### CERCETĂRI EXPERIMENTALE PENTRU TESTAREA COMPORTĂRII ÎN CONDITII INDUSTRIALE A PULBERILOR DE ACOPERIRE CENOTERM FOLOSITE LA TURNAREA CONTINUÀ A OTELULUI EXPERIMENTAL RESEARCH FOR TESTING THE BEHAVIOR IN INDUSTRIAL CONDITIONS OF CENOTERM COATING POWDERS **USED FOR CONTINUOUS CASTING OF STEEL**

#### CRISTIAN DOBRESCU, SÂNZIANA ITTU, NICOLAE CONSTANTIN\*, BOGDAN FLOREA, VALERIU RUCAI, DRAGOS FLORIN MARCU

University POLITEHNICA of Bucharest, 313 Spl. Independentei, Bucharest, Romania

The goal of this paper was to analyze the industria behavior of CENOTERM coating powders used in continuous casting of steel. CENOTERM powder is made using thermal power plant ash in the manufacturing recipes. The thermal power plant ash is part of the range of industrial waste. In the context of this paper, CENOTERM coating powder was used for continuously casting steel under industrial conditions. Industrial experiments with powder recipes for the thermal power plant ash-based dispenser were carried out at MECHEL Târgoviște.

Testing of coating powders at an economic agent where continuous casting of steel is carried out has been carried out with a view to finalizing these powders' manufacturing technology. The paper presents the analysis of the behavior in industrial conditions of coating powders made from indigenous raw materials, some of which are even landfilled waste. The research carried out revealed the functions of the powder on the surface of the liquid steel and the final effects of the powders on the quality of the steel.

Această lucrare a avut drept scop analiza comportării în condiții industriale a pulberii de acoperire CENOTERM folosită la turnarea continuă a oțelului. Pulberea CENOTERM este realizată utilizând în rețetele de fabricație cenușă de termocentrală. Cenușa de termocentrală face parte din gama deșeurilor industriale. În cadrul prezentei lucrări s-a folosit în condiții industriale pulberea de acoperire CENOTERM la turnarea continuă a oțelului. Experimente industriale cu rețetele de pulberi pentru distribuitor pe bază de cenușă de termocentrală s-au desfășurat la MECHEL Târgoviște.

Testarea pulberilor de acoperire la un agent economic unde se practică turnarea continuă a otelului, s-a efectuat în vederea definitivării tehnologiei de fabricație a acestor pulberi. În lucrare se prezintă analiza comportării în condiții industriale a pulberilor de acoperire realizate din materii prime indigene, unele fiind chiar deșeuri depozitate în halde . Cercetările efectuate au pus în evidență funcțiile exercitate de pulbere pe suprafața oțelului lichid și efectele finale ale pulberilor asupra calității oțelului.

Keywords: coating powder, secondary materials, thermal power, fly ash, steel, continuous casting.

#### 1. Introduction

In the conditions of maintaining or even increasing the world steel production, the steel industry is an important field for the economic development of Romania. Increasing the purity of steel is a permanent goal of applied research. There are a lot of factors that influence the quality of steel, namely its purity.

One method of increasing the quality of steel is the use of technological powders in the dispenser.

These powders have the role of thermally insulating the liquid surface of the steel.

Casting powders must retain endogenous and exogenous inclusions thus contributing to the purification of the steel.

The purpose of the experimental research presented in this paper was to finalize the obtaining of advanced materials with optimal characteristics to be used as coating powders in the dispenser.

Good characteristics for coating powders can

be obtained if proper importance is given to the research stage of the raw materials, regardless of their provenance.

Those that possess physic-chemical properties compatible with those of the expected product, will be therefore used as basic materials and the others will focus the chemical composition in the proposed field. [1-4]

The range of potentially useful raw materials for the manufacture of powders is wide, starting with refractory brick waste, waste, left over from other technological flows or natural deposits.

