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**INVESTIGATIONS ON THE REDUCTION LEVEL OF THE CONVERTER SLAG
DURING ITS MELTING IN AN ELECTRIC ARC FURNACE**

**BADANIA ZMIAN STOPNIA REDUKCJI SKŁADNIKÓW ŻUŻLA KONWERTOROWEGO
W CZASIE JEGO PRZETAPIANIA W ELEKTRYCZNYM PIECU ŁUKOWYM**

Recently, new methods for utilization of converter slag have been sought. Slag processing by reduction in an electric arc furnace is one of such methods. However, the state of the relevant investigations is rather poor. This was the reason for carrying out study aimed at developing a new technology of the process under industrial conditions. The study presented allows chemical composition of non-metallic and metal phases and the reduction level of the converter slag components during process run in an electric arc furnace to be determined.

Od kilka lat poszukuje się nowych sposobów zagospodarowania żużla konwertorowego. Jednym z takich sposobów jest przerób żużla metodą redukcji w elektrycznym piecu łukowym. Stan badań w tym zakresie jest jednak bardzo skromny. Z tego powodu przeprowadzono badania na podstawie których można opracować technologię procesu prowadzonego w warunkach przemysłowych. Prezentowane badania pozwalają na określenie zmian składu chemicznego fazy niemetalicznej i metalicznej oraz stopnia redukcji składników żużla konwertorowego w czasie procesu prowadzonego w elektrycznym piecu łukowym.

1. Introduction

The existing methods of utilizing converter slag are considered to be not much effective so other methods of processing and utilization are developed. A reduction method of slag processing [1-3] may be one of such methods. However, the research into this problem is scarce and the available literature does not contain publications that could have been a basis for making guidelines to run process optimally under industrial

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conditions. Recently, a research is carried out financed from European Union funds and aimed at development a cost-effective method of converter slag reduction.

To obtain data necessary for developing technology and methods for utilization of the output metal and non-metallic phase, investigation was carried out on the converter slag reduction process in a single-electrode arc furnace. The study was the basis for determining the influence of the reducer contribution in the charge on the reduction level of slag components of large dissociation pressure, and therefore on the chemical composition of the obtained metal and non-metallic phase.[4]

The investigations on the converter slag reduction process were continued. They were aimed at the determination of the changes of chemical composition of metal and non-metallic phase versus process duration.

2. Methodology

The investigations were carried out in a single-electrode arc furnace with conductive bottom the diagram of which is presented in Fig. 1.

