Heraeus





Slag Management

The key to higher quality steels and lowering costs with measuring technologies in modern steel making

1 How to decrease costs by regular slag measurements with Heraeus Electro-Nite products

In modern steel manufacturing advanced process monitoring and control is essential to improve overall production efficiency and performance as well as operator safety, and finally to reduce energy and costs.

Why is slag management so important in steel manufacturing?

It is well-known that slag has many important functions. Besides being a barrier for atmospheric gases and reducing thermal losses slag functions as sink for oxides, inclusions and impurities and protects the liquid steel from atmospheric air reoxidation.

Especially for high-quality steel manufacturers, they need to control the slag process to be able to increase steel cleanliness, reach exact steel grades, increase desulfurization efficiency, optimize production efficiency and safety, and finally control costs.

1.1 Celox SLAC®

Celox SLAC[®] allows for an instant decision to add slag modifiers by measuring the oxygen activity in the slag.

Celox SLAC[®] enables fast and accurate slag conditioner calculation to prevent steel reoxidation, aluminum fading or any waste of ferroalloys in secondary metallurgy.

It allows for:

- cost savings
- increased desulfurization efficiency
- improved steel cleanliness



1.2 Delta Dist[®] L

Delta Dist[®] L allows the steelmaker to optimize ladle filling, slag carryover detection and power consumption in the ladle furnace by measuring the slag thickness.

Delta Dist[®] L enables measuring the freeboard, slag thickness and bath level to optimize ladle filling and power consumption and increase the refractory lifetime in the ladle station, as well as detecting slag carryover and precise positioning of equipment, like injection lances and manipulators.

It allows for:

- energy saving
- increased production efficiency
- improved safety

1.3 QUSAS[®] Slag Samplers

QUSAS® Slag Samplers provide fast and safe sampling with the additional benefit that these samples are ready to analyze without sample preparation.

QUSAS[®] Slag Samplers enable fast and safe sampling of representative samples, as well as elimination of labor-intensive sample preparation, and use at BF, EAF, converter, ladle, LF, and degassing stations.

They allow for:

- cost savings
- improved safety
- time saving





2 How to improve steel cleanliness in secondary metallurgy

2.1 Slag conditioning to reach equilibrium of oxygen partial pressures in steel and slag

One of the important goals of good steel making practices is to neutralize the slag by setting oxygen partial pressures in steel and slag in equilibrium: pO_2 steel = pO_2 slag. In case the slag oxidation state is not in equilibrium with the steel, reoxidation will take place leading to fading of aluminum or other alloys added for certain steel grades.

Celox SLAC[®] allows the operator to optimize slag condition by measuring the oxygen activity in the slag whereas the standard Celox[®] sensor probe measures the oxygen activity in the steel. The electro-chemical cells used in both sensors are identical: the Celox[®] mV-signal is in direct relation with the pO₂ in the steel, whereas the Celox SLAC[®] mV-signal is directly related to the pO₂ in the slag.

Negligible reoxidation takes place if slag and steel are in equilibrium: mV (Celox[®]) = mV (Celox SLAC[®]).

Many steel producers of Low Carbon Aluminum Killed Steel (LCAK) underestimate the direct impact of the slag oxidation state on the total oxygen and the inclusion content of the steel.

STEEL REOXIDATION -

Steel reoxidation leads to:

- aluminum fading
- reduced ferroalloy yield
- increase of impurities and inclusions
- risk of nozzle clogging, especially for billet casters and thin slab casters

The consequences of nozzle clogging in CCM:

- decreased productivity
- increased costs due to tundish refurbishment and nozzle replacement
- decreased quality as particles from the clog buildup can become dislodged and lead to cleanliness defects

The figures 1 and 2 show that the oxygen content in the slag is directly related to the amount of alumina inclusions in the steel.

Celox SLAC[®] allows you to measure the active oxygen content (FeO + MnO) in the slag which is directly related to the amount of total oxygen dissolved in the steel.



Source: Ahlborg,K.C.; Bieniosek,T.H.; Tucci, J.H.: "Slagmaking practices at LTV steel Cleveland Works": Proceedings Steelmaking conference March 1993 Dallas, TX. / Freuhan R.J.: "Review of chemical thermodynamics": Carnegie Mellon University Pittsburgh, PA.

Figures 1 & 2

Celox SLAC[®] allows an instant decision to add slag modifiers by measuring the oxygen activity in the slag which influences the amount of total oxygen, impurities and inclusions in the steel.

