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INFLUENCE OF SLAG CHARGE CHEMICAL COMPOSITION AND REDUCER ON THE FeO REDUCTION EFFICIENCY

WPŁYW SKŁADU CHEMICZNEGO WSADU ŻUŻLOWEGO I RODZAJU REDUKTORA NA EFEKTYWNOŚĆ REDUKCJI FeO

The reduction of iron oxides in molten slag by means of solid reducing agents takes place during various stages of pig iron and steel production. It may also be used in other metallurgical technologies, e.g. for the utilization of metallurgical slag. The possibility of using the utilization methods requires an in-depth analysis of the phenomenon and specification of the optimal conditions for their industrial application. This article presents the results of experiments involving FeO reduction in metallurgical slag in an electric arc furnace. The experiments were conducted using slag melt mixed with various carbon reducing agents. The experiments determined the effects of different components of the molten slag on the effectiveness of the FeO reduction process

Proces redukcji tlenków żelaza z ciekłego żużla stałym reduktorem zachodzi podczas różnych etapów produkcji surówki i stali, może on być wykorzystywany w innych technologiach metalurgicznych np. do utylizacji żużli hutniczych. Możliwość zastosowania takiego sposobu utylizacji wymaga dokładnego poznania zjawiska oraz ustalenia optymalnych warunków do przeprowadzenia go w warunkach przemysłowych. Artykuł prezentuje wyniki badań procesu redukcji FeO z żużli metalurgicznych w elektrycznym piecu łukowym, w warunkach laboratoryjnych. W czasie badań zastosowano wsad żużlowy wymieszany z różnymi reduktorami węglowymi. Na podstawie przeprowadzonych badań stwierdzono, wpływ niektórych składników wsadu żużlowego na efektywność procesu redukcji tlenku żelaza.

1. Introduction

Steel production involves the generation of an oxide phase in the form of slag. If unprocessed, steel-making slag cannot be further utilized due to its chemical composition. Therefore it is stored in waste dumps in the vicinity of steel-works and has an adverse effect on the environment. One of the slag utilization methods involves the reduction of iron oxides in an arc furnace. The oxide phase obtained after the reduction may be used in cement production or as an artificial fertilizer in agriculture. The method of post-reduction utilization is determined by the chemical and mineral composition obtained after the process, which depends on the course and technology of the reduction process and the technical parameters applied. The process also generates a metallic phase, which does not affect the environment and may be used by the industry.

2. Effect of the chemical composition on FeO reduction

Factors influencing the FeO reduction rate in molten slag include [1]:

- reducing agent type and parameters,
- physical and chemical properties of the oxide and metallic phases,
- temperature.

Particle shape, type and dimensions as well as the reducing agent feeding parameters significantly influence the rate and environment of molten slag reduction. The reduction rate increases with the increase of the flow rate of the reducer volume and the rate of the carrier gas flow. The influence of the reducing agent particle size on the reduction rate is tightly related to the carrier gas blowing rate [2]. With high gas flow rates fine reducing agent particles increase the reduction speed. With low gas flow rates the reduction rate increases along with an increase in the reducing agent particle size. The study of

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the influence of volatile parts, ash and sulphur contained in the reducing agent prove that these factors highly influence the FeO reduction rate in slag [3]. Volatile parts change the reduction mechanism, which limits the reduction rate through FeO diffusion to the reaction surface or reaction stage act. Ash content in the coal significantly changes the wetting angle by the slag, which influences the reduction rate. Sulphur, as a surface active element causes reduction in the rate through lowering the bulk transport coefficient.

Physical and chemical properties of slag affecting the reduction speed include surface tension and viscosity [4]. When coal particles are blown into the slag bulk, along with an increase in their wettability and decrease in the surface tension, the number of coal particles involved in the reaction decreases, which accelerates the reduction rate. Slag viscosity, tightly related to basicity, affects the reduction rate in an indirect way. Decreased viscosity along with increased basicity of acid slag highly increases the reduction rate. On the other hand, as the basicity of alkaline slag increases, initially also the reduction rate increases, to radically drop once the basicity reaches 1.5.

