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THE APPLICATION OF ON-LINE GAS ANALYSIS BY MASS SPECTROMETRY TO SECONDARY STEEL MAKING [1]

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Abstract

This paper describes how fast on-line gas analysis by Process Mass Spectrometry is used in secondary steel production for better process control and end-point determination to reduce costs and product variability and to expedite process-turnaround. Process Mass Spectrometry is a very powerful analytical technique, providing very accurate and rapid multi-component analysis. Modern instruments are compact, low maintenance and very reliable even in the relatively harsh environment near a steel making furnace. Mass Spectrometry has been successfully applied to Argon Oxygen Decarburization (AOD), Vacuum Oxygen Decarburization (VOD) and Ruhrstahl-Hausen (RH) furnaces. In the AOD process, gas analysis is utilized to control the argon/nitrogen/oxygen mixtures used to decarburize the steel whilst minimising the undesirable oxidation of chromium. Measurements of evolved CO and CO_2 are used to determine the process end-point. In RH and VOD the process occurs under vacuum and mass spectrometry is easily adapted to these conditions as it is itself a vacuum technique. Decarburization end-point is more accurately determined. Mass spectrometry can measure all components in the off-gas: H_2, CO, N_2, O_2, Ar and CO_2. Additionally it can be used to monitor a tracer gas such as helium for calculating the extent of decarburization. As well as describing the benefits of using on-line gas analysis by Process Mass Spectrometry, this paper also describes the principles of the technique and discusses some of the installation considerations, such as gas sample conditioning, calibration requirements and data communications.

Key words: Mass spectrometer; Process optimization.

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1 INTRODUCTION: PROCESS MASS SPECTROMETER

A process mass spectrometer is dedicated to continuous on-line gas analysis measurements with minimal user intervention. These instruments are very rugged and reliable,[1,2] requiring only minimal maintenance and breakdowns are extremely rare. There are many processes in the iron and steel industry where analysis of evolved gases provides a means of monitoring and controlling the process. A process mass spectrometer measures multiple components very rapidly and precisely (normally measures all the constituents of a gas sample) and can be used on multiple sample gas streams, which it measures in sequence. The data are directly communicated with a control system. An example of a process mass spectrometer is shown in Figure 1.

Figure 1: Thermo Fisher scientific prima PRO mass spectrometers.

Figure 2 shows the six main parts to a mass spectrometer. The first is the sample selector to automatically introduce the different sample gas streams into the instrument. This is followed by a pressure reduction inlet because the mass spectrometer operates under vacuum. The ionization chamber converts the sample molecules into ions which are positively charged molecules or parts of molecules. These ions are then separated according to their mass by the mass filter by the action of electric and/or magnetic fields. The different mass ions are then quantified by the detector in accordance with the abundance of the signals at these masses. The vacuum system is an essential element of the instrument for ensuring that the ions in the instrument behave in a predictable way independently of the presence of other molecules, i.e. to avoid ion-molecule interactions.

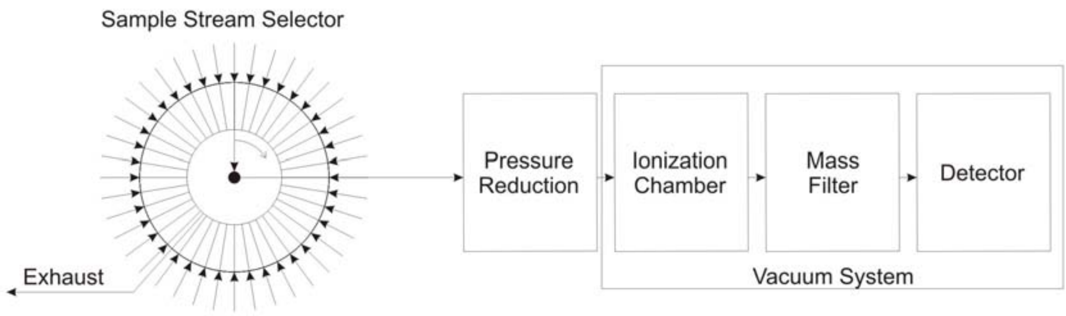

Figure 2: Components of a gas analysis mass spectrometer.

