Heraeus

ELECTRO-NITE



Celox® Hot Metal application report, 2011

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CELOX®
HOT METAL
APPLICATION REPORT

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01

ABOUT CELOX® HOT METAL SULPHUR

1.1 CELOX® HOT METAL SULPHUR MEASURING SYSTEM

The following sketch shows the hardware required for a sulphur measurement in hot metal:

- Celox® Hot Metal Sulphur (HM-S) sensor
- Immersion lance with inner compensating cable and external cable connecting the lance with the *i*M² Sensor Lab® instrument
- *i*M² Sensor Lab® instrument



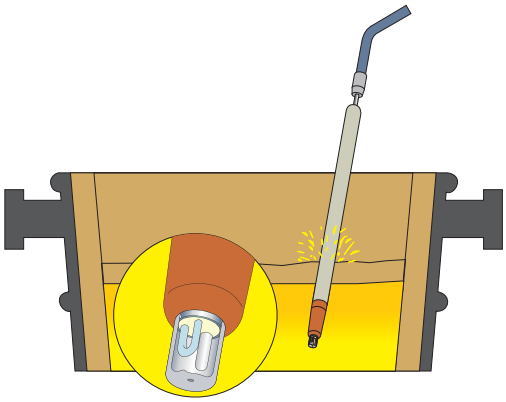


FIG. 1 : MEASUREMENT SYSTEM

1.2 SENSOR SPECIFICATIONS AND APPLICATION RANGE IN HOT METAL

- Temperature range: 1250°C to 1450°C
- S-range: 5-2000ppm
- S-accuracy: σ (1 sigma) <= 10% of actual S value, for example, for sulphur content S = 0.003% σ = 0.0003% for a co-injection process CaC2/Mg ratio of 1:4

IMPORTANT
The minimum required magnesium content in the reagent mix is 13%. The sensor will not work in mixtures with a magnesium content lower than 13%.

The measurement time depends on the temperature and varies between 7 and 15 seconds: for a given sulphur content, a higher temperature gives a shorter measurement time. The sensor is compatible with standard Heraeus Electro-Nite (HEN) contact blocks, sensor holders, and cabling.

1.3 GOOD OPERATING PRACTICES

- Keep sensors dry.
- Keep lances and cables dry and in good condition.
- Fix the sensor securely on the immersion lance notches.
- Immerse quickly through the slag into the metal.
- Immersion depth must be 30 to 40cm and 30 to 40cm away from the lining.

1.4 MEASUREMENT PRINCIPLE AND FORMULAE

The HM-S sensor does not measure sulphur directly: it measures an oxygen potential, which is related to the sulphur level through a special coating on the measuring cell.

The determination of the oxygen partial pressure around the coating is based on an electrochemical measurement. Magnesia-stabilised zirconia is used as the electrolyte. At high temperatures, this solid electrolyte allows the transfer of oxygen ions between the molten metal and the reference material in the electrochemical cell.

The following shows the principle of the HM-S measuring system:

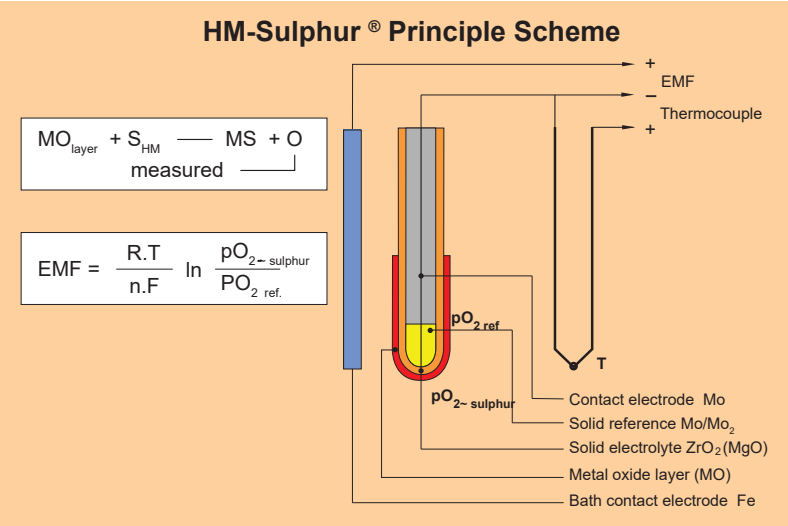


FIG. 2 : HM-SULPHUR PRINCIPLE

The oxides in the coating react with the free sulphur in the liquid metal and generate an oxygen partial pressure, which is in relation to the sulphur concentration. The oxygen partial pressure inside the cell is fixed by the Mo/Mo2 solid reference. The temperature is measured and as a consequence the measured EMF is a function of the sulphur content in the hot metal.

The following shows a typical HM-S measurement:

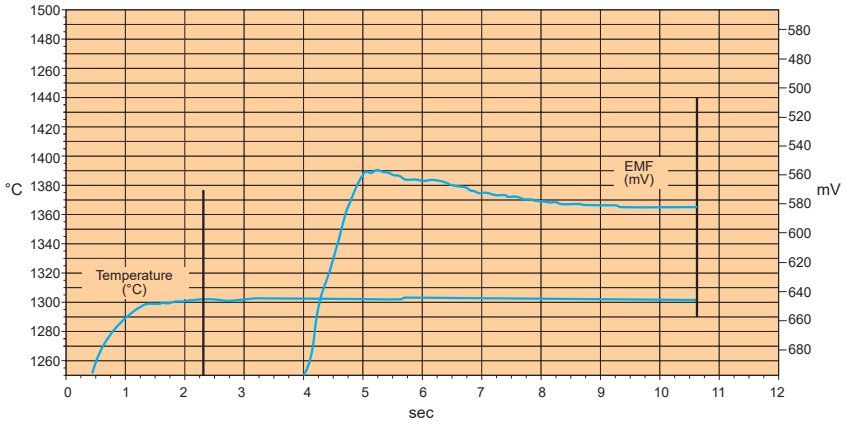


FIG. 3 : TYPICAL MEASUREMENT TRACE

The EMF trace appears after 4 seconds and, after an initial overshoot, the signal stabilises after 8 seconds. The measuring times depend mainly on the hot metal temperature. The initial overshoot depends on the sulphur level.

The formulae used to calculate the sulphur content are derived from empirical relationships between sample analysis and the temperature and EMF signals coming from the HM-S sensor rather than from thermodynamic principles.

The previous and next figures show an example of such an empirical relationship.

Typically, the relationship is: Log S = f(EMF, Temp, log Si)

The following shows a typical correlation between sample sulphur and Celox® HM-S:

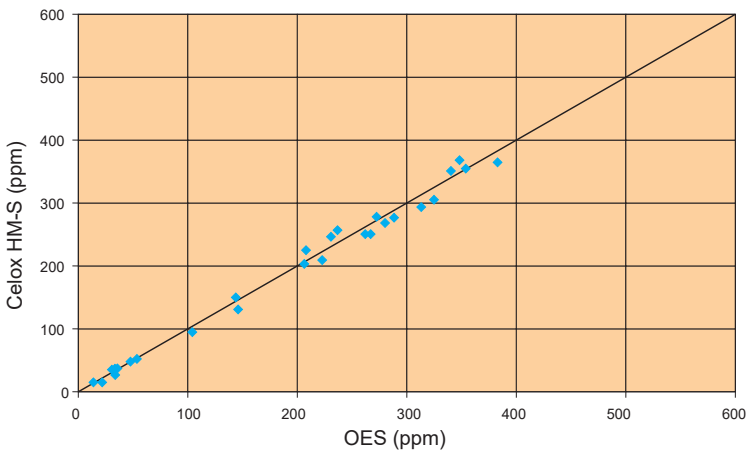


FIG. 4 : CORRELATION BETWEEN OES-S AND CELOX® HM-S

The following table shows a regression analysis for the following formula:

log S = A + B x %Si + C x T + D x EMF + E x EMF2

Before desulph: A = 23893.1 / B = 104.918 / C = 1.406935 / D = 84.04919 / E = 0.068813