Both surface tension and viscosity depend on the chemical composition. The effect of silica dioxide content on the FeO reduction rate in slag is presented in a publication by S.K. Tarby and W.O. Philbrook [5]. Their study involved three-component CaO-SiO_2-Al_2O_3 slag, with almost constant CaO content of 50%, and varied levels of SiO_2 and Al_2O_3, as well as two-component CaO- Al_2O_3 slag, at process temperatures of 1500°C and 1575°C. The experiments revealed two different reduction reaction states: a state of intensive slag-metal mixing resulting from the formation of a large number of CO bubbles and a laminar state characterized by a significantly lower number of CO bubbles. The reduction rate constant calculated for turbulence conditions was marked as K2, whereas that for laminar conditions - K1. The experiment results are presented in Figure 1. The points on the graph represent the mean values of the calculated reduction rate constant for a given slag temperature and chemical composition. As can be seen from the curves, in all cases, an increase in the primary content of SiO_2 in slag causes a decrease in the FeO reduction rate constant. Temperature growth and increasing flow intensity of the gas bubbles accelerates the reduction process. A similar study of the influence of silica content in slag on FeO reduction rate is presented in a publication by M. Sheikshab [6]. The study proves that an increase in the SiO_2 level in slag whose basicity amounts to 1.0—1.5, with primary FeO content of 10%, brings about an increase in the FeO reduction rate constant.

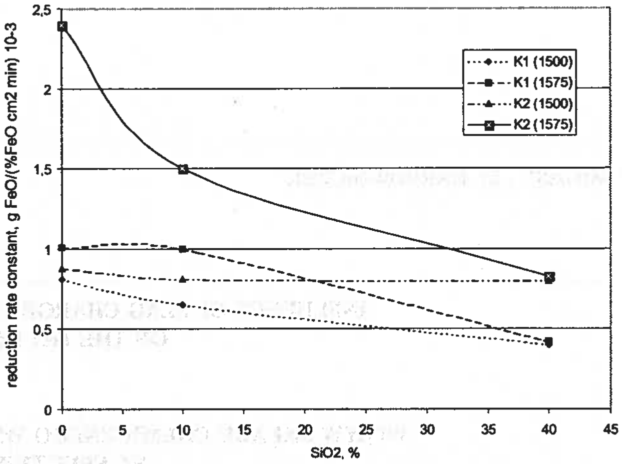

Fig. 1. FeO reduction rate constant in the function of silica in slag, 1500 and 1575°C [5]

A study of the effects of slag basicity (CaO/SiO_2) on the FeO reduction rate is presented by J. Mróz [7]. The results for the temperature of 1450°C, for controlled and uncontrolled reaction surface, are presented in Figure 2. As can be seen from the curves, an increase in the basicity of acid slag speeds up the reduction rate, regardless of the reaction surface. An increase in the basicity of alkaline slag decreases the reduction rate. The maximum reduction rate was observed for the basicity of 1.2 for controlled reaction surface and for the basicity of 1,6 for uncontrolled reaction surface.

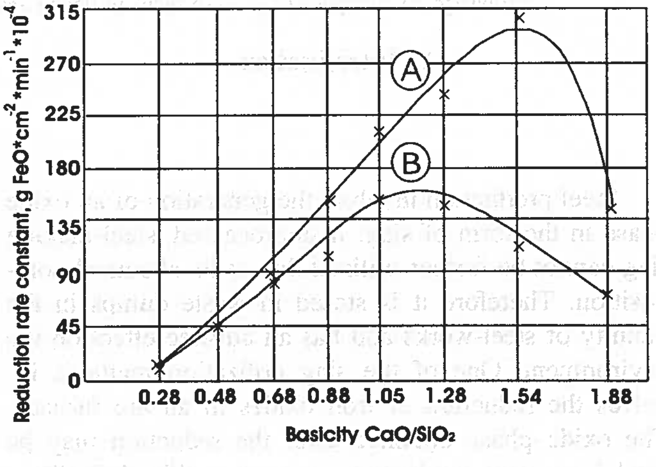

Fig. 2. Effect of slag basicity (CaO/SiO_2) on FeO reduction rate [7]