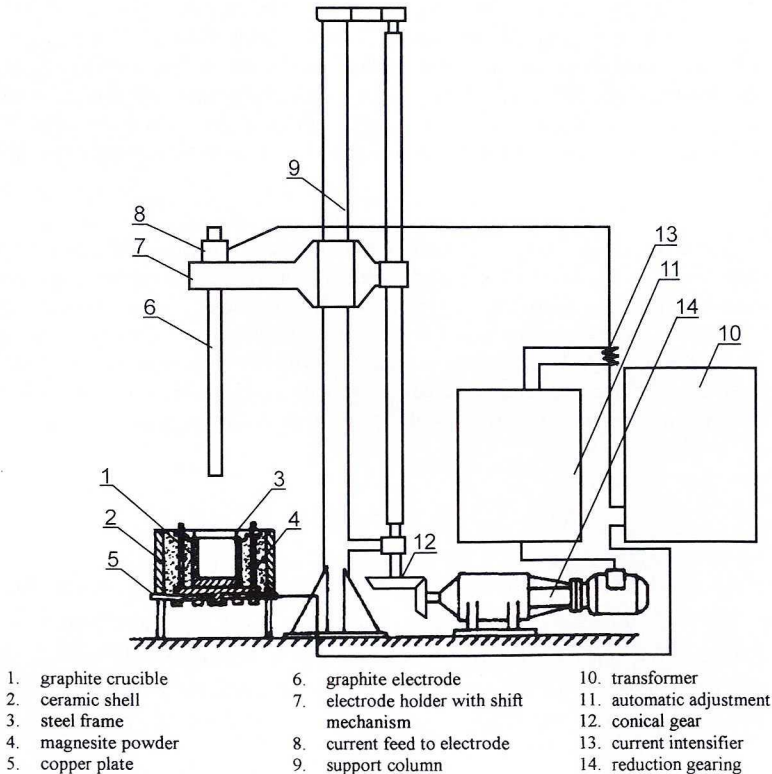


Fig. 1. Single electrode arc furnace

Milled converter slag and milled electrode were used in test melts. The mass of the slag was 1000 g, the mass of the reducer was 50 g. The slag was mixed with the reducer and the mixture was added in small portions into the melting pot during a 6-minute period. The foaming of the slag added ended after about two minutes from the end of slag addition, i.e. after eight minutes of process duration. In this period, the working current and voltage were 600 A and 40 V, respectively. From the moment the slag foaming ended, the current was gradually reduced to 400 A while the voltage was 45 V. The reduction durations after slag foaming end were 1, 5, 9, 13 and 17 minutes. For each duration three melts were performed, so the test material from 15 melts was obtained.

When the melt was finished, the metal phase from the bottom of the melting pot was separated from the overlying non-metallic phase. The latter was milled and then freed by the method of magnetic separation from the drops of the solidified metal that did not fall onto the bottom of the melting pot. Both phases were weighed and their chemical composition was determined.

The results obtained are presented in Tables 1 through 4.

After chemical composition of both phases was determined, the converter slag reduction level was calculated. Because it was expected that under industrial conditions the slag would not occur, it was decided that when calculating reduction level the chemical composition of the non-metallic phase on the metal bath should be used and the metal phase on the melting pot walls should be treated as losses. The reduction level of the converter slag components was calculated using the following equation:

$$R_x = \frac{\Delta m_{0_1}}{m_{0_2} - \Delta m_{0_3}} * 100\%,$$

where:

R_x — reduction level of component X, %,

Δm_{0_1} — oxygen mass reduction in the oxide of the component being reduced in the reduction process, g,

m_{0_2} — oxygen mass in the reduced oxide, g,

Δm_{0_3} — oxygen mass reduction in the reduced oxide resulting from the losses occurring because of the blow-out, g.

The results of converter slag reduction level are listed in Table 5.

3. Result analysis

The results obtained show that these components of slag are easily reduced with carbon which have a relatively weak affinity for oxygen. When the reduction process is finished, a non-metallic phase occurs and settles on the melting pot walls during intensive foaming of the slag. The mass of that phase increases because of outbursts caused by intensive liberation of exhaust gases and the non-metallic phase on the metal

TABLE 1

Chemical composition of non-metallic phase on the walls of the melting pot

No.	Melt	Time [min]	Phase mass. [g]	Chemical composition [%]											
				C	CaO _Σ	CaO _F	MgO	SiO ₂	MnO	ΣFe	FeO	Cr ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	ΣS
1.	converter slag		1000.0	—	44.50	1.68	5.26	16.63	5.40	18.04	23.19	0.16	1.68	1.24	0.11
2.	1-3	1	134.7	0.47	61.94	1.96	6.09	19.37	4.19	4.61	5.93	—	1.71	0.54	0.13
3.	4-6	5	265.3	0.28	61.71	1.30	4.24	23.25	2.84	3.35	4.31	0.007	2.64	0.44	0.08
4.	7-9	9	242.0	0.31	60.38	1.50	3.90	23.98	2.46	4.39	5.65	0.015	2.37	0.46	0.07
5.	10-12	13	215.3	0.48	62.31	2.03	4.44	23.27	1.95	3.74	4.81	0.007	1.93	0.51	0.07
6.	13-15	17	148.7	0.78	59.94	2.03	4.77	20.38	2.56	6.51	8.37	0.005	2.40	0.52	0.08