The multi-stream sampler like the rapid multi-stream sampler (RMS) shown in Figure 3 is used to collect the gas samples from multiple lines (systems can be supplied with up to 64 sample ports). Typically a few seconds is required for the analysis of each sample point. Each line connects to a different port and the gas samples flow continuously and internal volumes are kept to a minimum to maximise speed of response. At any one time only one sample is allowed to flow to the analyzer, while the other streams are still flowing through the sampler but to the exhaust in order to maintain good response. The sample is selected according to the position of the rotating arm, which causes the selected sample to be diverted into the analyzer. The position of the selector arm is controlled by a stepper motor and an optical sensor. This sampler can be heated up to 120 deg C. This particular device, the RMS was developed and patented by Thermo Fisher Scientific nearly 20 years ago and has proven to be extremely reliable with virtually no maintenance required.

Figure 3: Rapid Multi-Stream Sampler (RMS).

The main type of ion source used in process mass spectrometry is the electron impact ion source, where a thermionic filament is heated to over 1000 deg C and gives off electrons which are accelerated and then used to collide with the sample molecules, such that the molecules are caused to lose an electron and fragment to produce molecular ions and fragment ions. These ions are themselves accelerated

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before being introduced into the next stage of the mass spectrometer, the mass analyzer.
Figure 4 shows the spectrum of the ions used to monitor the main gas constituents of an example gas mixture of H_2, CO, N_2, O_2, Ar and CO_2.

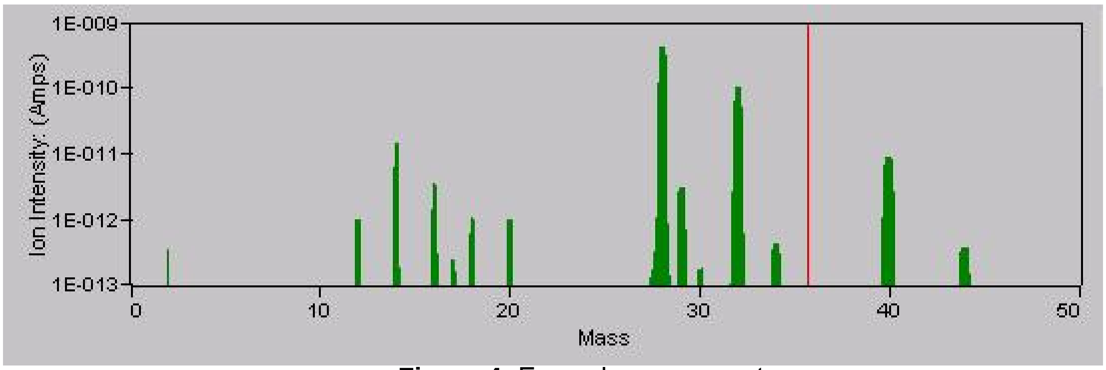

Figure 4: Example mass spectrum.

In practice the process mass spectrometer switches the magnetic field to the theoretical peak centers of certain peaks and then measures the ion current collected at the detector. The ion currents are normally within the range of nano- (10^{-9}) to femto- (10^{-15}) amp range, which provides 6 decades of measurement range.
The actual quantification is very simple: the peak height or measured ion current is directly proportional to the concentration. The instrument is calibrated using gas mixtures containing accurately known concentrations. These are normally gravimetric mixtures, i.e. mixtures prepared by weighing the different added gases into a mixture. One of the great strengths of mass spectrometry is that the sensitivities to different components do not vary very greatly – the difference between the most sensitive and least sensitive gas is approximately an order of magnitude. Mass spectrometry responds to almost any gas component. Some gases interfere with each other in that they produce ions at the same mass as other components. This is dealt with automatically by the calibration, however; this explains the need for more than a single calibration gas mixture since some fragment ratios need to be measured in isolation.
An example of the peaks used for analysis are shown in Table 1.

Table 1: Mass ion peaks corresponding to various gases

Mass	Gas responsible for signal at this mass	Description of positive ion producing this signal
2	H_2	H_2^+
12	$CO + CO_2$	$^{12}C^+$
14	N_2	$^{14}N^+$
32	O_2	$^{16}O_2^+$
40	Ar	$^{40}Ar^+$
44	CO_2	$^{12}C^{16}O_2^+$

It can be seen that most of the mass peaks are unique to one gas. The only exception is mass 12, which results from the C^+ ion which arises from the ionisation of both CO and CO_2. During calibration (which measures the magnitude of the peak height for a known concentration of gas) pure CO_2 is used for determining the ratio of the mass 12 peak to the mass 44 peak, so it is a simple correction to subtract the CO_2 contribution to mass 12.