Even low contents of surface active elements influence the reduction rate of iron oxides in slag. An example of the influence of P_2O_5 level in slag on the reduction rate constant is presented in Figure 3. With an increase in the P_2O_5 level the reduction rate constant decreases. The influence of different P_2O_5 levels in slag on the changes over time of FeO levels during reduction by carbon is presented in Figure 4. As can be seen in the figure, decreasing FeO levels during reduction are dependent on the phosphorus oxide levels. The higher the P_2O_5 content the slower the rate of FeO reduction. Similar decrease in the reduction rate constant was observed with increasing sulphur levels [9].

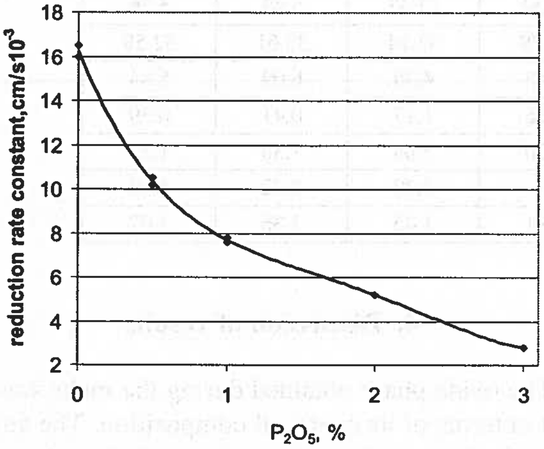

Fig. 3. Effect of P_2O_5 level in slag on the FeO reduction rate constant [5]

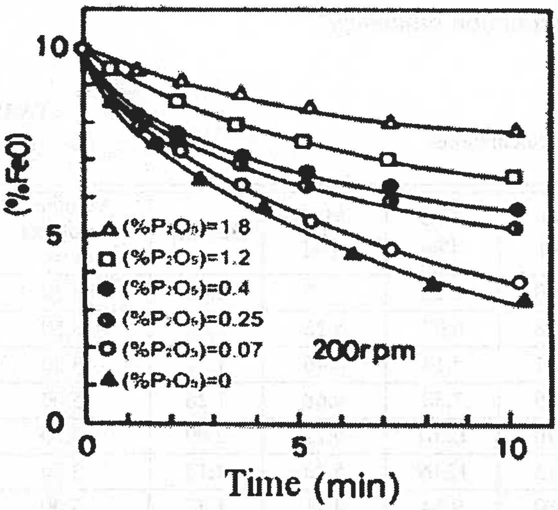

Fig. 4. Effect of P_2O_5 level on the changes in the FeO content in slag during reduction by carbon [8]

An important factor highly influencing the course and rate of iron oxide reduction is the temperature [1]. Apart from the direct effects on the course and kinetics of the reduction process itself, temperature also affects the physical and chemical properties of the slag and other parameters of the system in which the reduction takes place (surface tension, viscosity). This hinders a simple analysis of the influence of temperature on the reduction rate. As a rule, however, as the temperature grows also the FeO reduction rate increases.

3. Apparatus and methodology

The experiments were conducted in a single-electrode experimental arc furnace with a graphite crucible. The power of the supply transformer was 40 kVA, supply voltage 40 V, and the maximum current 1200 A. A 50mm-diameter carbon electrode was used. The unit was fitted with an automatic control system ensuring stable arc operation. The crucible is made of graphite and lined with a layer of alund-based refractory material. The crucible has the internal diameter of 310 mm, internal diameter of 220 mm and the refractory lining thickness of 40mm. Its total height is 400 mm, while the internal height is 315 mm.

