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Sulphur control as part of the steelmaking transition: challenge or opportunity

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Improving the quality of steel has been a matter of routine for metallurgical engineers and steelmaking companies in a demanding market for quality products. The traditional Electric Arc Furnace process has the lowest carbon emission compared to the integrated route, making it the best route for green steel production. In addition, the industry is focused on ensuring that high-quality steel products can be produced smoothly, immediately after the transition.
One of the challenges is controlling sulphur residual in steel, which is critical for certain applications and has "secondary / additional" impact on overall steel cleanliness. Lesson learned from market with different feasibility studies, investigations and accumulated know how from long list of projects for different flat products, including thick and thin casting processes are summarized and reported in article.

KEYWORDS: EAF PROCESS; SULPHUR CONTROL; SLAG QUALITY CONTROL.

INTRODUCTION: THE IMPORTANCE OF SULPHUR CONTROL

Sulphur influences microstructure primarily through the formation of MnS inclusions, which tend to segregate along grain boundaries and within the matrix. These inclusions can modify grain growth behaviour during hot working and heat treatment, often acting as pinning points that inhibit grain coarsening.
Mechanically, sulphur reduces toughness and ductility due to its embrittling effect, especially at higher concentrations. It can promote hot shortness, leading to cracking during hot working processes. Physically, sulphur presence can decrease thermal and electrical conductivity slightly, owing to the non-metallic inclusions. It also influences magnetic properties by affecting the microstructure of steel and inclusion distribution. Chemically, sulphur reduces corrosion resistance, especially in environments where sulphide inclusions act as initiation sites for localized corrosion. Oxidation behaviour is also affected, as sulphur compounds can promote scale formation and spallation during high-temperature oxidation.
In steel grades with a higher content of sulphur and aluminium it is difficult to form liquid inclusions with calcium, without forming CaS [1]. It is well known that the addition of calcium can prevent the precipitation of MnS.

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Compared to MnS, CaS inclusions are harder and less deformable. Duplex types of CaS or (Ca,Mn)S inclusions can exist as a single-phase inclusion. Since large oxide inclusions surrounded by calcium sulphide were identified as of primary origin [2], CaO-Al_2O_3, acts as nuclei for the precipitation of calcium sulphide, with the result that the CaS phase is confined to the outer surface.

Over-addition of calcium can lead to the formation of solid CaS inclusions which are detrimental to the castability of steel. Additionally, excess calcium can react with the alumina contained within slag and refractory, increasing the number of inclusions formed in the steel and reducing cleanliness [3].

SULPHUR CONTENT DURING PRIMARY AND SECONDARY METALLURGY PROCESS STEPS

Sulphur content from the primary melting unit

Charge mix evaluation for an EAF melt shop is based on steel quality requirements and on the refining capability of the chosen secondary metallurgy units. The integrated steelmaking process presents intermediate steps between the Iron Making and Steel Making division – Sulphur removal from hot metal. The capability to remove sulphur from hot metal is strong and final sulphur content prior to hot metal charging into the BOF could be low – up to 0.002%.

Tab.1 - Main reasons for having different sulphur content before tapping from primary melting unit.

	BOF (usually, sulphur content is lower)	EAF (usually, sulphur content is higher)
Raw material	Hot metal with low sulphur content	Different kind of raw material
Charge mix	High participation of hot metal	High participation of sulphur bearing material
Raw material quality	Controllable inlet sulphur content	Unpredictable sulphur content
Type of raw material	Hot metal, scrap and slag builders	Different charge mixes, slag builders, slag foaming agent
Slag basicity during steelmaking process	High / Favourable for sulphur removal	Low / Not sufficient for sulphur removal
MgO content in slag	Aligned with sulphur removal	Higher content - Based on slag basicity
Slag density	Higher - Better for sulphur removal	Lower - to control slag foaming
Oxides in slag	Lower content - Better for sulphur removal	Higher content
Carbon Vs. Oxygen	Closer to equilibrium	Higher content of oxygen with same carbon content
Steel temperature	Higher temperature before tapping	Lower temperature before tapping
Steel volume mixing	Stronger agitation	Less agitation

The impact of raw material quality on sulphur content control during the primary melting process can be observed in the case of the BOF process as well. With, on average, 20% of scrap participation in the charge mix, the impact of sulphur content in scrap and slag builders is strong. In the case of the EAF process, sulphur removal is lower and less predictable. The figures below report typical sulphur content before tapping from different primary melting units.

