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# Green Steel Initiatives Supported by Enhanced Slag Engineering Using High-Alumina Circular Metallurgical Additives

Desulphurisation in the steel ladle requires a reactive slag with high CaO dissolution. Conventional slag fluxing agents applied during this secondary metallurgical refining step include calcium aluminate additives and fluorspar to maximise the dissolved CaO. However, calcium aluminate additives can have a high carbon footprint due to their energy-intensive production process and the use of fluorspar is associated with both environmental concerns and refractory wear. Stahlwerk Thüringen (Germany) is committed to sustainability, with a green steel strategy that includes reducing resource use and implementing stepwise improvements in process efficiency. To support these initiatives, RHI Magnesita and MIRECO conducted an industrial feasibility study to determine if typical fluxes used during steel desulphurisation in the ladle could be replaced by a high-alumina circular metallurgical additive derived from recycled refractory material. This article describes the metallurgical consulting provided by RHI Magnesita during the trial series, as well as the e-tech slag engineering tools that were used for efficiency optimisation calculations and enabled an appropriate balance between desulphurisation rate, additive application, slag volume, and purging gas consumption to be determined. Furthermore, extensive steel and slag sampling was performed, and the chemical and mineralogical results enabled an in-depth evaluation of the metallurgical process during the sequential replacement of calcium aluminate and fluorspar with a cost-effective, low carbon footprint slag fluxing agent.

## Introduction

Stahlwerk Thüringen (SWT) is a steel plant in Germany with an annual capacity of approximately 1 million tonnes of high-quality steel. As part of CSN (Brazil), the steel plant comprises an electric arc furnace (EAF), ladle furnace (LF), four-strand beam-blank caster, and a rolling mill. It operates at 120 tonnes of steel per heat and an average of 24 heats a day. 100% scrap is charged in two buckets during each heat and the quality varies considerably, depending on availability and price. Slag forming agents such as lime and dolomite are added during the meltdown phase via a hole in the EAF roof. The average tap-to-tap time is up to 50 minutes and the EAF is relined 4 times a year. During EAF tapping, deoxidisers and slag forming additives such as CaO, Al<sub>2</sub>O<sub>3</sub>-containing materials, and CaF<sub>2</sub> are added to form calcium aluminate and calcium aluminosilicate-based slags. The LF treatment lasts up to 40 minutes, during which time the metallurgical specifications of the steel are adjusted accordingly. Typically, SWT produces steel grades with a sulphur content not exceeding 300 ppm as well as low-sulphur grades with <50 ppm of sulphur.

Sustainability is key to SWT and their Green Steel Strategy includes three pillars: Energy, logistics, and efficiency [1]. For example, 100% of the plant's electrical energy comes from renewable sources, rail transport is prioritised, and energy efficiency is continually improved. As a result, SWT Green Steel had a global warming potential of 335 kg CO<sub>2</sub> equivalent per tonne of steel (CO<sub>2</sub>e/tonne<sub>steel</sub>) in 2024, according to their Environmental Product Declaration [2], making SWT one of the most sustainable steel plants in Europe [3].

In line with the steel plant's strong commitment to reduce the carbon footprint of its products, improve efficiency, and mitigate environmental impact, several trials were conducted

with the full support of RHI Magnesita and MIRECO. In the EAF, this resulted in replacing the standard slag former with a circular metallurgical additive to achieve financial savings and CO<sub>2</sub> cradle-to-gate reductions per tonne of steel (i.e., ~10 kg CO<sub>2</sub>e/tonne<sub>steel</sub>), as well as determining areas for improvement that will increase the yield. Additionally, the secondary metallurgical process in the LF was evaluated and the following opportunities were identified:

- Replace the standard calcium aluminate additive with a low carbon footprint, high-alumina circular metallurgical additive.
- Eliminate the use of CaF<sub>2</sub> because it can cause environmental issues related to slag leaching and is detrimental for the refractory lining.
- Improve desulphurisation efficiency.
- Reduce alloy addition.

This article provides an overview of secondary metallurgy in the LF, comparison of a high-alumina circular metallurgical additive and calcium aluminate flux, in addition to describing the trial program that resulted in a more sustainable LF process and cost savings for the plant.

