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APPLICATION NOTE

Prima PRO process mass spectrometer

Improving product quality and process efficiency in basic oxygen steelmaking

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Key words

- Basic Oxygen Steelmaking (BOS)
- Basic Oxygen Furnace (BOF)
- Off gas analysis
- Decarburization control
- Slopping detection
- Gas recovery
- Magnetic sector

Introduction

Steel, an alloy of iron and carbon containing less than 2% carbon, is our most important construction and engineering material, with over 1.6 billion tonnes of crude steel produced in 2015[1]. About 70% of this steel is produced by Basic Oxygen Steelmaking (BOS), also known as the Basic Oxygen Process (BOP). The most common type of steel converters are known as Basic Oxygen Furnaces (BOF), also known as Linz Donawitz (LD) converters.

In the BOF, carbon-rich molten iron from the Blast Furnace is converted to steel by blowing oxygen through a top-mounted lance at supersonic speeds into the molten iron. Carbon in the molten iron reacts with oxygen to form carbon monoxide (CO) and carbon dioxide (CO_2). The process is known as basic because chemical bases of lime or dolomite are added to promote the removal of impurities and protect the furnace lining. Modern BOFs can handle several hundred tonnes of iron and convert it to steel in around 30-40 minutes, with the oxygen 'blow' typically lasting around 20-25 minutes. Scrap metal can be added to the molten iron to improve recycling. Some converters blow oxygen through the bottom of the furnace—these are known as Q-BOP (quick-quiet BOP) or OBM (Oxygen Bottom-blowing Maxhütte).

Steel is commonly described as mild, medium- or high-carbon, according to the percentage of carbon it contains, although this is never greater than about 1.5%. Table 1 shows the carbon content of these grades of steel. Adding metals such as nickel, chromium, and tungsten produce a wide range of alloy steels such as stainless steel.

Table 1 Carbon content of common grades of steel

Type of steel	Carbon content
Mild steel	Up to 0.25%
Medium carbon steel	0.25% to 0.45%
High carbon steel	0.45% to 1.50%

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In a highly competitive industry, steel producers have to ensure their furnaces are operating at maximum efficiency, maximizing product quality and process safety while minimizing energy consumption and environmental impact. A key requirement is to monitor, control and optimize the conversion of carbon to carbon monoxide and carbon dioxide, so analysis of the off-gas from the furnace is a vital part of the process control strategy.

Historically, two Non-Dispersive Infra-Red (NDIR) analyzers were used, one to measure CO, the other CO_2. Additional discrete analyzers were required to monitor oxygen and hydrogen – typically paramagnetic O_2 analyzers and thermal conductivity analyzers for H_2. Process mass spectrometers are now widely used for many important gas analysis applications on iron and steel plants, including blast furnace top gas analysis, coke oven gas analysis, secondary steel process control, fuel gas analysis and direct reduction iron processes[2]. Many steel producers have incorporated mass spectrometers into their manufacturing processes to provide improved dynamic process control. As well as carbon monoxide and dioxide, the MS analyzes oxygen, hydrogen, nitrogen and argon, providing a complete gas composition profile in seconds, replacing a number of discrete analyzers with a single reliable system.

An example of the off-gas profile obtained by a Thermo Scientific™ Prima PRO process MS is shown in Figure 1. The CO and CO_2 concentrations rise quickly at the start of the oxygen blow, whereas the oxygen level falls dramatically to virtually zero at the start, rising equally dramatically at the end of the melt as the CO and CO_2 levels drop.