After desulph: A = 40.997 / B = 0.455 / C = 0.002186 / D = 0.120075 / E = 0.0000839

ppm S = ...
Before Desulph

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0,96612389
R Square	0,93339537
Adjusted R Sq	0,90917551
Standard Err	18,084511
Observations	16

ANOVA

	df	*SS*	*MS*	*F*
Regression	4	50415,8926	12603,97	58,53842
Residual	11	3597,544902	327,0495	
Total	15	54013,4375		

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	23893,1011	10299,73362	2,319779	0,040594
% Si Spectro	104,918002	67,3805772	1,557096	0,147734
°C	1,40693536	0,280343639	5,01861	0,000391
mV	84,0491874	36,04666916	2,331675	0,039751
mV^2	0,06881305	0,031151892	2,208952	0,049309

Log S = ...
After Desulph

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0,990365287
R Square	0,980823402
Adjusted R Sq	0,969865346
Standard Error	0,063800203
Observations	12

ANOVA

	df	*SS*	*MS*	*F*
Regression	4	1,457341795	0,364335	89,50706
Residual	7	0,028493262	0,00407	
Total	11	1,485835056		

	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	40,99684079	6,617513021	6,195204	0,000447
% Si Spectro	0,454764934	0,236323166	1,924335	0,095717
T°C	0,002186112	0,001435281	1,523125	0,171546
mV	0,12007512	0,018500542	6,490357	0,000337
mV^2	8,39329E-05	1,39887E-05	6,000047	0,000542

FIG. 5 : REGRESSION ANALYSIS

It is important to know that silicon in the hot metal has a relatively large impact on the sulphur EMF signal. The silicon content has to be included in the regression analysis. The following graph shows the influence of silicon:

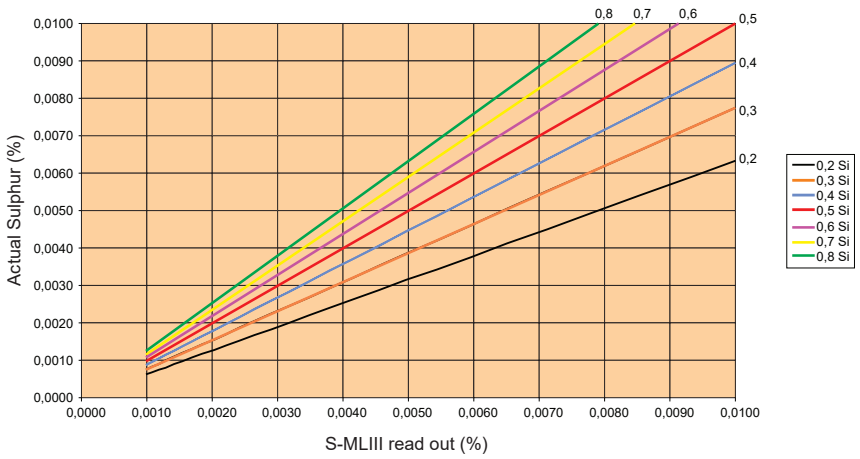


FIG. 6 : SILICON INFLUENCE

The following shows the reproducibility of the Celox® HM-S based on back-to-back measurements in a ladle:

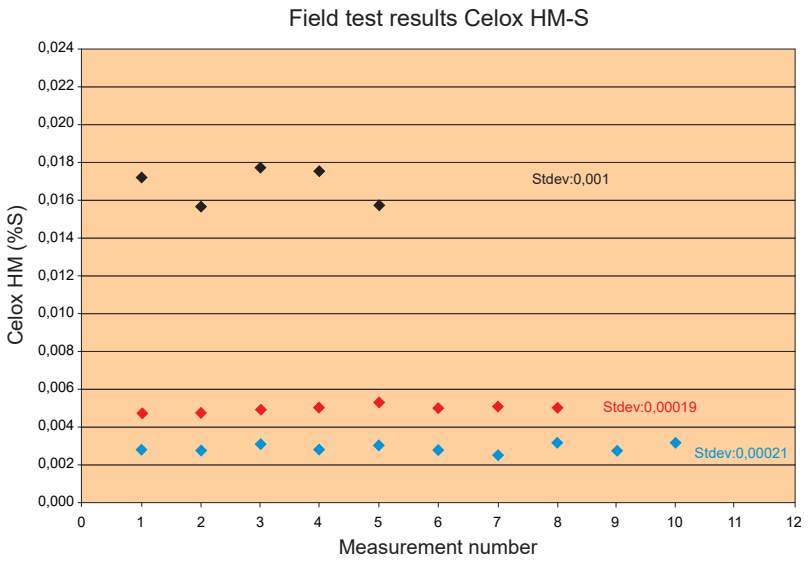


FIG. 7 : REPRODUCIBILITY TEST

1.5 SULPHUR DETERMINATION ON SAMPLES

The accuracy of the sulphur measurement is influenced by the following factors:

- Quality of the samplers and obtained samples; capping, sample dimensions...
- Sample taking; timing, depth, lance type (auto or manual)
- Method of sample preparation; milling, grinding, drilling,...
- Analytical equipment and its calibration procedures; XRF, OES, Combustion analysis...

Sample quality:
Adequate capping is essential in order to obtain slag-free samples. The standard capping (steel and cardboard cap) might need to be matched with the application.

Sufficient cooling capacity (air, water) is necessary in order to avoid segregation. When OES is used, we recommend using the SAHT08NA5 (8mm round sample, no lugs)

Sample taking:
First of all, the sample should be representative of the hot metal in the ladle torpedo. Sampling position and timing of the sample are equally important especially when samples are taken in the runner or torpedo. Stratification can also take place in a hot metal ladle when it is topped up with hot metal from a different torpedo.

Fast auto-lances (>0.3m/s travel rate) and sufficient immersion depth (>50cm) below the slag line give best results.

The following graph shows the sample after skimming (S22) and before skimming (S21):

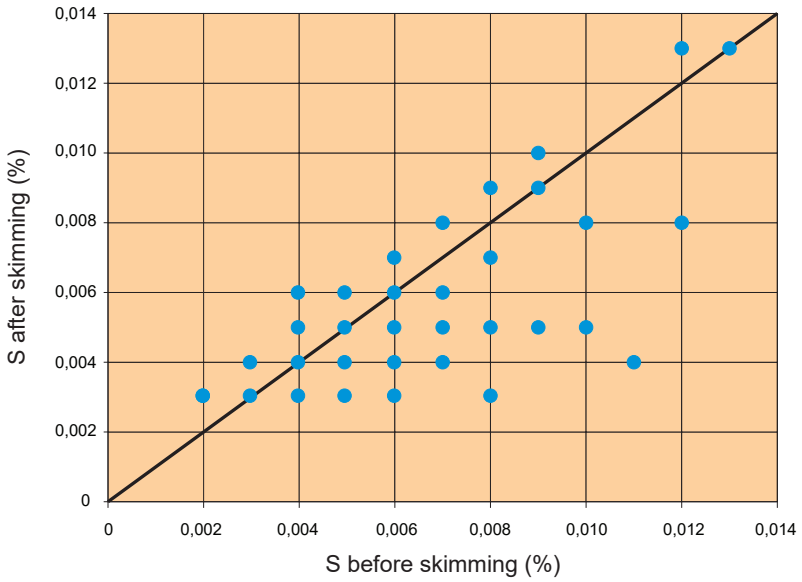


FIG. 8 : SULPHUR BEFORE AND AFTER SKIMMING

At the desulphurisation station, after desulphurisation, samples taken before or after slag skimming frequently give different analytical results. In general, samples taken after skimming give lower results and show less variation.