## Secondary Metallurgy and Slag Forming Additives

Secondary metallurgy is the steel production stage that starts with tapping the furnace into the ladle and continues until the ladle reaches the continuous casting platform. Within this period, the steel is refined and alloyed to achieve the targeted chemical composition and required casting temperature [4,5]. During the tapping phase, most steel grades are deoxidised with metallic aluminium, silicon, or both, forming Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, depending on the chosen deoxidiser. However, these oxides must be counterbalanced with metallurgical additives to achieve the required

steelmaking slag properties (e.g., basicity and viscosity) and to avoid refractory wear. Typically, using the mixing force of the tapping stream, this process starts with the addition of CaO, and dolomite if MgO is required, followed by various fluxing agents (e.g., CaAl<sub>2</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, FeSi, and CaF<sub>2</sub>), according to the targeted steel grade.

Sulphur is undesirable in almost every steel grade because it makes steel extremely brittle and can cause transverse cracking during casting [6]. Low sulphur contents can be achieved by steel desulphurisation in the ladle when the steel is fully killed (i.e., deoxidised), according to [7]:



Where CaO is dissolved in the slag and Al and S are present in the liquid steel.

In addition to high CaO dissolution in the slag being critical, other conditions that favour sulphur removal include [7]:

- Low FeO and MnO levels in the slag.
- Low initial sulphur content in the slag.
- Moderate temperature.
- Intense mixing of the slag and steel by argon purging.

The two common criteria used to characterise the efficiency of sulphur removal are the sulphur distribution ratio between the slag and steel at equilibrium ( $L_S$ ) and the slag's sulphide capacity ( $C_S$ ) [7]. The latter shows a good correlation with optical basicity over a wide range of slag compositions [8].

As CaO is the means by which sulphur is removed from steel in the ladle, liquid slags that are saturated with CaO are favourable for desulphurisation [7]. Depending on the specific slag chemistry, there are various approaches to increase CaO dissolution, including the addition of CaF<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> [9]. However, due to considerable environmental concerns associated with CaF<sub>2</sub>, the limited use of B<sub>2</sub>O<sub>3</sub> to boron-containing steel grades, and the detrimental impact of both these fluxes on basic refractory wear, the addition of Al<sub>2</sub>O<sub>3</sub> in sufficient amounts (i.e., 20–30%) is an established approach to dissolve CaO in the liquid portion of the slag [9].

## High-Alumina Circular Metallurgical Additives

The use of MIRECO's circular metallurgical additives contributes to green steel production, as the carbon footprint of these materials, derived from recycled refractories, is significantly lower (i.e., 0.05 tonne CO<sub>2</sub>e/tonne<sub>metallurgical additive</sub>) than that of standard slag formers [10]. Furthermore, these sustainable products are distinguished by their cost competitiveness, offering a price advantage of approximately 10%. Within MIRECO's portfolio of high-quality circular raw materials, there are several different high-alumina metallurgical additives that are an environmentally friendly alternatives to standard calcium aluminate and CaF<sub>2</sub> flux materials (Table I). Furthermore, the chemistry of these products can be tailored to the customers' specific metallurgical requirements, and they are available in various grain size distributions. TE 80 was selected as the most appropriate material for the SWT trials and therefore analytical investigations were performed on this material and the standard calcium aluminate additive used in the plant, providing a detailed comparison.

## Comparison of TE 80 and a Calcium Aluminate Additive

X-ray fluorescence (XRF), X-ray diffraction (XRD), mineralogical, and physical investigations of TE 80 and the standard calcium aluminate additive used at SWT were conducted at RHI Magnesita's Technology Center Leoben (Austria), on different grain size fractions. As detailed in Table II, the chemical composition of TE 80 was ~79% Al<sub>2</sub>O<sub>3</sub> with the predominant Al-containing mineral phase comprising corundum. In addition, minor amounts of other Al-containing phases such as mullite, magnesia-alumina spinel, diaoyudaoite, anorthite, and andalusite were detected. The calcium aluminate additive had an Al<sub>2</sub>O<sub>3</sub> content of ~64% and a higher CaO content compared to TE 80, with 4 mineral phases identified in the samples (i.e., calcium aluminate, grossite, magnesia-alumina spinel, and mayenite). Although corundum has a higher melting point than calcium aluminate, the good dissolution behaviour of TE 80 observed during the trials could be attributed in part due to its high specific surface area (3.59 m<sup>2</sup>/g), which was ten times greater than the standard additive (0.3 m<sup>2</sup>/g), as well as the SiO<sub>2</sub> content that results in lower melting point phases.

**Table I.**

Examples of MIRECO's high-alumina circular metallurgical additives, which can be adjusted to each customer's specifications. Abbreviations include tonnes of CO<sub>2</sub> equivalent per tonne of metallurgical additive (t CO<sub>2</sub>e/t).

