On-line Sulphur Immersion Sensor Improves Hot Metal Desulphurization Process

Steve Cook, Quality Manager
John Nicholson, Manufacturing Manager
Scunthorpe Works
Corus Construction & Industrial
PO Box 1, Brigg Road, Scunthorpe
North Lincolnshire UK DN16 1BP
Tel. +44 (0)1724 404040
Fax9 +44 (001724 405564
(Steve.cook@corusgroup.com)

Robert Hall, Sales Manager
Stephen Pagden, Project Leader
Heraeus Electro-Nite (UK) Ltd
655 Sheffield Road
Chesterfield, UK S41 9ED
Tel +44 (0)1246 454849
Fax +44 (0)1246 453898
(rhall@electro-nite.co.uk)

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INTRODUCTION

Scunthorpe Cast Products (SCP), part of the Corus Group in the UK, manufactures an extensive range of cast and rolled products; produced from the work's 4 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-sulphurized free machining grade steels. Current production is around 3.8 million tonnes per annum.

Iron is produced by three operational blast furnaces, with a fourth due to be reintroduced during 2006 in line with enhanced secondary steelmaking capacity, to allow a planned increase in output to 4.5 million tonnes per year.

Scunthorpe have long recognized that an on-line measurement of sulphur could improve the efficiency and reduce the cost of its Hot Metal Desulphurization process.

Desulphurization at 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 dependant upon the incoming sulphur level as determined from analysis of samples taken at the blast furnace and the aim steel sulphur.

A leading sensor manufacturer, Heraeus Electro-Nite, have recently developed a new immersion sensor based upon standard oxygen sensor technology for the measurement of hot metal sulphur (HM-S sensor), which effectively provides the on line measurement desired by Scunthorpe. This paper presents the initial experience with this new technique, moving through to regular use of the HM-S sensor since November 2003 and its cascade to the sister plant at Teesside.

THE HOT METAL DESULPHURISATION PLANT AT SCUNTHORPE

Hot metal desulphurization equipment at the BOS Plant was first commissioned in 1973, utilizing a torpedo injection system, progressing to the installation of a Polysius ladle injection system in 1979. Initially, this was used to inject calcium carbide/diamide lime mixes but was converted to inject magnesium in the early 1980's. In 1989, the present Simon-Macawber magnesium ladle injection system was installed.

Torpedo ladles arrive by rail from the blast furnaces, carrying up to 250 tonnes of hot metal (HM). The HM is poured into a transfer ladle whilst simultaneously adding a soda ash reagent. This serves to flux the slag as well as possessing limited desulphurization capacity in itself. Ladles are transported via overhead crane to the desulphurization plant.

The schematic in fig 1 shows the location of the desulphurization plant in relation to the rest of the primary steelmaking operations.
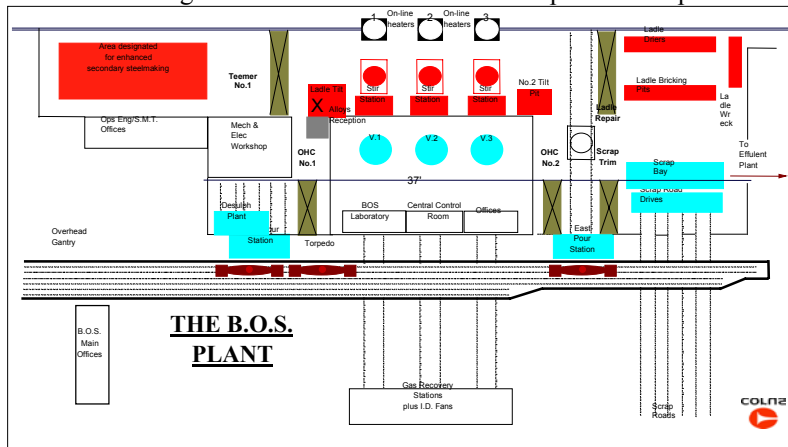

Fig 1 BOS plant layout, Scunthorpe Works

The desulphurization plant comprises two identical stations, each with two dispensers. One dispenser is filled with an inert pre-injection material, and the other is filled with the more expensive magnesium reagent.

