

# Re+Gen® an innovative technology for recovery and reutilization of Steel Slags

Authors: \*Pietrobon L.<sup>1</sup>; Miolo M.<sup>1</sup>; Carlesso F.<sup>2</sup>; Pizzato E.<sup>2</sup>; Artuso D.<sup>2</sup>

<sup>1</sup>Chemical Department of White Black Slag Technology S.r.l (Treviso, Italy)

<sup>2</sup>Engineering Department of White Black Slag Technology S.r.l (Treviso, Italy)

\*Corresponding author.

E-mail address: luca.pietrobon@wbstitalia.it

## Abstract

*In the steelmaking process, metallurgical wastes are produced, called slags, as a by-product of the steel. The conventional operations used for these wastes are typically slow cooling, mechanical separation, and landfill transportation, leading to safety hazards, dust emissions and excessive use of water. In this work, it is presented the technology of White Black Slag Technology S.r.l. (WBST), which allows the recovery and regeneration of different slag from the EAF furnace (black slag) and LF furnace (white slag). The proposed technology consists in an innovative treatment with a cooling system, separation of metal from the slag and recovery of useful materials in form of granulates. The tests carried out demonstrate the possibility of lowering the leaching values of heavy metals from EAF slag and the elimination of the dusting problem and water consumption well known for LF slag. Furthermore, this article presents the chemical and physical characterization of the materials obtained by cooling LF slag (Re+Lime®), which have been successfully used to partially replace the flux agents commonly used in EAF, thus contributing to reducing dependence on materials sourced from natural resources such as limestone and dolomitic lime.*

## 1. Introduction

In 2023, global crude steel production was recorded at 1.888 million tons. [1]

The steelmaking process involves the use of chemicals called fluxes, which perform several functions: removing impurities in the metal, separating the molten metal from atmospheric oxygen, and preserving the integrity of the furnace refractory materials. Fluxes are composed of a combination of calcium lime, dolomite lime and other chemical compounds (silicates and aluminates). Once these elements react, they generate waste commonly called "slag".

Conservative estimates suggest that, for every ton of steel produced, about 9-10% black slag is obtained from the electric arc furnace (EAF) and 3.9-4% white slag for carbon steels, rising to approximately 25% for stainless steels, from ladle furnaces (LF). Currently, only a small part of this waste is recycled, generating considerable disposal costs and still representing an environmental impact. [2]

Also, thanks to the push of the European Union with the expansion of the carbon emissions

trading system, the "circular" approach is gaining value. Of particular importance is the transformation of slag in order to extract and recover useful materials, which are then destined for the production of secondary products. By way of example, slag can be used as building materials, insulation materials, ceramics, pH regulators for soils, fillers for plastics, or as raw materials for other industrial processes. These processes not only reduce dependence on natural resources, they also contribute to a more sustainable and circular vision of the entire production cycle. [3] [4] [5] [6] [7] [8]

Black slag is mainly composed of a mixture of calcium oxide (CaO, 20-40%), silicon dioxide (SiO<sub>2</sub>, 10-20%), aluminum oxides (Al<sub>2</sub>O<sub>3</sub>, 10-20%), magnesium oxides (MgO, 5-15%), iron oxides (FeO, 15-30%) and other components present in smaller percentages [9].

To date, once the EAF furnace cap has been discharged, the slag is subjected to several treatment phases. First, the molten black slag must go through a cooling and solidification phase. This process, if left to its natural course, could take days or weeks. To speed up this procedure, normal industrial practice involves

the use of large quantities of water, which are sprayed on the molten material deposited in pits. Subsequently, the slag can be subjected to a separation process to remove and recover any metal residues that may still be present. To facilitate this operation and optimize the size of the particles, the slag can be subjected to a crushing and granulation phase. At the end of this process, which requires amounts of energy, the waste is typically disposed of in landfills. Alternatively, if these have certain chemical-physical characteristics, they could be used in construction sectors, for example as material for the construction of road substrates or to produce asphalt.

The typical composition of the white slag includes calcium oxide (CaO): 45-60%, silicon oxide (SiO<sub>2</sub>): 5-25%, aluminum oxide (Al<sub>2</sub>O<sub>3</sub>): 5-25%, magnesium oxide (MgO): 1-10%, ferrous oxide (FeO): 1-5%, manganese oxide (MnO): 1-5%, phosphorus oxide (P<sub>2</sub>O<sub>5</sub>): 0.5-3%, sulphur (S): 0.5-3%, titanium oxide (TiO<sub>2</sub>): trace -1%. [9] The management of white slag is more problematic due to a phenomenon, anticipated earlier, well known by both the academic and industrial worlds. In fact, during a slow cooling, the white slag is subjected to a phenomenon that leads to a "*self-pulverization*", generally called "*self-dusting*". This is related to their chemical and mineralogical composition. In particular, this phenomenon is due to the presence of a mineral that is formed during slag. During a slow cooling condition, an allotropic transition of dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>, 2CaO·SiO<sub>2</sub> or C2S) from the monoclinic phase  $\beta$  to the orthorhombic phase  $\gamma$ , to form the most energetically stable crystal structure. Unfortunately, the formation of  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> leads to an increase in the volume of the slag by 10-14% and a rapid pulverization of the slag (a few seconds). [10]