Product name	Al <sub>2</sub> O <sub>3</sub> [%]	CaO [%]	MgO [%]	SiO <sub>2</sub> [%]	Fe <sub>2</sub> O <sub>3</sub> [%]	TiO <sub>2</sub> [%]	C [%]	t CO <sub>2</sub> e/t
TE 80	78.0	2.0	3.0	11.0	2.5	2.0	2.0	0.05
TE 85	85.0		2.5	7.5	0.7	0.4	6.0	0.05
TE 90	90.0	2.5	2.5	1.8	0.8	0.1		0.05

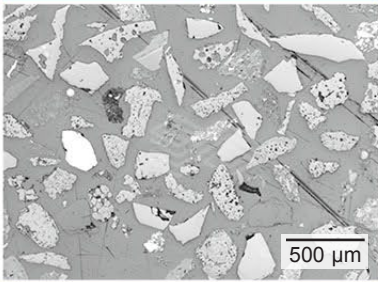
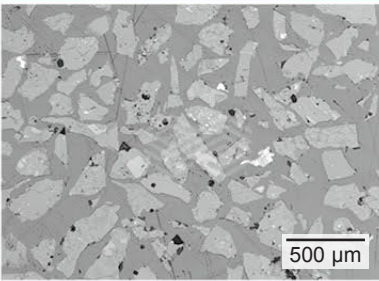
## Trial Setup

The first step of RHI Magnesita's slag engineering consulting to optimise the application of circular metallurgical additives is fact-finding. At this stage, the customer's standard operating procedure (SOP) is examined, improvement potentials are identified, and proposed operating procedures (POPs) are defined to achieve benefits within short-term trials [11]. As the literature and experiences in other steel plants had shown that it is feasible to use  $\text{Al}_2\text{O}_3$  from various sources as a flux, the first POP at SWT completely replaced the calcium aluminate additive with TE 80 but retained the standard  $\text{CaF}_2$  addition, and slightly increased the  $\text{CaO}$  content to target the same  $\text{CaO}:\text{Al}_2\text{O}_3$  in the final slag as the SOP.

During this and subsequent trials, the additives were applied during the final third of the EAF tapping procedure. Immediately after tapping, the ladle was moved to the LF where electrodes were used to increase the temperature and inert gas purging (i.e., argon stirring) was started. This further melted the slag formers and alloys as well as increased the interaction between steel and slag. After approximately 5 minutes at the LF, a Celox measurement was conducted to track oxygen activity. Subsequently, steel and slag samples were taken to check the steel chemistry and examine the initial slag composition (e.g.,  $\text{Al}_2\text{O}_3$  content and TE 80 dissolution). During the trials certain LF treatment parameters were kept stable, such as the purging rate. 10 minutes before sending the ladle to the caster another steel and slag sample were taken, enabling the steel sulphur

**Table II.**

Comparison of MIRECO's TE 80 circular metallurgical additive and the standard calcium aluminate used at SWT. Abbreviations include magnesia alumina (MA). The mineral phase estimates are based on Rietveld refinement.

Additive	TE 80	Calcium aluminate
Light microscopy		
<b>Chemical composition</b>		
$\text{Al}_2\text{O}_3$ [%]	79.7	63.9
$\text{CaO}$ [%]	2.2	30.5
$\text{MgO}$ [%]	3.8	3.9
$\text{SiO}_2$ [%]	10.4	1.1
$\text{Fe}_2\text{O}_3$ [%]	2.1	0.3
$\text{TiO}_2$ [%]	1.0	0.1
$\text{Cr}_2\text{O}_3$ [%]	0.5	0.1
$\text{MnO}$ [%]	0.1	0.1
$\text{ZrO}_2$ [%]	0.3	
<b>Mineral phase analysis</b>		
Calcium aluminate	$\text{CaAl}_2\text{O}_4$ [%]	56
Grossite	$\text{CaAl}_4\text{O}_7$ [%]	26
Mayenite	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ [%]	5
MA-spinel	$\text{MgAl}_2\text{O}_4$ [%]	14
Corundum	$\text{Al}_2\text{O}_3$ [%]	69
Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$ [%]	11
Diaoyudaoite	$\text{NaAl}_{11}\text{O}_{17}$ [%]	3
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$ [%]	3
Periclase	$\text{MgO}$ [%]	3
Cristobalite	$\text{SiO}_2$ [%]	1
Andalusite	$\text{Al}_2\text{SiO}_5$ [%]	2
Quartz	$\text{SiO}_2$ [%]	1
Silicon carbide	$\text{SiC}$ [%]	1
<b>Physical properties</b>		
Bulk weight [g/l]	1364	1243
Specific surface area [ $\text{m}^2/\text{g}$ ]	3.59	0.30

content to be determined and the slag evolution to be tracked. After sampling, CaSi wire injection was started and the ladle was sent to the caster. Since CaSi treatment serves as the last desulphurisation step, a steel sample was also taken at the tundish and the results were incorporated into the trial evaluation. Figure 1 provides a schematic overview of the secondary metallurgical process and the slag and steel sampling points during the trials.