When obtaining powders as mechanical mixtures, the quality of the finished product is determined by the physic-chemical properties of each individual raw material. [1,5,6]

The choice of raw materials is made according to the chemical composition, according to SR ISO 1953: 1999, the thermal characteristics, and some physical characteristics such as bulk density, volumetric mass, spreading area, according to SR

<sup>\*</sup> Autor corespondent/Corresponding author,

E-mail: nctin2014@yahoo.com

ISO 331:1994, and the cost price of each, including transport.

The raw materials used in casting powder production technologies are natural ores, secondary materials, or combinations of them.

Ores have the advantage of relatively stable chemical compositions, but their price is higher than secondary materials or waste. In addition, most deposits require additional technological operations, such as concentration in useful substance (as a sterile part removal operation).

These necessary operations increase production costs [7].

Secondary materials that can be used in the production of casting powders are powders captured in electro filters in steel mills or in the development of ferroalloys (amorphous silica), dumped waste (thermal power plant ash and furnace slag), waste from electrodes used in metallurgy, metallurgical coke residue remaining from loading furnaces, etc.

Among the mentioned secondary materials, power plant ash is a raw material successfully used in the technology of casting powders, for all types of casting powders, both for obtaining thermal insulation materials and lubricating ones. [8-10]

Thermal power plant ash is a waste resulting from the burning of coal in thermal power plants, being captured in a powdery, dry state, in electro filters.

The chemical composition of the fly ash was determined on the pre-calcined sample at 800 °C, following ASTM C618 standards, obtaining the following result in (%): mass: 51.6% SiO<sub>2</sub>; 20.1% Al<sub>2</sub>O<sub>3</sub>; 10.6% Fe<sub>2</sub>O<sub>3</sub>; 10.8% CaO; 1.9% MgO; 1.2% Na<sub>2</sub>O; 0.3% K<sub>2</sub>O; 2.8% SO<sub>3</sub>.

The chemical analysis of the power plant ash does not show the presence of heavy metals but only of *alkalis*.

The chemical composition ensures the presence of the main refractory oxides:  $SiO_2$ ,  $Al_2O_3$  and small amounts of basic oxides: CaO, Na<sub>2</sub>O, K<sub>2</sub>O in the structure of the coating powder for the dispenser.

The ash introduces small amounts of carbon into the composition of the casting power.

The raw material that brings carbon in the powder recipes is metallurgical coke. The quantity and quality of carbon are determined by the share of coke in the recipes.

Free carbon plays an important role in thermal insulation powders as the combustion of the coals takes place. Free carbon is a moderator of the melting rate of powders and at the same time increases the thermal insulation capacity through the caloric intake resulting from its combustion.

Thermal power plant ash is a waste with a strong ecological impact due to the large quantities in which it results and for whose storage large areas of land are removed from the agricultural circuit.

These considerations were the basis for conducting experimental research for the use of thermal power plant ash in the manufacture of casting powders.

Powders obtained as mechanical mixtures are oxidizing materials with physical and chemical properties determined by their components.

To determine the range in which the finished product must fall, for its use, the chemical analysis, then physical and high-temperature parameters, shall be used as the starting criterion. The free carbon content regulates the melting rate of the main oxides in the composition: SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>. At the same time, the free carbon-carrying material is a fuel, and its thermal contribution compensates partially the heat loss from the steel surface [10-12]

The research in this paper presents the use of dispenser powder obtained from the thermal power plant ash as a solution for solving the problems currently encountered in steel works.

The difficulty of the problem resulted in the correlation of the physical and thermal characteristics of the powder with the main parameters of the casting (quality/brand of steel, casting temperature, casting speed, dispenser capacity and free surface) correlated with the stationary time of the steel in the dispenser.

From a granulometric point of view, the ashes from CETs fall in a spectrum between 0.2 and 200µm.

The raw materials used in the manufacture of the coating powder for the CENOTERM dispenser can be separated into the following categories:

-basic raw materials, with refractory oxide content: power plant ash, [2-4]

-raw material with the role of loosening, reducing the volumetric mass perlite,

- fuel type raw material, carbon bearing metallurgical coke residue / oil coke / charcoal,

The technological process of powder manufacturing follows the stages of the technological flow mixing and homogenization.