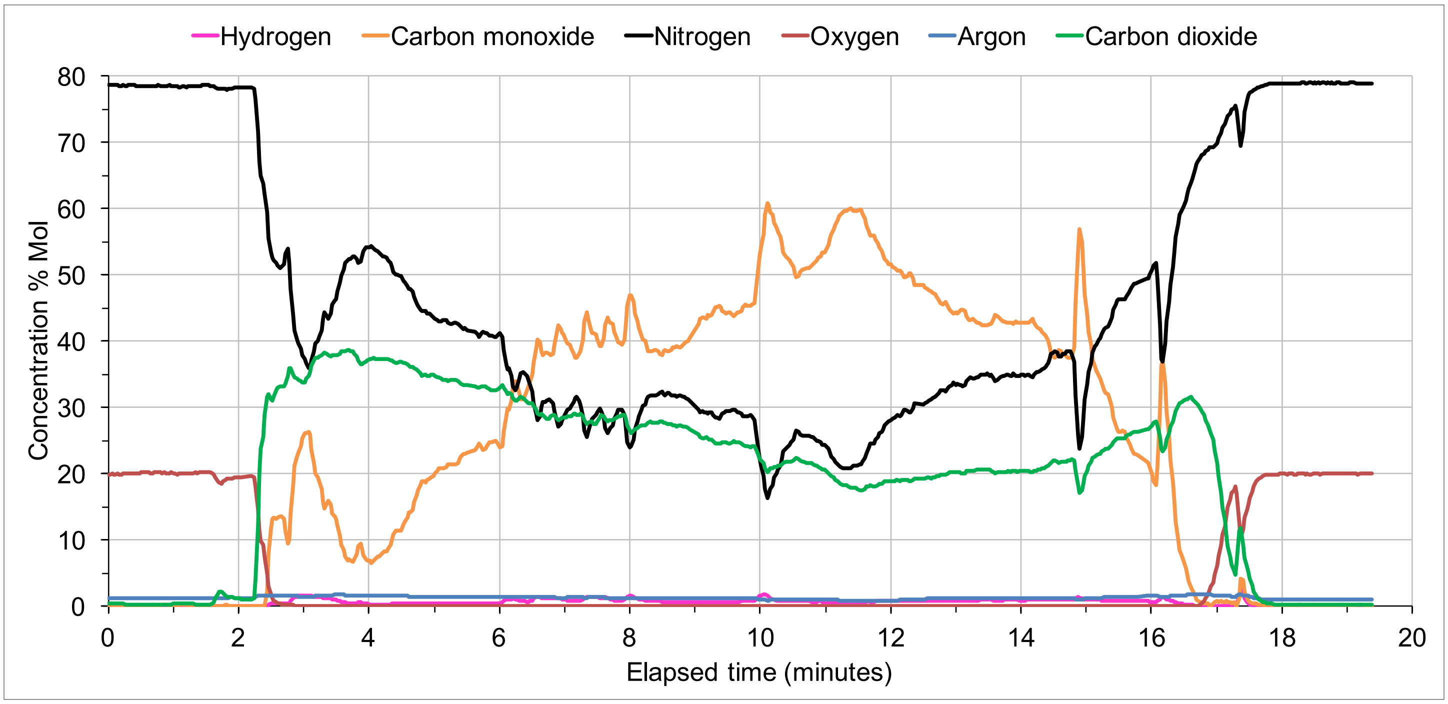

Figure 1 Example of BOS off-gas analysis by Prima PRO

Process control requirements

Fast, accurate, multi-component gas analysis provides much valuable information to the process control model, including decarburization rate, onset of slopping, oxygen lance position, hydrogen concentration, and waste gas recovery.

Decarburization control

Off-gas composition changes rapidly during the steel making process so gas analysis data must be acquired quickly. Using Prima PRO MS, this data can be updated in 2 seconds or less, compared with up to 20 seconds for conventional infrared techniques.

Decarburization can be expressed as:

$$\mathbf{dC/dt = constant} \times \mathbf{([CO] + [CO_2])} \times \mathbf{waste\ gas\ flow}$$

The ratio of CO to CO_2 in the waste gas gives an indication of carbon removal during the blowing phase. The study of these distinctive curves, together with the retained O_2, shows a pattern that correlates well with the beginning and end of decarburization. This reduces the need for re-blows and extra flux additions to the converter vessel, reducing costs and improving productivity. Carbon prediction hit rates of over 95% for carbon contents less than 0.1% have been reported using a Thermo Scientific process MS as part of a dynamic control model[3].

