Experimental Research for Operating Thermal Electric Plant Ash in Coating Powder Production Used in the Continuous Steel Casting Lines

Nicolae CONSTANTIN, Valeriu RUCAI*, Bogdan FLOREA, Cristian DOBRESCU, Dragoș Florin MARCU

Abstract: In this paper the authors present obtaining of a technological powder used for the continuous casting of steel. The powder is applied in the casting plant distributor to ensure thermal insulation, prevent oxidation of the steel and especially to capture the steel inclusions. The powder helps to purify the steel and thus improve its quality. The paper presents the physical and chemical characteristics of the power plant ash, which is a fine-grained waste, stored in dumps and which can be used for the production of coating powders. Several experimental recipes were made, in which the proportion of power plant ash was between 65-80%. To characterize the recipes, measurements were made to determine the humidity, volumetric mass, spread area, particle size analysis, melting temperature and chemical analysis. After analyzing the physical, chemical and thermal characteristics, pilot experimental batches were performed for testing in the steelworks. The favourable effects of the use of Cenoterm powder were highlighted by analyzing the slag samples taken from the experimental batches. These showed an increase in the MnO content of steel up to 3.0%, an increase in alumina, magnesium and a decrease in silica. They show that the molten powders in the formed slag are reactive and play a beneficial role in the quality of the steel. Consumption of ash-based coating powder was between 0.065 and 0.22 kg/t liquid steel.

Keywords: coating powder; continuous casting; disperser; steel; thermal electric plant ash

1 INTRODUCTION

Continuous improvement of the steel production requirements in terms of quality, the modernization of the steel elaboration and casting aggregates together with the developments in related technologies, lead to the implicit improvement of the disperser as part of the complex continuous casting plant equipment [1-4].

At the same time, there is a qualitative improvement in refractory materials ancillary to casting, which plays a very important role in ensuring the purity of steel through the functions they perform.

The processes that take place in the disperser during the casting of a batch, determine the purity of the steel. A proper understanding of the correlation of all technological factors contributing to superior quality of cast semi-manufactures (slabs, billets, plate slabs) is the realistic approach to continuous casting procedure [5-8].

The reduction of heat loss from the steel surface occurs by using coating powders.

They must take into account the constructional features of the distributor (shape, capacity, size of the surface of the liquid steel, number of wires) and its role as an intermediate link between the casting ladle and the casting plant.

Technological powders used to cover the liquid surface of steel in the distributor are oxidative powdery materials classified as thermal insulating materials and are part of multi-component systems of the SiO₂-CaO-Al₂O₃-Fe₂O₃-MgO-K₂O-Na₂O type and consisting of at least 15% free carbon in various forms for calorific intake and melting delay.

The performance of these powders influences the casting and solidification process of steel, including the accompanying dynamic processes, with effects on the quality of the surface and the internal structure of the continuous cast semi-finished product [2, 9-11].

The imported powder Accutherm T from Stollberg is currently used to pour large-scale slabs, for the uncovered distributor, at ArcelorMittal Galați, which has the following drawbacks:

- high specific consumption, 0.7-0.9 kg/t liquid steel;
- high price;
- the deficient melting forms viscous sinters and during the sequence from the third batch, forms solidified slag bark on the steel surface, sometimes blocks the operation of the ladle-stopper;
- it reacts with the disperser lining producing corrosion that can be seen at the end of its sequence; it remains glued against the top of the unit (slag area) which leaks to the bottom of the unit blocking some steel.

The analysis of the factors that influence the quality of cast steel by increasing steel purity in the disperser constituted a second threshold in evaluation of thermodynamic and chemical processes taking place during casting from the ladle to the distributor and then into the crystallizer [7, 12, 13].

In this respect, the conditions to be met by coating powder for the distributor and the correlation of its characteristics with the first casting parameters: steel brand, temperature and casting speed and the constructive features of the aggregate called disperser, were established. Free carbon plays an important role in thermal insulation powders, its quantity and quality being determined by the share of free carbon-bearing matter, metallurgical coke, oil coke or charcoal but also by its quality.