Prepared raw materials (dry and ground), dosed according to the manufacturing recipe, ash, and coke, will be introduced into the ball mill with a capacity of 100 or 150 liters, for mixing for  $\frac{1}{2}$  hour / charge. Perlite is added for homogenization with 5 min. before the end of homogenization.

The verification of the characteristics is done according to the in-force norms.

Finally, the selection of the batches used for the experiments is a very simple problem, there can be no errors and the reproducibility of the results can be ensured.

# 2. Experimental research for testing the industrial behavior of CENOTERM coating powders

2.1. Characteristics of industrial use CENOTERM coating powder

Table 1

CENOTERM powder manufacturing recipe/ Reţeta de fabricaţie a pulberii CENOTERM [1]

Raw materials	M.U.	VALUE
Thermal power plant ash	% by weight	60 - 70
Expanded perlite	% by weight	15 - 20
Metallurgical coke residue /Petroleum coke waste / Charcoal waste	% by weight	15 - 20

Table 2

Physical characteristics of CENOTERM powder batch/ Caracteristicile fiziice ale pulberii pentru distribuitor CENOTERM [1]

Rest, [%] on sieves:						Specific volume	Moisture [%]	Spreading	Melting		
1.0 [mm]	0.5 [mm]	0.2 [mm]	0.09 [mm]	0.06 [mm]	< 0.06 [mm]	[g/cm <sup>3</sup> ] SR ISO 5069-1994	SR ISO 331: 1994	area, [cm²/g] SR ISO 1953: 1999	temperature, [ºC] SR ISO 5069- 1994		
0.4	0.4	6.4	28.4	13.2	51.2	0.48	0,53	818.30	1330-1350		

Table 3

Composition of CENOTERM powder/ Compoziția pulberii CENOTERM [	<sup>.</sup> 1]
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% by weight,											
SiO <sub>2</sub>	$AI_2O_3$	CaO	MgO	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K2O	MnO	P.C.	LOI*	
50.35	17.48	4.0	3.42	0.79	6.13	0.61	2.50	0.09	14.63	0	
56.00	19.30	1.69	-	-	5.60	-		-	15.40	2.01	
62.01	19.87	3.97	3.51	-	7.60	-		0.08	0.16	2.8	

\*) loss of ignition

The physical and chemical properties of the made powders are essential in assessing their quality. The analysis of the powders' behavior on the liquid steel surface is very important for both assessing product quality and the completion of the powder manufacturing technologies.

To produce the pilot experimental batch, the raw materials were dispensed according to the proportion of the recipe presented in Table 1.

The physical and chemical characteristics of the experimental CENOTERM powder batch are shown in Tables 2 and 3. The relative measurement errors of the physical-mechanical properties are 0.1%.

## 2.2. Experimental conditions and casting technological parameters

The testing of the coating powders made based on thermal power plant ash at the continuous casting of steel, was performed to finalize the manufacturing technology of these powders.

Experiments in casting construction steels were carried out to perform industrial experiments of powder recipes created in the laboratory.

The physical and chemical properties of the made powders are essential for their quality evaluation.

To appreciate a thermal insulation powder, the behavior when using powders on the surface of the steel meniscus is very important. For preliminary experiments, the laboratory recipes of the powders based on thermal power plant ash were used in the casting of construction steels.

The experimental conditions at the electric steelworks, the continuous casting section, were:

Casting pot with magnesium brick lining, capacity 70-75 t liquid steel:

-casting, without protected jet,

-pouring time 80-85 minutes, under normal conditions,

-casting temperature of steel in dispenser: 1555-1565°C,

-cast steel quality: PC 52, grade 60 steel; these steels are not deoxidized with aluminum, the deoxidation is done with silico-manganese, Si-Mn,

-the last temperature range measured in the pot,

-tuning in sequence, minimum 2 loads, maximum 4 loads.