Both dispensers have screw feeders to give precise control over the material flow rate. The gas pressure either side of the screw is equal so that pressure cannot influence the material flow rate. The carrier gas is nitrogen.

Maximum desulphurizing efficiency from the magnesium is only achieved when it is injected deep into the hot metal. It is for this reason that the inert material is used at the start of a treatment while the carrier gas reaches its normal working pressure and flow, and while the lance is entering the hot metal. Once the lance is at its deepest within the ladle (about ½ metre from the ladle bottom), injection of inert material is replaced by magnesium reagent.

Magnesium continues to be injected until the demand weight is reached, at which stage the magnesium feed stops and the lance automatically withdraws.

The carrier gas remains on for up to 10 minutes after withdrawal from the hot metal to cool the lance and extend its life.

Optimum magnesium injection rate is approximately 10kgs per minute to avoid problems of excessive reaction at high feed rate, which reduces efficiency and lance life; and the converse problem of excessive hot metal temperature drop and reduced tonnage throughput at lower feed rates.

Magnesium efficiency is inevitably less than 100%, and may be defined as:-

$$\frac{\text{'theoretical' amount of Mg required to remove x \%S}}{\text{'actual' amount of Mg required to remove x \%S}}$$

It is affected by:

- The residual magnesium left in solution

- The amount used to deoxidise rather than desulphurize the hot metal

- The amount lost as vapour in the carrier gas

- The starting level of sulphur, a higher starting sulphur content favours a higher efficiency.

- The amount of magnesium reagent added depends on the start sulphur (ie, the post pour sulphur), and also on the required final sulphur (ie, charge sulphur). The computer prediction must also take account of scrap type and weight and typical skim efficiency.

It is well known that the desulphurization process is ultimately affected by the ability to remove slag during skimming. Skimming is achieved by a mechanical rabbler.

Typical analyses pre and post desulphurization are given in table I:

	%C	%Si	%Mn	%P	%S	Temperature
Pre-Desulphurization	4.55	0.55	0.44	0.091	0.028	1357
Post-Desulphurization	4.54	0.54	0.44	0.091	0.013*	1324
* Sulphur range Post Desulphurization is 0.002-0.015%S						
Pour Weight is typically 282 tonnes and 60%-70% of ladles are treated dependant upon grade mix						

Table I: Input and output Hot Metal parameters at Scunthorpe

Over £5 million per year is spent on iron desulphurisation, £4 million of which is reagent costs, 80% of which can be attributed to magnesium. Therefore, it is essential that the process is operated at maximum efficiency, with minimum wastage.

The average treatment cost build up per ladle is shown in table II.

Parameter	Proportion of Cost
Soda ash	13%
Magnesium reagent	60%
Inert injectant	1%
Operating costs	26%

Table II: Desulphurisation process cost breakdown at Scunthorpe

It is clear from an analysis of the cost breakdown that the key drivers in any process improvement initiative would be reduction in magnesium usage and also reduction in operating costs. Additional operational benefits may be obtained should the process timing improve.

The current method of process monitoring had been by solid sample optical emission analysis or combustion Leco analysis with samples sent by Lamson tube to the BOS laboratory. The location of the laboratory in relation to the desulphurization plant can be seen in figure 1. A typical wait analysis time is around 4 minutes, but the complete sampling process turn round time is closer to 10 minutes.

Scunthorpe have identified two key issues arising from this analysis wait time:

- There is a tendency for operators to "overblow" the desulphurization process to ensure that the hot metal achieves specification, resulting in waste of material and time.

- The wait time increases the potential for causing a bottleneck at vessel charging, as the charge balance is not known until the hot metal analysis is known. The planned production output increases at Scunthorpe will increase the pressure on desulphurization treatment time.