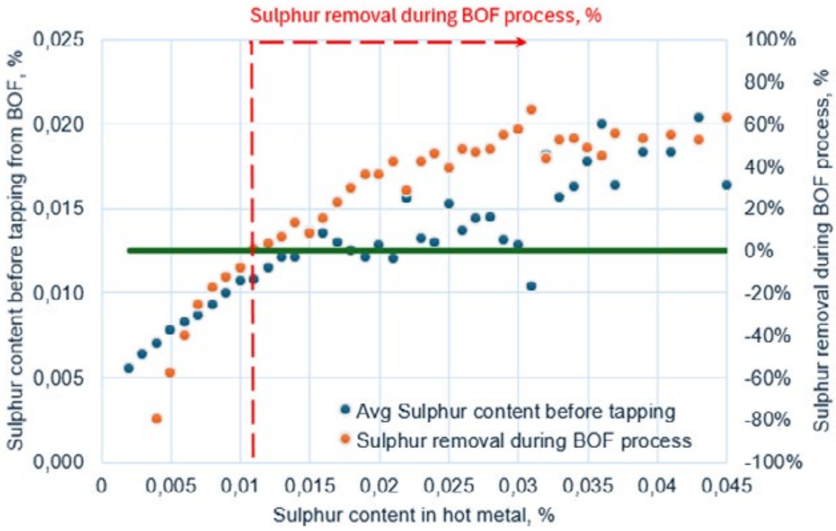


Fig.1 -Typical (average) sulphur content before tapping from BOF (internal database).

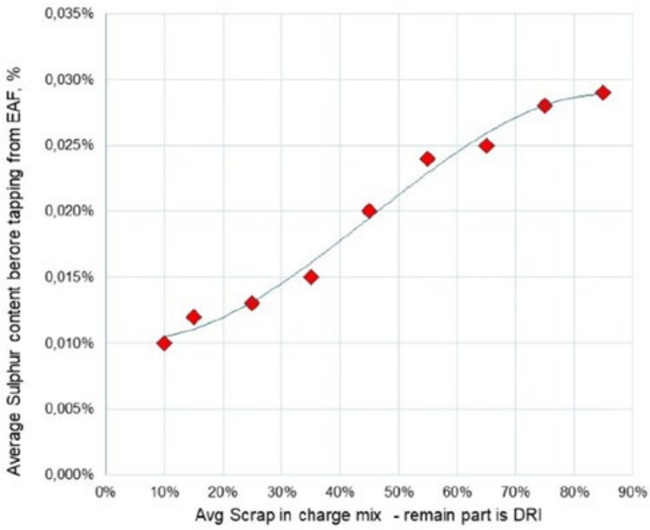


Fig.2 -Typical (average) sulphur content before tapping from EAF (internal database).

Scrap participation in the EAF charge mix is linked to the refining capability of the secondary metallurgy process and with steel quality requirements.

SULPHUR REMOVAL DURING THE SECONDARY METALLURGY PROCESS

The Electrical Arc Furnace process could have the same productivity as the BOF process has. A different charge mix and different primary steelmaking metallurgy result in different outputs from the primary melting unit. Obviously, a higher sulphur removal rate is required in the case of the EAF based process and it could require a longer process time and higher stirring energy. Stronger contact between steel / slag and refractory material could have an impact on steel quality (i.e. generated MgO based inclusions or higher refractory wearing). To overcome this issue, a tailor-made melt shop must be designed, and a dedicated steelmaking practice must be applied. Metallurgical preconditions for sulphur removal are slag basicity, low content of free oxygen and low oxides content in slag, temperature, and stirring energy. Natural, strong mixing during tapping, together with extended mixing time after tapping, will promote a higher sulphur removal rate and could provide a "suitable" initial sulphur content for the ladle furnace process. This is possible to do with a proper layout design.