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An important part of a process mass spectrometer is the software that controls the measurements of the instrument and needs to have the flexibility to fully utilize the analytical power of the analyzer. It is normally a two-computer system with an on-board stand-alone industrial computer that actually controls the instrument and communicates with other devices. The second is the user interface PC for data display, storage, configuration, diagnostics and tuning.

The main justifications for investing in a process mass spectrometer are the following:

- Analysis response time is very fast (as fast as 1 second for analysis of 6 components).
- It is multi-component – all components of interest are measured on a single instrument.
- It is multi-stream – multiple sample gases are measured on the same instrument
- The high analytical performance in terms of sensitivity, precision, stability and linearity.
- There is a definite cost benefit in incorporating composition gas analysis or derived data into the plant control strategy.

2 APPLICATIONS

2.1 Basic Oxygen Converter

In a steel plant the basic processes for conversion of iron (from the blast furnace) and scrap into steel are removal of sulphur and reduction in the carbon content to the required level.

In the basic oxygen steel making process (often referred to as BOS, BOF or LD) the carbon content is typically reduced from 4% to 0.05%. In this process high purity oxygen is blown through molten hot metal via a lance at super sonic speed, in a process that lasts only about 30 minutes. The oxygen reacts with carbon to produce CO and CO_2; analysis of these gases is used to control operation of the lance to improve process efficiency and also to detect the process end point. The process end-point is determined by calculating the carbon content based on measurement of total evolved carbon oxides by MS and measured waste gas flow rate. The benefits are great: process turnaround is improved, re-blows are avoided, as is undesirable oxidation of the metal.[3] Typical process measurements are shown below in Figure 5.

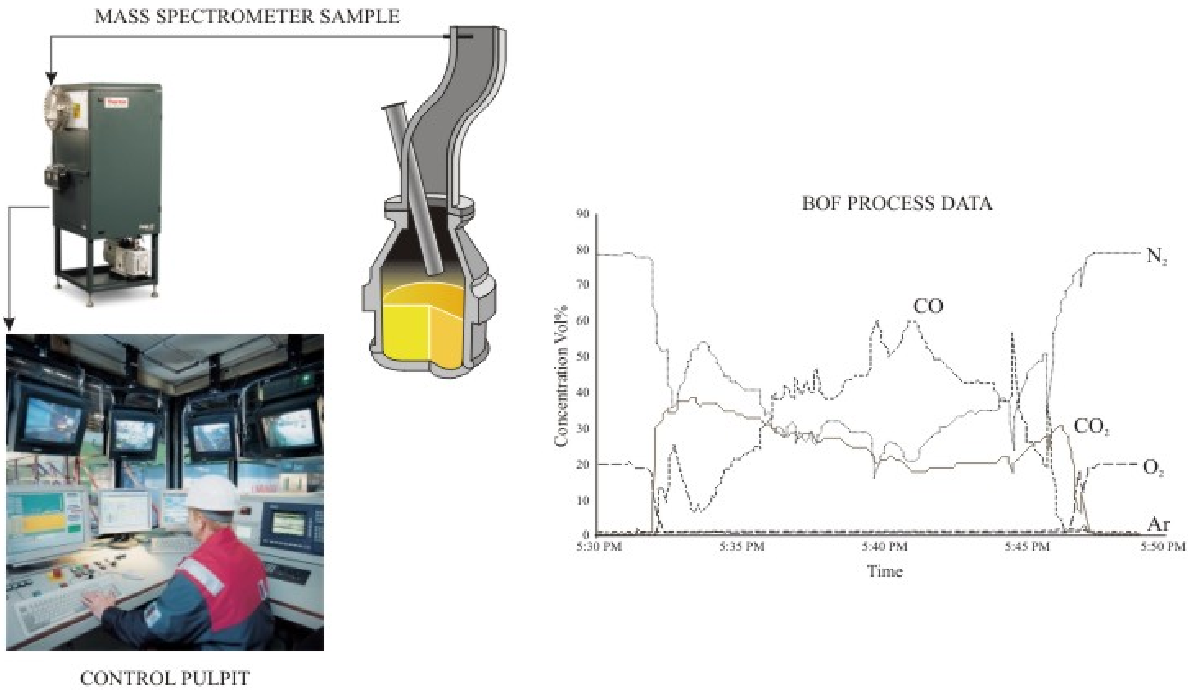

Figure 5: Representation of process MS on a BOF plant and typical data.