Sample preparation and analysis:
The reproducibility of combustion analysis was checked on standards :

- Standards usually give a +/- 10% relative scatter.
- On a standard containing 50ppm S, we found a scatter of 2ppm.
- On a standard containing 500ppm S, we found a scatter of 15ppm.

The very best result we obtained on real life samples was about twice the scatter on standards: 4ppm on a 50ppm S level and 30ppm on a 500ppm S level.

In the lab, the recommended procedure is to mill the samples (0.7mm) and drill afterwards. Analyse the obtained turnings by combustion analysis.

For sample analysis (besides combustion analysis), OES rather than XRF is recommended.

When using OES, it is essential to obtain a well-chilled sample, otherwise graphite will form. The graphite precipitations interfere with the spark and provide less reliable results. This can be avoided by selecting a sample thickness of 8mm. Graphite formation is more likely with higher temperatures and thicker samples.

Porosity and slag inclusions also interfere with the spark and should therefore be avoided.



FIG. 9 : Example of a white (top) and grey (bottom) solidified hot metal sample



FIG. 10 : Microstructure of a hot metal sample taken in the desulphurisation station with a pocket sampler. The presence of needles and very few graphite inclusions indicates a good white solidified sample structure.

The graphite precipitation is highest in the middle of the sample.

Combustion analysis on lugs, although easy to use, gives a relatively large scatter on the analytical results.

Comparison between different analytical techniques:
The following graph shows OES (HEN) versus combustion analysis (plant Y)

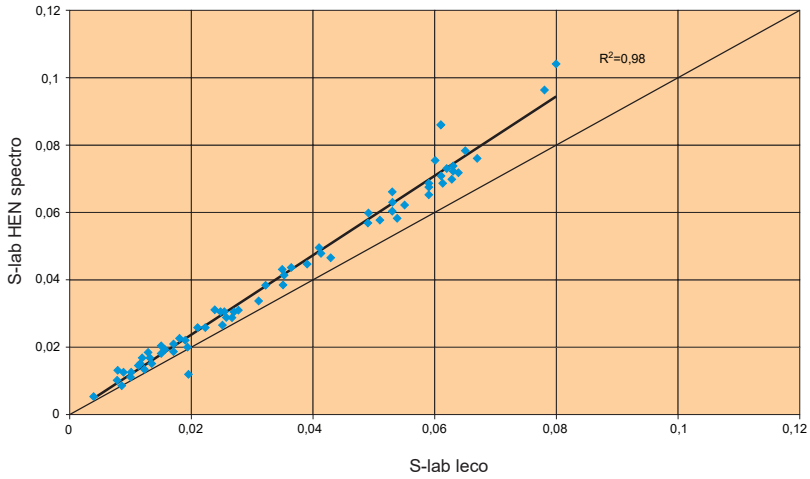


FIG. 11 : COMPARISON BETWEEN OES AND LECO

The sample had been milled (1mm) and analysed with a calibrated OES. The same sample was carefully drilled in order to obtain solid parts suitable for combustion analysis. Note that the standard deviation of both systems is small. On the other hand, there is a clear offset between the two. The offset increases as S levels increase.

The following shows OES (plant X) versus combustion analysis on lugs (plant X):

Both methods do not show an offset (45° line), but there is a larger scatter over the entire sulphur range. Above 0.06% S, the relationship disappears.

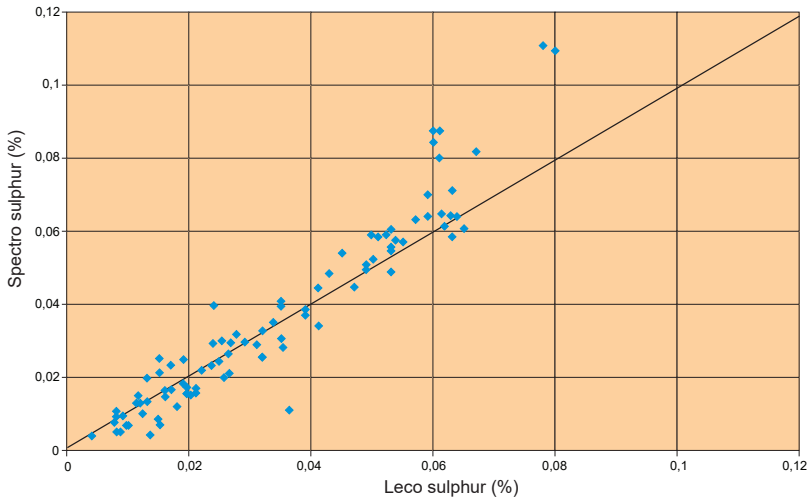


FIG. 12 : COMPARISON BETWEEN OES AND LECO

In plant Z, XRF and OES analyses were performed on the same sample:

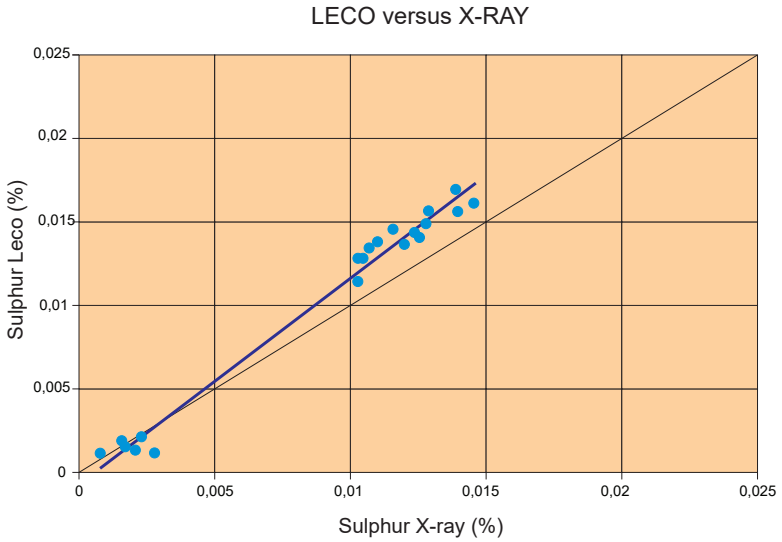


FIG. 13 : COMPARISON BETWEEN LECO AND X-RAY

The following shows OES results on the same sample in different labs:

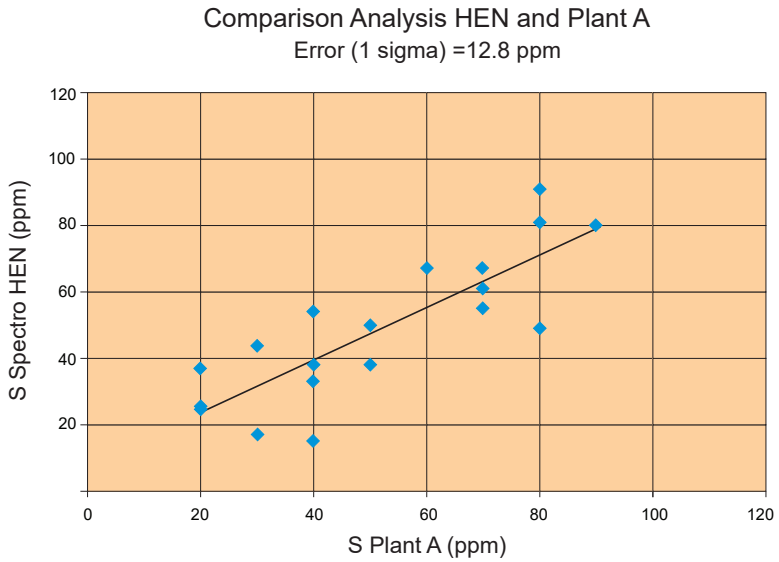


FIG. 14 : COMPARISON BETWEEN LABS

In this case the samples were first analysed using OES at Heraeus Electro-Nite and afterwards using OES from plant A.