### Trial Results

Results of the first trial showed that an equivalent desulphurisation efficiency could be achieved when TE 80 replaced the standard calcium aluminate additive. Therefore, further trials were conducted in which TE 80 completely replaced the calcium aluminate and the CaF<sub>2</sub> was decreased to zero in a stepwise manner. Additional TE 80 and CaO were added to maintain a similar slag CaO:Al<sub>2</sub>O<sub>3</sub> as the SOP.

XRF and XRD investigations were performed on all the slag samples at the Technology Center Leoben. These analyses were evaluated in combination with heat report figures, steel chemistry results, and the Celox analysis to provide an in-depth picture of the desulphurisation efficiency, average treatment time, inert gas purging and power-on times, as well as the temperature at the beginning and end of the LF treatment.

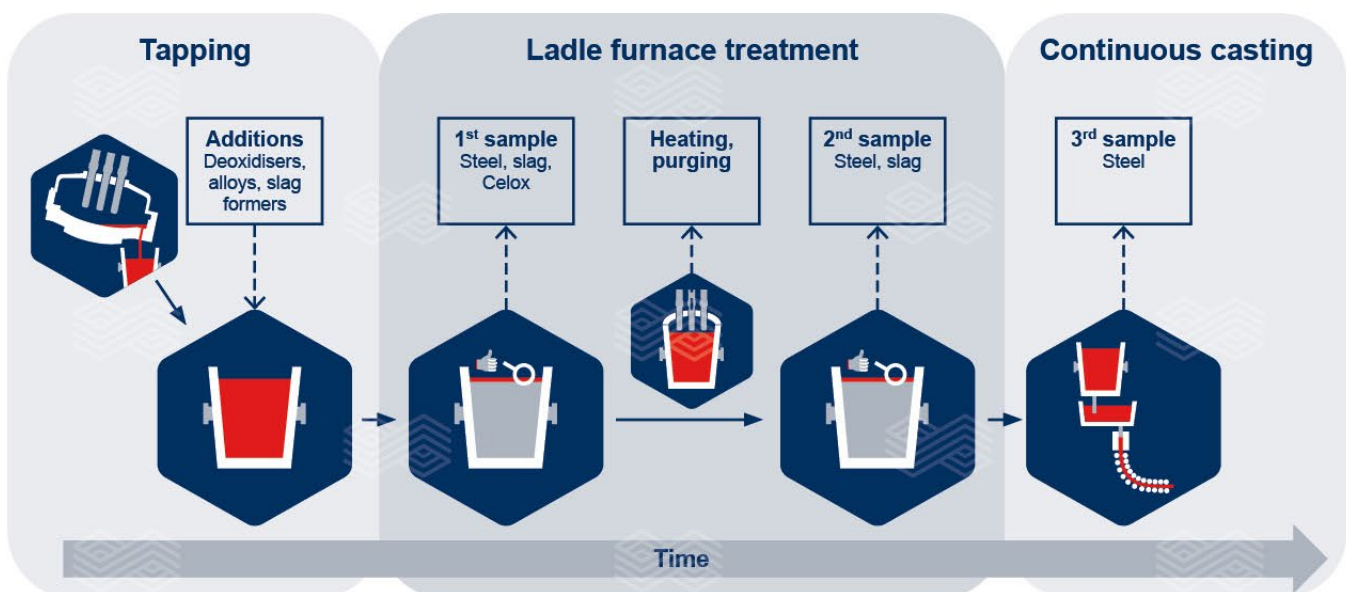
By observing the final slag composition and steel sulphur content, it was concluded that TE 80 dissolved appropriately in the slag and provided the necessary fluxing effect to achieve the same desulphurisation efficiency in the ladle as the calcium aluminate additive. Furthermore, the

step-by-step elimination of CaF<sub>2</sub> caused no significant change in the slag's desulphurisation capacity. These outcomes demonstrated that it is technically feasible to replace the standard calcium aluminate with a circular metallurgical additive and that CaF<sub>2</sub> can be completely avoided by using TE 80, even for low sulphur steel grade production. A total cost of ownership (TCO) calculation revealed that a six-digit annual saving in euros could be achieved by introducing TE 80 in the plant, as well as CO<sub>2</sub> cradle-to-gate reductions per tonne of steel (i.e., ~1 kg CO<sub>2</sub>e/tonne<sub>steel</sub>), potential lining wear decrease, and the avoidance of ground water pollution from slag containing fluorine.