Slopping detection

Slag is formed in the furnace as silicon, manganese and iron are oxidized and form an emulsion with metal droplets, fluxes and the refractory lining. As off-gases pass through the emulsion, an expanding foam is formed. Under certain process conditions, this excessive foam is forced out through the furnace opening, a process commonly known as slopping. Slopping results in loss of valuable metal, damage to process equipment, lost production time, pollution and even potential safety risks for plant personnel.

The ability to detect successfully the onset of slopping is one of the most significant advantages that MS has over conventional techniques. The steel producer needs to know precisely how much oxygen remains in the converter in order to predict when slopping will occur. The MS measures nitrogen directly, providing an accurate determination of the quantity of air leaking into the converter through the hood. This, in turn, will yield a much more precise measurement of the oxygen leaving the converter.

$$\text{Remaining } O_2 = O_2 \text{ blown in} - \int [O_2]\ \% \times \text{gas flow}$$

This precise oxygen measurement allows steel producers to use mathematical modeling techniques to predict when slopping will occur. At sites where Thermo Scientific mass spectrometers have successfully been installed, this modeling predicts slopping with a success rate of over 81%[4].

Oxygen lance position

The curves for CO/CO_2 and retained O_2 also give an indication of slag development and can therefore assist with lance positioning at the beginning of the blow, also O_2 rate and lance height control towards the end.

Hydrogen analysis

Furnaces are fitted with water cooling systems which control process heat. These cooling systems are critically important, because faults or failures can affect the process and damage (or even destroy) the furnace. If water leaks into the furnace during a melt, it will dissociate to hydrogen and oxygen; plant personnel are then at serious risk from a resulting explosion. Prima PRO provides significantly faster and more accurate hydrogen analysis than a thermal conductivity detector, enabling rapid detection of water leaks into the furnace. It can also be used to determine the water content in flux additions.

Fuel cost savings through efficient gas recovery

The normal Prima PRO sampling point is directly on top of the waste gas duct, before the gas cooling and dust extraction systems. A typical installation scheme is shown in Figure 2.

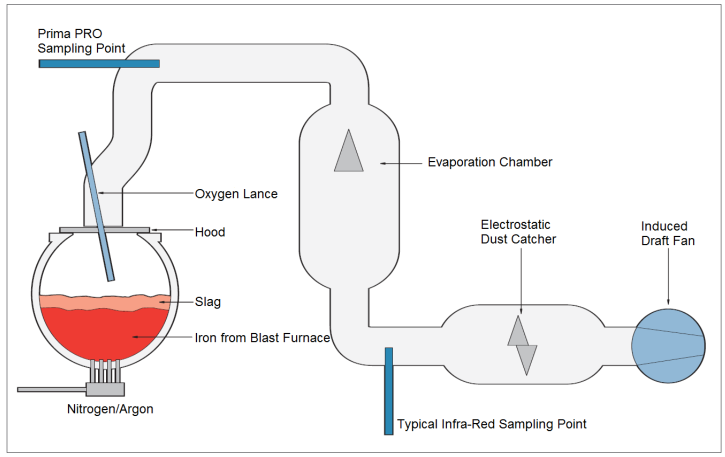

Figure 2 Typical Prima PRO installation scheme

This close-coupled sample point, combined with Prima PRO's exceptionally fast gas analysis, enables the steel producer to begin recovery of the valuable waste gas up to 20 seconds sooner at the start of the melt, and prolong the recovery for 20 seconds at the end. With a typical gas flow rate of 150,000 Nm^3/hour, the steel producer can save over 1,600 Nm^3 on each charge, resulting in a significant saving in plant fuel costs as the recovered gas is collected, mixed with other process gases and used as fuel.

Thermo Scientific process mass spectrometers have been used to provide fast, on-line, accurate analysis of the properties of a wide range of fuel gases on integrated iron and steel works for many years[5]. Table 2 shows a site acceptance test for a Prima PRO measuring BOF gas as a fuel gas; the MS measured component concentrations and also calculated standard energy parameters as Derived Values, including Calorific Value (Upper & Lower), Specific Gravity, Wobbe Index and Density according to ISO 6976. A certified calibration cylinder was analyzed periodically over 8 hours and results compared with specified values; Prima PRO passed the acceptance test easily.