The σ standard deviation is 12ppm S.

02

HOW TO MAKE UP A CUSTOMISED SULPHUR ALGORITHM

2.1 INTRODUCTION

The algorithms used to calculate the sulphur content are derived from empirical relationships between sample analysis and the temperature and EMF signals coming from the HM-S sensor, not from thermodynamic principles.

1 algorithm alone cannot be used for the full sulphur range. 2 different algorithms must be used to determine the sulphur content before and after desulphurisation. Data must be collected carefully depending on the application. Data collection is the first step in the process of algorithm creation.

Collecting data can be time consuming: at least 50 measurements are needed for a reliable regression analysis, therefore requirements must be defined exactly. For example:

- If a measurement before desulphurisation is required, the focus should be on taking measurements before desulphurisation only.
- Various reagent mixtures are used to desulphurise. Focus on the one that is used most frequently.

2.2 IMPORTANT: ERRATIC SAMPLE ANALYSIS

Due to the potential errors generated by sample taking, preparation, and analysis, the correlation between the Celox® HM-S and the lab might not be straightforward and show a scatter. It is therefore recommended to take additional samples with each measurement and send these samples to Heraeus Electro-Nite Int. N.V. where it can be prepared and analysed using OES. It might also be advisable to use two or more HM-S probes in order to check the reproducibility and accuracy of the probes.

2.3 REQUIRED DATA FOR REGRESSION ANALYSIS

- Measurement number
- Heat number
- Blast furnace number
- Indication whether before, during, or after treatment
- Desulphurisation reagent: for example, CaC2/Mg 4:1
- Injection rate in kg/min, for example, 25
- Temperature (°C)
- EMF signal (mV)

Analytical results on sample: at least %Si, %Mn, %S, and, if available %Mg, %C, and %Ti.

FIG. 15 : DATA COLLECTION

No.	Heat No.	Blast Furnace No.	Meas. timing	Desulph. reagent	Temp. ° C	EMF mV	Analysis by spectro lab					
							[C] %	[Si] %	[Mn] %	[P] %	[Mg] ppm	[S] ppm
1	002	A	After treat.	CaC2/Mg 1:4 (25kg/min)	1329.9	−576	4.59	0.26	0.20	0.108	50	200
2	003	A	After treat.	CaC2/Mg 1:4 (45kg/min)	1370.2	−594	4.69	0.30	0.20	0.107	20	60
3	006	B	After treat.	CaC2/Mg 1:4 (35kg/min)	1287.3	−621	4.94	0.31	0.24	0.117	35	20
4	008	A	Before treat.		1360	−569	4.14	0.39	0.21	0.117	0	350
5		B	After treat.	CaO/Mg 1:5(60kg/min)	1349.1	−599	4.98	0.35	0.21	0.111	45	104
6	012	C	After treat.	CaO/Mg 1:4(55kg/min)	1364.9	−600	4.29	0.32	0.20	0.112	23	39
7	014	B	Before treat.		1381	−578		0.43	0.23	0.114		250
8		B	After treat.	CaC2/Mg 1:4 (28kg/min)	1371	−597	4.51	0.41	0.22	0.115	90	65
9	016	B	Before treat.		1371.3	−570	4.99	0.33	0.22	0.114		320
10		A	After treat.	CaC2/Mg 1:4 (15kg/min)	1356.1	−601	4.36	0.34	0.22	0.115	100	70
11	018	A	Before treat.		1371.2	−565	5.10	0.33	0.24	0.117		300
12		B	After treat.	CaC2/Mg 1:4 (25kg/min)	1360.7	−594	4.17	0.35	0.24	0.109	150	117

03 THE DESULPHURISATION PROCESS

3.1 TREATMENT SEQUENCE

The following graph shows a typical treatment sequence at a ladle desulphurisation station:

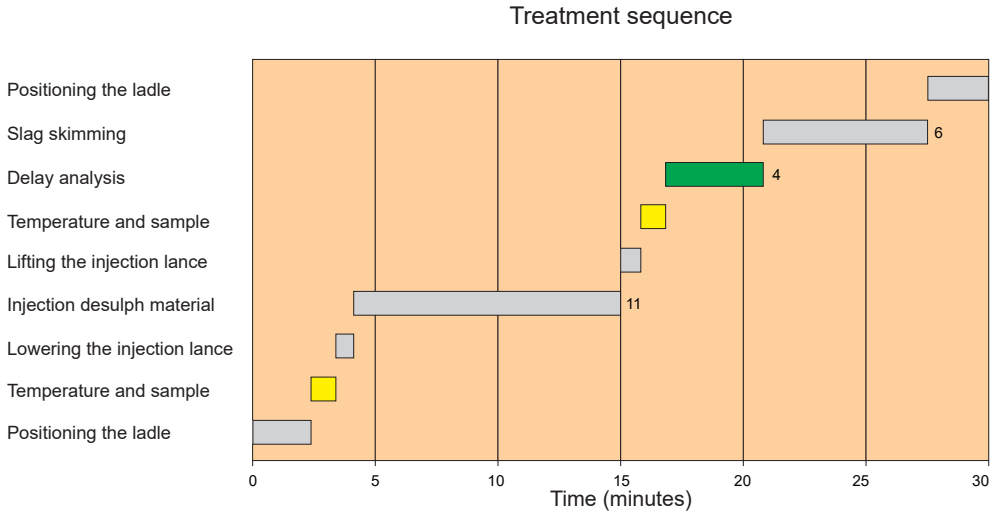


FIG. 16 : TREATMENT SEQUENCE

Most steel plants take a sample and a temperature measurement before the desulphurisation process starts. The desulphurisation model however calculates the required amount of reagent based on the average sulphur content being based on the analysis results of samples taken in the runner or torpedo at the blast furnace.

The waiting time for the results depends on the priority in the lab. If the waiting time is shorter than the injection time, the amount of reagent can be adjusted to the correct value.

After the calculated amount is injected, a second sample and temperature measurement is taken. Usually, because of time constraints, the second sample is taken directly after lifting the injection lance. Waiting time for the sample is on average more than 4 minutes.

The ladle is skimmed right after the sample is taken. If the sample analysis is below the S target, the ladle is sent to the converter. If not, an additional treatment and slag skimming is applied.

3.2 INJECTION PROCESS

The following shows a bench mark injection process:

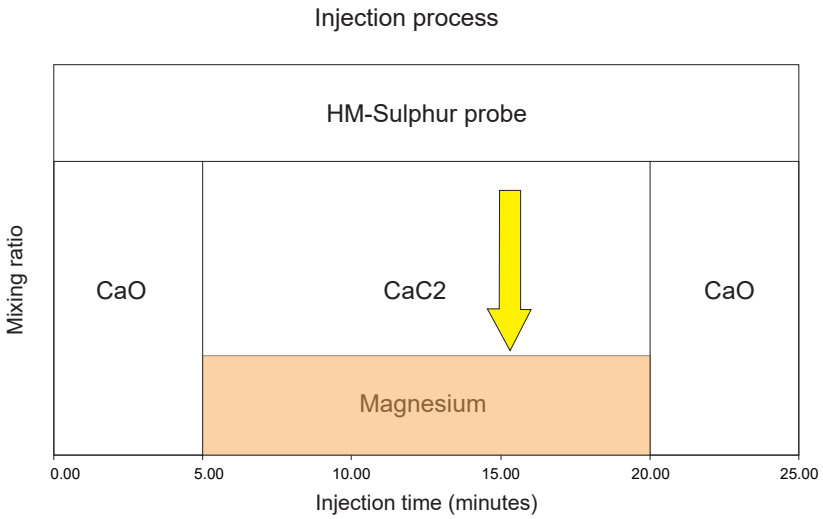


FIG. 17 : INJECTION PROCESS

1. Pure lime is injected.
2. Mg is injected to speed up the desulphurisation. The oxygen content is lowered to enable desulphurisation to achieve low S targets. The CaC2/Mg or CaO/Mg ratios and injection rates can be adjusted according to the S targets and time requirements downstream.
3. CaO is injected to maximise the Mg yield and the removal of the remaining inclusions in the hot metal.