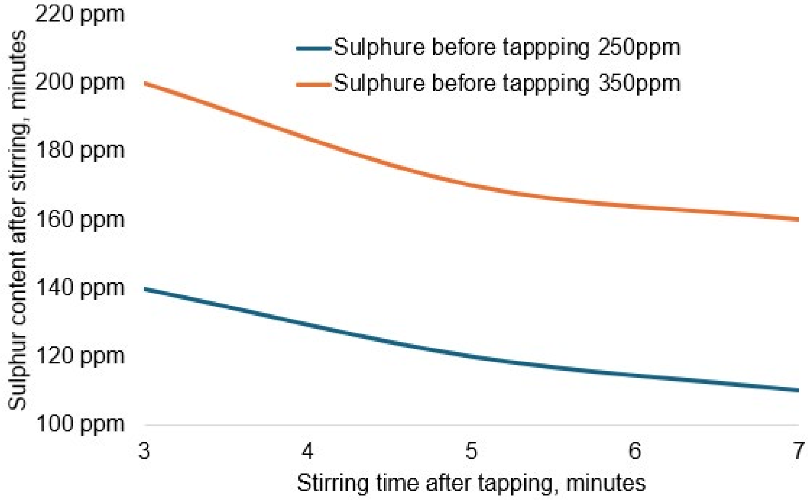


Fig.3 - Case study: Impact of stirring time after tapping on sulphur removal during tapping and during mixing after tapping.

Strong sulphur removal during the secondary metallurgy process is influenced by slag quality, stirring energy, and equipment design. For example, with the same melt shop productivity, the twin ladle furnace solution enables a longer available process time and higher sulphur removal rate. The main reason for a higher, available process time are "hidden" operative steps by presence of two roofs and two transfer cars.

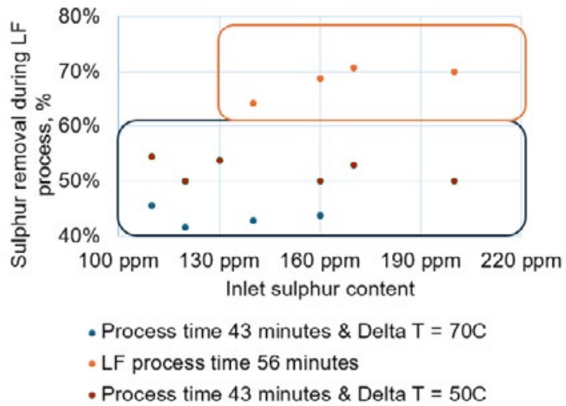


Fig.4 - Impact of different process time durations and different super heats on sulphur removal rate – based on top slag sulphur removal practice – Case study.

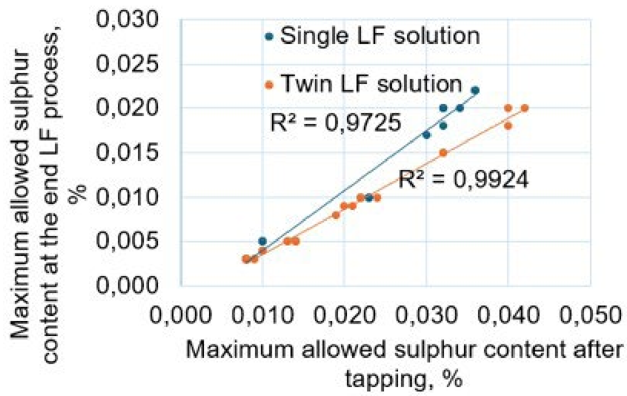


Fig.5 - Different sulphur removal with the same metallurgical conditions: Single ladle furnace versus Twin ladle furnace design – Case study.