Free carbon is a moderator of the melting rate of the powder and at the same time increases the thermal insulation capacity through the calorific intake resulting from its combustion.

The carbon as a chemical element is found in the metallurgical coke used in the powder, in max. 88%, typically Cfree = 80%, while petroleum coke, even waste, has more than 95% free carbon, so using the last type of coke, the oil one, is beneficial.

The delay by carbon of the melting process of the major oxides in the powder composition such as Al₂O₃, SiO₂, CaO results in a low consumption rate, or the specific powder consumption will be lower and the thermal insulation (by stratified powder) of the steel surface will be optimal.
As a reducing agent, C, especially in the presence of CO (formed by contact with slag oxides), can influence the quality of the steel when the powder, due to turbulence, is temporarily embedded in molten steel [7-9].

In the thermal electric plant ash, the content of iron oxides of type Fe₂O₃ is up to 10% and there is no FeO ferrous oxide.

The iron content of the ash is entirely in the form of Fe₂O₃ because a process of total oxidation of the fuel components takes place when the coal is burned.

The fineness of the grinding of the coke or charcoal used influences both the melting speed and the solidification range of the liquid slag. The use of ash powders, with added graphite, nanometres, if possible, increases the dust sinter-melting time, as well as a decrease in the slag solidification (vitrification) speed, which is beneficial for the steel in the disperser.

The metallurgical coke residue, used in the coating powders obtained in the present work, has compositional variations within relatively small limits.

In the coating powder manufacturing technology, a limitation of the compositional variation for raw materials is required, as follows:

- for metallurgical coke, a maximum of 10% ash is required and the free carbon is at least 90%,
- for the thermal electric plant ash introduced in the raw materials recipe, contents of maximum 10% for Fe₂O₃ and maximum 20% for Al₂O₃ are required.

2 EXPERIMENTAL RESEARCH TO OBTAIN COATING POWDERS
2.1 Analysis of the Characteristics of the Thermal Electric Plant Ash
2.1.1 Determination of the Physical Characteristics of the Thermal Electric Plant Ash

The ash is a waste from the combustion of coal in thermal power stations, being sprayed, dry, in electro filters. The ash introduces the main oxides of the coating powder structure Al₂O₃, SiO₂, CaO as well as carbon into the casting powder composition [1, 11, 12].

To be used as a raw material in the molding powder technology, the ash must be kept under special ventilation conditions and without the possibility of attracting atmospheric humidity, since it is hygroscopic.

For good use, it is necessary to comply with certain values for physical characteristics, namely:

- humidity, max. 0.55 %
- volumetric mass 0.60 - 0.65 / g/cm³
- spreading surface min. 400 / cm²/g
- sintering interval 1200 - 1250 / °C
- melting range 1260 - 1350 / °C.

Thermal electric plant ash drying is carried out in several stages, since it is warm after drying and temporarily deposited in identified bags (until dosing and mixing is carried out) it has been found to increase its humidity by more than 0.4%.

Several successive determinations of humidity, volumetric mass and spreading area have been carried out in the laboratory, the mean values of which are given in Tab. 1 and in the graphs in Figs. 1 to 3.

Figs. 1 to 3 show the graphical interdependence of these parameters.
It can be observed that the humidity has a negative effect on the spreading capacity and the bulk mass/volumetric mass of the ash, as well.

The chemical compositions of thermal electric plant ash from Doicesti were determined in the laboratory and are shown in Fig. 4 [2, 4].

2.1.2 Analysis of the High Temperature Performance of Doicesti Thermal Electric Plant Ash

Using a furnace in which the evolution of the temperature can be perfectly controlled, as laboratory furnace coupled with an optical microscope that visualizes the sample inside the furnace, the high-temperature behavior of Doicesti-source thermal electric plant ash was investigated.

Microscopic images of the ash sample, which is heated up to 1358 °C, are shown in Fig. 5.

It is noted that it deforms as the temperature increases.