2.2 How to enable instant decision on slag modifier addition and control steel reoxidation to prevent inclusions and impurities

To prevent a high oxygen content in the slag one needs to calculate the exact amount of deoxidizer needed to kill the oxygen and improve steel cleanliness. This can be done by using Celox SLAC[®] measuring the oxygen activity in combination with Delta Dist[®] L allowing to calculate the slag volume by measuring the slag thickness.

2.2.1 Celox SLAC[®] – What needs to be considered for representative results

Celox SLAC[®] needs to be immersed through liquid slag at a depth of about 40-50cm into the steel in a similar way as a Celox[®] sensor as close to vertical perpendicular to the slag/steel surface as possible. It is recommended to firstly measure with Celox SLAC[®], and in a second step measure in the steel with Celox[®].

Both measurements need just up to 20 seconds and you see an immediate result with iM² Sensor Lab[®] or other measuring instruments offered by Heraeus Electro-Nite. This allows you to instantly decide if slag modifiers need to be added to reach equilibrium of oxygen activity between slag and steel. There is no need to wait for the result of a slag sample analysis.

2.2.2 When and how to use Celox SLAC[®] to prevent steel reoxidation in secondary metallurgy

The first Celox SLAC[®] measurement is recommended after the initial argon stir homogenization or/and initial preheating which allows to check converter or furnace slag carryover and enables to decide on the next action: slag skimming or slag conditioning.

Slag treatment (deoxidation) prior to steel deoxidation enables better and faster control of aluminum or alloying additions. Additionally, time can be saved since a second trim addition will not be required.

Regardless of initial slag oxygen potential, many steel producers add the same amount of slag deoxidizers. This results in over deoxidation or under deoxidation of the slag and causes reduction of some elements (Mn, Si etc.) and Al fading. At the end of a ladle treatment the reoxidation potential can be measured with Celox SLAC[®] and corrected if needed.

As a result, the aluminum costs per ladle can be reduced by setting the aluminum targets to a medium level in the specifications and avoid the extra costs of the 'safety margins'.

EXAMPLE -

A target is to have 0.028% aluminum content in 200t ladle. The logical action is to add 56kg of aluminum. But if the ladle has 1.5t of top slag with 15% FeO which contains 51kg $O_{2^{1}}$ all added aluminum will react entirely with the slag, as a result, there would be no residual aluminum in the steel.

2.3 How to save costs by using Celox SLAC[®] to reduce the amount of deoxidizer and eliminate sampling

VALUE-IN-USE

SAVING COSTS BASED ON CUSTOMER CASE

Predicting the exact amount of aluminum deoxidizer you need to condition the slag can save €375k of 'extra safety margins' annually:

- only saving 20kg of AI = 20 × €2.5/kg
 = €50/heat
- €50 × 25 heats/day × 300 days/year = €375k annually
- If Ca wire is used as deoxidizer you can save 20-30m of Ca wire and will also save more than €50/heat

Additional costs can be saved as the fast and accurate measurement of oxygen activity can replace slow, expensive and sophisticated X-Ray analysis of samples. This saves process time, but also additional costs and labor of samplers, sample preparation and analysis.

3 How to reach exact steel grades



Source: Andersson, M.; Hallberg, M.; Johnsson, L.; Johnsson, P.: Slag/metal reactions during ladle treatment with focus on desulphurization. Sixth International Conference on molten slags, fluxes and salts.

Figure 3

3.1 How to avoid aluminum fading and increase ferroalloys' yield

Proper slag treatment is the precondition to reach exact steel grades. In LCAK steel grades the active oxygen in the slag reacts with aluminum in the steel which leads to aluminum fading or decreases the recovery of ferroalloys added for certain steel grades.

To reach exact aluminum content or alloyed steel grades containing Ti, Ca, Zr, B, Nb, Ni, Cr, or V, and to improve ferroalloy recovery, Celox SLAC[®] allows adequate slag conditioning which prevents excess oxygen from reacting with ferroalloys.

The figure 3 shows the dramatic reoxidation effect depending on the slag condition:

- If the FeO + MnO is less than 1%, almost no aluminum fading occurs.
- With 10% content of FeO + MnO in the slag the soluble aluminum content in the steel will be halved 30 minutes after ladle opening.
- The optimum slag and steel oxygen potential for minimum alloy fading can be determined with plant trials.

Celox SLAC[®] allows to control steel reoxidation, fading of aluminum and protects added ferroalloys from oxidation losses, which in the end is reducing costs and improving the production efficiency.

4 How to increase desulfurization efficiency

4.1 Precondition for deep desulfurization is deep deoxidation of steel and slag

The influence of the oxygen content of the steel on the sulfur removal efficiency is well known, but the influence of the oxygen content of the slag on the steel is underestimated.