It is for these reasons that it was decided to investigate the potential offered by the HM-S sensor system to provide an on-line measurement. Some results and experience with the new system are presented later in this paper.

SENSOR DESIGN AND BACKGROUND

The HM-S sensor is a development of the existing Celox single immersion oxygen activity sensor. Its principle design features are shown in fig 2.
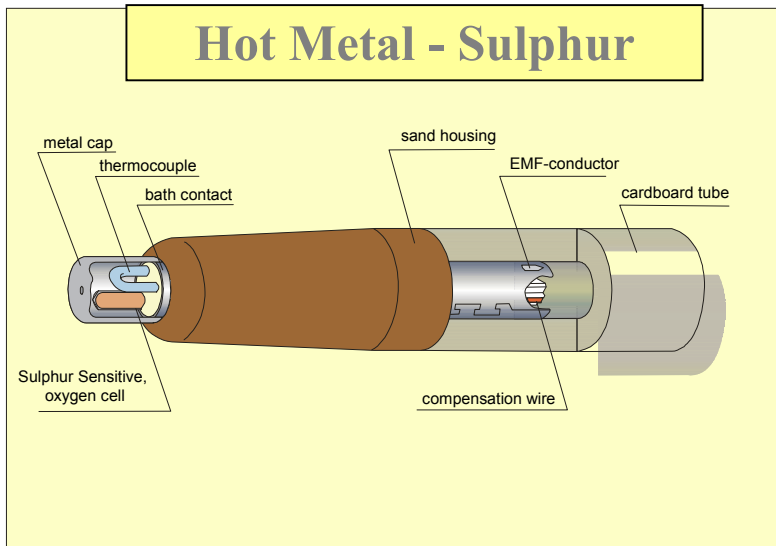
Fig 2: Schematic cutaway of the HM-S sensor

Dimensional standardisation mean that the sensor immersion system is compatible with standard immersion thermocouples and combined 2in1 sample and thermocouple sensors, and the dedicated instrumentation system will work with each.

The sensor delivers thermocouple and cell emf signals, and from these the instrument can predict temperature, sulphur, silicon and carbon. Results are generated within 15 seconds, making it a true on line measurement.

It is the modification to the electro chemical cell which is the key to obtaining a sulphur measurement. A special coating on the zirconia electrochemical cell sets up a partition between oxygen and sulphur at the coating surface on immersion into hot metal, resulting in a potential difference between the bath and the cell reference which is a function of the sulphur content. Successful measurement depends upon the properties of the coating.

A brief qualitative review of the measurement thermodynamics is presented in the Appendix to demonstrate how the sensor responds to variation in hot metal sulphur content. A direct measurement of sulphur is not possible, so that practical formulae have to be derived from empirical relationships rather than by application of thermodynamic principles..

A successful formulation for a practical formula is shown in eq. 1. It can be seen that the sulphur prediction is a function of the temperature T and the cell emf output E. Derivation of plant specific formulae requires the calculation of modified coefficients.

$$Log([Sppm]) = 6.51136 + (0.000445*T) = (0.010029*E) + 2.91*10^{-6} *E^2 \qquad \text{(Eq.1)}$$

Experience during development of the sensor[2] suggested that the sensor was sensitive within the range of sulphur 5-1000 ppm (0.0005% - 0.1%), and experience suggested repeatability levels where 1 Std.Dev would be better than 10% of the actual S value. For example, if the sulphur level is 0.003% , then the expected standard deviation of repeat measurements would be 0.0003%.