At the beginning of the experimental melting process 1kg of a charge mixture (oxide phase mixed with the reducing agent) was inserted into the crucible. On switching the power on and the melting process began. After the molten phase was formed the remaining part of the mixture was inserted into the crucible by portions until the total bulk was melted (in total 3kg were used for all melts). The study was performed using three melting mixtures based on utilizable metallurgical slags. These were assigned the following symbols:

1. W — metallurgical slag produced during carbon steel production (92%), heat and power station — ash (5%) and reducing agent (3.5% or 5%),
2. WD — metallurgical slug produced during carbon steel manufacturing (82%), convector ash (10%), heat and power station — ash (5%) and reducing agent (3.5% or 5%),
3. S — metallurgical steel produced during high-chromium steel manufacturing (72%), arc furnace dust produced during chromium steel manufacturing (20%), heat and power station - ash (5

The chemical contents of melting mixture are presented in Table 1. Coke (K), anthracite (A) and coal-graphite waste (CGW) were used as reducing agents.

The melting time was approx. 6 min. Subsequently, the reduction process started, which was characterized by intensive foaming. The duration of reduction was varied from 6 to 10 minutes. After the oxide phase, foaming stopped, the power supply was cut off, as it was assumed that the reduction process finished. The slags and metal phases were poured into an ingot mould. After self-cooling, the oxide and metal phases were weighed.

TABLE 1

Chemical composition of the melt used in the experiments.

Components	Charge W		Charge WD		Charge S	
SiO_2	22.93	27.74	18.69	22.80	26.19	30.38
Al_2O_3	3.28	8.17	3.77	5.81	4.68	7.04
FeO	10.10	13.30	17.51	17.43	5.42	5.56
CaO	45.15	32.74	35.79	33.14	35.61	32.58
MgO	2.63	4.33	4.45	4.38	6.09	5.84
P_2O_5	1.71	1.16	1.26	1.17	0.41	0.39
Mn_3O_4	3.66	3.05	3.30	3.08	1.36	1.27
Cr_2O_3	0.43	0.41	0.39	0.39	6.32	5.78
Basicity	1.97	1.18	1.91	1.45	1.36	1.07

The samples of both phases were collected for chemical analysis. In order to examine the effects of particular oxides and reducing agent types and their amounts on the oxide phase reduction, 43 experimental melts were performed for various primary levels of particular charge oxides.

4. Discussion of results

The oxide phase obtained during the melts was analyzed in terms of its chemical composition. The analysis results for iron oxide were used to calculate the weight in grams. Also the differences between the FeO phase weight of the charge mixture and the FeO weight produced by the oxide phase after the reduction process were calculated. The difference is referred to as „the FeO reduction efficiency".

TABLE 2

List of experiment results and calculations.

	Symbol	Melts	Type of reductor	loss of FeO [g]	SiO_2 [%]	P_2O_5 [%]	FeO [%]	MgO [%]	Basicity	Volume of reductor %
1	KW	W	K	176.30	24.23	1.490	6.20	5.17	2.00	3.50
2	AW	W	A	188.79	24.23	1.488	6.07	5.22	2.03	3.50
3	KW	W	K	274.30	28.04	0.691	7.14	4.46	1.27	5.00
4	AW	W	A	269.15	28.50	0.779	7.38	4.68	1.26	5.00
5	KWD	WD	K	292.84	20.71	1.070	12.01	6.73	2.09	3.50
6	AWD	WD	A	284.90	20.68	1.015	12.09	5.42	2.13	3.50
7	KWD	WD	K	357.28	25.69	0.880	9.54	4.71	1.47	5.00
8	AWD	WD	A	360.81	24.67	0.919	9.41	4.44	1.49	5.00
5	KS	S	K	80.67	28.43	0.600	3.88	7.10	1.43	3.50
6	AS	S	A	104.08	28.27	0.380	3.23	8.26	1.44	3.50
8	AS	S	K	99.42	31.79	0.328	3.44	6.57	1.13	5.00
9	KS	S	A	86.76	31.36	0.330	3.75	6.27	1.13	5.00
10	AA39P	W	CGW	249.12	27.52	0.780	8.10	4.79	1.43	5.00
11	AA46LC	W	CGW	281.06	27.12	0.640	7.03	4.35	1.35	5.00
12	AC45LP	W	CGW	280.76	25.77	0.620	6.99	4.76	1.33	5.00
13	AC42LW	W	CGW	262.17	28.52	0.705	7.62	4.71	1.32	5.00
14	AC47LC	W	CGW	277.18	27.52	0.655	7.13	4.39	1.31	5.00