To ensure proper sulfur removal efficiency steel makers should keep oxygen levels of the steel and the slag as low as possible.

$$L_{s} = \frac{(W_{s})}{[W_{c}]} = \frac{C'_{s}}{[h_{c}]}$$

C's: Modified sulfide capacitiy ho: Oxygen activity of steel and slag

Source: Secondary Steelmaking: Principles and Applications, Ahindra Ghosh, 2001 CRC Press LLC.

This equation shows, that the lower the oxygen activity of steel and slag, the greater is the distribution coefficient of sulfur between slag and metal. This means that the minimum values of oxygen activity of steel and slag create the most favorable conditions for steel desulfurization.

Desulfurization treatment

Figure 4 shows that deep desulfurization, meaning S<0.005%, is only possible if the content of FeO and MnO is less than 1%.

An increase of the initial FeO content in the top slag significantly lowers the desulfurization rate. Checking and controlling the initial oxidation state will be beneficial if you practice top slag desulfurization:

- saving treatment time
- increasing the desulfurization efficiency
- allowing more precise end sulfur prediction

INFLUENCE OF FeO CONTENT IN THE SLAG ON DESULFURIZATION



Source: Andersson, M.; Hallberg, M.; Johnsson, L.; Johnsson, P.: Slag/metal reactions during ladle treatment with focus on desulphurization. Sixth International Conference on molten slags, fluxes and salts.

Figure 4

Celox SLAC[®] allows to deoxidize the slag properly to ensure efficient desulfurization saving treatment time and costs.

4.2 How to ensure effective Ca-treatment

Many steel makers try to improve their steel quality by additional Ca-treatment at the refining station. Also, effective Ca-treatment requires a low oxygen slag.

Based on an initial Celox SLAC[®] reading before starting the Ca-treatment, the slag can be conditioned with aluminum prior to calcium resulting in a higher Ca-yield, as well as cost savings, as calcium wire is up to three times more expensive than aluminum.

5 How to optimize production efficiency and safety

5.1 How to increase production efficiency and annual revenue

5.1.1 Delta Dist $^{\odot}$ L – One sensor measuring freeboard, slag thickness and bath level



Graphic showing the use of Delta Dist® L

The Delta Dist[®] L (DDL) is used on automatic immersion lances with an encoder which measures movement at a known constant speed. The slag thickness and freeboard are determined by the sensor measurement and the encoder position measurements, or calculated by the time interval and speed of the lance.

The DDL is using existing hardware for Celox[®] probes. The measurement is made with iM² Sensor Lab[®] and the calculation can either be made with appropriate Heraeus Electro-Nite instruments, e.g. iM² Sensor Lab[®] or by means of steel plant's level 2.

5.1.2 Delta Dist[®] L – What needs to be considered for representative results

The DDL works in a two-step method: In a first step, by moving down the lance, the slag level is detected by use of a small steel strip providing the contact. As the probe continues down, it will pass through the slag and detects the presence of steel.

The measurement time is typically less than 2 seconds. Top slag conditions will certainly influence the accuracy. Liquid slag will enable slag thickness measurements within 1 to 2cm.

VALUE-IN-USE

INCREASING PRODUCTION EFFICIENCY BASED ON CUSTOMER CASE

By measuring the freeboard with Delta Dist[®] L you can decrease the safety margin and increase your production efficiency. This example shows the saving potential for a 160t ladle:

- In case of a 1.5m freeboard one can easily add +5% (+8t) of steel to each ladle, meaning in total 168t.
- With 25 heats per day = 25 × 300 days × 8t
 = 60,000 t/year.
- This leads to an annual increase of steel production of 60,000 tons, resulting in an annual revenue increase of €60m (60,000t × €1,000).

Delta Dist[®] L enables to optimize ladle filling to increase production efficiency and annual revenue by measuring the freeboard. **5.2 How to optimize power consumption in ladle furnace** For most efficient power use the arc coverage by slag should be optimized. If the slag thickness is too low, the arcs will heat the walls and lid of the ladle furnace. If the slag thickness is too high the arcs will overheat the slag. The thickness of the slag should be 20-30% more compared to the arc length. Furthermore, this will increase also the refractory lifetime.

VALUE-IN-USE

SAVING ENERGY AND COSTS BASED ON CUSTOMER CASE

This example shows how much energy and costs can be saved if the slag thickness is optimized using DDL for a 150t ladle:

- Heating up the ladle to 80°C needs 6.2MWh, leading to costs of €1,984 (6.2 × €320 energy costs).
- If 3% of power can be saved, the result is a saving of ~€60 per heat, leading to annual savings of ~€450,000 (€60 × 25 heats × 300 days).