TABLE 2

Chemical composition of non-metallic phase on metal bath

No.	Melt	Time [min]	Phase mass. [g]	Chemical composition [%]											
				C	CaO _Σ	CaO _F	MgO	SiO ₂	MnO	ΣFe	FeO	Cr ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	ΣS
1.	converter slag		1000.0	—	44.50	1.68	5.26	16.63	5.40	18.04	23.19	0.16	1.68	1.24	0.11
2.	1-3	1	510.2	0.26	62.74	1.65	4.49	23.75	2.99	2.23	2.87	—	1.49	0.32	0.12
3.	4-6	5	379.0	0.37	66.36	1.81	3.40	24.36	1.41	1.02	1.31	0.001	2.05	0.41	0.08
4.	7-9	9	345.0	0.63	70.09	10.64	2.82	22.39	0.05	0.76	0.99	0.001	2.21	0.37	0.10
5.	10-12	13	316.0	1.69	71.89	11.10	2.22	21.09	0.04	0.18	0.23	—	2.23	0.39	0.09
6.	13-15	17	222.7	2.03	75.08	13.20	1.72	18.40	0.05	0.19	0.25	0.011	1.49	0.35	0.08

TABLE 3

Chemical composition of metallic phase

No.	Melt	Time [min]	Phase mass. [g]	Chemical composition [%]							
				C	Fe	Si	Mn	Al	Cr	P	S
1.	1-3	1	171.4	1.08	92.07	0.65	3.84	0.005	0.42	1.49	0.026
2.	4-6	5	177.6	1.44	92.42	0.57	3.41	0.005	0.19	1.40	0.021
3.	7-9	9	181.9	2.25	90.63	0.58	4.86	0.005	0.21	1.33	0.043
4.	10-12	13	183.7	4.48	87.23	0.72	5.66	0.013	0.18	1.15	0.047
5.	13-15	17	185.2	4.85	86.77	1.11	5.77	0.017	0.21	0.95	0.109

TABLE 4

Losses of converter slag components

No.	Melt	Time [min]	Losses of converter slag components [%]						
			CaO	MgO	SiO ₂	MnO	FeO	Al ₂ O ₃	P ₂ O ₅
1.	1-3	1	28.07	56.44	25.72	56.30	6.22	53.57	38.82
2.	4-6	5	43.48	75.49	43.18	75.90	6.87	52.53	41.22
3.	7-9	9	45.66	81.50	52.13	98.90	7.20	53.45	45.29
4.	10-12	13	48.95	86.65	58.25	85.40	10.90	56.79	51.20
5.	13-15	17	51.19	92.72	72.66	74.70	10.70	79.38	60.44

TABLE 5

Reduction ratios of slag components

No.	Melt	Time [min]	Reduction ratios of slag components [%]					
			Fe	Si	Mn	Al	P	R _Σ
1.	1-3	1	93.07	1.96	36.33	0.21	78.69	22.93
2.	4-6	5	97.69	2.29	59.60	0.23	78.64	28.60
3.	7-9	9	98.15	2.87	99.15	0.22	73.65	31.00
4.	10-12	13	99.64	4.05	99.02	0.61	79.46	32.98
5.	13-15	17	99.73	9.77	99.14	1.77	83.81	42.33

bath. Moreover, those drops of metal that did not fall onto the bottom of the melting pot remained in the non-metallic phase. Their mass decreased as the process duration increased from 1 to 17 minutes from the moment slag foaming ends. At the same time the total mass of the metal phase increased from 171.4 g to 185.2 g while that of the non-metallic phase decreased from 510.2 g to 222.7 g. This was caused by the losses increasing with time, caused by the outbursts and evaporation in the electric arc influence zone.

The metal and non-metallic phases were carburized during slag reduction. When the process duration increased from 1 to 17 minutes, the carbon content in the metal and non-metallic phases increased from 1.08% to 4.85%, and from 0.26% to 2.03%, respectively. At the same time the loss of mass of the electrode and melting pot increased from 27.7 g to 71.3 g, and from 21.3 to 123.7 g, respectively.

It results from the dissociation pressure of the oxides of the slag that under the investigation conditions ferric oxides, MnO, Cr₂O₃ and P₂O₅, and, to some limit, SiO₂ and even Al₂O₃, should be reduced. This finding is confirmed by changes in mass and chemical composition of the obtained metal phase. As the reduction duration increases, the mass of this phase increases and the iron content decreases in this phase from 92.07% to 86.77%.