The parameter characterizes the intensity of the reduction process under experimental conditions. The oxide phase components (SiO_2, P_2O_5, MgO) were determined as well as their basicity, which affected the efficiency of the FeO reduction process. The slag phase components (except FeO) were expressed as mean values understood as the mean value of the percentage of a given component in the ingot mixture before the reduction and that of the component after the reduction. The experiment results and measurements obtained according to the procedure described above are presented in Table 2. Graphic interpretation of the results is presented below in the figures.

4.1. FeO content in molten slag

The loss of FeO, that is the relation between the decrease in the weight of FeO in grams after the reduction process and the primary weight of the FeO bulk is presented in Figure 5. The Figure presents data for all experimental melts, regardless of the type and amount of the reducing agent. As can be seen from the data, the loss of FeO increases proportionally to the increase in the amount of FeO inserted, i.e. the reduction efficiency decreases. The tendency is observed regardless of the amount of the reducing agent applied. On the other hand, what clearly matters is the type of charge used. The greatest loss was observed for the WD charge, which contains the highest proportion of FeO, next for the W charge, which contains the medium amount of FeO; the lowest loss was observed for the S charge, which contained the lowest amount of iron oxide.

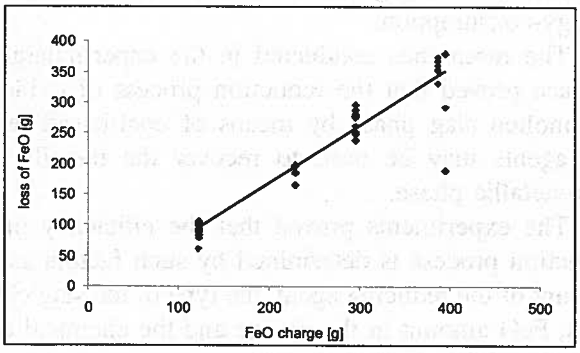

Fig. 5. Changes in the loss of FeO depending on the FeO content in the charge

Figure 6 presents the loss of iron monoxide in the oxide phase after reduction for different amounts and types of the reducing agent and for the 3 types of charges. In view of the data presented in the figure, anthracite is for most part the best reducing agent for charges W and S. This tendency persists regardless of the amount of anthracite used. For the WD charge the tendency is different: in two cases it was reverse, which means that the K-coke type reducing agent is better. In conclusion, it can be stated that anthracite is the most effective reducing agent for melts containing lower amounts of iron oxides, whereas for higher levels of iron monoxide in the melt, factors other than the reduction agent type and reduction conditions are more important.

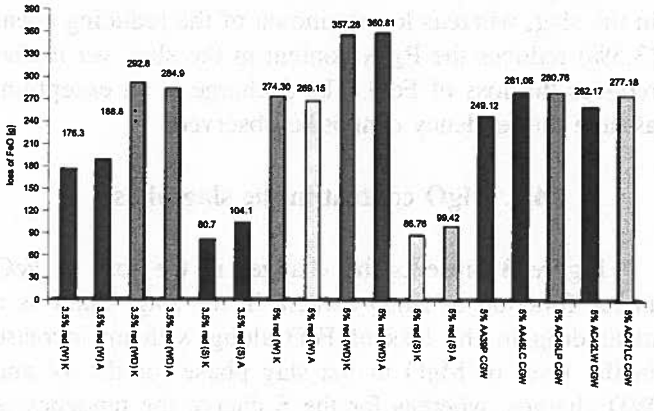

Fig. 6. Characteristics of the changes in the loss of FeO for particular: charges, reducing agent type and the amount of reducing agent