This is shown in fig 3 for a range repeat measurements at different sulphur levels.
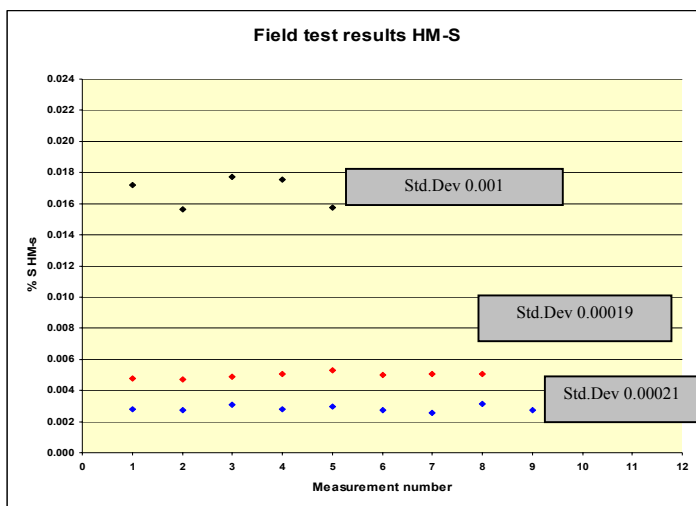
Fig 3: repeatability measurements at different hot metal Sulphur levels

An unexpected finding from early trial work was a correlation between cell output and hot metal silicon and carbon. If this benefit could be realized, then the new sensor would indeed become a powerful tool for providing on-line data for the BOS charge balance model. Subsequent experience has shown that the relationship between S, Si, and C depend upon individual blast furnace operation and subsequent hot metal treatment practice, and may not be applicable where hot metal is sourced from multiple blast furnaces, and where a pre-treatment is performed, such as at Scunthorpe. It has proved possible to use the correlation to predict hot metal silicon at Scunthorpe's sister plant at Teesside, as shown in fig 6. Teesside is fed by a single 12m hearth blast furnace and does not pre-treat the hot metal.

Correlations between sample and sensor prediction for S, Si and C are are shown in figs 5-7 in the section on "Measurement Results and Cost savings".

Due to differences in blast furnace operation and desulphurization practice and sampling technique, plant specific empirically derived equations are usually required.

OPERATIONAL EXPERIENCE AND PRACTICE DEVELOPMENT

The expected performance of the sensor, and familiarity with the capability of oxygen sensors in the steel plant was sufficient for Scunthorpe to justify plant trials, with expectations of achieving the benefits shown in table III

Anticipated Benefit	Result
Elimination of the Laboratory sample	Achieved November 2003
Reduction in reagent usage	Average 30kg reduction per ladle
In process S measurement	Yes, via interrupted blow practice
Si and C prediction for BOS charge balance model	No, soda ash pre-treatment weakened the expected S, Si, C ex blast furnace correlation
Increase in throughput through the hot metal station	An average time saving of 4 minutes per treatment has been realised

Table III: Summary of anticipated benefits and results achieved

Following a preliminary demonstration trial conducted by the sensor manufacturer under Corus supervision, extensive plant proving trials with the new sensor were begun at Scunthorpe. The plant measurement systems on both injection stations were upgraded and a dedicated instrumentation system was installed for measurement interpretation and display. The instrument provides a traffic light sequence to guide the operator through the measurement sequence and output analysis data directly to the plant level process control computer

Plant operators at Scunthorpe were already familiar with the use of immersion sensors and the typical "traffic light" measurement sequence, so no special re-training in the use of the sensor was needed, though application experience has been built into operational practice. Recommended operational procedures are listed in table VIII.

Plant re-configuration proved to be reasonably straightforward, and involved changing the 2-wire thermocouple holder and wiring system to a 4-wire system required for the thermocouple and cell of the HM-S sensor , integrating the instrument "traffic light" system with the existing immersion lance drive control systems, and generating a measurement result input into the plant Vax computer systems.

Plant personnel were trained in the use of the new sensor by the manufacturer, whose personnel also assisted in the trial monitoring.

The treatment sequence in operation is shown schematically in fig 4. The standard measurement practice in place had been to use the analysis of a "2in1" sample taken at the Iron Pour Station as the basis for reagent quantity prediction at the desulphurization station. The ladle would normally be blown according to the treatment model and the judgement of the operator based upon the predicted demand. The ladle requires skimming prior to taking the post desulphurization 2in1sample to confirm the sulphur content; as it has not proved possible to rely on the analysis of samples taken pre-skim, due to the variability of analysis caused by sulphur pick up from the slag. Therefore time would be wasted if a re-treatment and re-skim were required. The ladle is held until the laboratory analysis is confirmed.