The iron content in the slag was 18% and decreased during the non-metallic phase to 2.2% after elapsing one minute from the end of slag foaming to less than 0.2% after 13 and 17 minutes. The iron oxide reduction level increased from 93% after one minute to more than 99.5% after 17 minutes. However, with increasing process duration, the iron losses increases from 7.2% in the 9th minute to 10.9% in the 13th minute.

The character of the iron oxide reduction changes resulted from the development of the reduction process as early as in the period the sample was added and very low FeO content in the non-metallic phase after one minute from the end of slag foaming was obtained. At low content of iron oxides, the reaction rate is probably controlled by their transport in the slag. This is why increasing the iron oxide reduction level to above 99% requires a substantial longer process duration. Unfortunately, longer duration results in increase of losses of iron and when their value is greater than the mass of the reduced iron, the reduction rate would be negative.

Chromium oxide, Cr₂O₃, is a slag component that can be easily reduced. Consequently, in the first minute after the end of slag foaming the chromium content in the metal phase was 0.42%, and in the non-metallic phase was lower than the admissible error of determination ($\pm 0.01\%$). The losses of Cr₂O₃ exceeded 50% in the first minute after the end of slag foaming and increased to over 75% in the 17th minute of the process.

The chromium oxide reduction ended in the period of sample adding and slag foaming. A decrease in chromium content to about 0.2% in the metal phase after the end of slag foaming period was connected with a mass increase of this phase and chromium losses caused by blow-outs and chromium evaporation in the zone of the electric arc.

Manganous oxide cannot be not so easily reduced as iron and chromium oxides. In the first minute after the end of slag foaming its content in the non-metallic phase was 2.99%, and the reduction level was about 36%. In 9th minute, the MnO content in the

non-metallic phase decreased to 0.05%, and the reduction level increased to over 99%. Increasing process duration did not influence essentially the MnO content in the non-metallic phase and the reduction level, which shows that the end of the reduction in the 9th minute after the end of slag foaming.

The manganous oxide reduction resulted in increased manganese content in the metal phase. In the first minute, the manganese content in this phase was 3.8% and increased to 4.9% in the 9th minute, and to about 5.7% in the 13th and 17th minutes. At the same time the manganous oxide losses increased from 56% in the first minute to about 75% in the 5th minute of the process. The quantities of losses suggest intense evaporation of manganese as early as during the slag adding period.

After 1 minute from the end of slag foaming the P_2O_5 content in the non-metallic phase was 0.32%, while the phosphorus content in the metal phase was 1.49%. The P_2O_5 reduction level was over 78%. Further increasing of reduction time resulted in decreasing to zero of the rate of phosphorus pentoxide reduction to metal phase. Reduction of phosphorus had not been observed from the 3rd minute after the end of slag foaming. The phosphorus content in the metal phase decreased in the 17th minute to 0.95%. This was caused by the losses of phosphorus increasing from about 39% in the first minute to over 60% in the 17th minute.

The SiO_2 content in the non-metallic phase increased to 23.7% in the first minute after the end of slag foaming, which was caused by a mass decrease of the reduced slag and low (1.96%) level of silicon reduction. Lengthening of the reduction time to 17 minutes resulted in an increase of reduction level to about 10%. At the same time, the SiO_2 content in the non-metallic phase decreased to about 18.5%, and in the metal phase it increased to over 1%. The losses of SiO_2 in the non-metallic phase decreased to about 18.5%, the silicon content in the metal phase increased to over 1%. The losses of SiO_2 in the 17th minute of the process were very high and amounted to over 70%.

When reduction time was increased, the aluminum content in the metal phase increased to 0.017%. The aluminum reduction level in the 17th minute was 1.0%. The losses of Al_2O_3 were very high at that time and amounted to about 80%.