![Microscopic images of the ash sample during determinations](image)

Analysis of high temperature optical microscopy images shows that the ash, on melting, does not become fluid, remains viscous, and there is no regular flow for an oxidizing material. No image of the flattened half sphere, typical of flow.

The appearance of this melted ash is glossy-free, dark gray to black, and the melt easily detaches from the support plate upon which it melted.

Generally, the so-called "fly ash" casting powders melt harder, have higher viscosity and lower melting speed.

Ash is still an important raw material, with a large share in the composition of casting powders (still predominantly used in powder technology in Europe) due to the following advantages:
- it is a cheap raw material;
- found in a powdery or pulverization state, using it as such and no longer requires additional energy consumption for grinding;
- has good flow and spreading properties;
- it can be transported pneumatically, directly to the storage bunkers.

The chemical composition ensures the presence of the main refractory oxides: SiO₂, Al₂O₃ and small amounts of basic oxides: CaO, Na₂O, K₂O [2, 4].

The ash melts heavily, the molten state is viscous; it has a sinter-melting range of approximately 1000 °C, which is ideal for the ash used in the casting of steel.

2.2 Experimental Laboratory Research to Produce the Coating Powder Using the Thermal Electric Plant Ash as Raw Material

The most used coating powders for the dispenser have acid composition.

Accutherm T and Accutherm T 20 powders are acidic powders containing silica (SiO₂) and alumina (Al₂O₃) more than 70%.

Thermal electric plant ash powders have higher silica content than these powders and lower alumina content.

Being a mechanical mixture of oxidizing materials, it has physical and chemical properties determined by its components; the physical characteristics are transmitted to the finished product in proportion to their weight. Chemical reactions between components occur on melting, certain networks of silicoaluminates are formed which can incorporate and dissolve various steel inclusions, usually oxides but also sulphides or sulphates formed earlier.

The formation of the SiO₂MgO or SiO₂Al₂O₃ refractory spinels increases viscosity and density of slag.

For this reason, the slag is usually removed from the dispenser at least once per batch to take the viscous slag down.

By subsequent application of the coating powder, a new slag is formed by partial melting upon contact with the steel bath, which is fluid and capable of capturing other inclusions or of retaining any trace of gases.

The characteristics of the powder, both as a powder and as a melt in liquid slag, determine its behaviour at the interface with steel.

Chemical analysis of the components helps to establish the approximate scope of the application, but also to assess the thermal characteristics and the mode of melting behaviour.

The alumina, magnesia, and silica compositions free of founding oxides such as Na₂O and K₂O, even Fe₂O₃, will have high sinter-flow temperatures; those with silica and alumina, i.e., the thermal electric plant ash powders have melting temperatures around 1280 °C.

The experimental recipes are presented in Tab. 2.

### Table 2 Recipes for raw materials to produce coating powder

| Materials/Recipes | R₁ | R₂ | R₃ | R₄ |
|-------------------|----|----|----|----|
| Thermal electric plant ash | 70-80% | 70-80% | 60-70% | 65-75% |
| Expanded perlite-perlysol assortment | 5-15% | 10-20% | 15-25% | 10-20% |
| Metallurgical coke residue | 15-25% | 10-20% | - | - |
| Oil cokes | - | - | 15-20% | - |
| Charcoal waste | - | - | - | 15-25% |

The main physical characteristics of the experimental materials are presented in Tab. 3.

### Table 3 Physical characteristics of the raw materials used [1]

| Material name/ Feature | Humidity / % | Volumetric mass / g/cm³ | Dispersal surface / cm²/220 g | Granulometry, / % |
|------------------------|--------------|--------------------------|-------------------------------|-------------------|
| Ash - Doicesti source | 0.31 | 0.55 | 560 | 100% < 1.0 mm |
| Metallurgical cokes | 0.72 | 1.0 | 230 | 80% < 0.09 mm; 20% < 1.0 |
| Perlite-perlysol | 0.70 | 0.12 | 3070 | Min 15% > 1 mm; max 85% < 1.0 |

The experimental recipes are presented in Tab. 2.
To characterize the recipes, determinations were made for humidity, volumetric mass, dispersal surface, particle size analysis, melting temperature and chemical analysis. The results of the determinations performed are presented in Tabs. 4 and 5.