The highest efficiency of FeO reduction in the WD charge, may result from the physical properties of slag, the changing chemical composition, but may also result from the highest levels of iron oxides. The positive effect of the amount of the reducing agent can be observed regardless of the types of melt: with 3.5% the loss of FeO is lower than with 5%.

4.2. P_2O_5 content in the slag phase

Figure 7 presents the effect of medium-level P_2O_5 content in the slag phase on the loss of FeO, showing the efficiency of the reduction process for various reducing agent types and amounts and for the 3 types of charges involved.

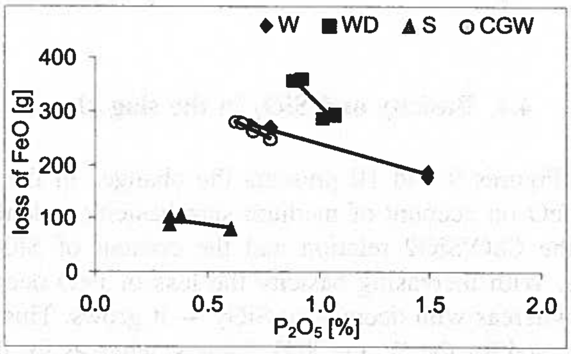

Fig. 7. Changes in the loss of FeO depending on the P_2O_5 content in the charge

Along with FeO also P_2O_5 was reduced. Therefore the calculated mean content of P_2O_5 in the oxide phase is lower than that in the charge, the greatest changes in P_2O_5 occur in the WD charge, next in the W charge, and the lowest in the S charge. For each melt type there is a clear tendency of FeO loss reduction due to increasing P_2O_5 content in slag.

Increased amount of the reducing agent (5%) causes an increase in the loss of FeO and reduces P_2O_5 content in the slag, whereas lower amount of the reducing agent (3.5%) reduces the P_2O_5 content in the slag, yet it also reduces the loss of FeO. The S charge is an exception, as here the tendency cannot be observed.

4.3. MgO content in the slag phase

Figure 8 presents the changes in the loss of FeO in the function of MgO content in the slag. There is a clear drop in the loss of FeO along with an increase in the level of MgO in the slag phase for the W and WD charges, whereas for the S charge the tendency is reverse. The changes in the loss of FeO resulting from the amount of the reducing agent are the same as in the previous figure for the W and WD charges. Along with an increase in the amount of particular reducing agents, the loss of FeO increases. In the case of the S charge, no visible influence of the amount of the reducing agent on the loss of FeO can be seen.

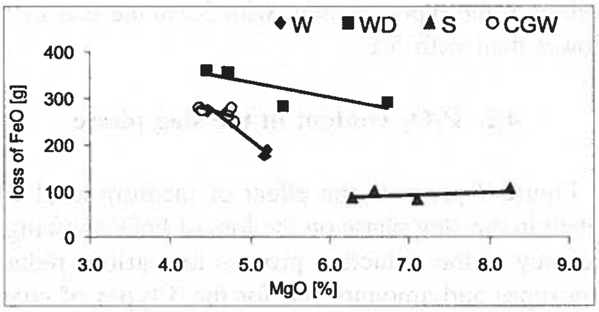

Fig. 8. Changes in the loss of FeO depending on the MgO content in the charge

4.4. Basicity and SiO_2 in the slag phase

Figures 9 and 10 presents the changes in the loss of FeO on account of medium slag basicity, calculated as the CaO/SiO2 relation and the content of SiO_2 in slag. With increasing basicity the loss of FeO decreases, whereas with decreasing SiO_2 — it grows. This was observed for the W and WD charges, whereas for the S charge no changes in the loss due to increased basicity and SiO2 content were observed.