The effectiveness of sulphur removal during secondary steelmaking is influenced by the available process time under conditions that favour sulphur transfer from the metal phase to the slag phase. A critical aspect is the time-balance between two competing process requirements:

- the time required for reheating (thermal compensation);

- the time available for intensive steel–slag mixing (mass-transfer driving stage).

The ratio between reheating vs. strong mixing time directly affects the degree to which the slag can be fully activated (high CaO activity, low FeO), the mass transfer of sulphur across the interface, and the approach toward equilibrium sulphur levels. A high reheating-to-mixing ratio reduces the efficiency of desulphurization even if slag composition is optimal.

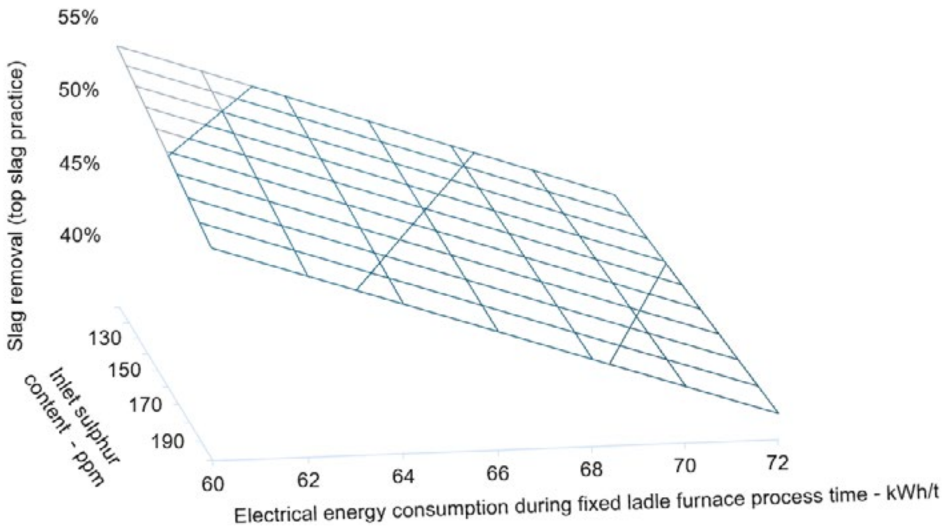


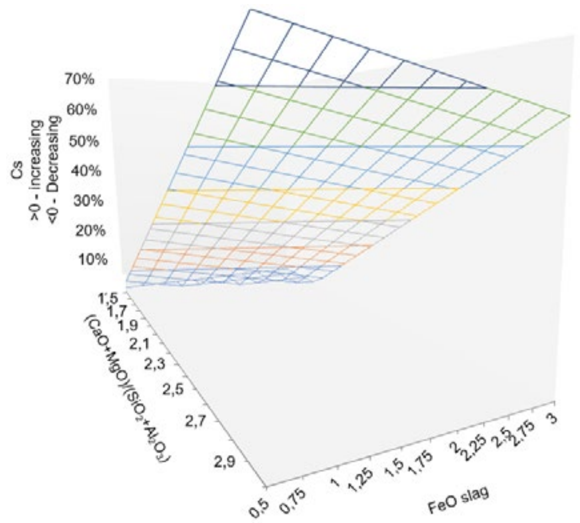
Fig.6 - Case study: Impact of different power on time duration, expressed as consumed energy on sulphur removal (fixed process time with fixed applied power).

Slags in ladle metallurgical processes are designed to maximize their refining capacity, which includes an optimized chemical composition as well as physical properties. In a clean steel process slag should not contain excessive amounts of unstable reducible oxides (FeO, MnO). The effective viscosity of the slag increases by addition of refractory oxides (MgO and CaO) beyond the liquidus composition, whereas the addition of fluxing oxides increases the fluidity of the slag. The higher the oxidation potential, the smaller the sulphur distribution ratio between steel and slag. Thus, oxygen in the form of oxide in slag, and oxygen in metal significantly reduce the degree of desulfurization.