Administration of CENOTERM powder in the dispenser with lid.

The experimental powders were applied, by the usual procedure, administration through the holes of the dispenser's lid, after filling it with liquid steel. The amount of powder used was on average 20 kg / batch (for a single batch); when necessary, a 5 kg bag was added. then 15 kg/load. When casting in sequence, 2-4 batches, no powder was administered starting with the second batch, because its effectiveness would have been very low.

Experimental batches and the casting main parameters are shown in Table 4.

The first sample was collected about 10 minutes after the start of the casting procedure and the following at about 70 minutes. If two charges were sequent cast, another sample was taken towards the end of the sequence casting, i.e., the minute 150.

The chemical analyses carried out indicated changes between the initial composition of the powder, the composition of the first slag sample (liquid + sintered) at the beginning and at the end of the casting.

During the performed tests, the slag capacity to capture the inclusions of MgO, MnO and  $Al_2O_3$  was studied. The determinations were performed by

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Crt.	Crt. Batch no	Steel Grade	Pot temperature,	Dispenser	Powder type/	Quantity of cast					
No.	Daten no.	Oleci Olade	(LF)[ <sup>0</sup> C]	temperature, [ <sup>0</sup> C]	quantity, [kg]	steel, [t]					
1	53604	Grade.60	1613	1560-1555	RI/30	71					
2	53605	Grade.60	1613	1555-1547	0	68					
3	53612	P.C.52	1613	1560-1555	RII/16	70					
4	53613	P.C.52	-	1560-1555	0	68					
5	63406	P.C.52	1613	1560-1555-1555	RII/16	78					
6	63407	P.C.52	1610	1560-1555-1555	RIII/16	78					
7	53621	P.C.52	1613	1560-1555-1555	RIII/16	75					
8	53622	P.C.52	-	1550-1555-1550	RIII/16	78					
9	53848	Grade.60	1610	1565-1560-1560	RIV/10	75,4					
10	53849	Grade.60	1605	1560-1555-1555	0	75					
11	53850	Grade.60	1607	1550-1560-1560	RIV/10	78					
12	53851	Grade.60	1610	1565-1560-1560	0	76,8					

Parameters recorded during testing batches with experimental CENOTERM powder

Table 5

Table 4

Evolution of the oxide composition of experimental slags in the use of experimental recipes Evolutia compozitiei zgurilor experimentale la utilizarea retetelor experimentale [1]

	Batch no	Oxide composition, % by weight									
Crt. No.	sample no.	SiO <sub>2</sub>	Iron oxides	$AI_2O_3$	$V_2O_5$	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	
R I composition		55.05	6.70	16.03	-	-	-	< 0.05	8.52	6.70	
min 10 - R I	53604- P1	55.2	7.36	16.7	0.03	0.66	0.04	2.6	8.3	2.85	
min 70 - R I	53605- P2	39.5	7.02	8.4	-	0.55	0.20	26.7	3.6	4.31	
R II composition		56.95	6.90	16.33	-	-	-	< 0.05	6.95	3.22	
min 10 - R II	53612- P3	56.0	6.8	16.2	0.02	0.63	0.09	4.3	6.8	2.72	
min 70 - R II	53612- P4	43.8	6.33	6.3	0.02	0.55	0.54	31.0	3.0	4.74	
min 150 - R II*	53613- P5	35.3	12.8	4.7	-	0.42	0.57	23.9	8.8	7.34	
RIII composition		42.00	0	15.90		-	-	-	3.64	3.73	
min 15 - R III	63406– P1			7.65				13.1		6.34	
min 70- R III	63407- P2			7.04				22.04		7.19	
R IV composition		47.76	6.52	15.00		0.63	-	-	3.57	3.00	
min 10 -R IV	53848- P1	42.19						9.51		1.70	
min 70 - R IV	53848- P2	37.71						36.83		6.35	
min 95- R IV	53849-P3	34.55						37.87		5.5	
min 150- R IV	53849- P4	36.85						37.38		5.89	
min 10- R IV	53850- P1	46.87						13.85		0.90	
min 70- R IV	53850-P2	47.87						36.93		5.50	