In special cases, the phenomenon of delayed self-pulverization can also be witnessed. The latter pulverization is linked to a very similar event but involving free lime and magnesium oxide present in the slag. These two elements, reacting with air humidity and carbon dioxide, can increase their volume and lead to the pulverization of the slag. In this case, the phenomenon occurs over a period of months. This phenomenon limits the possibility of recovery and reuse of this material, which otherwise could be reintroduced into the

production cycle of the steel mill or used in the cement industry to produce binding materials. The self-dusting, in addition to being a problem for the integrity of the slag, also represents a risk for the safety of workers. In fact, the presence of fine particles suspended in the air and the related risk of inhalation, can cause potential respiratory problems and other negative health effects. [11]

To reduce or avoid these risks, steel mills are forced to adopt dust control measures, which require, in some cases, a high consumption of water to break down suspended particles with the aim of reducing their environmental impact.

In recent years, thanks to the collaboration of academia and industry, several strategies for repurposing waste have been examined. Even though numerous strategies based on dry slag cooling are being studied and tested in the industrial landscape, it is not always easy to be able to "scale-up" technologies, which seem to be promising on a laboratory scale.

The Baoshan Iron & Steel Co. Ltd. It has developed a slag cooling technology based on heat exchange between the molten slag and a heat-absorbing material. This strategy involves mixing the slag coming out of the refining furnace with steel balls at room temperature. Heat exchange makes it possible to accelerate the solidification process of the slag, avoiding the problem of "*dusting*" [12] [13]. Unfortunately, this technique involves several additional steps. In fact, after cooling it will be necessary to crush and grind the solidified material to recover the spheres, thus increasing management times and costs. Tenova S.p.A. has developed a cooling technology that consists of using a high-pressure jet of air to cool the molten material to a thermal shock, which leads to the formation of a granular material that can be amorphous or crystalline, depending on the cooling speed. Due to the conformation of this technology, which uses the parabolic motion of the granules of incandescent slag in the air, it is plausible to hypothesize that for a matter of worker safety, it is necessary to set up dedicated work areas, a circumstance that for logistical reasons is not always possible in all industrial plants. [14] [15] [16]

WBST's Re+Gen® technology provides for indirect dry cooling of the molten slag

immediately under the furnace, by means of heat exchange with a cooling fluid (water) in a closed cycle. This plant configuration makes it possible to solve the problem of slag pulverization by obtaining a crystalline material separated by grain size, and, at the same time, allows the separation of the metal residues still present in the slag.

This technology has been successfully used in various production contexts of carbon steels and stainless steels present in Italy Duferco TPP, Industrie Riunite Odolesi I.R.O. S.p.A., NLMK Verona (NLMK Group), Alfa Acciai S.p.A., Acciaieria Valsugana (Acciaierie Venete S.p.A.), Acciaierie di Calvisano S.p.A. (Feralpi Group), Acciaierie di Verona S.p.A (Pittini Group), Acciai Speciali Terni (Arvedi Group), Siderpotenza (Pittini Group), Nunki Steel S.p.A., Italfond S.p.A. (GIVA Group), for the cooling and regeneration of white and black slag.

For black slag, it has been observed that the cooling performed with Re+Gen®, supports the formation of mineralogical phases belonging to the spinels family, able to significantly limit the leaching of heavy metals from the granulated material, thus facilitating the introduction of the granulated product into other production contexts, such as the construction industry, thus avoiding landfills.

The cooling of the white slag, on the other hand, made it possible to stabilize the crystalline forms of  $\text{Ca}_2\text{SiO}_4$  in stable phases such as  $\beta\text{-Ca}_2\text{SiO}_4$ . This material can be used in the production of binding materials.

In addition, due to the average elemental composition of the white slag, replenishments were successfully carried out in the EAF furnace, partly replacing the virgin slag used during production.

The resulting material, composed of 45-60%  $\text{CaO}$ , resulted in a reduction of at least 30% in the use of lime from natural resources, without making any changes to the regular production process.