The sulphide capacity of slag (CS) is one of the most important characteristics of refining property of the slags applied during extra-furnace steel processing. This value is determined as the function of slag temperature and composition, i.e. this value is experimentally determined and thermodynamically evaluated. Figure 7 reports the impact of slag composition on sulphide capacity. Reference conditions for the study reported below is as follows: slag with FeO = 0.5% and $(CaO+MgO)/(SiO_2+Al_2O_3)$ = 1.3.

Deep sulphur removal is possible during the ladle furnace process by applying an injection of materials which have strong affinity towards the sulphur. Splashing during material injection consequently has a high nitrogen pick up and shall be considered as a kind of "secondary re-oxidation". Certainly, the best process is sulphur removal based on "top slag practice" only, if total steel residence time and applied stirring energy do not affect final steel quality.

Sulphur is well known as a surface-active element in molten steel, meaning it strongly affects reactions occurring at the metal-gas interface, where nitrogen is removed during vacuum degassing. A kinetic study on nitrogen removal under reduced pressure showed that sulphur, as a surface-active element, reduces the surface reaction rate of nitrogen. Confirmation for this statement has been found by statistical evaluation of internal databases from different projects with the same metallurgical conditions.



$$Ls = \frac{(\%S)_{slag}}{[\%S]_{metal}} = C_s \ x \ \frac{f_s \ x \ K}{a_0}$$

$$a_0 \uparrow \leftrightarrow \ FeO \uparrow$$

Fig.7 - Evaluated impact of slag composition on sulphide capacity of slag (internal data evaluation) [4]
Note: Chart must be considered as indication only; multiple R = 0.65; P-value for each coefficient $6.4x10^{(-8)}$ or less; reference sulphide capacity based on FeO content = 0.50%.

It is well known that sulphur removal does not exist during the RH (recirculation) vacuum process which has an impact on limited nitrogen removal under vacuum, compared with the application of the vacuum tank degassing process. In the case of an RH-type degassing unit, an extremely low sulphur content—in the range of 20÷30ppm prior to degassing—must be obtained. A strong agitation needed for deep sulphur removal, with fixed available process time, could have an impact on steel quality (flat products with high required formability).

Thanks to intensive contact between steel and slag, continuous slag reduction and continuous sulphur removal are part of the vacuum tank degassing process. Sulphur removal during the vacuum process has an impact on nitrogen removal as well. The figure below reports the impact of "effective surface" on nitrogen removal under vacuum (vacuum tank degassing) together with the impact of different, inlet nitrogen content.

$$\text{Effective surface} = f\,(\frac{\textit{Exposed steel surface under vacuum}}{\textit{Concentration of active surface elements: free oxygen and sulphur}}$$

Higher concentation of free oxygen and / or sulphur content as result has reduction of nitrogen removal capability

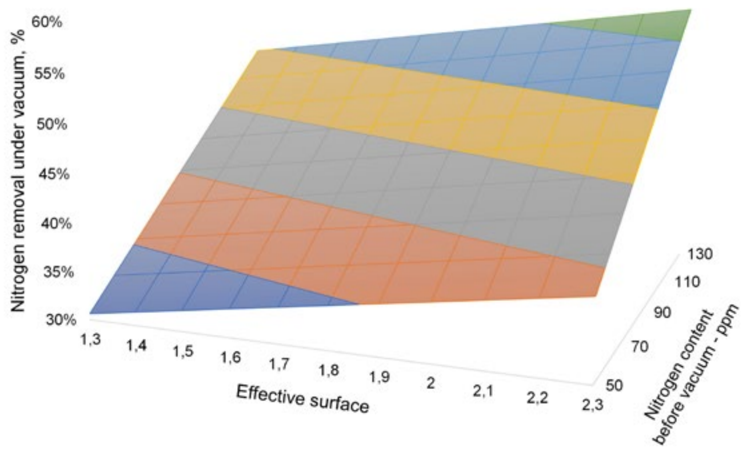


Fig.8 - Nitrogen removal under vacuum [4].