spectral analysis in the steel laboratory, only significant in influence oxides of the analyzed slag sample. The determination of SiO<sub>2</sub> by spectral analysis was done outside the calibration curve for this compound, for this reason there may be some errors in the value of this oxide. However, the tendency manifested in the composition of the slag is important, and these preliminary tests aimed at studying the behavior of the molten powder but also the evolution of the chemical composition of the slag. MnO and CaO values were determined by spectral analysis.

The obtained results were compared with those given by wet chemical analysis.

Similar values were obtained on both types of analyzes. The values shown in Table 5 represent the collected slag compositions taken from the dispenser's meniscus. No slag samples have been taken for the last 4 batches.

The industrial parameters investigated during the studies with CENOTERM coating powders were, as follows:

-thermal insulation capacity, -ability to capture inclusions, -powder consumption. Melting the powder in a short time and maintaining a permanent layer of liquid slag determines the use of the coating powder only for the first batch of the sequence; for the next batch there is already a layer of liquid slag covering, which provides protection against oxidation and capture of inclusions.

In the analysis of the behavior of the tested powders, emphasis was placed on the absorption capacity of the inclusions, because this is a very important function for the purification of steel and that the tested powders have successfully fulfilled. The uptake of MnO in slag up to 16% showed that both the manganese steel oxidized strongly when poured with open wire, without jet protection tube but also that the slag has a composition suitable for absorbing inclusions.

The average powder consumption was 130 / 891.2 = 0.15 kg powder/t liquid steel, cast iron. The maximum specific consumption was 0,22, kg/t poured billet, recorded for the RI recipe.

The study of these industrial parameters was made to highlight the major effect of the use of CENOTERM coating powder on the quality of cast steel.

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Fig. 1 - Temperatures measured in the dispenser Temperaturile măsurate în distribuitor [1].



Experimental sample number

Fig.3 - Content of SiO2, MnO and MgO (% by weight) in the experimental samples / Conţinutul de SiO<sub>2</sub>, MnO şi MgO (procente masice) în probele experimentale [1].

The graph in Figure 1. shows the temperatures measured in the dispenser for the batches for which three measurements were taken, and the graph in Figure 2 shows the quantities of cast billet for each charge.

#### 2.2.1.Analysis of taken slag related to the initial compositions of experimental powders

The main changes that take place in the composition of the molten slag on the dispenser's meniscus are the following:

a) Increasing the MnO content

The MnO content increases strongly from 2.6 % to 26.7 % for batch 53604, where the R I powder was used.

The graphs in Figure 3 show the values for  $SiO_2$ , MnO and MgO (% by weight) in the experimental samples 53848-P<sub>1</sub>, 53848-P<sub>2</sub>, 53849-P<sub>3</sub> and 53849-P<sub>4</sub>. The graphs in Figure 4 show the values for  $SiO_2$ ,  $Al_2O_3$ , MnO and MgO (% by weight) in the experimental samples 53604-P<sub>1</sub>, 53605-P<sub>2</sub>, 53612-P<sub>3</sub> and 53612-P<sub>4</sub>.

When testing with recipe R II, MnO increased from 4.3% in the first sample taken, 10 minutes after the casting start, to 31 % at the end of the charge.

At the end of the next charge casting, the second in the sequence, the MnO content has dropped to 23.9 %.



Fig. 2 - Quantities of cast billets for experimental batches/ Cantitățile de țagle turnate pentru șarjele experimentale [1].



Experimental sample number

Fig. 4 - Content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO and MgO (% by weight) in the experimental samples / Conţinutul de SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO și MgO (procente masice) în probele experimentale [1].