In the graph in Fig. 6 the spreading surfaces of the experimental samples are presented in a suggestive manner compared to the Roeno TTC dust - the reference dust from MECHEL Targoviste.

### Table 4 Physical characteristics of experimental recipes

| Powder type | Particle size analysis / % | Volumetric mass / g/cm³ | Dispersal surface / cm²/220 g | Humidity / % | Melting temperature, / °C |
|-------------|---------------------------|-------------------------|-------------------------------|--------------|---------------------------|
| R₁          | 1.6 / 11.2                | 0.51                    | 854.4                         | 0.41         | 1200                      |
| R₂          | 3.2 / 10.1                | 0.42                    | 977.3                         | 0.37         | 1200-1220                 |
| R₃          | 3.7 / 10.3                | 0.45                    | 862.1                         | 0.19         | 1200-1250                 |
| R₄          |                          | 0.58                    | 629.5                         | 0.47         | 1200-1220                 |
| Roeno TTC   | 5/10 Rolleke             |                         |                               |              |                           |

**Note:**
- over 40% > 0.5
- cca. 60% > 0.09
- 0.41
- 497.8
- 0.15
- 1300

### Table 5 Chemical analysis of the experimental recipes

| Powder type | Chemical composition / % | Chemical composition / % |
|-------------|--------------------------|--------------------------|
|             | CaO | Al₂O₃ | MgO | SiO₂ | Fe₂O₃ | Na₂O | K₂O | TiO₂ | C lib | P.C. |
| R₁          | 7.60 | 14.29 | 2.64 | 49.08 | 5.97 | 1.45 | 2.32 | -   | 16.53 | 16.6 |
| R₂          | 6.36 | 14.96 | 2.95 | 52.16 | 6.32 | 1.13 | 2.41 | -   | 11.43 | 13.7 |
| R₃          | 3.92 | 17.11 | 4.02 | 45.19 | 5.92 | 0.98 | 2.52 | -   | 13.52 | 20.3 |
| R₄          | 3.57 | 15.00 | 3.00 | 48.16 | 6.52 | 0.79 | 2.73 | 0.63 | 11.15 | 19.6 |
| Roeno TTC   | 0.95 | 5.86  | 0.84 | 89.9  | 0    | 0.08 | 2.17 | -   | 4.50  | 0.20 |
| Accutherm T | 2.5  | 19.5  | 1.6  | 35.5  | 6.5  | 5.3  | -    | -   | 18.0  | -    |
| Accutherm T5| 4.0  | 21.5  | 1.6  | 41.5  | 7.0  | 5.5  | -    | -   | 6.0   | -    |

*The carbon was analysed separately, the initial samples were calcined, and the calcination losses, P.C. have resulted.*

### Figure 6 Dispersal surfaces for experimental recipes and reference powder

A lower value of humidity determines a lower value of the volumetric mass of the sample.

The "light" and dry masses have a very good ability to discharge and disperse, thus ensuring an efficient thermal insulation.

Fig. 7 shows the values of the preponderant oxide compounds and combustible parts for made powder recipe. The melting temperatures have been found to be in the low range of 1200 to 1250 °C, and in this respect need to be experienced by the addition of calcium oxide or by increasing the content of metallurgical coke.

The R₃ recipe has the highest melting temperature of the prepared recipes. The coke used is different from blast furnace coke, it has been contaminated with sand and therefore all recipes have shown a low melting temperature.

The chemical analysis of the recipes reflects the compositional dosage for experimental powder and is crucial for the use behaviour of each powder.

