

Improved Monitoring of Slag Chemistry for Steel Production Quality Using X-Ray Fluorescence Spectroscopy

For steelmakers seeking to manufacture steel more profitably, it is essential to adopt technologies and processes that allow for monitoring and sampling slag more efficiently and cost effectively. Because of the highly integral role of slag in steel manufacturing, it is critical that these prospective technologies and processes are, at a minimum, reliable, repeatable and accurate, and that they function properly in difficult manufacturing environments.

Current Challenges of Monitoring Slag

Historically, the manufacturing of steel has been more of an art than a science, as one of the major challenges for steel manufacturers has been monitoring and controlling the chemistry of slag in determining batch quality. Operators of steel furnaces have typically accomplished this by primarily relying on visual cues.

In monitoring slag formation and the quality of individual steel batches, operators check to verify that such impurities as silicon, manganese and phosphorus are dispersed when iron ore is inserted into the individual vats and the various components begin to melt. They also monitor the two different basicity rates, the V ratio and the B3 ratio, to determine how basic the slag is relative to the amounts of oxide that are present.

The Challenge of Individual Operator Analysis

As a result of increasing demands from customers for greater standardization in steel metallurgy, steel manufacturers are having to change their processes to rely less on individual operator judgment and more on scientific production methods. Manufacturers that rely on individual operator judgment typically end up producing steel batches where each batch is different to varying degrees, no matter how qualified or skilled the individual operator. The practice of relying on individual operator judgment also makes training more difficult in that there are fewer objective or quantifiable steps that can be communicated to new operators.

In-Line vs. After-the-Fact Analysis

With the continued emergence of electric arc and ladle metallurgy furnaces, steel manufacturers have an opportunity to conduct analysis in real time, or “inline” during the actual process of steelmaking, instead of after the fact. By analyzing batch chemistry during manufacturing, composition can be monitored more closely and adjustments can be made to the process more quickly and easily. Steel manufacturers using blast furnaces must conduct analysis after the fact, which ultimately affects quality and productivity as it takes longer to make process and batch adjustments.

The Drawbacks of ICP, AAS Methods

Currently many steel manufacturers with blast furnaces conduct slag analysis after the fact in laboratories using inductively coupled plasma (ICP) and atomic absorption spectroscopy (AAS) methods. The disadvantage of these two methods is that they cannot be performed inline so feedback is slower, which impacts quality and productivity as it takes more time to make process and batch adjustments. The other disadvantage of these two methods is that they use lots of consumables and generate byproducts that require proper environmental disposal. As a result, they also require special handling and training.

XRF Technology: the In-Line Solution

X-ray fluorescence (XRF) analysis is a fast, non-destructive and environmentally friendly analysis method with very high accuracy and reproducibility. All elements of the periodic table from beryllium to californium can be measured qualitatively, semi-qualitatively, and quantitatively in powders, solids and liquids. Concentrations of up to 100% are analyzed directly, without any dilution, with reproducibilities better than $\pm 0.1\%$. Typical limits of detection are from 0.1 to 10 ppm. Most modern X-ray spectrometers with modular sample changers provide fast, flexible sample handling and adaptation to customer-specific automation processes.

XRF spectrometry is the most effective way to perform multi-element analysis of slag, as it offers a number of key benefits to steelmakers seeking more efficient and productive manufacturing methods. The key advantage is that it can be used inline during the manufacturing process, allowing operators to take a sample, analyze it and then quickly return it to the batch. As a result of this capability, operators get automatic feedback that they can use to make critical adjustments during production, which greatly enhances efficiency and productivity as well as individual batch quality.

Another benefit of XRF technology is that it does not use acids in the course of sample preparation, unlike the ICP and AAS methods. XRF technology is clean and generates no byproducts that create disposal challenges.

XRF Technology—What to Look For

When evaluating a specific XRF spectrometer, the following criteria should be considered:

Element range. The instrument should be able to analyze virtually all elements of the periodic table from boron to uranium. To easily extend the range of analytical routines, the instrument should include specialized pre-calibrated analytical and universal programs, as universal programs enable users to analyze nearly all elements of the periodic table.

Concentration range. The instrument should be able to measure sub-ppm to 100% for light and heavy elements in solids and liquids. The key to this capability is the X-ray tube, the instrument's core technology. A high-intensity X-ray tube should provide the specific excitation energy for every element. This includes high-energy X-rays for the analysis of heavy elements and low-energy X-rays for light elements.