The explanation for this phenomenon may be that the *steel is heavily oxidized during free casting, without a protective tube*, and the manganese content of the steel (1%Mn), is not changing for the 71-tone ladle.

Assuming that this process is entirely due to oxidation, which is excluded, the insignificant decrease of manganese by burning, as a steel alloying element, is inferred as follows:

15 kg R I powder is converted into 13.6 kg liquid slag containing 26% MnO -(free coke carbon burning, i.e., 80%, has entirely taken place) i.e., approx. 3.53 kg MnO.

This amount has been formed by burning about 2.7 kg manganese.

Compared to 710 kg manganese contained in the steel in the ladle, the 2.7 kg represents 0.38 %, or in other words this decrease is insignificant for the chemical composition of the steel.

The origin of MnO in the slag on the dispenser's meniscus may also be due to the penetration of the MnO steel existing inclusions in the casting ladle.

Quantitative evolution of the MnO content immediately after the change of the casting ladle gives precise indications on the provenance of this oxide. For recipe R IV, the difference between the MnO content at the end of the first charge casting ,36.83%, compared to the beginning of the second charge casting ,37.87%, is approximate 1%.

The MnO ratio is lower in the R II slag sample at the end of the second charge casting, 23.9%, than at the end of the first batch, 31.0%, all due to the penetration of a quantity of basic slag from the ladle, which enriches the slag with CaO and diluting the other components, including MnO, consequently.

b) Decreasing the following oxides values:  $SiO_2$ ,  $Al_2O_3$ , CaO because of the increasing of MnO content by dilution.

c) Increasing the MgO content of slags, which has an increasing evolution from the beginning of the casting to the end of second charge casting, which means that there is a superficial reaction of the slag with the lining of the dispenser or, small breaks from the lining can arrive in the liquid steel from the casting ladle, lined with magnesite brick.

The appearance of the dispensers after casting processes shows that there were no corrosions of their lining in the slag layer. Both the slag and the melting steel have "glazed" the walls of the dispenser after the last casted charge.

#### Specific consumption recorded

A quantity of 891.2 tons of billet was cast in the 12 charges by using 130 kg of coating powder as experimental recipes. The average consumption was 130/891.2 = 0.15 kg powder per ton of liquid steel, casted billet.

At first casted charge, the RI powder was provided in a larger quantity, of 30 kg, but in the following charges RI, RII and RIII, less powder was obviously provided.

In the first charge, the calculated specific consumption was 0.423 kg/tone of liquid steel, and 15 kg/charge were used for the following charges.

The last casted charges with RIV powder have counted a consumption of 10 kg/2 charges. When pouring in a sequence of 2 charges, no more powder was applied to the dispenser for the second batch except for the following charges: 63406, 63407, 53631, 53632.

*The specific consumption per net billet* has not been calculated, but the losses being generally very small, it would possibly exceed by max. 15 % the counted consumption for liquid steel.

The recorded consumptions were, as following:

R I: 30 kg /139 t = 0.22 kg / t liquid steel

R II, R III 16kg /138t or 16kg / 75t = 0.12-0.21kg / t liquid steel

R IV: 20 kg / 305.2 t = 0.065 kg / t liquid steel

The powder consumptions for the dispenser, measured in kg, and the quantity of cast billet, in tones, are shown graphically in Figure 5.



Fig. 5 - Actual powder consumptions for each charge and the corresponding amount of billet cast/ Consumurile efective de pulbere pentru fiecare şarjă și cantitatea de țaglă corespunzătoare turnată [1].

#### 2.2.2. Analysis of the slag compositions taken from the dispenser; inclusions capture Slag samples were taken as follows:

- the first slag sample and steel, respectively, at about 10 to 15 min after providing the melted powder.

- the second sample at the halfway point of the first charge casting.

- the third sample, at approx. 5 min before the completion of the first charge casting.

- the fourth sample, at the beginning of the second charge casting, (after emptying the second ladle), in sequence casting procedure.

- the fifth sample at the halfway point of the second charge casting.