### *1.1 Engineering section*

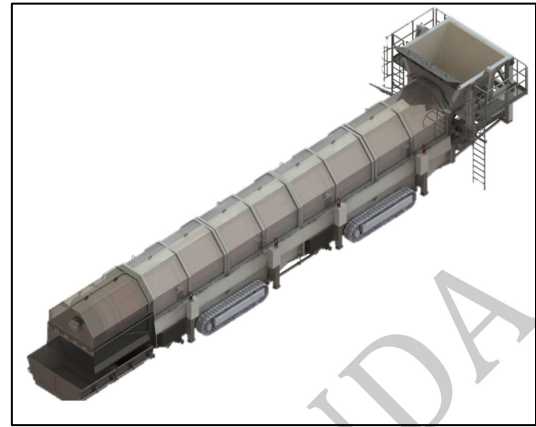


Figure 1, rendering Re+Gen®

WBST's patented Re+Gen® technology consists of a special plant, suitably sized, capable of carrying out a controlled cooling of the steel mill slag using a dry cooling method through the heat exchange of a rotating drum and a coolant fluid (typically water), in a given period of time and with a specific thermal profile. The liquid slag is conveyed inside the rotating drum, where the cooling process begins. As it passes through the drum, the slag advances in a "sawtooth" motion, which ensures optimal contact between the slag and the inner surface of the rotating drum. The coolant, lapping the external surface of the drum itself, allows the absorption of the heat of the slag by indirect heat exchange. The temperature of the slag and the regenerating fluid is constantly monitored through a PID (Proportional Integral-Derivative) retroactive control system. This allows the flow rate of the refrigerant fluid to be adjusted in real time to maintain the desired thermal profile, ensuring efficient and uniform cooling of the slag.

A further distinctive aspect of Re+Gen® technology is the possibility of designing the plant as a mobile solution. This flexibility allows the cooling unit to be moved according to the



Figure 2, loading of molten slag in Re+Gen®



Figure 3, fine fraction of white slag (a), Coarse fraction of white slag (b), recovered metal scrap (c)

operational needs of the steel mill, making it possible to use the plant in different areas of the production site. This feature not only increases operational versatility but helps to improve overall process efficiency by reducing downtime and quickly adapting to changes in the steel mill's production conduct.

At the exit of the regenerator, the cooled slag can be divided according to two different particle sizes thanks to the presence of a screen and a sub-screen. This system, which can be assisted using a magnetic screen, also allows the recovery of any large metal scrap, optimizing the slag management process and improving metal recovery.

The design of the Re+Gen® is based on the imposition of a specific thermal gradient between the cooled material and the drum shell, in the hypothesis of direct contact between them, according to a "sawtooth" motion model validated and confirmed by experimental field tests.

Once the quantity, the physical properties of the slag and the coolant are known and the inlet and outlet temperatures of both have been set, the temperature trend is obtained in a logarithmic manner between the inlet and outlet according to the following formula:

$$d(t' - t'') = (t'_i - t''_u)e^{-KA_x M}$$

Where:

1.  $t'$ : slag point temperature;
2.  $t''$ : point temperature of the drum coolant;
3.  $t'_i$ : temperature of the slag entering the drum;
4.  $t''_u$ : temperature of the coolant leaving the drum;

5.  $K$ : global heat transfer coefficient;
6.  $A_x$ : point heat exchange area;
7.  $M$ : is a combined thermal resistance factor defined by:

$$M = \left( \frac{1}{c' \dot{m}'} + \frac{1}{c'' \dot{m}''} \right)$$

8.  $c'$ : specific heat capacity of the slag;
9.  $\dot{m}'$ : mass flow rate of the slag;
10.  $c''$ : specific heat capacity of the coolant;
11.  $\dot{m}''$ : mass flow rate of the coolant.

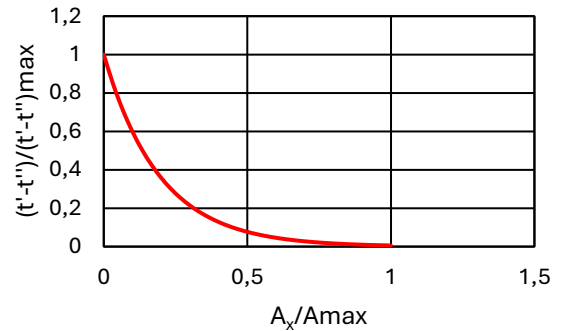


Figure 4, dimensionless temperature difference between slag and coolant

In Fig.3 it can be seen how the temperature difference between the slag and the refrigerant decreases exponentially from the maximum inlet value, as the exchange area increases, until it asymptotically reaches the thermal equilibrium for  $A_x = A_{max}$ .

From the integration of the above equations, it is possible to derive the maximum area  $A_{max}$  of heat exchange between slag and the refrigerant fluid, thus determining the flow rate of the fluid and the sizing of the drum itself.

Subsequently, through the application of the first law of thermodynamics, a thermal balance is carried out of the refrigerator collection tank located on the lower area of the machine, to size the tank itself and determine the temperature of the outgoing liquid, which will then be reintroduced into the steel mill circuit.