Delta Dist[®] L allows the steelmaker to optimize power consumption enabling energy and cost savings by measuring and enabling to optimize slag thickness.

5.3 How to detect slag carryover and to precisely position instruments for the production process

If a slag cut-off system is out of order the Delta Dist[®] L probe is a back-up system which can exactly detect the amount of slag carried over to the ladle. Additionally, you can use DDL as a calibration tool to adjust the sensitivity of the slag cut-off system. Furthermore, if you use skimming stations the DDL sensor shows if all slag was removed efficiently.

DDL assists to accurately position the vacuum chamber of the RH degasser and precisely position injection lances which in the end then leads to a higher efficiency of injected materials. Moreover, DDL enables you also to accurately determine the immersion depths for manipulators, e.g. automated Hydris[®], Celox SLAC[®], and QuiK-Spec[®] samplers.

Measuring instrument iM² Sensor Lab[®] and Delta Dist[®] L sensors



5.4 How to increase safety and reduce costs by automated sampling

5.4.1 QUSAS[®] Slag Samplers – What needs to be considered for representative results

There are three different QUSAS[®] Slag Samplers available: QUSAS[®] Slag Cup Sampler for blast furnace or EAF for manual use and two QUSAS[®] Immersion Slag Samplers for converter, ladle, LF, RH and degassing stations for manual or automatic use.

QUSAS[®] Samplers: <u>Quick Samplers for Slag</u>

The QUSAS[®] Samplers are composed of a sand body with a conical filling chamber. When passing through the slag, the slag is collected in the chamber and pressed through a small gate into the sampling house.

The sample can easily be removed when breaking the sand body after immersion. The sample is captured into a protective steel ring and this solid sample coin is immediately ready for transport and XRF analysis.

A vertical immersion and liquid slag are crucial to get a representative sample. The sampler should be held for 5-8 seconds in steel with a minimal immersion depth of 40cm. The sample should be taken before temperature or oxygen measurement and before steel sampling. After stirring you should wait at least 1 minute before sampling.

QUSAS[®] Slag Samplers provide fast and safe sampling – ready to analyze without sample preparation reducing costs.



QUSAS® Slag Cup Sampler for EAF or BF

5.4.2 QUSAS[®] Slag Cup Sampler for EAF or BF

The slag is sampled by a spoon and poured into the QUSAS[®] Slag Cup Sampler. The slag solidifies in the cup. Within a few minutes, the sand cup is crushed and the slag sample can be picked up. In order to cope with the foamy EAF slag, it is recommended to use the slag cup with a reinforced sheet. Thanks to the special design of the mould for EAF or converter application you get representative samples of even foamy slag.

The slag sample is protected by a heavy-duty steel ring and instantly ready for XRF analysis which saves up to 10 min time giving the possibility to immediately correct the process.

QUSAS[®] Slag Samplers eliminate labor-intensive slag sample preparation and allow further cost savings as QUSAS[®] samples do not require sophisticated and expensive sample preparation equipment.

QUSAS[®] Slag Cup Samplers for EAF or BF allow fast manual sampling also for foamy slag and eliminate sample preparation saving costs.

5.4.3 QUSAS[®] Immersion Slag Samplers for automated sampling in converter & LF

QUSAS[®] Immersion Slag Samplers can be used with manipulators which makes the sampling process completely safe. As the slag sample can be also directly analyzed without any sample preparation these samplers save process time and costs. A 10mm tall chamber is available for samples being directly analyzed on the XRF, and a larger 24mm chamber is available for safely collect bulk slag for conventional slag preparation and analysis.

QUSAS[®] Immersion Slag Samplers allow you to take the top slag only, which leads to a representative slag sample. The graphite coating of the QUSAS[®] Slag Samplers for ladle and converter application ensures a good slag transfer.

The sampling method is more reliable than the traditional way of immersing a steel rod or bar. Automated sampling reduces process and operator variables and the ready-to-analyze-sample reduces the risk of contamination.

VALUE-IN-USE

INCREASING PRODUCTION EFFICIENCY AND ANNUAL REVENUE BASED ON CUSTOMER CASE

Increasing production efficiency and sales:

- QUSAS[®] Slag Sampler saves at least 2 min per heat.
- instead of 30 heats/day it enables 31 heats/day
- with 180 t/heat and USD 165,000 extra finished goods production per day = USD 50m annual sales increase

QUSAS[®] Immersion Slag Samplers for converter & LF allow fast and safe sampling and eliminate sample preparation saving costs.



 $\mathsf{QUSAS}^{\circledast}$ Immersion Slag Samplers for automated sampling in converter and ladle furnace

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