It can be envisaged that the safest course of action for an operator would be to "overblow" the ladle to ensure that sulphur specification was achieved in one treatment, as this approach better achieves the priority of maintaining caster sequences, and gives better Mg efficiency than reblowing.

The HM-S practice was initially based upon a similar regime, with a pre treatment and post treatment measurement, but with the post treatment measurement being taken pre skim. During the initial trial period the standard sampling practice was maintained to build a comparative database .
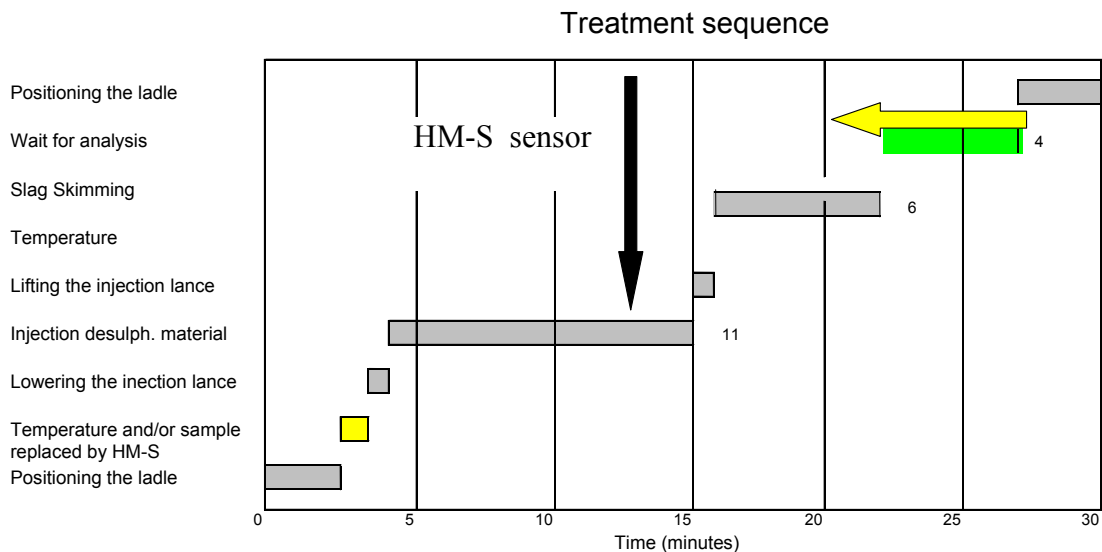


Fig 4: Schematic process flow chart

Once plant specific empirical equations had been established and operators had gained confidence in the reliability of the HM-S system, an "interrupted blow" practice was adopted with a measurement taken close to the expected end of treatment. Based on the result, the treatment is completed with the demand Mg trimming addition based upon the Vax computer prediction if required. The measurement taken as part of the interrupted blow practice is indicated in fig 4 by the vertical arrow which bisects the injection time period at about 80% of the predicted demand. The time saving resulting from elimination of the sample wait period is indicated by the horizontal arrow.

This new practice, enabled by the ability to obtain accurate sulphur predictions prior to skimming, immediately enabled the process to be operate with a tendency to under treat compared to demand, which has proved the key to the successful ongoing reagent savings obtained.

Initially the in process treatment measurement was taken dynamically during the latter stages of the blow, however, despite some encouraging results in early trials, this practice was abandoned as reliability was low compared to the "interrupted blow" practice, due to poor traces, measurement failures and inconsistent results.