3.3 MATERIAL COSTS AND RELATED COST SAVINGS

The following graph takes as an example the most common co-injection process with CaC2/Mg mixture. Initial S is 0.05% and target S is maximum 0.005%. It shows that approximately 80% of the material costs are reagent costs, although the iron loss cannot be ignored either:

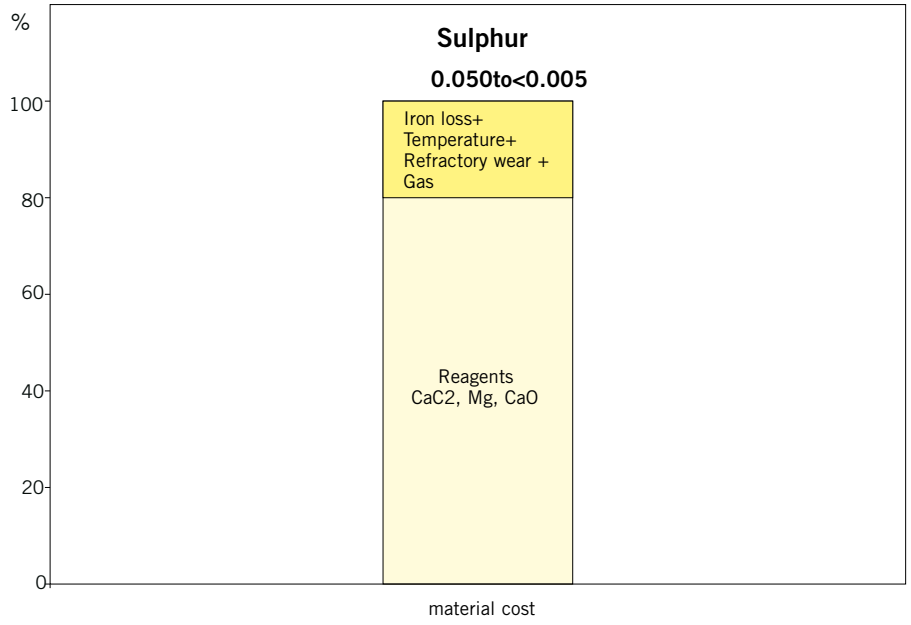


FIG. 18 : COST STRUCTURE

Magnesium is the most expensive component in the reagent mixture. The magnesium consumption increases exponentially as sulphur targets are lowered:

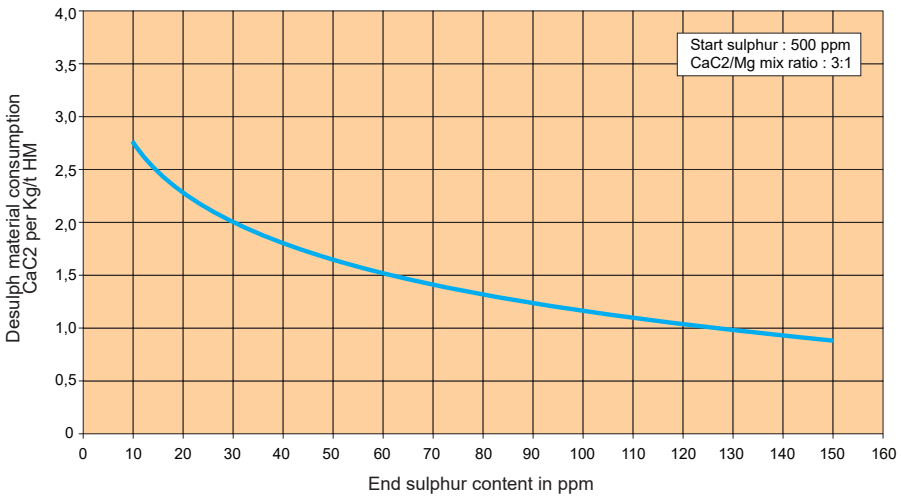


FIG. 19 :REAGENT CONSUMPTION

The following trace shows the cost of overtreatment as a function of the S target in a 300 ton ladle. For example: 0.001% S (10ppm) overtreatment at an S target of 0.0030% (=30ppm S) costs approximately 120 Euros:

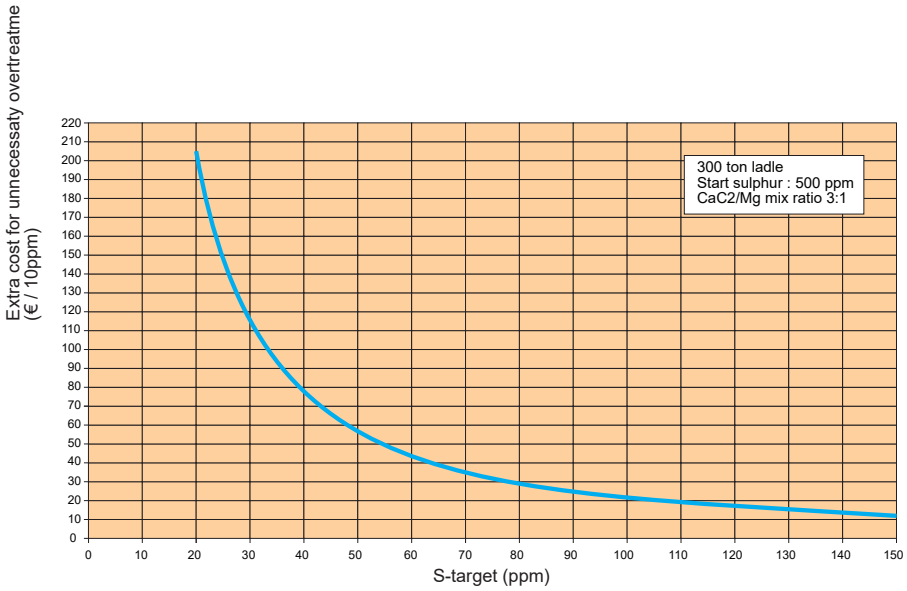


FIG. 20 : OVERTREATMENT COST

3.4 PROCESS PREDICTABILITY AND RELATED COST SAVINGS

The following Gauss trace shows a typical sulphur distribution after a desulphurisation process in the ladle using a bench mark co-injection process with a 4:1 CaC2/Mg mixture.

The S max of 0.005% S corresponds with a target of 0.0035%. Typically, the bench mark process deviation is 0.0005% for a 0.005% S level.

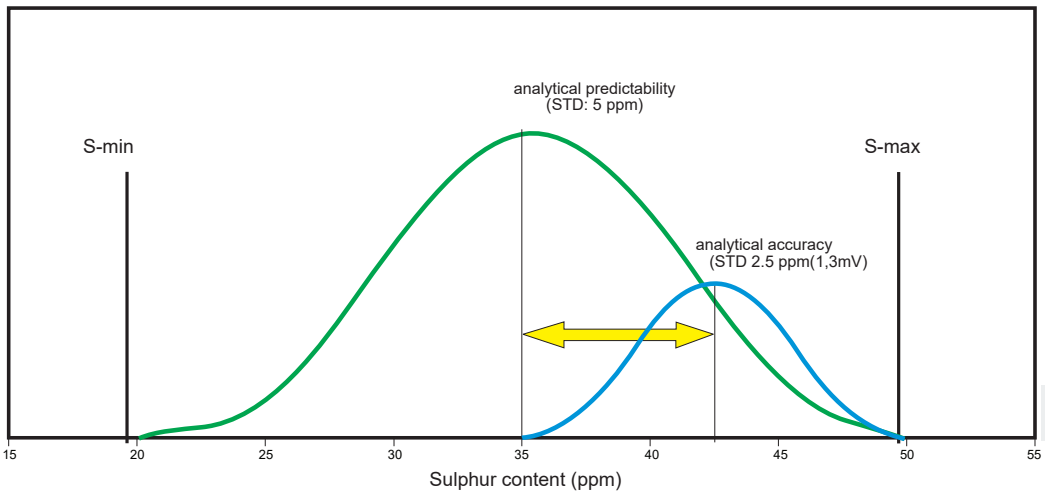


FIG. 21 : PROCESS PREDICTABILITY

The target S level ensures that the maximum specification is never exceeded. In theory, the S target should be 3 standard deviations below the maximum in order to achieve a 100% success rate (0.0035 = 0.005 – 3 x 0.0005%).