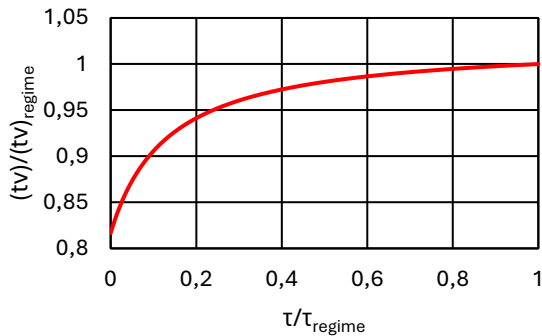


Figure 5, dimensionless temperature trend in the cooling tank

As shown in Fig.4, the temperature trend of the refrigerant  $tv$  inside the tank increases, starting from the initial temperature, in a logarithmic manner with a high slope during the first period of time  $\tau$  and then stabilizes at full capacity once thermodynamic equilibrium is reached. From the comparison of the parameters  $tv$  and  $\tau_{\text{regime}}$  with the requirements of the steel mill, the heat exchange area or the dimensions of the tank are then determined.

## 2. Experimental Section

### 2.1 Materials and methods

Using Re+Gen® technology, an extensive trial was carried out involving over 1000 samples from the main steel mills located in Italy. The molten slag, at temperatures ranging from 1100°C to 1400°C, was subjected to a targeted cooling process in order to obtain a granular material known as Re+Lime®, which is stable over time. Materials from the black and white slag generated in both the production of carbon and stainless steels were selected and recovered. To ensure the representativeness of the data, samples ranging in size from 5 to 20 kg were taken for each casting, which were then homogenized, subjected to magnetic screening to remove any traces of metal and reduced by

quartering to 1 kg to be subjected to chemical and mineralogical analysis.

### 2.2 XRF and XRD Chemical Analysis

Each sample, dried at 105 °C for 24 hours, was crushed using a jaw crusher (ROCKBITER C18) to reduce the particles to a size of less than 4 mm. Subsequently, the material was subjected to further grinding via a planetary ball mill (2500 rpm for 1 hour), reaching a final size of 63 mm before being subjected to chemical and mineralogical analysis. Chemical composition analysis was conducted by X-ray fluorescence (XRF) spectrometry using a Thermo Scientific™ Niton™ XL2 Plus instrument, with a silver anode. The mineralogical composition was determined using X-ray diffractometry (XRD) analysis performed with the PANalytical Empyrean instrument. The  $2\theta$  angle range considered was from 5 to 100 degrees, with an increment of 0.05 degrees, using CoK radiation. To conduct the quantitative analysis of the phases present in the samples, refining with the Rietveld method was adopted.

### 2.3 Leaching Test

Samples resulting from the black slag cooling process were subjected to a leaching examination by ICP, in accordance with Italian environmental regulation for landfill disposal of inert granular waste (Uni EN 12457-2:2004) [17]. The analyzes were conducted at an accredited analysis laboratory, Catullo Lab Srl - environmental chemical analysis (Italy).

### 2.4 EAF Replenishment Test

Due to the average CaO content in Re+Lime® of about 50%, experiments were conducted to partially replace the lime used in EAF furnace. As part of the experiments conducted, the substitution of a weight fraction of lime calcium (CaO), commonly used in EAF furnace, with two weight parts of Re+Lime® was considered to determine the maximum amount of lime that could be replaced.

## 3. Results and discussion

### 3.1 Chemical characterization

The samples, as shown in Figure 1, are in the form of granular material, ranging in color from



dark gray to yellow-brown, ranging in size from 0,5 to 5 cm.



Figure 6, Re+Lime® samples obtained by cooling white slag via Re+Gen®

Table 1 shows the average elemental composition of the analyses carried out on the individual castings in different steel mills, which is consistent for this type of material [3] [7] [9] [10]. Re+Lime® materials derived from white slag cooling are predominantly composed of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO, with an average CaO concentration of more than 50%.

formulations of the slag used in the various production plants and to the different types of steel produced, such as Al-Killed steels, Si-Killed steels and special steels (e.g. stainless steel). Mineralogical analyses by X-ray diffraction (XRD) were performed for all the samples of granular material collected. Despite the error associated with the Rietveld refining process, estimated to be between 5% and 10% due to the large number of steps involved, the quantitative analysis is congruent with the elemental analysis obtained by X-ray fluorescence spectrometry (XRF). The mineralogical composition of white slag can differ depending on the refining process from which it derives and the type of steel produced, but the main phases observed for white slag are: celite (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, 3CaO·Al<sub>2</sub>O<sub>3</sub>), larnite (in β-Ca<sub>2</sub>SiO<sub>4</sub> form for granular material, in γ-Ca<sub>2</sub>SiO<sub>4</sub> form for pulverized material), periclase (MgO), mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, 12CaO·7Al<sub>2</sub>O<sub>3</sub>), brownmillerite (Ca<sub>2</sub>(Al,Fe)<sub>2</sub>O<sub>5</sub>,