MEASUREMENT RESULTS AND COST SAVINGS

Plant experience with the sensor confirmed some of the predicted performance claims 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 empirical relationship derived for sulphur at Scunthorpe, and the sample-sensor correlation obtained is shown in fig 5.
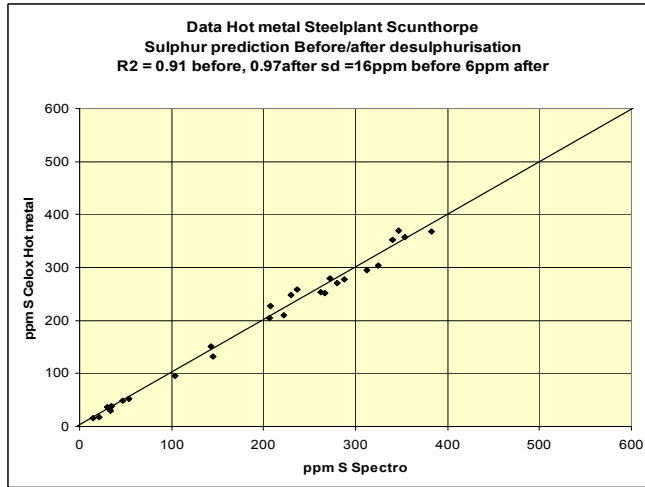
$$\text{Sulphur (\%)}=10\text{^}(41.979 +(0.000504*T) = (0.11607*E) + 8.131*10^{-5} *E^{2})$$
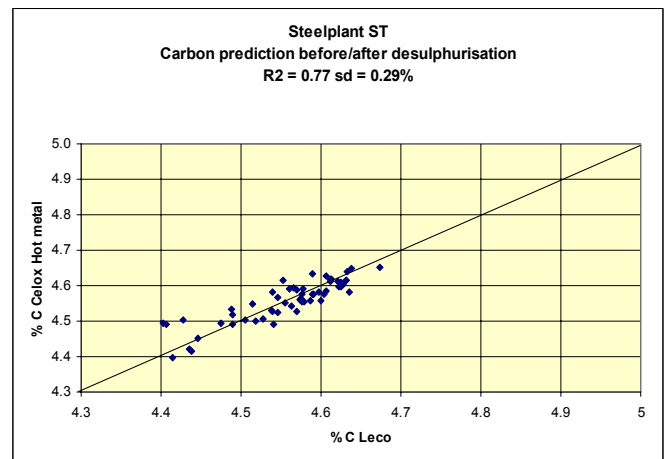
Fig 5: Sensor-lab correlation for sulphur at Scunthorpe following derivation of a prediction equation

Typical correlations and empirical relationships for Si and C are shown in figs 6 and 7. Figure 6 shows the correlation for Si obtained at CC&I's Teesside plant where Si measurements are taken pre-treatment. It can be seen by comparison that the Si equation contains similar terms to the S equation, and that the C prediction is derived from the Si and temperature.
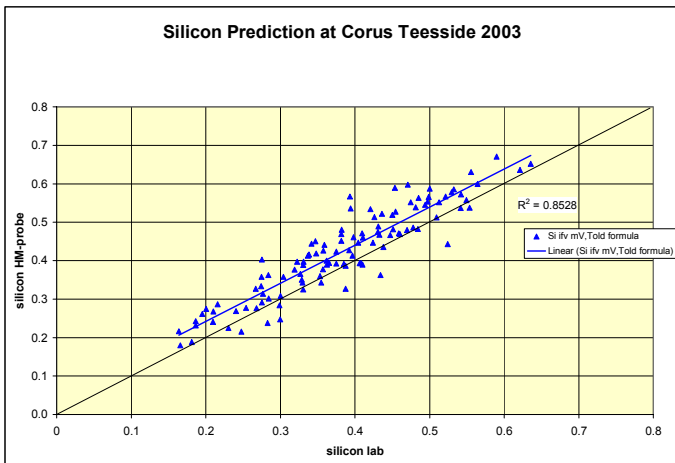
$$\text{Si \%} =10\text{^}(24.293-(0.000832*T) +(0.0915*E) + (8.78*10^{-5}*E^{2})$$

Fig 6: Sensor-lab correlation for silicon at Teesside

$$\text{C \%} =10\text{^}(1.887+ (0.00215*T) –(0.2094*Si)$$

Fig 7: Typical Sensor-lab correlation for carbon

At Scunthorpe, the hot metal is pre-treated with soda ash on pouring from the torpedo prior to sending to the treatment station. The desulphurizing effect of the soda ash reagent proved sufficient to disrupt the expected blast furnace S, Si, and C correlations and thus render Si and C predictions unreliable.