Analysis of results values given in Tab. 5 leads to the following assessments:

- the values of Al₂O₃ are around 15%, (max. 17.11% for R₃) and show (theoretically at least) that the powder has the capacity to capture inclusions and is not saturated in alumina. Accutherm T powder has alumina values of around 20%, but Na₂O content is over 5%. Na₂O is a very good flux and fluidizer on the silicate grid;
- low values of MgO, below 4.0% which may mean that the melt will have a low viscosity (increasing the MgO ratio increases viscosity);
- the content of iron oxides is below 6.5 %, which for powder obtained from ash is the limit of a good composition;
- free carbon has much higher values than Roeno TTC powder with 5-12%, but comparable to Accutherm T powder. For powder used in the dispenser, restrictions on carbon content very rarely exist when pouring a pearlitic steel, with very low carbon content, susceptible to crust carburization;
- the values of physical and chemical characteristics determined for the experimental recipes compared to the imported powder from Rolleke, Roeno TTC 5/10 which were presented in Tabs. 4 and 5, are different. The high content in SiO₂ shows that the powder is very strongly acidic, siliceous, the composition of which is different from that of the experimental silico-aluminous powder.

The visual appearance of the powder is that of a mass of rice husks mixed with graphite flakes, a powder like the Thermostil type.

The disadvantage of this powder is that at the melting it forms very little slag, the thickness of the layer being insufficient to capture and incorporate the slag inclusions.

The analysis of made compositions to select a recipe with the best characteristics is based on their values and the $R$ type. The third favourable effect is to better thermal insulation and to capture non-metallic inclusions from the previous dump's locations.

- The advantage of this powder is that at the melting it forms very little slag, the thickness of the layer being insufficient to capture and incorporate the slag inclusions.

The granulometry indicates an advanced fineness of the powder because of mixing in the ball mill, although the ball load was 20% (of the total balls) which led to the advanced grinding of the coke and partly of the perlite; it is necessary to reduce the mixing time, to 15-20 minutes, and to add the perlite only 5 minutes before the end of the homogenization.

- Granulometry indicates an advanced fineness of the powder because of mixing in a mill with balls, although the ball load was 20% (of all balls) which led to the advanced milling of the coke and partly of the perlite; it is necessary to reduce the mixing time to 15-20 minutes and to add the perlite only 5 minutes before the end of mixing.

- The volumetric mass and spreading area are conditioned by performing advanced drying and have optimum values for a thermo insulating powder.

The finalization of the coating powder technology for the dispenser, the powders based on thermal electric plant ash, can only be done after industrial use tests.

3 RESULTS AND DISCUSSION

Analysis of the characteristics determined on the experimental batch will lead to the following assessments:

- The first aspect is the much lower cost of ash as a raw material, being a production waste category, than traditional raw materials, with implications on the manufacturing cost of the coating powder.

4 CONCLUSIONS

In order to research and make products of this type, with indigenous raw materials that include electric plant ash, the most widely used imported coating powders were taken as a reference in terms of composition, structure and properties.

For the purposes of research and development of such products with indigenous raw materials including thermal electric plant ash, reference was made to the composition, structure and properties of the most used imported coating powders.

The use of this fine-grained waste deposited in dumps near coal-fired power plants a threefold beneficial effect has been obtained.

The first aspect is the much lower cost of ash as a raw material, being a production waste category, than traditional raw materials, with implications on the manufacturing cost of the coating powder.

A second favourable effect is that on the environment, the ash stored in dumps, having a very fine grain, is driven by air currents, and is polluting the air in a large area. Making the most of this waste is also greening the areas of the previous dump's locations.

The third favourable effect is to better thermal insulation and to capture non-metallic inclusions from continuously cast steel due to the slow melting of the coating powder that has had also thermal power plant ash in the raw materials recipe.

The results of the experimental research presented in this paper confirm the validity of the stated results and create the technological framework for the recovery and use of thermal electric plant ash as raw materials in the production of coating powders.

5 REFERENCES

[1] Ittu, S. (2013). Increasing the purity of steel by the efficient use of oxidic powders in the continuous casting plant dispenser. PhD thesis, Bucharest.