- the sixth sample, as the final one, occurred just before the end of the second charge casting.

The samples were chemically processed, and the six representative samples were spectrally analyzed. The samples were investigated by the SEM / EDS method by using a scanning electron microscope model XL 30 ESEM (3.5 nm resolution), coupled with an EDAX Sapphire energy dispersion spectrometer (128eV resolution). The values of the determinations on the taken slags are shown, as percentages in Table 6.

Determination of values for MnO, CaO and  $SiO_2$  were done by spectral analysis (XRF method).

The values determined by spectral analysis for MnO and CaO were verified by the classical, wet

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Chemical analysis, 2 analyses /sample/ Analiza chimică, 2 analize /probă [1]

	Batch	SiO <sub>2</sub>	CaÓ	$AI_2O_3$	Fe*	MnO	MgO	TiO <sub>2</sub>	P.C.
1	65202 P1	51.25/	1.96/	19.27/	23.84/	2.22/	2.87/		1 17
	05292- F 1	53.30	2.76	20.00	9.46	2.14	1.37		1.17
2	65202 02	48.22/	2.38/	17.60/	1.63/	11.22/	4.91/		2 5 2
2	05292- F2	52.00	2.53	18.30	5.52	10.00	2.20		2.52
2	65202 02	40.58/	1.96/	12.82/	2.72/	32.50/	6.23/	Ī	
3	05292- P3	42.50	1.32	9.52	5.73	27.80	5.13	0.27-	
4	65202 D1	38.33/	3.21/	9.70/	6.73/	31.06/	4.87/	0.28	
4	05295- F 1	40.20	3.10	7.80	8.70	30.20	6.03		
5	65202 02	33.84/	2.35/	7.51/	5.04/	34.88/	5.11/		
5	05295- FZ	38.00	2.29	6.67	6.75	33.60	5.67		
6	65002 D2	24.30/	1.96/	7.20/	10.60/	38.83/	6.38/	]	
0	05295-P5	40.50	1.80	6.31	11.21	33.20	6.09		

chemical procedure. The chemically determined values were very close to the spectral ones.

Therefore, these preliminary tests were based on the behavior of the molten powder as well as the evolution of the chemical slag composition.

The analysis by electron scanning microscopy of the slag samples taken from the reference charge sequence - 65292 - 65293 – as presented in the following figures, shows both images of each analyzed sample and the points at which the components were analyzed qualitatively and quantitatively, as well (EDS elementary analysis).



For most of the analyzed samples, the carbon content is very high because the samples were SiC sanded which partially impregnated the surface. If we remove the SiC "mark" from the slag sample, we have the real picture of its real composition.

Figures 6 and 7 show the images accompanied by elementary analyses at three different points, for sample P3 in charge 65293, the last slag sample of the charge sequence.

It is noticed the MnO values of 26.82% in a very light coloration area, off-white (Fig.6 left) and in a black particle, a well-defined globular inclusion,



Fig. 6 - Image and composition of slag particle with 17.3% Si and 26.8% Mn (left), respectively slag with 14.54% Si and 43.87% Mn (right), % by weight / Imagine şi compoziție particulă de zgură cu 17.3% Si(stânga) şi 26.8% Mn, respectiv, zgură cu 14.54% Si şi 43.87% Mn (dreapta), (procente masice) [1].

Table 6



Fig. 7 - Image and composition of slag particle with 20.62% Si and 31.22% Mn, respectively slag with 20.07% Si and 31.57% Mn (% by weight)/ Imagine şi compoziție particulă de zgură cu 20.62% Si şi 31.22% Mn, respectiv, zgură cu 20.07% Si şi 31.57% Mn (procente masice) [1]

MnO is equal to 31.22% (Figure 7 left). In another analyzed area (Figure 6, right) the black globular formation, covered by a white, non-homogeneous film, MnO is equal to 41.83%. The oxygen content level of all samples is high, which shows that the slag elements are mostly oxides.