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. The new practice continues in use during 2004 to date.

Introduction and establishment of the interrupted blow practice enabled its impact upon process costs to be assessed.

Table IV 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 Vax prediction	Approximate saving (annualized)
New practice (3 months data mid 2003)	200	£98000

Table IV: Average daily reagent saving resulting from under treatment via the interrupted blow practice[3]

Ongoing assessment of the process for 2004[4] indicates that on average operators are finding it acceptable to stop the process 30kg of reagent earlier than the Vax prediction requires.

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

Treatment period and ladles		10 kg usage reduction		20 kg usage reduction		30 kg 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**

Table V: Savings projections based upon 2004 treatment data[4]

In November 2003, post skim sampling finally stopped. The cost of operating the HM-S sensor is approximately equal to that of the cost of sampling plus laboratory analysis, thus the new practice incurs virtually no net cost compared to the previous sampling regime. This enabled realization of the time saving generated, estimated as 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.

The process histogram on fig 4 suggests a typical treatment time of around 30 minutes, thus a 4 minute saving represents a 15% saving in time, and consequent real "no cost" increase in desulphurization capacity. CC&I Scunthorpe is scheduled to increase output from 3.8mtpa to 4.5 mtpa during 2006, a ~20% increase in output, so this boost to plant capacity is timely..

FUTURE DEVELOPMENTS

An improved regression equation and process model are being built to predict more accurately the Mg quantity to hit the desired sulphur aim without the need for reblows.

The current Vax desulphurization reagent addition model has not been updated to take account of the improved precision in achieving specification offered by the HM-S sensor, so the current rules are currently based on the capability of the process to achieve specification. The current process capability results in process aim sulphur levels being far lower than required by grade, simply to ensure a "right first time" ladle in specification and on time ready for charging.

The potential advantage of basing the new model on the sensor capability is shown in table VI. A set of rules is proposed for the sulphur grades covered by the current 0.002% S process aim grade. The projected material savings are quantified.

S Max	3*Std Celox	Current Process Sulphur Aim	Proposed Sulphur Aim (S Max- 3*Std Celox)	Difference	Potential Mg Savings kg	Value of Savings £
0.003	0.0009	0.002	0.002	0.000	0	0
0.005	0.0015	0.002	0.004	0.002	60	77
0.008	0.0024	0.002	0.006	0.004	105	134
0.01	0.0030	0.002	0.007	0.005	110	141

Table VI: Proposal for revised process aim rules based upon sensor rather than process reproducibility

The average charge sulphur level resulting from this practice will be higher than historical averages, so other factors which affect final tap sulphur, such as skimming efficiency , variable sulphur levels in the scrap charge and retained vessel slag, must be taken into consideration. Thus the chance of breaking the tap aim S becomes more significant as the treatment aim is increased.

Further developments which will impact upon the Desulphurization plant are as follows:

Consideration is being given to introducing an improved slag skimming practice. This will use a porous plug to agitate the surface layers followed by application of a slag coagulant into the slag free "eye", thus enhancing slag removal.

The use of soda ash reagent at the pour station will be curtailed for environmental and engineering reasons.

Initial trials with an electro-chemical Silicon probe post desulphurization have been undertaken. Further trials are planned.