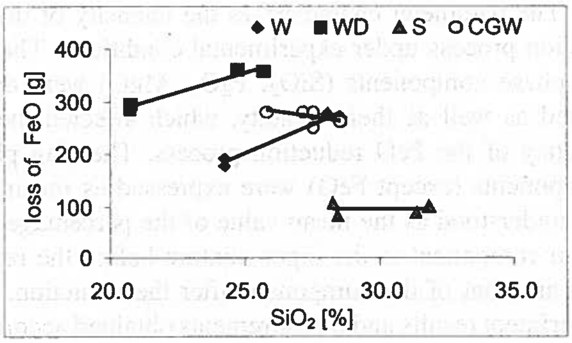

Fig. 9. Changes in the loss of FeO depending on the SiO_2 content in the charge

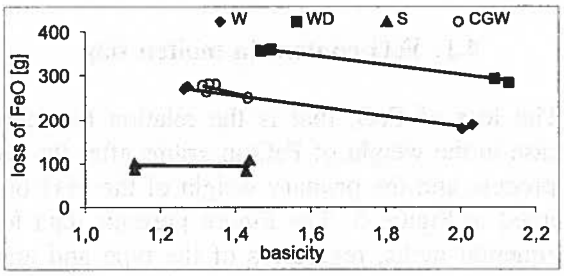

Fig. 10. Changes in the loss of FeO depending on the basicity of slag

5. Summary and conclusions

The possibility of the utilization of such post-production waste as slimes, dust, metallurgical slag requires a study and characterization of the reduction mechanisms and the influence of chemical composition of the reaction system on reduction kinetics and efficiency. There is also a need to develop new technologies and optimize the existing ones in view of cost reduction and energy-consumption.

The researches conducted in the experimental arc furnace proved that the reduction process of oxides in the molten slag phase by means of coal-based reducing agents may be used to recover the metallic and non-metallic phase.

The experiments proved that the efficiency of the reduction process is determined by such factors as: the amount of the reducing agent, the type of the slag charge used, FeO amount in the charge and the chemical composition of the reaction system.

Conclusions:

- An increase in the amount of the reducing agent to 5% causes increased loss of FeO, i.e. it increases reduction efficiency,
- It cannot be clearly stated which type of reducing agent — K (coke) or A (anthracite), improves reduction efficiency.
- Clear is the influence of FeO amount in the melt on the efficiency of the reduction process, the more iron ox-

ide in the molten slag, the bigger the loss of FeO, (regardless of the amount of the reducing agent added), i.e. the yield of the metallic phase after the process is higher,

- The graphs shows the influence of selected oxides on the loss of FeO: increased P_2O_5 content decreases the loss of FeO, which may prove the data provided in reference sources — presented in figure 3 — the reduction in the „k" constant — rate of FeO reduction resulting from increased P_2O_5 content,
- What can be observed for the S charge is the lower influence of chemical composition and basicity on the loss of FeO as compared to the two other charges — W and WD,
- Basicity of 1.2–1.5 seems to be most suitable for the W and WD charges to obtain maximum FeO loss, beyond this value reduction efficiency drops, which may prove that the process control is of diffusive nature,
- With the MgO content of 4.2–5.0% maximum loss of FeO was observed. This MgO level is optimal for the W and WD charges.

All figures show a slight decrease in the loss of FeO along with an increase in the amounts of the parameters examined. The conclusions drawn here will help us understand and describe the reduction mechanism and the effects of certain factors on the phenomenon. It should be stated, however, that it is necessary to continue the research in view of kinetics reduction in terms of quantitative chemical composition of the reaction system. This will help obtain the best conditions for the reduction process, which will enable effective utilization of metallurgical slag at minimum cost and energy.

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