Speed of analysis is particularly critical for BOF monitoring. The above components need to be measured in less than 2 seconds. The precision of measurement at this analysis speed is better than 0.1% absolute. The mass spectrometer provides a significant additional benefit for closed-hood systems where it can detect the potential buildup of explosive mixtures. If only a single explosion is avoided then the entire mass spectrometer installation will pay for itself many times over. In open-hood converters, mass spectrometry offers the only means of accurately measuring the carbon that is being ejected from the steel since it can measure, and account for, the dilution of CO and CO_2 caused by the ingress of air into the hood. The process MS can achieve this by directly measuring the nitrogen, oxygen and argon.

2.2 Argon Oxygen Decarburization

Argon Oxygen Decarburization (AOD) is a process used to produce stainless steel, i.e. steel containing approximately 17% chromium and carbon at less than 0.02%. As well as stainless steel, AOD is also used to produce most wrought and foundry-grade ferrous alloys. Successful commercial production of silicon, tool, nickel-base, cobalt-base, military specification, and other specialty alloys have also been accomplished with AOD. Typical raw material or 'charge' in an AOD vessel contains 1.5% carbon and 18.5% chromium. The object of the process is to reduce the carbon level via oxygen decarburization without chromium loss occurring. If only oxygen blowing is used for decarburization the chromium level is reduced to about 3% as the carbon level reduces from 1.5% to 0.02%. Chromium oxidation is dependent on the carbon monoxide partial pressure and temperature; therefore process conditions are maintained to control the CO partial pressure and exothermic reactions. The key to the AOD process is to dilute the oxygen used for blowing with argon, to reduce the partial pressure of the evolved carbon monoxide. Oxygen is progressively diluted with argon, which controls the temperature rise in the vessel and ensures that almost all of the chromium present in the starting charge is retained while carbon is removed

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to the desired levels. Rapid, accurate gas analysis is vital to monitor the gas stream so that the end-point of each blowing period can be determined.
Air separation plants are used to generate the pure oxygen, pure argon and pure nitrogen required for primary and secondary steel conversion. Molecular sieve is used in the pre-purification unit (PPU) where water, CO_2 and oxides of nitrogen are removed. The dry air entering the cold box consists of 78.11% N_2, 20.95% O_2 and 0.94% Ar. The distillation columns cryogenically separate the three gases and residual oxygen is removed from the argon in a second distillation stage. The cost of argon generation is therefore approximately 80 times that for nitrogen so N_2 is the preferred inert stirring gas. Unfortunately, low carbon sheet steels, intended for special applications such as automobile body panels, require very low nitrogen contents (20 to 50 ppm) so it is necessary to use argon once the nitrogen limit has been reached. The mass spectrometer is invaluable for accurate control of the switchover from nitrogen to argon.
Many of the benefits of the converter gas application also apply to the AOD process. Before MS was implemented, the process was difficult to control efficiently. The operator would judge the end-point by eye – looking at the flame color; not a very objective method. This often resulted in re-blows. Another approach was to always use longer blows, to make sure the end-point had been reached, but this is inefficient and gives a poorer product, due to chromium oxidation. Yet, another approach that was used was to interrupt the process and take several samples – this lowers production rate. After implementation of process MS on an AOD process, instrument payback has also been calculated to be as short as 3 months.

2.3 Vacuum Processing

2.3.1 Vacuum Oxygen Decarburization (VOD)

The unrefined steel is often converted into stainless steel or other high-quality, ultra-low carbon steel using the VOD process. Once the ladle has been charged, the converter top is closed. This consists of a vacuum hood that includes an oxygen lance and a hopper for adding desulfurizing slag treatments and alloying elements. The pressure in the vessel is lowered from atmosphere (1,000 mbar) down to 1 mbar or less using large multi-stage steam ejectors or 3-stage dry pumping systems. The lance blows oxygen over the melt while argon is bubbled up from the bottom in order to purge the carbon oxidation products and remove impurities. The mass spectrometer's sample tap is incorporated into the vacuum system so that decarburization and degassing can be monitored directly to enable optimum process control. The mass spec can also be used to calculate total gas flow from the vessel by use of an accurately metered helium injection as shown in Figure 6.