Detection limits. The instrument's detection limits should extend to the ppb level. The instrument should be able to provide optimized beam paths for the smallest samples and the best possible detection limits for small samples. Key features that support this level of detection performance include sealed proportional counters with high-transmission windows, high-efficiency flow counters for light element detection and high-sensitivity scintillation counters for optimal heavy-element detection.

Ease of use. To minimize training time and to ensure optimal ease of use, the instrument should feature controls, such as intuitive touch screen interfaces, that can be quickly understood and operated. In addition to being easy to operate, smaller XRF instruments for near or at-line process control should generally be simple to install, require low maintenance and take up a minimum of floor space.

Sample handling. The instrument should be designed to facilitate the safe handling of solids, powders and liquids, and it should be flexible enough to allow for easy switching between solid and liquid samples. Modern X-ray spectrometers often come with a process automation sample magazine, which is designed to quickly and safely handle powder samples or different-sized samples, including liquid samples.

Advanced design. The instrument should have features that support accurate, reliable and timely elemental analysis, which can include a high-intensity tube, an optimized beam path and high-performance detectors.

Time-to-result. This is the actual time from sampling to final qualitative and quantitative results. The instrument should involve simple sample preparation and direct, non-destructive analysis—the two key factors for optimum time-to-result speed. Instruments that also offer user friendly features, such as intuitive touch screens, can enhance their time-to-result speeds.

Sample throughput. For optimal efficiency and production, the instrument should be capable of processing 25-30 samples per hour (depending on the application).

Reliability. The instrument should be able to provide the same result on successive trials, regardless of the process or however harsh the operating environment. In addition, the instrument should be designed so that only minimal maintenance is required.

Precision. Because of its inherent X-ray fluorescence principles, a lower analytical error rate can be expected with an XRF instrument compared to an ICP or AA instrument. The instrument should also be able to provide excellent analytical performance in situations where faster turnaround times are required or desired.

Accuracy. The instrument should provide a high degree of conformity of a measured quantity to an absolute value. To ensure the best accuracy, all spectrometer parts should interact seamlessly.

The Bruker AXS Solution—S2 RANGER

Bruker AXS offers an innovative solution for steelmakers seeking a scientific, accurate way to monitor and sample slag quickly and easily. The S2 RANGER is a compact, benchtop-style energy dispersive X-ray fluorescence (EDXRF) spectrometer, with easy-to-use, touch-screen features, requiring only a mains power supply. It is designed to help operators of blast furnaces as well as electric arc furnaces achieve reliable and repeatable results when monitoring and sampling slag.

Short measuring times, extreme analytical flexibility, and high accuracy and precision are just some of the important advantages of the S2 RANGER. In addition, with the S2 RANGER measurement tasks are quickly defined and started with minimal operator input based on intuitive touch-screen operation. No special technical training or expertise is required to achieve precise results from the very first day the S2 RANGER is used by a particular operator.

The S2 RANGER also offers enhanced communication capabilities for operators or other staff wanting to use the results in their software environment. The S2 RANGER is fully open for communication and can be easily integrated into any network

Case Study: Nucor Corporation

Nucor Corporation is the largest steel producer in the United States, with net sales of \$12.7 billion in 2005, and it is also the nation's largest recycler. In 2004, Nucor recycled approximately 17 million tons of scrap steel, which included 5 million tons of scrap steel from discarded automobiles. Today Nucor has operating facilities in 17 states, and it continues to pursue growth opportunities in both the United States and abroad.

Challenge: Finding a Superior Elemental Analysis Solution to Improve Production

In 2004 the management at the Nucor steelmaking facility in Berkeley County, South Carolina, decided that it needed to improve certain aspects of the plant's operations, including its performance in monitoring slag chemistry, which is a critical factor in the quality of the steel that is ultimately produced. According to Eugene Pretorius, the plant's steelmaking specialist, Nucor was looking for an elemental analysis instrument that could provide superior reliability and accuracy, and that could help enhance the production process. The company also wanted an instrument that was easy to use and that only required a minimal amount of training.

The Solution: Bruker's S2 RANGER

After evaluating and then switching to the Bruker S2 RANGER, Nucor quickly attained the higher performance level that it was seeking. Pretorius says that the S2 RANGER succeeded in proving itself as a vital tool in helping to control slag impurities as well as with analyzing and verifying slag chemistry specifications.

"The S2 RANGER has been very reliable, and we have gotten very good slag results with it in a very short amount of time," Pretorius says. He adds that the instrument the facility used previously was satisfactory at a functional level, but it was not at the level of the Bruker S2 RANGER regarding accuracy, speed and overall performance.