**Tab. 1** Elemental analysis of average XRF samples collected in the main Italian steel mills. Samples marked with \* are related to stainless steel production

| Re+Lime® elemental analysis from white slag |      |      |                                |                  |      |                                |      |                 |
|---|------|------|--------------------------------|------------------|------|--------------------------------|------|-----------------|
| Entry                                       | FeO  | CaO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | MgO  | Cr <sub>2</sub> O <sub>3</sub> | MnO  | SO <sub>3</sub> |
| 1   | <0.1 | 61,6 | 20,2                           | 13,5             | 4,2  | <0.1                           | 0,2  | 0,3             |
| 2   | <0.1 | 61,1 | 20                             | 13,4             | 4,2  | <0.1                           | 0,1  | 1,3             |
| 3   | <0.1 | 55,6 | 9                              | 29,4             | 4,5  | <0.1                           | 0,5  | 1               |
| 4   | <0.1 | 50,6 | 14,2                           | 26,8             | 8    | <0.1                           | <0.1 | 0,4             |
| 5   | <0.1 | 57,3 | 17,9                           | 16               | 8,3  | <0.1                           | 0,2  | 0,3             |
| 6   | <0.1 | 53,1 | 10                             | 28,8             | 7,4  | <0.1                           | 0,6  | 0,1             |
| 7   | <0.1 | 57,8 | 27,6                           | 7,4              | 6,3  | <0.1                           | 0,1  | 0,8             |
| 8*  | <0.1 | 58,5 | 2,6                            | 29,6             | 5,3  | 0,8                            | 1,3  | 1,9             |
| 9*  | 0,2  | 51,2 | 5,5                            | 37,7             | 1,3  | 2,9                            | 0,5  | 0,7             |
| 10  | 1,4  | 54,2 | 5,6                            | 30,9             | 6,8  | <0.1                           | 0,3  | 0,8             |
| 11*   | 0,5  | 56,3 | 16,5                           | 20,1             | 2,8  | 3,2                            | 0,4  | 0,2             |
| 12*   | 1,7  | 50   | 23,6                           | 9,2              | 15,1 | 0,1                            | 0,1  | 0,2             |
| 13  | 0,8  | 57,2 | 22,2                           | 14,1             | 5,1  | <0.1                           | 0,3  | 0,3             |
| 14  | 2,2  | 57,5 | 20,9                           | 12,5             | 4,5  | 0,1                            | 0,5  | 1,8             |
| 15*   | 1,3  | 43,1 | 23                             | 17,1             | 11,7 | 1,8                            | 1,6  | 0,4             |
| 16*   | 0,3  | 56,3 | 24,2                           | 7,6              | 10,7 | 0,2                            | 0,4  | 0,3             |

As can be seen from the results, there are variations in the percentages of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, which can be attributed to the different

4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>, merwenite (Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>, 3CaO·MgO·2SiO<sub>2</sub>), free lime (f-CaO) and oldhamite (CaS).