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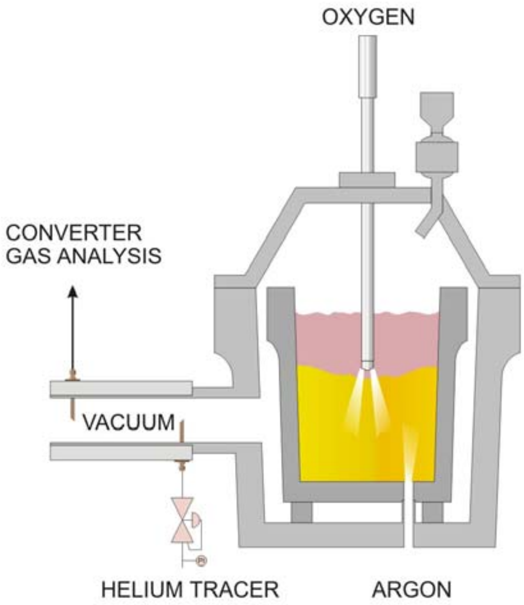

Figure 6: Measurement of total gas flow using helium tracer.

The amount of decarburization (C kg) is accurately calculated by integrating the area of the plot of dC/dt versus time, which can be expressed as

$$C\ (kg) = \sum 0.012 \times ([CO] + [CO_2]) \times F \times (1 / [He]) \times (1 / 22.415) \times dt$$

where [He], [CO] and [CO_2] are the mean values of successive concentration measurements by the mass spectrometer, F is the flow rate of Helium introduced (via a mass flow controller) and dt is the time difference between successive measurements.
This arrangement provides comprehensive data for the kinetic control models. In the production of ultra-low carbon steel (less than or equal to 30ppm) a mean error of 1ppm in the carbon content can be achieved when magnetic sector mass spectrometry is used to provide data to the advanced process control system.

2.3.2 Recirculating degassing (Ruhrstahl-Hausen process)

The purpose of the degassing process is to remove hydrogen, nitrogen, oxygen and carbon which reacts with the oxygen when the vacuum is applied. This reduces the number of inclusions in the steel which in turn improves toughness, fatigue strength and machinability. Better control of the steel's cleanliness is also a prime benefit of degassing. Alumina, inherent in all steel-making processes, is a major source of poor steel cleanliness. The use of slags that have an affinity for alumina enables the production of very clean steel products. In the R-H version of this process an evacuated vessel is lowered into the ladle and hot metal is drawn up through one of a pair of snorkel tubes into the vacuum chamber where the degassing takes place. Argon is injected into one leg in order to initiate a vigorous recirculating and boiling of the hot metal.

2.4 Electric Arc Furnace

The electric arc furnace (EAF) (together with the basic oxygen furnace) is one of the two modern ways of making steel. Unlike the basic oxygen process, the EAF does not use hot molten metal. It is charged with solid material. This is normally steel scrap and DRI. The steel scrap is first tipped into the EAF from an overhead crane. A retractable roof is then swung into position over the furnace. This cover contains electrodes which are lowered into the furnace. An electric current (supplied by a 100MW transformer typically) is passed through the electrodes to form an arc. The heat generated by this arc melts the scrap. Oxygen can also be lanced into the scrap or wall-mounted oxygen-fuel burners can be used to provide additional chemical heat. The roof includes a hood that diverts the gases through a post-combustion section and a dust removal system. As with other steel processes, burnt lime and dolomite are added to form a slag that blankets the molten steel and absorbs impurities. The slag also covers the arcs, preventing damage to the furnace roof and sidewalls from radiant heat. Carbon (in the form of coke or coal) is lanced into this slag layer, partially combusting to form carbon monoxide gas, which then causes the slag to foam, allowing greater thermal efficiency, and better arc stability. Once the meltdown is complete, the oxygen lance is used to burn out impurities (Si, P, S, Al, Mn and Ca) and their oxides are absorbed by the slag. Finally, the carbon content is lowered by the oxygen from the lance. Once the process is complete, the furnace is tilted and the molten steel is tapped into a pre-heated ladle.