A good process has a smaller standard deviation and the target can be set closer to the S max. Better process control reduces the process variation allowing for improved setting of the S target.

The ability to lower the S target can generate huge cost savings as previously explained and calculated.

The process variation can be reduced by implementing an accurate, online sulphur determination before, during, or after desulphurisation.

Overtreatment is common practice nowadays because of lacking online and accurate sulphur determination.

Due to production pressure, steel plants cannot afford to wait for the sample analysis in order to release the ladle from the desulphurisation station.

Undertreatment is completely unacceptable since initiating a second injection process including a second skimming of the slag can generate loss in productivity, temperature, and desulphurisation reagent.

Online sulphur determination, preferably during treatment, enables a better use of the desulphurisation time switching over to lower injection rates and/or higher CaC2/Mg ratios. Reagent efficiency decreases with higher injection rates.

04

EXISTING CELOX® HM-S APPLICATIONS AND BENEFITS

The Celox® HM-S sensor allows the hot metal desulphurisation process to be optimised by:

- **Cost savings** on reagents: The standard over addition (safety margin) becomes obsolete thus saving up to 15% on material (on average 40 Euros in a 250-ton ladle) per treatment.

- **Time savings**: With Celox® HM-S, results are obtained in seconds compared to the long waiting time required for lab sample analysis.

- **Chemistry**: Celox® HM-S measures the 'true' sulphur and silicon content and is not influenced by non-metallics. It is well known that non-metallics influence the final result in the case of hot metal samples.

- **Plant logistics**: Hot metal analysis using the fast and easy-to-use Celox® HM-S sensor can lead to improved plant logistics.

4.1 CELOX® HM-S IN THE TORPEDO

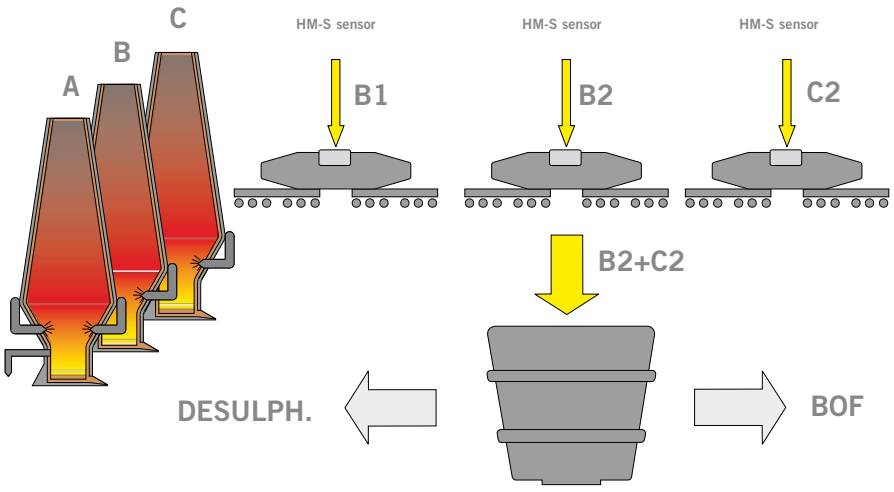


FIG. 22 : LADLE LOGISTICS

Depending on the BOF specification, some hot metal heats in the torpedo require desulphurisation and some do not. Celox® HM-S enables an instant decision on what to do: send the ladle to the desulphurisation station or directly to the BOF.

Desulphurisation can also take place in the torpedo. Usually, mono-injection with pure CaO or CaC2 is used in these cases.

There is a clear tendency to use a mono-injection of CaO/Mg mixture. If the Mg content in this mixture is larger than 13%, the Celox® HM-S can be used for measurements after desulphurisation.

4.2 CELOX® HM-S IN THE LADLE BEFORE DESULPHURISATION

The following figure shows the Celox® HM-S measurement taken before starting the injection process:

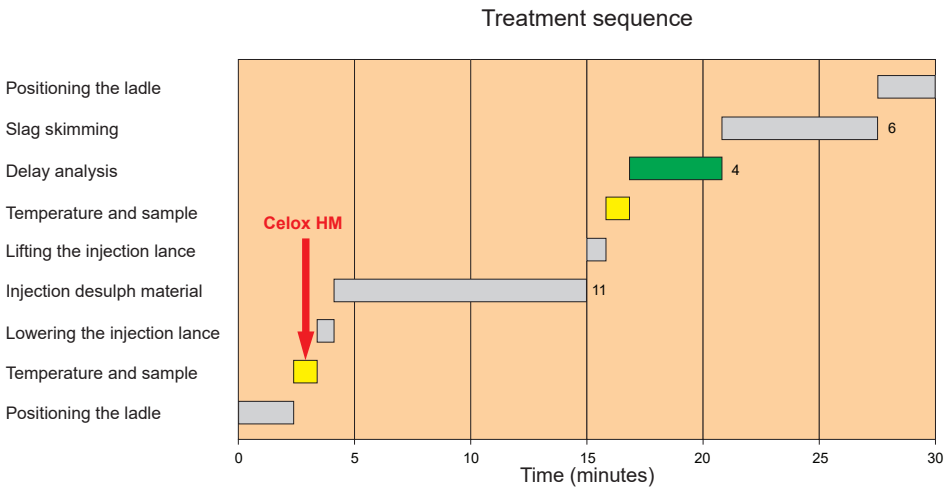


FIG. 23 : CELOX® HM-S BEFORE DESULPHURISATION

Many shops use a weighted average estimate for the initial S content. These results are usually inaccurate and prone to flyers. The inaccuracy and the amount of flyers can be large if the weighted average is based on a sample in the blast furnace runner. During the blast furnace tap, the composition might vary strongly. Stratification could occur in the torpedo.

An accurate knowlege of the sulphur content at the start is essential in order to reach the sulphur target. However, accurate sulphur analysis is difficult to obtain since it requires high priority being placed on the samples. The potential analytical problems are described in section 1.5 on page 5.

In many cases, for example, high injection rates, low incoming sulphur, or high sulphur target, the analysis of the incoming sample arrives when the injection process is finished. In some cases the operators are not allowed to stop the injection process until the start sample arrives. In the latter case a lot of reagent is wasted.

Sample analysis and combustion analysis can be extremely expensive – sometimes more than 18 Euros.