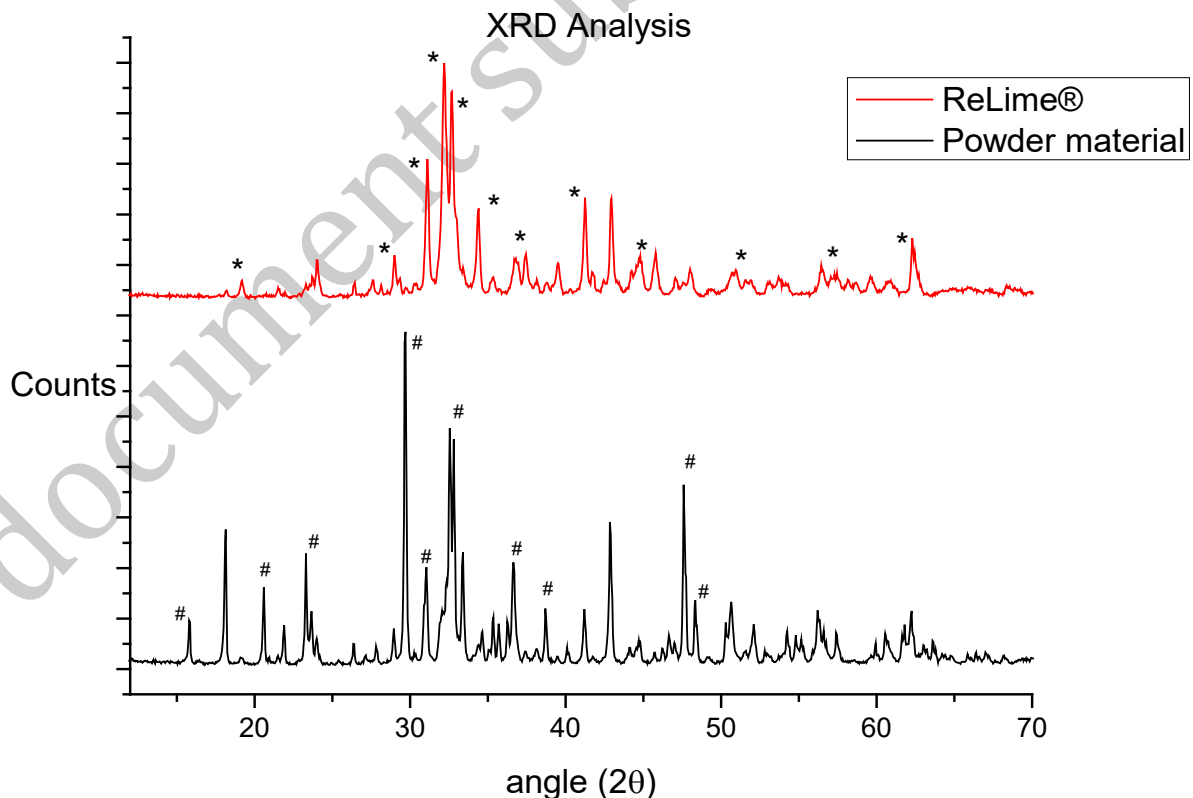
The phenomenon of white slag dusting [18] is a widely recognized problem in the steel mill industry, due to the allotropic transition of dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ) during its solidification from the molten state.  $\text{Ca}_2\text{SiO}_4$  has up to five allotropic transitions, whose crystal structures are a function of temperature. For the pure compound, the equilibrium temperature between the liquid and solid state, in its  $\alpha$ - $\text{Ca}_2\text{SiO}_4$  (hexagonal) conformation, is 2.150°C. At 1.425°C, the compound rearranges into the shape  $\alpha'$ H (orthorhombic), followed by a transformation to  $\alpha'$ L (orthorhombic) at 1.177°C.

At 675°C, this structure reaches equilibrium with the  $\beta$  (monoclinic) conformation, and at temperatures below 500°C, the  $\text{Ca}_2\text{SiO}_4$  undergoes a reorganization in the structure and its crystal cell parameters to lead to the formation of the most stable form  $\gamma$ , resulting in an increase in volume [18].

In naturally cooled LF slag, this increase in volume induces internal stresses culminating in

the pulverization of the material. In the real case, where the slag has a high mineralogical complexity, it is difficult to determine how the composition and temperature of the molten material can affect the phenomenon of dusting. Experimentally, it has been observed that the cooling operated by Re+Gen® is able to stabilize the metastable crystalline form of  $\beta$ - $\text{Ca}_2\text{SiO}_4$ , to the detriment of the energetically more favored phase of  $\gamma$ - $\text{Ca}_2\text{SiO}_4$ , in molten white slag samples entering Re+Gen® at temperatures between 1.100°C and 1.400°C.

As shown in Graph 1, there is a marked difference in mineralogical composition between a sample of Re+Lime® and a sample corresponding to the same casting but cooled by conventional methods. In the first sample, dicalcium silicate occurs in the  $\beta$ - $\text{Ca}_2\text{SiO}_4$  phase, giving the material greater volumetric stability over time and ease of handling, both in terms of production process management and work safety. On the contrary, the sample cooled by traditional techniques, and subject to self-pulverization, presents the  $\gamma$ - $\text{Ca}_2\text{SiO}_4$ .



Graph 1 XRD Analysis Difference Chart. In the red line there is the analysis related to the Re+Lime®, in the black line there is the faded sample. \* =  $\beta$ - $\text{Ca}_2\text{SiO}_4$ , # =  $\gamma$ - $\text{Ca}_2\text{SiO}_4$

The cooling process implemented by Re+Gen has also been applied to treat the black slag produced by the EAF furnace. Re+G(arnet)x® obtained by cooling the black slag, is a granular material with a color ranging from grey to black (figure 6).

This type of material has a slightly different chemical composition than that of LF slag. In particular, there is a non-negligible percentage of iron oxides, expressed in the form of FeO, which can reach values even higher than 30%. In addition, for samples obtained from stainless steel production, the presence of heavy metal oxides, such as Cr<sub>2</sub>O<sub>3</sub>, is observed (table 2).