Having established the parameters to achieve cost savings at SWT using a low carbon footprint slag fluxing agent, the possibility for additional process improvements, including increasing the desulphurisation rate, became apparent after onsite fact-finding and slag modelling. As a result, SWT requested efficiency optimisation calculations to be performed, based on the eco-friendly process parameters, to determine the most appropriate balance between the desulphurisation rate, amount of additive application (e.g., CaO), slag disposal costs, and purging gas consumption. This was performed with the support of RHI Magnesita's e-tech slag modelling tools described in the following sections. The resulting parameters significantly decreased the final sulphur content within the same treatment time, optimised the slag towards CaO saturation, and increased the inert gas purging rate. Although these conditions lead to increased costs regarding CaO use, slag disposal, and argon consumption, the TCO calculation indicated that an additional six-digit annual saving in euros could be achieved due to the decreased alloy requirement, bringing the combined potential savings to over €1 million per year.

Figure 1.

Schematic overview of the secondary metallurgical process and the slag and steel sampling points during the trials.



### Desulphurisation Slag Modelling Tools

The e-tech platform is a collection of online slag modelling tools available in RHI Magnesita’s Customer Portal [12], the secure online environment enabling access to data including order tracking, refractory performance reports, scope 3 CO<sub>2</sub> emissions from consumed refractory products, and gunning consumption figures [13]. The e-tech tools used to determine potential process improvements in the LF at SWT were “Slag Optimisation” and “Kinetic Desulphurisation”.

### Slag Optimisation Tool

The Slag Optimisation tool (Figure 2) calculates refractory compatible, fluid slags for optimised desulphurisation at specific temperatures and is applicable to magnesia-carbon and doloma refractories. It is possible to select whether the calculated slag should be CaO saturated, MgO saturated, or dual saturated. The tool is based on published phase diagrams and utilises statistical and mathematical approaches to describe the liquidus phase relationships as a function of temperature and composition for basic slags compatible with basic refractories. The Slag Optimisation tool has been designed to work with most EAF, BOF, and ladle reducing slags and utilises the concept of optical basicity and its correlation with sulphide capacity to calculate the final sulphur content in the steel. The calculated final sulphur content represents a “best case” scenario since thermodynamic equilibrium conditions are assumed and no kinetics are included. Therefore, the calculated final steel sulphur content will be achieved with the defined slag chemistry when there is sufficient time for the reactions to reach equilibrium. One output of this tool—the sulphur distribution ratio at equilibrium—is an input parameter for the Kinetic Desulfurisation tool that considers aspects such as time, kinetics, and inert gas purging during the desulphurisation process. Figure 2 shows the input mask for the Slag Optimisation tool, which can be used for both single heats and multiple heats simultaneously.

To demonstrate how the Slag Optimisation tool functions, the chemical analysis of a slag sample from the trials was

input to generate a Slag Optimisation Report (Figure 3). The output showed that the slag would require an additional 306 kg of CaO to have an optimum desulphurisation capacity. The data fields include:

- Initial slag: The chemical composition of the slag sample obtained from XRF analysis.
- Adjusted slag: Predicted slag composition if the recommended 306 kg of CaO are added.
- Desulphurisation results: The calculated slag basicity (CaO:SiO<sub>2</sub>), optical basicity, sulphide capacity, sulphur distribution ratio, and the final steel sulphur content (predicted for equilibrium conditions) of the initial and adjusted slag.