The elemental silicon, with a share of 14-17% corresponds to a content of approx. 30 to 34.5% SiO<sub>2</sub>, which is close to the chemical and spectral performed analyses. The margin of error due to carbon is its very share, i.e., 3-5%, up to even 10%.

#### 3. Discussion

Analysis of the main slag oxides,  $SiO_2$ ,  $Al_2O_3$ , MgO, CaO, coming out from the initial composition of the powder, as well as those ended up as inclusions, MnO and partially MgO, highlights their evolution during the casting of a slag sequence.

By comparison with the initial composition of the molten powder vs. the compositions of the successively taken slag samples when casting in sequence, the share, and the evolution of the MnO content are particularly pointed out.

The experimental results have indicated some changes between the initial composition of the powder, the composition of the first slag sample at the beginning of casting (about the 10 th minute) and those of the following taken samples during the charges casting.

The powder coating of the metal bath was easily achieved by maintaining a dark coloration for 10 to 12 minutes, after which the powder was transformed into a layer of liquid slag, evenly distributed on the meniscus of the dispenser.

The use of the cap dispenser is one of the major advantages of improving this aggregate, in terms of reducing the heat loss of the liquid steel mirror, by radiation to the atmosphere.

Thermal insulation was good, but analysis of the temperature gradient in the dispenser, i.e., a maximum 15°C decrease between T1 and T3, shows that there were heat losses in the dispenser, which did not affect the casting process, finally.

The possible reason of the assumption mentioned before might be both the low casting speed and small interruptions of casting wires, resulted in prolonging the steady state of the steel charge in the dispenser up to 1h and 45 minutes. (e.g., charge no. 65293).

When the casting time lasted one hour and ten minutes the temperature loss was lower, of about 5 to 10°C, maximum. At the last charges, only one temperature was measured in the dispenser due to a lack of measuring instruments (thermocouples sheaths).

The positive effects of powders on the crystallizers are, as follows:

- Increasing the cast steel quality by purifying it into the dispenser. [10-12]

- Decreasing the steelworks production costs by replacing the imported powders, such as Accutherm or Thermotect, with the much cheaper CENOTERM product.

Considering the estimated production costs, the sales price of CENOTERM powder, in €/t, is 2.3 times smaller, by comparison with price of the current imported powders: (the company Metallurgica or Stollberg).

- Reducing environmental pollution coming from steelworks by using powders without harmful dispenser components to the human body.

#### 4.Conclusions

CENOTERM-type coating powder manufacturing technology contributes to environmental protection by using thermal power plant ash, metallurgical coke residues, with a grain size of less than 3 mm, which remains after the furnace is loaded and can no longer be used as fuel for individual consumers or economic agents.

The raw materials used in the manufacture of powders for the dispenser are not harmful, do not contain quartz, asbestos or other toxic substances that can be inhaled during crushing, grinding, drying and handling operations. Even if during technological operations, especially when crushing, a small, very fine part of the material comes out of the machine inside the pilot station, they are not dangerous for the breathing of the working people.

By analyzing the slag samples the high capacity of capturing inclusions by the coating powder can be noticed.

At the same time it can be assessed that the thermal power plant ash-based powders have been reactive, with a major effect on cast steel quality.[10-12]

It can be said without any doubt that CENOTERM powder is optimal for purifying the melted steel in the dispenser. +++

The results of the experimental research presented in this paper created the technological framework for the use of thermal power plant ash as raw materials to produce coating powders.

Due to the good performance of CENOTERM powder in industrial tests, the manufacturing technology can be finalized.

The results of the experimental research presented in this paper create the technological framework for the recovery of thermal power plant ash as raw materials in the production of coating powders.

As a result of the CENOTERM powder 138691. capabilities in terms of steel casting production tests, the manufacturing technology can be finally occured.

The implementation of the technology does not produce negative effects on the main environmental issues: soil, microclimate, surface waters, vegetation, fauna; no noice inconveniences, as well.

CENOTERM powders have as main beneficiaries the economic agents producing steel.

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