Figure 7, Re+G(arnet)x® samples obtained by cooling black slag via Re+Gen®

**Tab 2** XRF Elemental Analysis of XRF Samples Re+G(arnet)x® collected in the main Italian steel mills.

| Re+G(arnet)x® elemental analysis |      |      |                                |                  |      |                                |      |                 |
|----------------------------------|------|------|--------------------------------|------------------|------|--------------------------------|------|-----------------|
| Entry                            | FeO  | CaO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | MgO  | Cr <sub>2</sub> O <sub>3</sub> | MnO  | SO <sub>3</sub> |
| 7                                | 20,6 | 47,3 | 11,8                           | 18,6             | 0,1  | <0.1                           | 1,5  | 0,1             |
| 8*                               | 2,4  | 28,3 | 7,1                            | 25,3             | 17,6 | 11,9                           | 6,9  | 0,6             |
| 12*                              | 12,1 | 47,6 | 7,1                            | 27,4             | 4,5  | 1                              | <0.1 | 0,4             |
| 13                               | 12,7 | 46,6 | 17                             | 14,6             | 4,2  | <0.1                           | 3,6  | 1,3             |
| 16*                              | 34,6 | 31,5 | 14,9                           | 9,7              | 6,5  | 1,2                            | <0.1 | 1,6             |

Samples marked with \* are related to stainless steel production

The mineralogical composition of the material obtained by cooling the black slag may vary according to the type of production, the quality of the scrap and the formulation of the slag used in the EAF furnace, but the main phases observed in this type of samples are larnite ( $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>, 2CaO·SiO<sub>2</sub>), brownmillerite (Ca<sub>2</sub>(Al,Fe)<sub>2</sub>O<sub>5</sub>, 4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>), gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>, 2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>), wustite (FeO), the RO phase (defined as a solid solution formed by MgO, FeO, and other divalent metal oxides such as MnO), and magnesium (CaMgSiO<sub>4</sub>, CaO·MgO·SiO<sub>2</sub>) and iron (MgFe<sub>2</sub>O<sub>4</sub>, MgO<sub>2</sub>) and iron (MgFe<sub>2</sub>O<sub>4</sub>, MgO·Fe<sub>2</sub>O<sub>3</sub>).

This material, which is not subject to the problem of self-dusting, is generally destined for landfill. However, black slag, due to its chemical-physical characteristics, could find application in the asphalt and concrete industry.

The effective management of such waste, both as a by-product in industrial applications and as waste, requires compliance with strict environmental regulations.

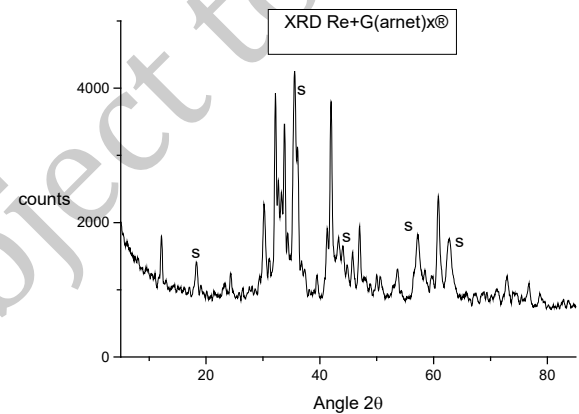
Regarding the management of waste as waste, Italian legislation imposes very strict limits for the release of heavy metals. Table 3 shows the results of the leaching tests conducted in accordance with EN 12457-2, comparing samples of slag cooled both by the traditional method and using the Re+Gen® system, both coming from the same casting. As can be seen, for most heavy metals and for Ba, Cr and V, the cooling operated by WBST technology is able to greatly limit the leaching value.



**Tab 3** Leaching test values according to EN 12457-2 expressed in  $\mu\text{g/l}$

| metal | Re+Gen® | Traditional cooling | Limit value in $\mu\text{g/l}$ |
|-------|---------|---------------------|--------------------------------|
| As    | 1,4     | <1                  | 50                             |
| Ba    | 54      | 147                 | 1000                           |
| Co    | <1      | 1,4                 | 10                             |
| Cr    | 4,82    | 18,4                | 50                             |
| Ni    | <1      | 1,19                | 10                             |
| Pb    | 1,36    | 27,3                | 50                             |
| Se    | 2       | 5,9                 | 10                             |
| Cu    | <0.001  | 6,2                 | 50                             |
| V     | 15,3    | 45,2                | 250                            |
| Zn    | 7       | 97                  | 3000                           |

Typically, heavy metals such as Chromium, Vanadium, Barium, Lead, etc., if present in low concentrations, tend to enter the crystal lattices of minerals forming defects, and depending on the type of mineralogical phases that are formed, there is a different stabilization of these metals at the release tests. The cooling carried out by Re+Gen, on black slag, is able to promote the formation of magnesium and iron spinels, which are able to incorporate heavy metals such as chromium, making the latter more stable to the phenomenon of leaching due to the lower reactivity of these crystalline phases towards water [19].



Graph 2 XRD analysis chart black slag cooled with Re+Gen technology. S= spinel ( $\text{MgFe}_2\text{O}_4$ ).