Table 2 Site acceptance test for BOF fuel gas analysis

	H_2 %	CO %	N_2 %	O_2 %	Ar %	CO_2 %	CV lower kcal/nm³	CV upper kcal/nm³	Specific gravity	Wobbe index kcal/nm³	Density kg/nm³
Cylinder certificate	2.01	24.93	54.09	2.02	1.99	14.96	805.4	814.8	1.0439	788.3	1.35
Mean MS reading	2.0056	24.9468	54.0884	2.0168	1.9870	14.9555	805.8	815.2	1.0439	788.7	1.35
Standard deviation	0.0021	0.011	0.0093	0.0018	0.0016	0.0095	0.2822	0.2736	0	0.2864	0.0001
Specified standard deviation	0.005	0.03	0.05	0.002	0.002	0.02	2	2	0.003	2	0.004

Figure 3 shows energy values generated by Prima PRO during an 8-hour run on a BOF converter gas. For safety reasons the recovered gas cannot contain oxygen if it to be used a fuel; Prima PRO's fast, accurate oxygen analysis ensures the oxygen levels in the extra 40 seconds of recovered gas are quite safe. For example, the average oxygen value over the 8-hour run in Figure 3 is less than 0.2%.

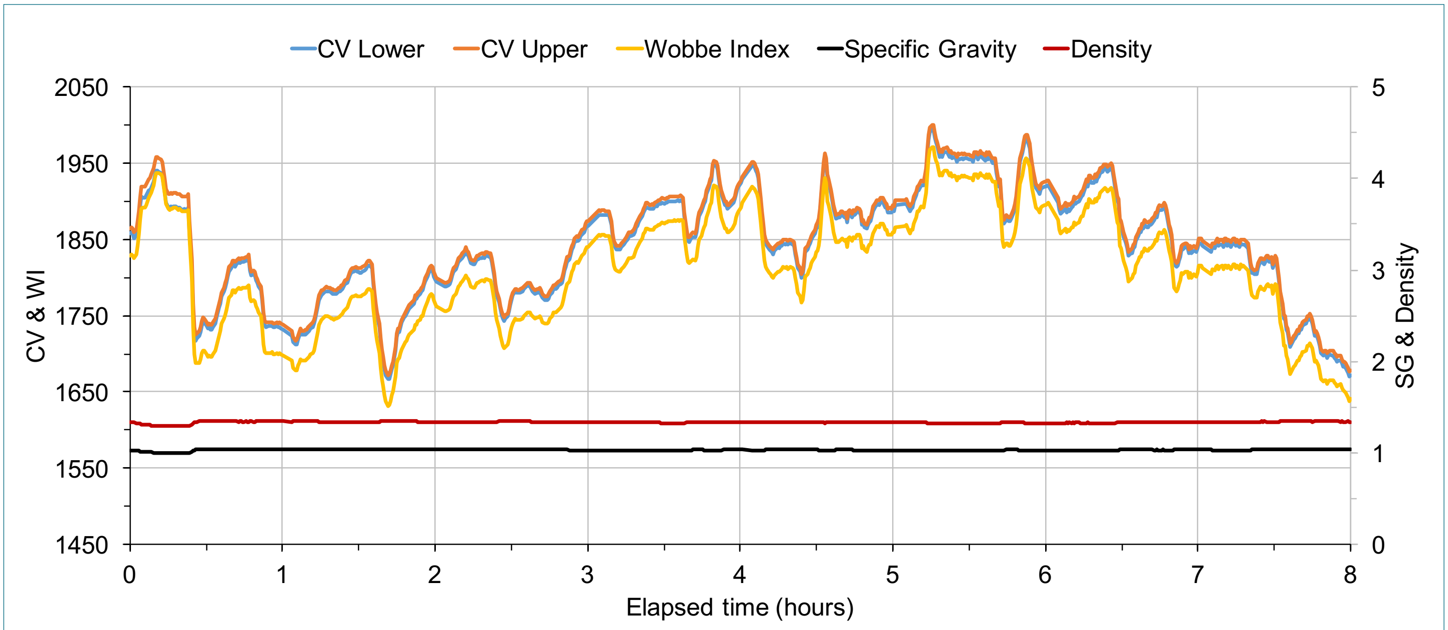

Figure 3 Energy values of recovered BOF gas measured over 8 hours

Benefits of Prima PRO magnetic sector analyzer

Prima PRO's magnetic sector analyzer uses technology which has been proven over many years in a wide range of iron and steel applications. There are essentially two types of mass spectrometers available for continuous process gas analysis and Thermo Fisher Scientific is unique in that we offer both types of MS systems, magnetic sector and quadrupole.

Magnetic sector has proven more successful for a wide range of industrial process applications, because of its superior stability and lower maintenance requirements.

Both types of MS use electron impact ionization to generate positive ions. These are then separated, either in a varying magnetic field (magnetic sector MS) or a varying RF/DC field between four parallel rods (quadrupole MS).

The magnetic sector MS operates with ion energies of 1000 eV, providing extremely rugged performance in the presence of gases and vapors that could contaminate the analyzer. Quadrupole analyzers operate at ion energies of typically just 5-10 volts—this can give rise to ion interactions within the MS, causing poorershort-term precision.

In a magnetic sector analyzer, the signal intensity at any specific mass position appears as a flat top peak. This means that any small drift in the mass scale will not result in a change in signal intensity. This is not the case with quadrupole mass spectrometers, which produce round top peaks.

Quadrupole analyzers also suffer from a phenomenon known as 'zero blast', making the analysis of light gases such as hydrogen problematic. Magnetic sector analyzers do not suffer from this effect, ensuring hydrogen can be analyzed with maximum accuracy for safety.