[2] Demir, I., Sevim, O., Ozel, G., & Dogan, O. (2020). Microstructural, physical and mechanical properties of aerated concrete containing fly ash under high temperature
and pressure. *Romanian Journal of Materials*, 50(2), 240-249.

[3] Volcean, E., Volceanov, A., & Sandu, S. M. (2019). Influence of poplar ash and willow ash admixture on plastering mortar properties. *Romanian Journal of Materials*, 49(4), 591-600.

[4] Woraphot, P. & Abideng, H. (2011). Feasibility study of cement composites with para wood particle wastes: strength and durability. *Global Nest Journal, 13*(2), 182-191. https://doi.org/10.30955/gnj.000768

[5] Ittu, C., Constantin, N., Miculescu, F., & Dobrescu, C. (2009). Insulating powder used in iron and steel industry. *Metalurgia International, 14*(4), 25-28.

[6] Ardelean, E., Lăscuțoni, A., Ardelean, M., Socalici, A., & Heput, T. (2016). Simulation of solidification process for billet with φ350 mm section, continuous casted. *IOP Conference Series: Materials Science and Engineering, 106*(1). https://doi.org/10.1088/1757-899X/106/1/012034

[7] Lohenkilpi, S. et al. (2003). Effect of thermophysical material data on heat transfer in continuous casting. *Modeling of casting, welding and advanced solidification processes-X, 733-740.

[8] Ittu, S. et al. (2021). Experimental research for testing the behavior in industrial conditions of cenoterm coating powders used for continuous casting of steel. *Romanian Journal of Materials, 51*(2), 291-299.

[9] Palomo, A., Maltseva, O., & Fernandez. A. (2016). Ultra reactive ash: a new concept of fly ash leading to the production of durable and cheap eco concrete. *Romanian Journal of Materials, 46*(3), 259-268.

[10] Ardelean, M., Lăscuțoni, A., Ardelean, E., & Socalici, A. (2016). Liquidus temperature, optimization, powder coating, powder molding, steel continuous casting. *Solid State Phenomena, 254*, 176-181. https://doi.org/10.4028/www.scientific.net/SSP.254.176

[11] Cbudziński, A. (2020). Physical modelling of fluids’ interaction during liquid steel alloying by pulse-step method in the continuous casting slab tundish. *Ironmaking & Steelmaking, Processes, Products and Applications, 47*(10), 1189-1198. https://doi.org/10.1080/03019233.2019.1708670

[12] Pineda Huitron, R. M., Ramirez Lopez, P. E., & Vuorinen, E. (2019). Converging criteria to characterize crack susceptibility in a micro-alloyed steel during continuous casting. *Materials Science & Engineering A, 772*, 138691. https://doi.org/10.1016/j.msea.2019.138691

[13] Ardelean, E., Lascutoni, A., Ardelean, M. et al. (2015). Technological aspects at continuous casting of semi-finished products with phi 270 mm. *IOP Conference Series-Materials Science and Engineering, 85*, 012002. https://doi.org/10.1088/1757-899X/85/1/012002

**Contact information:**

**Nicolae CONSTANTIN**, Professor, PhD
University POLITEHNICA of Bucharest,
313, Splaiul Independentei, 060042
E-mail: nctin2014@yahoo.com

**Valeriu RUCAI**, Associate Professor, PhD
(Corresponding author)
University POLITEHNICA of Bucharest,
313, Splaiul Independentei, 060042
E-mail: vrucai@gmail.com

**Bogdan FLOREA**, Lecturer, PhD
University POLITEHNICA of Bucharest,
313, Splaiul Independentei, 060042
E-mail: florea_b2004@yahoo.com

**Cristian DOBRESCU**, Lecturer, PhD
University POLITEHNICA of Bucharest,
313, Splaiul Independentei, 060042
E-mail: cristiandobrescu@yahoo.com

**Dragoș Florin MARCU**, Associate Professor, PhD
University POLITEHNICA of Bucharest,
313, Splaiul Independentei, 060042
E-mail: dragos.marcu@arasnet.ro