With the LF-VTD (vacuum tank degassing) secondary metallurgy process route overall sulphur removal can be divided in three steps: during tapping, during the ladle furnace process, and during the vacuum process, so optimum sulphur removal during each process step could be applied. In this way it is possible to achieve the ultra-low final sulphur content needed for grades like pipe grades for sour applications and at the same time to have controllable agitation and applied stirring energy during the ladle furnace process. Due to the need to control the "intensive" contact between steel / slag and ladle refractory material, as part of the steelmaking transition, existing ladles are quite often modified. Several types or different numbers of porous plugs are added to release the mechanical stress on the refractory material through a higher specific argon flow rate.

Figure 9 shows the possible critical sulphur content to be achieved during the ladle furnace process and additional sulphur removal under vacuum in the case of the vacuum tank degassing process. With the twin ladle furnace design (or application of two stations) it is possible to achieve an extremely low sulphur content at the end of ladle metallurgy process. However, production running costs, together with steel residence time, must be considered as parameters as well.

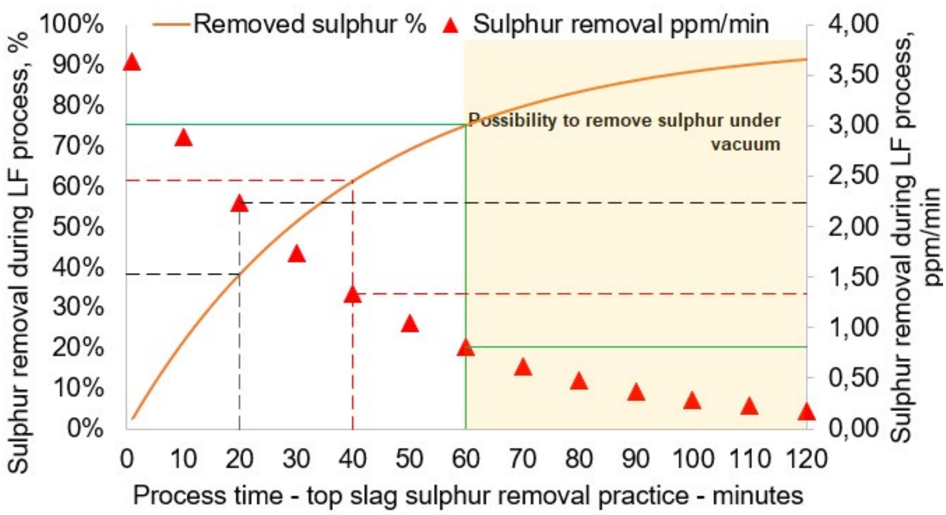


Fig.9 - Case study: Sulphur removal during secondary metallurgy process.

CONCLUSION

The removal of sulphur in secondary metallurgy is a crucial refining step aimed at improving steel quality. Sulphur is an undesirable impurity because it causes hot shortness, reduces toughness and ductility, and deteriorates weldability.

For the integrated steelmaking process, sulphur control is based on sulphur removal from hot metal. As part of the steelmaking transition, the secondary steelmaking process must be modified as well, and the sulphur removal process (by keeping the same final steel quality) must be considered as an important part of the steelmaking transition step.

Shortage of clean material consequently has an impact on higher sulphur content prior to tapping from the Electric Arc Furnace. Temperature control together with proper slag forming (on time), ladle design, maximum allowed and optimum steel residence time, together with proper design of vacuum degassing station must be considered as crucial steps during Best Available Technique development.

The Electric Arc Furnace process is confirmed as a "green steel technology". Circular economy, raw material supply, steel quality control, and tailor-made or modified secondary metallurgy process together with an EAF design based on quality and productivity needs are important steps needed to keep high steel quality as it is with integrated process.

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