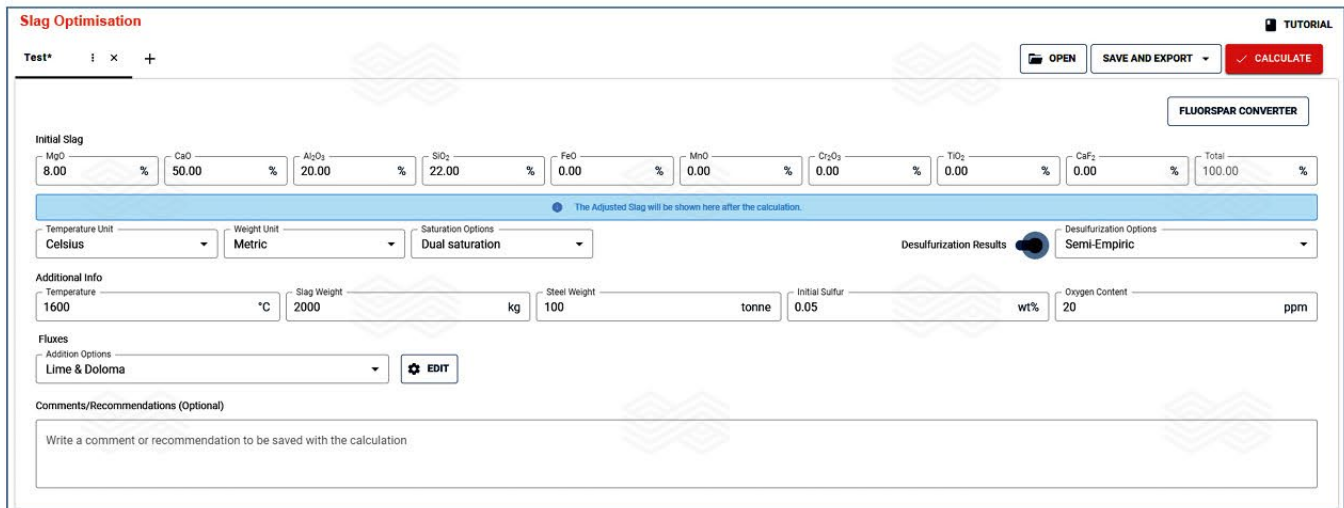
Figure 3.

Slag Optimisation Report generated using the chemical analysis obtained for a slag sample from the trials.



Figure 2.

e-Tech Slag Optimisation tool input mask [12].



## Kinetic Desulphurisation Tool

The Kinetic Desulphurisation tool calculates the steel sulphur content at equilibrium and predicts the desulphurisation rate for specific operational parameters. The model also enables comparison of two different cases (A and B) at three time points (I, II, and III), where the time and rate of inert gas purging, slag mass, sulphur distribution ratio, and initial steel sulphur content can be varied to evaluate the effect. The kinetic calculations are based on empirical correlations published in the literature [8] and although these correlations were derived from specific conditions and are not universally applicable, they still provide a useful estimate of the sulphur removal rate and its sensitivity to specific parameters. Figure 4a shows a comparison of the steel desulphurisation rates for the initial and adjusted slags generated by the Kinetic Desulphurisation tool and Figure 4b illustrates the impact of increasing the inert gas purging rate.

In summary, this tool can be used to decrease the LF treatment time, increase the desulphurisation rate, and evaluate the impact of CaO supersaturation. Furthermore, combining both tools is an excellent approach to achieve very low steel sulphur levels in the most time- and resource-efficient manner.

## Conclusion

Currently, steelmaking accounts for over 7% of global greenhouse gas emissions, highlighting the urgent need to decarbonise this industry [14]. SWT is committed to green steel production, with multiple initiatives aimed at reducing

the carbon footprint of its grades, including using renewable energy sources and continual efficiency improvements. To support these efforts, RHI Magnesita and MIRECO recently conducted industrial trials to determine if traditional fluxes used for steel desulphurisation in the ladle could be replaced by a high-alumina circular metallurgical additive made from recycled refractory material. Using the comprehensive metallurgical consulting provided by RHI Magnesita, the standard calcium aluminate and  $\text{CaF}_2$  were replaced by a circular metallurgical additive, generating both cost savings and a carbon footprint reduction. After the successful introduction of this flux material, efficiency optimisation calculations were conducted based on the newly defined eco-friendly process parameters. These calculations, performed with RHI Magnesita's e-tech slag modelling tools, were focused on determining the optimal balance between the desulphurisation rate, additive use, slag disposal costs, and purging gas consumption. As a result, the final sulphur content could be reduced within the same treatment time and potential savings of over €1 million per year were estimated from introducing the circular metallurgical additive and reduced alloy costs.

MIRECO offers a comprehensive range of sustainable additives for the steel production process, facilitating the reintegration of used refractory products into the supply and value chain. In addition to direct sales, the "CERO Waste" service is also available, enabling customers to benefit from MIRECO's expertise and implement closed-loop recycling to significantly decrease  $\text{CO}_2$  emissions [15]. The approach complies with the European Waste Framework Directive and focuses on optimising refractory collection, material sorting, and recycling to minimise landfill (Figure 5).

**Figure 4.**

Comparison of the steel desulphurisation rates calculated for the initial and adjusted slags using the Kinetic Desulphurisation tool using (a) the standard argon purging rate and (b) an increased argon purging rate.