Benefits

Pretorius cites several key benefits that the S2 RANGER has provided Nucor. "The first is reliability—the operators trust the machine. The results that they see are correct," he says. "Secondly, the machine is easy to use. Everybody can use it and it only takes a few minutes to get data on slag samples. And the speed of the S2 RANGER is an important factor as well."

Pretorius says that the S2 RANGER has helped the Berkeley facility take another step from steelmaking as an art to steelmaking as a science. "The S2 RANGER is one of the tools that we use to help us quantify what we are doing. It helps us make the necessary adjustments during production," he says. Pretorius also notes that the S2 RANGER has performed very well in the harsh operating conditions around the facility's scrap furnace.

To further demonstrate the critical importance of the S2 RANGER to Nucor's operations, Pretorius says the facility's management decided to purchase a second instrument as a backup after realizing how much it relied on the S2 RANGER in performing day-to-day monitoring and analysis.

S2 RANGER – Analysis of Blast Furnace Slags

The table below shows the analytical performance of the S2 RANGER for blast furnace slags, especially regarding analytical accuracy and short term reproducibility.

Sample preparation

Typically, slag samples are milled and prepared on pressed pellets with the addition of a binder to ensure a stable specimen. For this particular performance, the samples were prepared with the addition of 20% wax. Five grams of the mixture were pressed with a pressure of 10 tons for 20s.

Measurement

The measurement was performed using the predefined and precalibrated slag solution of the S2 RANGER with a total measuring time of 300s.

Chemical Composition	Chem. Conc. (%)	XRF Conc. (%)	Absolute Deviation (%)	Relative Deviation (%)
MgO	5.20	5.08	0.12	2.4
Al ₂ O ₃	4.40	4.28	0.12	2.8
SiO ₂	11.66	12.16	0.50	4.3
P ₂ O ₅	2.44	2.39	0.05	2.1
S	0.146	0.137	0.009	6.6
K ₂ O	0.44	0.43	0.01	2.3
TiO ₂	0.50	0.48	0.02	4.2
CaO	40.29	39.94	0.35	0.9
Cr ₂ O ₃	0.48	0.46	0.02	4.4
MnO	5.45	5.35	0.10	1.9
Fe	19.59	19.34	0.25	1.3

How to Use Slag Analysis Data

Once slag monitoring and analysis data has been obtained, there are a number of ways it can be used to enhance and improve slag formation and the quality of individual steel batches. For example, this information can be used to help determine the mass balance of slag related to elements being removed, such as phosphorus and sulfur, and those being injected, such as oxygen and carbon.

In addition, this data can be used to help better optimize flux inputs to create the proper slag chemistry while reducing FeO and Fe₂O₃. Regarding FeO content specifically, this information can be used to help control FeO formation by lowering O₂ injection and by reducing FeO in bulk slag by injecting carbon.

This data can also be very useful in monitoring and analyzing the key factors for creating the “right” foaming slag: optimum slag viscosity, sufficient levels of FeO to react with carbon and generate CO gas bubbles, and sufficient MgO to minimize refractory wear and prolong foaming.

Finally, this data can also be very helpful in analyzing and monitoring factors that contribute to poor foaming, such as out of control FeO, scrap variability (Si and Al), dirt or gangue in scrap charge, recycled EAF dust, and different steel grades (low vs. high C).

S2 RANGER On-Line Status: Technical Data

Elemental range: Sodium to uranium.

Concentration range: ppm to 100%.

Sample types: Powders, solids, liquids, pastes, coatings, slurries, films, filters, cuttings, etc.

Operation modes: Vacuum for solids (pump integrated) and Helium flushing for liquid samples or loose powders (external Helium supply required).

X-ray Tube: Pd anode, max. 50 W, 2mA or 50 kV.

Filter changer: Nine positions for primary beam filters.

Detector: Peltier cooled detector (no need for liquid Nitrogen), typical resolution <155eV @ Mn K.

Display & Printer: Integrated 12” TFT touch screen and thermal printer.

Room planning made easy

Mains: 110 or 240 V, 50/60 Hz, max. consumption 1kVA.

Dimensions: 65 cm (25.4”) x 80 cm (31.3) x 60 cm (23.4”), 80 kg (height x width x depth, weight).

Quality & Safety: DIN ISO 9001 / EN 29001, CE certified, Fully Radiation Protected System (e.g. DIN 54113).

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