Typical Prima PRO analytical specification

Table 3 shows the typical analytical performance for Prima PRO analyzing the six components normally monitored in the BOF process. Precisions are measured with a certified calibration gas over 8 hours, with an analysis cycle time of just 1.6 seconds.

Table 3 Typical Prima PRO steel converter performance specification

Component	Typical composition %mol	Prima PRO standard deviation %mol
Hydrogen	0 – 10	≤0.01
Carbon monoxide	0 – 85	≤0.1
Nitrogen	0 – 100	≤0.1
Oxygen	0 – 25	≤0.02
Argon	0 – 10	≤0.01
Carbon dioxide	0 – 40	≤0.04

Plant integration

The Prima PRO is normally located at the top of the converter in an analyzer shelter, taking its sample from the waste gas duct. Prima PRO's cabinet is sealed to prevent dust ingress, cooled by a side mounted air conditioner that stabilizes the temperature within the cabinet to within ± 0.5°C, and can handle ambient temperatures between 12°C and 40°C. An on-board processor provides embedded processing power for true, stand-alone control of all mass spectrometer functions; it can connect to a local or remote PC as a Graphical User Interface (GUI), and three additional configurable serial ports are provided for remote communication. Modbus RTU slave protocol communication is supplied as standard, with additional protocols such as Profibus DP and Modbus Ethernet TCP/IP available as options. 13 digital input channels and 13 digital output channels are provided as standard, additional analog and digital hardware is available as an option.

Sample conditioning is typically the same as for conventional analytical techniques, consisting of dust filtration and water removal. The sampling system has two probes, one probe is sampling while the other is being cleaned, with automatic switchover between probes scheduled to take place between blows.

Summary

Prima PRO provides accurate, real time off-gas analysis data to furnace control systems and dynamic control models, resulting in significant process benefits. A 1% increase in throughput is worth around $20,000 a day for a plant producing 10,000 tons of steel a day, so payback is extremely fast.

- Improve end-point detection
- Minimize oxygen use
- Optimize lance position
- Reduce tap-to-tap time
- Minimize re-blows
- Detect slopping
- Remove requirement for hot metal sampling during blowing
- Increase recovery of waste gas
- Improve process safety

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