmaking **19**, 1, 45-49 (1992).
[5] M. Dziarmagowski, Archives of Metallurgy and Materials **47**, 3, 287-295 (2002).
[6] M. Dziarmagowski, Archives of Metallurgy and Materials **48**, 2, 201-207 (2003).
[7] M. Dziarmagowski, Archives of Metallurgy and Materials **49**, 1, 73-81 (2004).
[8] M. Dziarmagowski, Archives of Metallurgy and Materials **49**, 3, 699-704 (2004).
[9] J. Geisseler, 6th International Conference on Molten Slags, Fluxes and Salts, Stockholm-Helsinki, 12-17 June, 2000, 1-14.

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The diagram of Al_2O_3 content in the reduced slag and metallic phase is presented in Fig. 4. It follows from the curves in the diagram that the Al_2O_3 content in the metallic phase is lower than in the reduced slag. It is observed that the Al_2O_3 content in the metallic phase is lower than in the reduced slag. It is observed that the Al_2O_3 content in the metallic phase is lower than in the reduced slag.

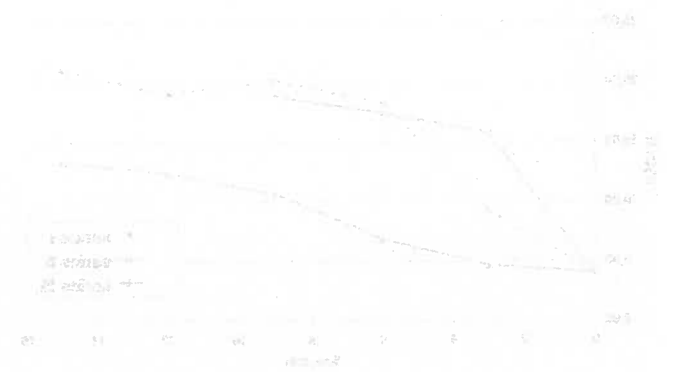


Fig. 4. Al_2O_3 content in the reduced slag and metallic phase.

The investigation of obtaining non-metallic phase was carried out in series I after 15 minutes of the reduction process. It was carried out by very low phosphorus content of 0.01% and low content of FeO and MnO, which being respectively 1.5% and 2.0% were lower than the content of these components in the series II and III.