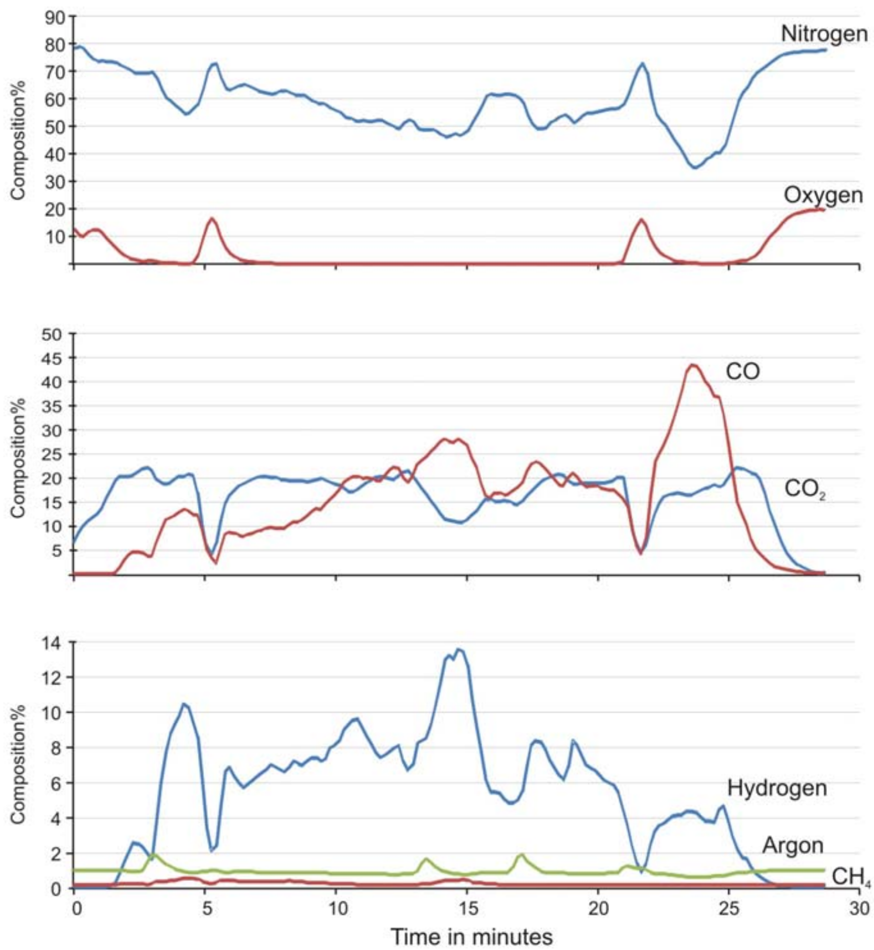

Figure 7: Electric arc furnace off-gas mass spectrometer data plots.

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The main control goals are to minimize energy usage, provide consistent steel specifications, achieve environmental compliance and to ensure safe operation. Furnace off-gas composition is measured in real-time and is used to continuously optimize chemical energy and to control post-combustion; primarily for bag house safety and environmental compliance reasons. The gas measurement is achieved by use of an extractive system that employs rugged water-cooled probes and a sophisticated sample conditioning system that provides a reliable off-gas sample for the mass spectrometer. The analyzer provides precise gas composition measurement for dynamic, model predictive, process control.

3 CONCLUSIONS

Process Mass Spectrometry provides fast on-line accurate analysis of the properties of a wide range of process gases, especially those encountered in the traditional iron and steel works. The modern mass spectrometer is highly reliable and easy to own yet it provides rapid and complete lab-quality analysis for real-time optimization of many hot metal processes within the mill. When the integrated steel mill uses waste process gases for fuel then these measurements include calorific value, density, specific gravity, Wobbe Index, stoichiometric air requirement and CARI as well as complete and precise compositional analysis. The short installation payback times and the superior measurement quality provided by a modern magnetic sector mass spectrometer have made this the analytical technology of choice for gas analysis throughout the industry.

Benefits of Gas Analysis by Process Mass Spectrometer

- Improved Hit-Ratio (for increased steel throughput)
- Minimize Tap-to-Tap Times (for minimum energy consumption)
- More Consistent Steel Quality
- More Accurate Kinetic Model Performance
- Best Available Speed and Precision for Model Development
- Total Flow Calculation c/o Helium Tracer Gas Analysis
- Precise Measurement of Fuel Gas Properties
    - To minimize natural gas use
    - Extend burner lifetime
    - Reduce scaling in re-heat furnace
- Rapid Installation Payback

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