Cost Effective Process and Quality Control by XRF for better Lifetime of Ceramic and Refractory Products

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To expand the lifetime of refractory products the elemental composition must be analyzed accurately and precisely during development and in production. It is a challenging task to achieve precise results in daily routine not only in the central laboratory, but also close to the mining of raw materials and in the process labs. The success depends on the one hand on the instrumentation. Even more important is to establish the same calibration and analytical quality control regime worldwide at each production site. Latest developments, like new multilayer X-ray optics and instrument design, will expand the analytical range, where flexible sequential X-ray fluorescence spectrometers can be used. New software functionalities, like the centralized global calibration concept, will support companies to achieve the same high product quality worldwide in all their operations.

1 Introduction

Ceramic materials are very highly valued in many sectors of modern industry. They are used where metals have reached the limits of their suitability and components are exposed to very high thermal, mechanical or chemical stresses. Ceramics are absolutely essential in high-temperature industrial processes such as the production of steel, cement, glass, non-ferrous metals and in energy generation. It's not only the temperatures which are extreme in these manufacturing processes. Abrasion, thermal expansion and chemical attack also take a heavy toll on these technological systems. For their protection, machinery and furnaces are lined with refractory materials selected for the specific process. These materials can withstand temperatures of about 1800 °C.

Every application is different, which means that the compositions for these refractory materials are also different. Shaped and unshaped materials with which to line the machinery and furnaces are made from the process-specific mixes of refractory raw materials. Chemical analysis of the raw materials as well as composition of the refractory products influence to a great extent the service life of the linings. For example, steel production makes very heavy demands on the thermal resistance of systems. Steel melts at about 1530 °C. Therefore, the lining of the ladle from which the steel is poured at the end of the process must be able to withstand these extreme temperatures. The lining is made of a mixture of refractory oxides such as magnesium oxide (melting point (mp) 2800 °C), calcium oxide (mp 2570 °C) or aluminium oxide (mp 2040 °C). However even the best refractory products wear out over time. For example, a steel ladle is ready for complete renovation after around 60 – 100 batches – and consider that it is 8 m high and 4 m across. A steelworks always has several of these ladles which can weigh up to 300 t in circulation. To ensure consistent processing conditions and product quality, the refractory lining also has to remain of a consistently good quality – not an easy task. Ensuring the highest possible standards of quality for the ceramic products and meeting all requirements for refractory products must be first priority. This objective can only be achieved on the one hand with permanent technological improvements and secondly by continuous enhancement of the quality assurance infrastructure. The main global acting companies, such as *RHI* or *Kerneos*, are producing their huge range of shaped and unshaped refractory products worldwide. At each production site, no matter if this plant is located in Asia, America or Europe, a strict quality regime with the same rules has to be established. The mining operation for raw material is shown in Fig. 1.

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Fig. 1 Mining operation for raw materials

Fig. 2 Sequential wavelength dispersive X-ray fluorescence spectrometer S8 TIGER

2 Sequential wavelength dispersive X-ray fluorescence spectrometry for industrial process and quality control

The chemical and mineralogical composition of raw materials, intermediate and finished products has to be determined to control and optimize the process achieving finally a constant high product quality. Raw materials from the quarry, additives, the intermediates and finally the refractory products must be analyzed to get detailed information about the elemental composition. This information is important to drive e.g. the mining process in the most efficient way for highest raw material quality. But not only major elements are important, also traces/impurities may cause later problems during the production and usage of the ceramics.

One of the most advanced analytical techniques for process and quality control in cement production is wavelength dispersive X-ray fluorescence analysis (WDXRF). No other technique can compete with the accuracy and precision, the ease of use, the simple and fast sample preparation and finally the high grade of automation and integration into any process control strategy.

Simultaneous WDXRF spectrometers with a limited number of fixed channels – one for each single element – are used ensuring a high sample throughput and a high analytical speed allowing a close monitoring of the process. Typically designed with a tube-above-sample geometry and with less moving parts, this kind of instruments is seen as reliable achieving a high instrument uptime. By default these units are used to get instant results for one specific, well defined application in process control, where analytical speed and precision counts – the mining and mineral processing.