### 3.2 Re+Lime® reintegration into the EAF Furnace

Due to the elemental composition of Re+Lime®, more than 150 make-up tests have been successfully performed in the EAF furnace, both in carbon steel production plants and in stainless steel production plants. During the initial stages of these experiments, particular attention was paid to the behaviour of the EAF furnace in relation to the acidic components present in the Re+Lime®. In order to balance the acidic components such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{MnO}$ , approximately 500 kg of Re+Lime® were introduced without any change in the amount of  $\text{CaO}$  commonly used in the smelting process. During this preliminary phase, no abnormal wear of the furnace electrodes or refractories

was found. However, after about a week of operation, an estimated increase in the specific electrical consumption of the EAF furnace was observed, equal to about 8-10 kWh/ton, mainly attributable to the introduction of additional material, particularly  $\text{CaO}$ , which requires a high energy input to be brought to the molten state (959 kJ/kg). The analysis of the material balance showed an increase in the quantity of black slag in line with the quantity of slagging materials introduced into the EAF furnace.

Subsequently, a weight fraction of calcium oxide ( $\text{CaO}$ ) was replaced with twice the amount of Re+Lime®, without observing any manifestation of abnormal degradation in the refractories or electrodes, nor an increase in the energy required in the electric arc fusion (EAF)

process. In these tests, an average of about 1.725 kg of CaO, 500 kg of Re+Lime® and about 750 kg of dolomite lime were loaded. The only variation observed by the steel mill involved in the trial concerns a slight decrease in the viscosity of the molten slag produced, which was promptly corrected by the addition of small quantities of slag formers (about 5 kg of CaSi<sub>2</sub> per casting) and by a slight modification of the introduction of lime which, instead of being loaded together with the scrap to be melted (first basket), It was introduced during the refining phase of the melting furnace, thus ensuring the optimal viscosity of the molten slag and keeping the energy consumption of the furnace unchanged. From the analyses of the experimental data with the special steel production site, it emerged that about 7 kg of Re+Lime® were used for each ton of steel produced for the tests carried out.

A slight increase in the use of lime was noted in the LF refining furnace, probably due to the reintroduction of sulphur into the production cycle. However, the combination of the two processes, smelting and refining, has resulted in a saving of over 155 kg of virgin lime and 20 kg of dolomite lime used in the conventional production process. This experimentation has been extended to all types of stainless steel produced, without compromising their quality. In addition, a technical comparison with the steel mill revealed the possibility of increasing this quantity of Re+Lime® to 10-14Kg/ton, thus reintroducing 750-1.000 kg to replace 375-500 kg of lime for casting.

Similarly, the experiment was also carried out at a carbon steel production plant where, under standard operating conditions, between 1.300 and 1.500 kg of lime should have been used for casting. By using 1.000 kg of Re+Lime® instead of about 500 kg of calcium CaO, out of a set of one hundred kiln reintroduction tests, the actual use of lime in the EAF kiln was only 88 tonnes compared to the 116 and 134 tonnes of CaO theoretically required, thus resulting in savings of between 25% and 35%.

## **4 Conclusions**

The Re+Gen® cooling technology, developed by WBST, is confirmed as an innovative and effective solution for slag management in the steel industry. Based on an indirect dry system,

which exploits heat exchange with a cooling fluid (water) in a closed cycle, this technology has proven its value in various production contexts in Italy. It has been successfully used for the cooling and regeneration of black and white slag from the production of carbon and stainless steels.

By turning what is commonly considered waste into a profitable opportunity, the Re+Gen® technology offers numerous operational and economic benefits to steel mills. It has been shown to effectively solve the problem of white slag self-pulverization (LF-Slag), caused by the transition of the crystalline cell from  $\beta$ -C2S to  $\gamma$ -C2S, resulting in optimized logistics, reduced handling of materials to be cooled, and significant savings in water resources.

The product obtained from the cooling and regeneration of LF slag, known as Re+Lime®, has been effectively used to reduce the consumption of slag within the steel mills. It has been successfully used as a partial substitute for virgin materials in the electric arc melting furnace (EAF), with an estimated saving of at least 25-35% of CaO of natural origin. Currently, studies are underway to evaluate its use as a partial substitute for raw material charging in clinker kilns for cement production, in order to reduce CO<sub>2</sub> emissions in the cement industry.

In addition, the product resulting from the cooling of molten black slag, called Re+G(arnet)x®, which has mineralogical phases belonging to the family of iron and magnesium spinels, can trap environmentally harmful heavy metals, such as Cr, V and Ba, within its crystal lattice.

This characteristic, combined with its hardness, makes it versatile in various sectors, such as road construction, granular concrete, asphalt and the production of sandblasting products.

These results are testament to the considerable potential of the Re+Gen® technology, which aims to become a Best Available Technology (BAT) in guiding the steel industry towards a more sustainable future. By integrating innovative practices to address current environmental challenges and promote a circular economy, this technology is confirmed as a key pillar for the transformation of the sector.

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