4.3 CELOX® HM-S IN THE LADLE AFTER DESULPHURISATION

The following figure shows the Celox® HM-S measurement taken after starting the injection process:

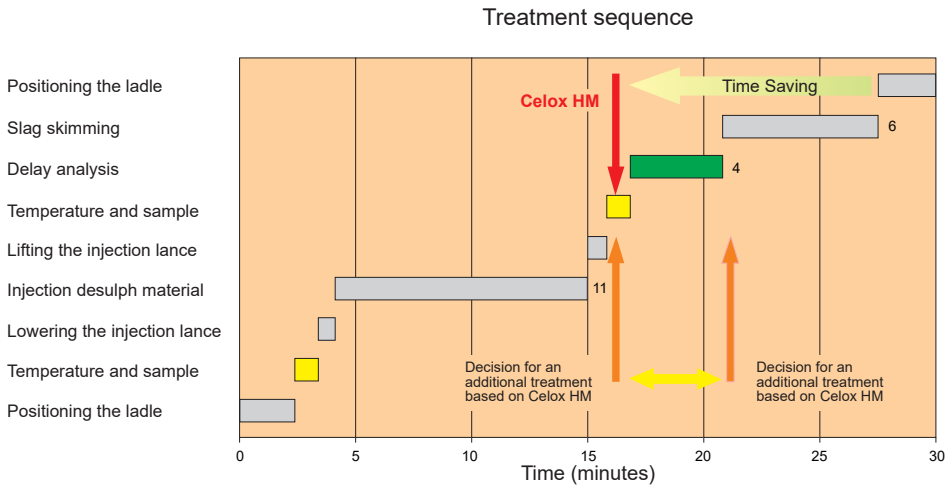


FIG. 24 : CELOX® HM-S AFTER DESULPHURISATION

Based on a quick sulphur check after the injection process and before slag skimming, the ladle can be released to the BOF. The time saving is at least 4 minutes. When taking the sample after skimming, the time saving increases to 10 minutes.

The problems and analytical issues of taking samples directly after injection are described in section 1.5 on page 5. The Celox® HM-S is a straight-forward, accurate measurement and using the HM-S sensor, overtreatment and the costs involved can be eliminated (see section 3 on page 11). A better decision can be taken about whether an additional treatment is required.

05 IMPLEMENTATION OF CELOX® HM-S AND HM-SI SENSORS IN STEEL PLANTS: PAPERS

5.1 HOT METAL PROCESS IMPROVEMENTS AT MITTAL STEEL, SPARROWS POINT, USA

The following is taken from a paper presented at AISTech 2006 - The Iron & Steel Technology Conference and Exposition, Cleveland, Ohio, and published in the AISTech 2006 Proceedings. It was written by:

- Rick Fash, division manager - steel producing
- William Howanski, division process manager
- Danny Neith, process engineer - BOF, Mittal Steel USA - Sparrows Point, Md.
- David Patterson, sales service engineer
- Randall P. Stone, senior product manager, Heraeus Electro-Nite Co., Langhorne, Pa.
- Mark Borsody, salesman, Hart Metals, Tamaqua, Pa.

The initial advantages of using an HM-S sensor at the Sparrows Point desulphuriser included accuracy and repeatability, as well as significant time savings to the operation. As the sensor became part of the standard operating procedure, a cost saving from the decreased amount of reagent was also recognised.

Projects that maximise steelmaking productivity while preserving capital expenditures are key to reducing operating costs in today's volatile market. Several constraints limit the steelmaking operation at Mittal Steel USA Sparrows Point. These include the ability to utilise existing infrastructure within the shop, the availability of hot metal, and increased demand for hot metal desulphurisation. All these challenges needed to be addressed at Mittal Sparrows Point in order to maintain the current production goals. Several options were examined to maximise hot metal throughput, including implementation of a sensor-based sulphur determination system for desulphurisation process input and control.

At its inception, the BOF at Mittal Sparrows Point was designed with the capacity to desulphurise approximately 30% of the total heats. Changing blast furnace conditions and the consistency of raw materials worked to drive the incoming sulphur higher to the BOF. Market forces and the need to stretch hot metal pressed the BOF to lower its final sulphur targets.

The product mix has changed with market demand over the years, increasing the demand for D&I grades. The typical target hot metal sulphur of 0.01% S in the year 2000 hovered in the 0.006% S range. While this alone placed a heavy burden on the shop, the recent trend of sulphur from the blast furnace increased from an average 0.020% S to 0.030%. The BOF was affected by this, while the infrastructure within the shop remained essentially unchanged.

The combination of these factors directly affected the shop's performance by increasing the desulphurisation rate to about 90% of all heats. This change impacted the shop throughput by increasing the time required to process hot metal. Therefore, improvements in hot metal processing were required to maintain production goals.

These factors, coupled with a fixed infrastructure, required a creative process optimisation strategy. In order to accommodate the requirements driven by the changing market, a thorough analysis of BOF practices and procedures was conducted. It became clear that the most obvious bottleneck in the shop centred on the desulphurisation practice. It was common to have several ladles from the hot metal station sitting "on the bank" waiting to be desulphurised. This delay caused a significant disruption to the flow of metal to the BOF vessels.

Changing market forces and an evolving product mix placed an unexpected burden on the BOF to process hot metal in a more efficient manner. A BOF equipped only to desulphurise 30% of its total heats was now expected to desulphurise nearly 100% of its total hot metal. Mittal Sparrows Point met this challenge by improving the hot metal processing efficiency. Steps taken to increase the hot metal throughput included a proposed second desulphurisation station, a primary side desulphurisation screen, alternative methods of desulphurisation, enhancements to the existing skimming operation, and the implementation of a sulphur sensor.

The most significant and recognisable change in the desulphurisation practice was the implementation of the sulphur sensor. The sensor system acted as a catalyst, enabling many advantages over the traditional method. They are as follows:

- *A significant reduction in the final sulphur standard deviation was observed. This can largely be attributed to the accurate and timely nature of obtaining a sensor-based sulphur reading. The previous method required several labour-intensive steps that relied on analytical equipment that needed to be properly calibrated and maintained on a regular basis. The new sensor-based practice requires very little maintenance and recalibration.*
- *Total reagent usage was reduced primarily through changes made in the reagent shot charts based on the standardised sensor practice. Due to the non-linear nature of the charts, each family of curves had to be individually tuned.*
- *A significant time saving was one of the most obvious benefits from the sensor implementation. Obtaining a sulphur value in less than 1 minute versus the previous 10 minutes represented a significant reduction in process time. The bottleneck that was evident before desulphurisation shifted to post-desulphurisation.*
- *In an effort to stretch hot metal, double scrap charges were ordered in conjunction with increased coal usage. This, in turn, required a lower final hot metal sulphur target, which involved additional injection time and material to desulphurise. The new sensor practice gave the operator more confidence to shoot to the target final hot metal percentage S without the additional reagent "insurance policy" typically used in this practice.*
- *Additional improvements in the hot metal processing efficiency included more changes to the primary side coordination screen, skimming practice, and desulphurisation method. A silicon sensor practice that began in the first quarter of 2006 provides additional time savings and efficiencies to the shop.*

In total, all the changes, both proposed and those already implemented, have proved to effectively address the demand issues that faced Mittal Sparrows Point.

5.2 IMPACT OF NEW ONLINE HOT METAL SILICON AND SULPHUR SENSORS

The following is taken from a paper that discusses the impact of new online HM-Silicon and HM-Sulphur sensors on iron transfer operations, iron desulphurisation, and overall BOF shop productivity. It was written by:

Randall P. Stone, Sr. Product Manager, Heraeus Electro-Nite Co., Langhorne, PA, USA
Danny Habets, R & D Engineer, Heraeus Electro-Nite Intl., B-3530 Houthalen, Belgium
Rudi Maes, Product Application Manager, Heraeus Electro-Nite Intl., B-3530 Houthalen, Belgium
Peter J. Koros, Principal, Koros Associates, Inc., Pittsburgh, PA, USA

There are 2 new sensors available for online analysis of sulphur and silicon in hot metal. They operate in a manner similar to that of the immersion oxygen sensor and are in production use in several major steel plants. The silicon sensor provides timely silicon analyses in pre-treated iron. The sulphur sensor measures the full range of hot metal sulphur, both before and after desulphurisation.