As the process of reduction in the non-metallic phase developed, the CaO content increased reaching 44.5% in the slag. After 1 minute from the end of slag foaming, the CaO content in the non-metallic phase was 62.7% and increased to 75% in the 17th minute of the process. At the same time the content of CaO not bounded with silica maintained at the level similar to that in the converter slag, and exceeded 10% after 9 minutes. The losses of CaO in the first minute were 28% and increased to 51% in the 17th minute.

The MgO in the non-metallic phase decreased with increasing process duration and equaled to 4.49% in the first minute after the end of slag foaming, and 1.72% in the 17th minute. At the same time the losses of MgO increased from about 56% to over 92%. This suggests magnesium evaporation under conditions of the study.

The tests made indicate that the process of converter slag reduction commences during the period of its adding. The result is intense slag foaming caused by occurring of CO bubbles in the generated liquid. Continuous slag adding determined further course of

reduction and stabilization of the generated foam. The most important factors stabilizing the generated foam include the viscosity of liquid slag, presence of dispersed molecules of the reducer and generated metal phase, and generation of adsorption layers at the boundary of the slag and metal drop or CO bubble. Literature data on the mechanism of foam generation and stabilization is given in many papers [5–8].

After slag was added a spontaneous disintegration of foam followed because of the coalescence of gas bubble and falling drops of the reduced metal phase. These processes led to the complete separation of the generated phases.

Reduction of all components of converter slag began at adding of converter slag and its foaming. The chromium oxide was reduced completely in this period. The manganese oxide reduction terminated practically in the 9th minute of the process, and the iron reduction level was 98.5%. When the process duration was extended, the iron reduction level increased to over 99.5% in the 13th minute after the end of slag foaming. Extension of process duration to over 13 minutes resulted only in increasing reduction of silicon and aluminum oxides. Reduction of other components shall be considered terminated. Moreover, when reduction time is extended, the content of sulfur in the metal phase increases from 0.0043% in the 9th minute of the process to 0.109% in the 17th minute. This was connected with an increased use of the graphite melting pot that contained 0.032% of sulfur and reacted with a generated metal phase.

The losses of the converter slag components resulted mainly from blow-outs and evaporation in the electric arc zone. The quantity of the losses point at the necessity of designing the arc furnace adjusted to the conditions of reduction process. The investigations were carried out in a melting point where the diameter of the electric arc influence zone was practically equal to the pot diameter. This was the reason for very high losses of slag components. In order to reduce the losses, a unit should be designed where the ratio of the electric arc influence zone area to the total area of generated liquid would be small. Also, a condition of low depth of the liquid compared to the height of the furnace should be met. A unit of such a type was applied by a Swiss firm vonRoll to process industrial wastes of various types.

4. Conclusions

Based on the investigations on the converter slag reduction process made in a single-electrode electric arc furnace the following was found:

1. The chemical composition of the obtained metal and non-metallic phases depends on the process duration. If the duration increases, the slag reduction level also increases, as well as the carburization of both phases and the content of manganese, silicon and aluminum in the metal phase.

2. Reduction of oxides of iron, manganese, phosphorus and chromium began under conditions of the study in the period of slag melting and foaming. Small reduction of oxides of silicon and aluminum also occurred in this period. The process resulted practically in termination of reduction of chromium oxides. The reduction level of iron

and phosphorus was 93% and 79%, respectively. Manganese was reduced to lesser extent and its reduction level was 36.3%.

3. If the time after slag foaming period was extended to 9 minutes, the reduction level of iron and phosphorus increased to 98.5% and 99%, respectively. The phosphorus reduction level was not significantly altered in this period, although the losses of phosphorus increased.

4. The reduction level of iron oxides increased to over 99.5% in the 13th minute after the end of slag foaming period while the manganese reduction level remained unchanged. If the process duration was extended to over 13 minutes, reduction of oxides of silicon and aluminum occurred only. Reduction of other components should be considered terminated.

5. Compared to the converter slag, the obtained non-metallic phase contains more CaO and SiO₂, and less MgO. As process duration increases, the content of oxides with high dissociation pressure in this phase decreases.

6. The changes of the reduction level of the converter slag components, determined based on the obtained results, allow to select the moment of process termination depending on the required chemical composition of metal and non-metallic phases.

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