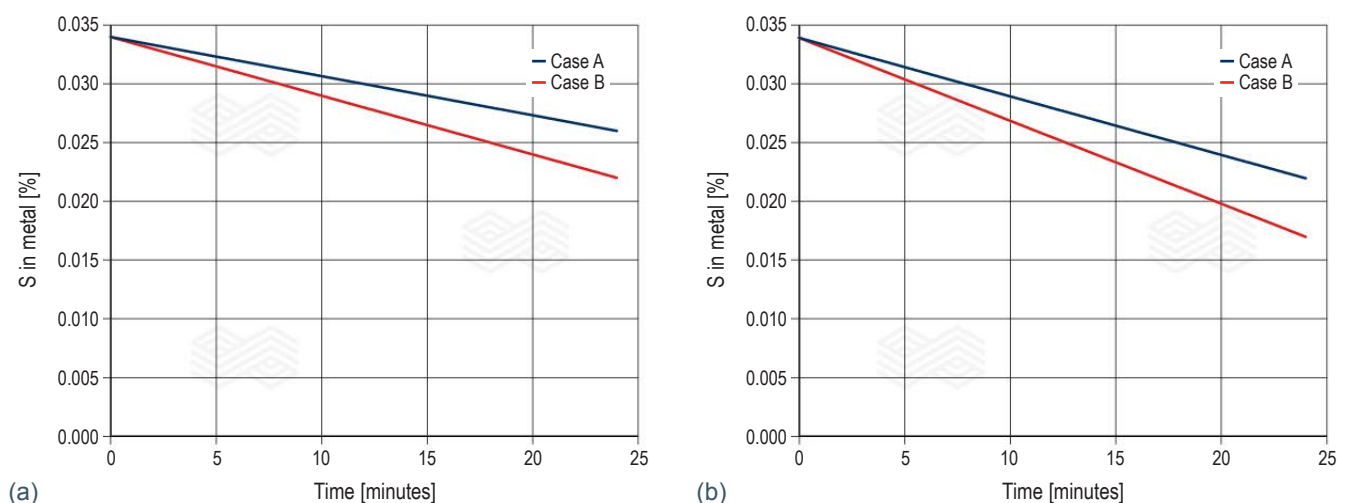
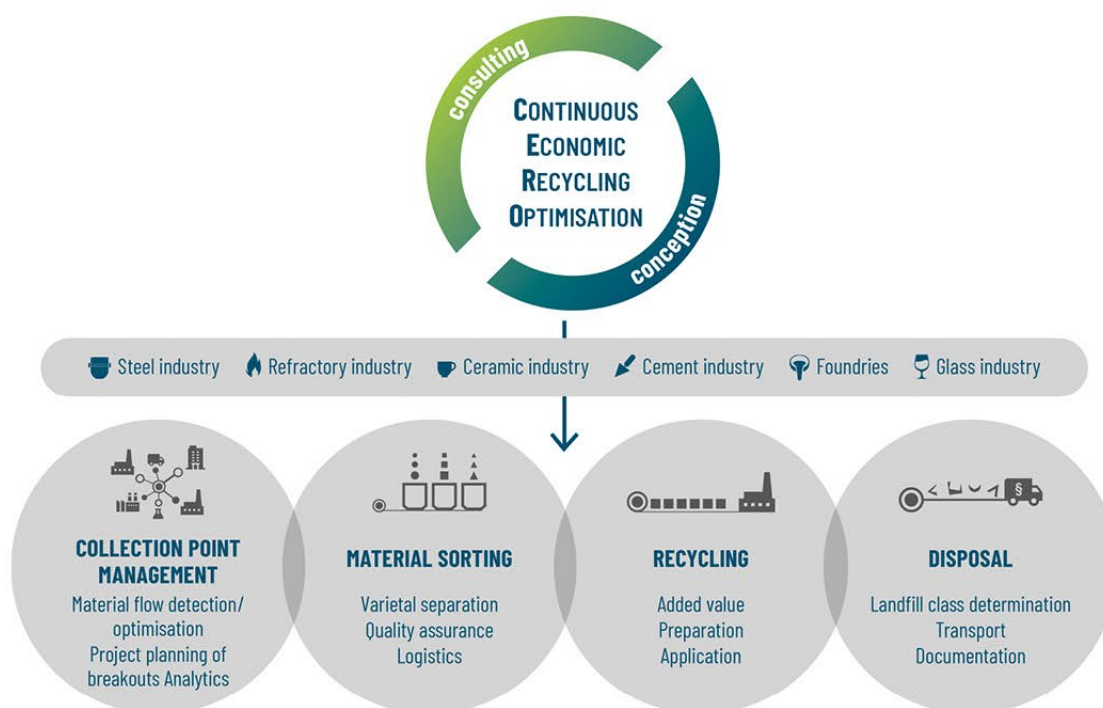


Figure 5.