APPLICATION NOTES

Measurement Range	Temperature: 1100-1400 degrees C S: 5-1000ppm, 0.0005%-0.1%.
Immersion Time	approximately 15s
Immersion Conditions	- Agitate or treat the slag to break up or flux any crusting. - Measurement during treatment is best avoided* - Fix the probes securely on the probe holder - Immerse quickly through the slag about 30-40cm into the metal. - Immerse about 30 to 40 cm away from the ladle lining
System Maintenance and Housekeeping for optimal performance	- Keep probes dry and avoid rough handling - Regularly inspect lances and cables to ensure they remain dry and in good condition
* Trials of a "dynamic" in treatment measurement were carried out at Corus Scunthorpe, but this practice was abandoned due to low measurement success rate.	

Table VII: Recommended operating parameters[5]

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APPENDIX

The HM-S sensor does not measure sulphur directly, rather it measures an oxygen potential which is related to the sulphur level through the properties of the special coating on the cell. Successful measurement depends upon the stability and reproducibility of this coating as much as on the cell itself. Practical formulae have to be derived from empirical relationships rather than true thermodynamic principle.

The cell emf measurement may be represented by the Nernst equation[1]

$$E = RT/4F * \ln((pO_2)meas/(pO_2)ref) \tag{Eq.A1}$$

This equation implies that at constant temperature T the cell emf E will vary with the oxygen content of the system being measured. Provided that the thermodynamic characteristics of the internal reference material and the cell material are reproducible, and the sensor is measuring in a dilute solution of oxygen then it is possible to base the oxygen content of a system as a simplified empirically derived function of cell emf and temperature rather than as a function based upon thermodynamic data.

$$\ln[O]\ meas = f(E,T) \tag{Eq.A2}$$

In the HM-S sensor, the cell emf is a measure the local oxygen content, but this is controlled by the partition with sulphur generated at the coating. The partition of sulphur and oxygen between the coating and the hot metal may be represented by the same equilibrium which governs a slag-metal desulphurization reaction. This can be represented by a partition between solute in the melt [x] and anion in the coating (x^{y-}).

$$[S] + (O^{2-}) = (S^{2-}) + [O] \tag{Eq.A3}$$

The equilibrium constant for the partition may be written as in Eq.A4, with the equilibrium constant k determined largely by the cation composition of the coating:

$$k = \frac{(S^{2-}) * [O]}{(O^{2-})*[S]} \tag{Eq.A4}$$

Re-arranging in terms of [S]:

$$[S] = \frac{(S^{2-})}{k * (O^{2-})} * [O] \tag{Eq.A5}$$

Taking logs

$$\text{Ln}([S]) = \ln(k) + \ln ((S^{2-})/(O^{2-})) + \ln ([O]) \tag{Eq.A6}$$

$\ln(k)$ in Eq.A6 can be shown to be a function of T, $f(T)$, related to the cation content of the coating,

and from Eq.2 $\ln([O])\ meas = f(E,T)$, so the relationship could be reduced to an empirical formulation:

$$\text{Ln}([S]) = \ln ((S^{2-})/(O^{2-})) + f(E,T) \tag{Eq.A7}$$

In order to achieve a reproducible response of the cell to a changing sulphur level, it is implied that:

- The equilibrium constant k and hence $\ln(k)$ for the partition is a stable function, which implies that the cell coating must possess reproducible thermodynamic characteristics across the measurement range and within different treatment systems (Ca based, Mg based, Na based).

- That the anion compositions within the coating reach equilibrium so that the term $\ln((S^{2-})/(O^{2-}))$ in Eq.7 varies reliably with changing levels of sulphur and effectively disappears.

If these are achieved, then it is reasonable to write an equation (eq. A8) which says no more than the cell responds to a change in sulphur level and temperature, and to derive the relationship between these empirically rather than from rigourous thermodynamic principles.

$$Ln([S]) = + f(E,T) \qquad (Eq.A8)$$

A typical empirical relationship will be similar to that shown in Eq. A9:

$$Log([Sppm]) = 6.51136 + (0.000445*T) = (0.010029*E) + 2.91*10^{-6} *E^2 \qquad (Eq.A9)$$