Applications like the quality control of the final products and support of the product development in R&D laboratories are demanding a higher degree of analytical flexibility. Modern sequential WDXRF models, like the S8 TIGER of Bruker AXS, offer today to users not only the performance for the routine, but also the analytical speed and precision, reliability and instrument uptime for all analytical tasks in a modern refractory production site. Typical problems of conventional sequential WDXRF instruments on the market were identified. These topics were addressed during development to present with the introduction of modern instrument generations. The S8 TIGER is shown in Fig. 2, the flexible X-ray beam path with all optical components ensuring the optimum setup for each element and its respective concentration range is shown in Fig 3.

Using sequential wavelength dispersive X-ray fluorescence (WDXRF) each element is analyzed under optimal measurement conditions. For this purpose individual combinations of measurement parameters are set corresponding to the concentration range: The X-ray source and primary radiation filter guarantee that each element in the sample is optimally excited. The collimators are used for improving resolution. A crucial role is played by the analyzer crystals. They break down the multiple-frequency fluorescence spectra into the specific wavelengths for the elements. This signal separation is crucial for the outstanding resolution and sensitivity of WDXRF. For the detection of light elements a proportional counter and for the heavier elements a scintillation counter is used. Both detectors are perfectly suited to the respective energy range. Automatically and quickly these parameters are adjusted to achieve the maximum analytical performance regarding the precision and detection limit.

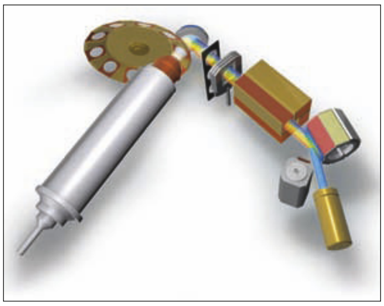

Fig. 3 Analytical flexibility: Instrumental setup of sequential wavelength dispersive X-ray fluorescence spectrometers

3 Precision and analytical speed of WDXRF

Ensuring highest precision on results in combination with high analytical speed seems to be magic for a sequential WDXRF instrument. Several drives for the crystals, detectors, collimators must be adjusted at the same time quickly and precisely.

The influence of changing temperatures must be suppressed, otherwise e.g. the expansion of traditional analyzer crystals will cause differences in intensity, and last but not least the sample positioning must be very accurate ensuring the same tube to sample distance every time a sample is

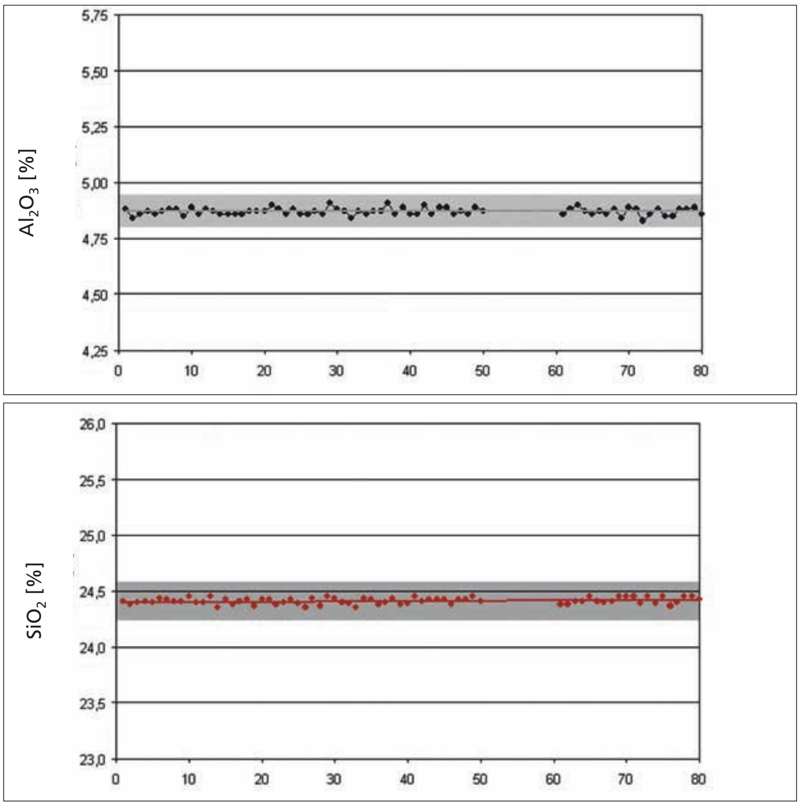

Fig. 4 Precision trial for Al_2O_3 and SiO_2 for a raw material

Fig. 5 Simple operation of analytical instruments by new software and operation concepts – shown TouchControl

placed in the chamber. This is under tough conditions e.g. in tropical countries not an easy task.