Overview of the “CERO Waste” concept that encompasses the collection, sorting, reuse assessment, disposal, and legal management of reclaimed refractory material.



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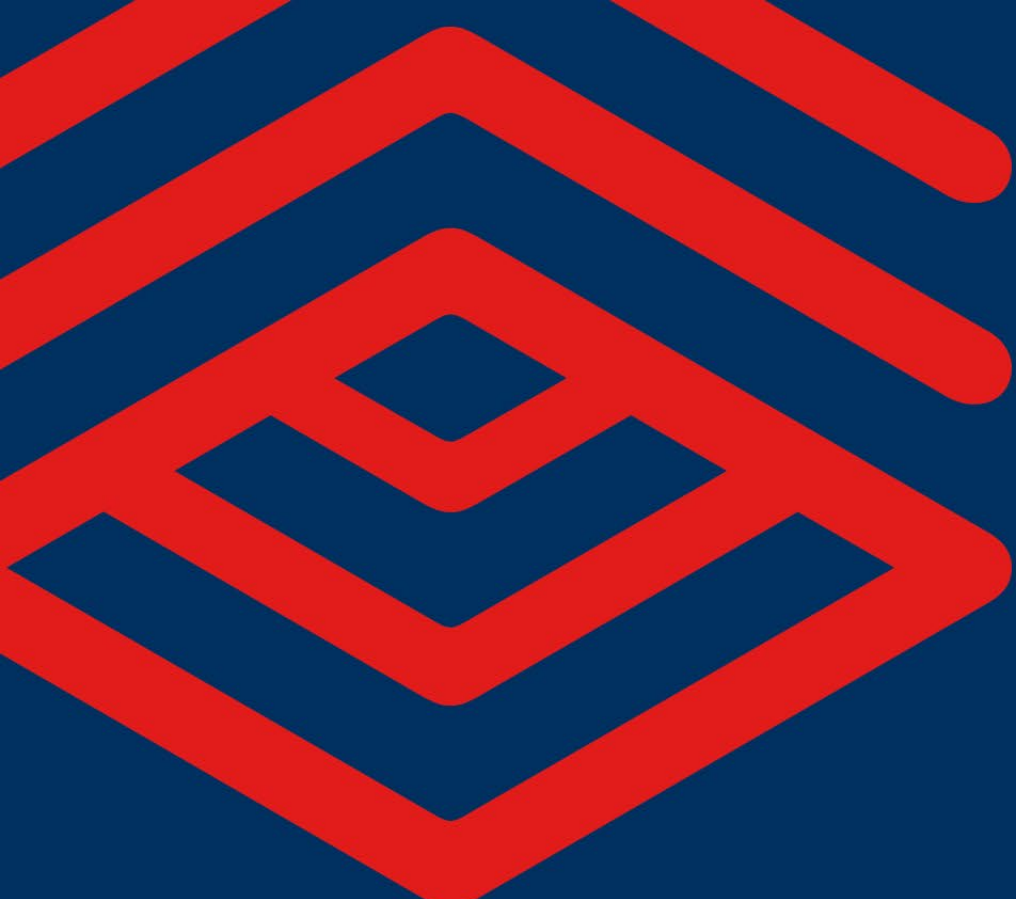
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**Cover picture:** The image depicts the lower section of a RH degasser, a secondary metallurgical unit used in steel plants. In the RH degassing process, snorkels are submerged into liquid steel contained in the casting ladle. Argon gas is purged through the inlet snorkel, creating a suction effect that draws liquid steel into the lower vessel of the RH degasser, where a vacuum is applied. The steel treated in the lower vessel flows back to the ladle through the outlet snorkel, creating a continuous steel circulation between the ladle and the RH degasser. The strong negative pressure (vacuum) within the RH degasser facilitates various metallurgical processes that enhance steel quality, with the key process steps including degassing, decarburisation, deoxidation, and alloying under vacuum. Rail steel, flat steel for the automotive industry, and steel plates for shipbuilding are just a few examples of products that benefit from the RH degasser. Prefabricated snorkels, which RHI MAGNESITA manufactures ready for use and delivers to our globally operating customers, are essential components of the RH degasser.