These sensors have the potential to streamline hot metal transfer operations, replacing timeconsuming sampling and chemical analysis for these key elements. The silicon sensor allows for instantaneous online calculation of the charge balance of the BOF heat. Utilising the sulphur sensor prior to desulphurisation provides timely input into the desulphurisation calculation model. The same sensor can be used immediately after the desulphurisation injection treatment to obtain final sulphur content to confirm the accuracy of the treatment or to initiate corrective re-injection prior to slag skimming or raking. This paper presents the current state of hot metal processing, potential sensor-based scenarios for improved process control, and discussion of the resultant benefits in manpower reduction, process reliability, materials consumption, and savings in processing time.

Conclusions

- *Consistency and stability of sensors for determination of the silicon and sulphur contents of hot metal has been demonstrated in several BOF shops in the US, UK, and continental Europe.*

- *Speed and reliability of the pre-treatment sulphur value provided by the sensor allows adjustment of the "injection chart" to eliminate the typical "over treatment" that is built in (upwards of 10 to 20% depending on the target final %S) to minimise the chances of the need for a costly ladle re-injection. This adjustment results in a significant saving in desulphurisation reagent consumption, labour cost and cycle time: accurate tests can betaken immediately after secession of injection, and, if a desulphurisation re-injection blow is needed, it can be started prior to slag raking, reducing this process step to a single event (for conservation of yield, time, and temperature.)*

- *Gains in BOF shop production are made possible by the speed up in processing that results from the use of sensors as this leads to the reduction of the hot metal cycle time and its attendant losses in temperature. This results in increased scrap melting and reduced consumption of hot metal thereby to boost steel production from a given amount of hot metal.*

- *Replacement of traditional sampling and chemical analyses has resulted in major gains in operations as well as work force reduction, work simplification, and improvement in process control. It is now possible to have a totally sensor-based BOF process control solution: from hot metal transfer, desulphurisation through BOF blowing, and steel ladle filling.*

5.3 MEASURING METHODS FOR PROCESS CONTROL IN THE STEEL PLANT

The following is taken from a paper written by Norbert Bannenberg und Helmut Lachmund in "Metallurgical Techniques and Trends".

The modern steel plant uses diverse measuring methods. Whereas the development of process models has in recent years been the prime emphasis of most research activities, it is now vital, as a result of ever-increasing demands on the quality of steel, as a material, to guarantee rapid assessment of the quality of the product - online wherever possible - and, under ever more intensive cost pressure, to minimise auxiliary process times to the greatest extent possible and thus to enhance the steel plant's productivity.

Today's steel technology is designed to minimise the consumption times of the various ancillary aggregates. This leads to improved performance and economies of scale in the steel mill process. Fast analysis and temperature measurements are necessary. Moreover, the mill process must drive reproducibility in terms of quality. This requires procedures that enable a quick quality judgement of intermediate and final product. The following are examples of some innovative methods used in steelworks, which meet the twin demands of reducing downtime and making a rapid judgement of quality.

The determination of dissolved oxygen by means of EMF measurement in steel mill technology has been going on for about 20 years. Heraeus Electro-Nite has built on this knowledge and developed a measurement method analogous to the determination of oxygen that permits a sulphur determination. The innovative sensor can measure sulphur content in cast iron before and after hot metal desulphurisation.

Results verify that in principle the determination of sulphur in cast iron using an EMF measurement is possible. As determined by 2 methods, sulphur has a spread before pig iron (1σ) of ± 87ppm and after pig iron of ± 42ppm. These variations are not exact enough to predict the target sulphur content after hot metal desulphurisation. Further development is needed to ensure the accuracy and reproducibility of sulphur determination in pig iron using EMF measurements.

The required variances before the hot metal desulphurisation of ± 30ppm and after hot metal desulphurisation of ± 15ppm must be reached. With the help of such a rapid determination of sulphur content in the pig iron, the actual period of time the pig iron can be treated is increased and the need for chemical analysis is eliminated. The hot metal desulphurisation process is optimised by a more efficient inblow rate.

5.4 IMMERSION SENSORS MEASURE SULPHUR ONLINE IN HOT METAL DESULPHURISATION

The following is taken from a paper written by:

Robert Hall, Sales Manager and Stephen Pagden, Project Leader
Heraeus Electro-Nite (UK) Ltd, 655 Sheffield Road, Chesterfield, UK S41 9ED

And reviewed by the quality and manufacturing managers of an integrated steel works referred to here as plant x.

Plant x manufactures an extensive range of cast and rolled products; produced from the work's casters feeding downstream markets as diverse as rod and wire, rail, plate, sections, bar, and narrow strip. A large proportion of the grades produced impose maximum sulphur specifications, although the plant also produces re-sulphurised free machining grade steels. Production is around 4 million tonnes per annum.

Plant x has long recognised that an online measurement of sulphur could improve the efficiency and reduce the cost of its hot metal desulphurisation process.

Desulphurisation takes place in the transfer ladle after pouring from the torpedo. The practice is based upon the deep injection of set amounts of Mg-based product into the ladle dependent upon the incoming sulphur level as determined from analysis of samples taken at the blast furnace and the target steel sulphur.

Plant experience with the sensor confirmed some of the predicted performance targets made by the manufacturer. Plant-specific empirical relationships between laboratory sample and the sensor were established and programmed for sulphur, but operationally successful carbon and silicon correlations were not obtained.

The positive initial results obtained for the sulphur prediction and the uptake of the sensor by the operators, led to an extended trial and the rapid assimilation of the HM-S sensor into use as the process control tool for the interrupted blow practice.
Introduction and establishment of the interrupted blow practice enabled its impact upon process costs to be assessed.

The following table presents cost savings data from the initial 3-month monitoring period calculated from "under treated" heats. These are heats where the reagent addition was less than the predicted demand weight, and result from the introduction of the sensor measurement and interrupted blow practice. By definition, the previous standard practice

relied upon blowing until at least the demand weight had been added, so the savings shown are effectively savings compared to the old practice.

Trial period	Under addition kg Mg reagent per day compared to prediction	Approximate saving (annualised)
New practice (3 months data mid 2003)	200	£98 000

Ongoing assessment of the process for 2004 indicated that on average operators found it acceptable to stop the process 30kg of reagent earlier than the prediction required.

The savings generated by the 30kg actual reduction in reagent usage and by projected reductions of 10kg and 20kg on the ladles treated in the first 5 months of 2004 are shown in the following table. From this data an annual projection was made. Savings in the range of £120 000 to £360 000 per annum were projected, substantially greater than suggested by the earlier findings presented in the previous table. The promise of the initial trials has been borne out in practice, and quantifiable savings in material usage were generated.

Treatment period and ladles		10kg usage reduction		20kg usage reduction		30kg usage reduction	
2004	Total ladles treated	Mg saving kg	Saving £	Mg saving kg	Saving £	Mg saving kg	Saving £
Jan	785	7852	10051	15705	20102	23557	30153
Feb	707	7066	9045	14132	18089	21198	27134
Mar	1005	10054	12869	20108	25739	30163	38608
Apr	743	7431	9512	14863	19024	22294	28536
May	723	7231	9256	14463	18512	21694	27768
5 month total	3964	39600	50700	79300	101500	118900	152200
12 month projected savings		**95000**	**121700**	**190300**	**243600**	**285400**	**365300**

In November 2003, post-skim sampling finally stopped. The cost of operating the HM-S sensor was approximately equal to that of the cost of sampling plus laboratory analysis, thus the new practice incurred virtually no net cost compared to the previous sampling regime. This enabled realisation of the time saving generated, estimated at about 4 minutes per treatment, as a result of being able to take a sensor measurement pre-skimming, and therefore not needing to wait for laboratory analysis.

A typical treatment time is around 30 minutes, thus a 4-minute saving represents a 15% saving in time, and consequent real "no cost" increase in desulphurisation capacity. Plant x was scheduled to increase output from 3.8mtpa to 4.5mtpa during 2006, a ~20% increase in output, so this boost to plant capacity was timely.

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