Finally the latest development for analyzer crystals is solving major issues with long term stability, especially for the critical elements like aluminum and silicon. Traditionally analyzed using an organic PET analyzer crystal users know about the loss of intensity by time with aging of the crystal. Additionally the long time for thermal stabilization after each service intervention causing a delay typically of several hours after the instrument is started again. This is overcome with new analyzer X-ray optics based on multilayer technology. New multilayer crystals, like the XS-CEM answer these questions and make the WDXRF spectrometers independent from thermal influences and resistant against X-rays, air and oxidation – ensuring a stable sensitivity over the lifetime of the instrument.

The result of a precision study for Al_2O_3 and SiO_2 is shown in Fig 4 the intensities are recorded with the XS-CEM with a seq. WDXRF instrument.

The clear benefit for the use in ceramic production plants is time: less time need for drift correction measurements, less time-out periods during service and maintenance interventions.

Finally the better analytical precision allows a closer control of the elemental composition of the ceramic products.

4 Reliability and robustness

During 24 h, 7 d a week, 365 d a year a WDXRF instrument is used to analyze samples, mainly prepared as pressed powders. This means that in some plants more than 150 000 samples a year are analyzed. There is no doubt that it is only a matter of time that particles from the sample will fall on the X-ray tube or into the goniometer damaging the sensitive drives and optical components. The solution to prevent these damages and ensuring the same quality of results without interruption is to protect the sensitive components efficiently. With the S8 TIGER e.g. during loading and unloading of samples two metal contamination shields are moved in front of the goniometer entrance and the X-ray tube. Released particles will fall down and are collected safely without harm to the spectrometer in the dust reservoir.

A dust sealed instrument cabinet, the secondary water circuit to buffer short fluctuations and interruptions in cooling water supply, self diagnosis capability of the instrument firmware and powerful instrument tools as well as the online remote diagnosis connection to the service centers are the next important factors for unrivalled instrument uptime of the sequential wavelength dispersive X-ray fluorescence spectrometers.

5 The same analytical quality – worldwide

Only WDX systems can reach the demands on accuracy that is necessary to get high quality products. How do they ensure that all the devices deliver the same analysis results?

X-ray spectrometry is a relative method; the spectrometer itself only supplies intensities of the characteristic X-ray lines. Calibration with test specimens of known composition ("standard specimens") then allows the concentrations to be determined. The same results on different equipment?

Why not simply measure the same standard specimens on all the spectrometers installed at production site? That sounds simple, but with different locations worldwide that would mean parallel working, a large number of identical sets of specimens or the specimens would have to spend a lot of time travelling. In cooperation with RHI and Kerneos Bruker AXS has therefore perfected a much more simple method: A single system sets the tone – the master spectrometer in the technical center. All standard specimens are calibrated centrally on the master spectrometer and then transferred to the "daughter" spectrometers worldwide – pure CAQ (computer aided quality control). What does that mean in practice? A specialist carries out the central calibration on the master spectrometer with a large number of specimens. This calibration is easily transferred to all the daughter devices with the help of a few reference specimens. This ensures that the same results are achieved with the same accuracy overall. The testing equipment, including the X-ray spectrometers, is monitored constantly and if necessary, any intensity drift is corrected, which takes into account the aging of the instrument, for example. This drift correction is based on worldwide identical sets of reference specimens and ensures that the results agree over longer periods. Industrial users say, the ease with which the clear structure and the flexibility of recent software packages, like SPECTRAplus, allows the integration of X-ray spectrometers in quality management systems is unrivalled. Almost all the parameters can be replaced and shared. Each daughter spectrometer can receive calibrations from the master instrument easily and quickly. This ensures that absolutely identical analytical results can be achieved with all the spectrometers – whether they are in Europe, South America or China. To guarantee the same high quality on a permanent basis the same standard has to be applied on every production site. Fig 5 is showing the simple operation of today WDXRF instrumentation.

6 Conclusions

The direct feedback of analytical results on the process and quality is important for the high quality and cost effective production of refractories. The sequential wavelength dispersive X-ray spectrometers available today, like the S8 TIGER of Bruker AXS, offer analytical performance, reliability and flexibility in combination with unrivalled ease of use, especially regarding simple sample preparation. This overall performance is making these spectrometers the perfect analytical tool for the industry. Clever solutions, like the centralized calibration approach, so setting a new standard to support users establishing the same high analytical quality control all over the world. A worldwide acting company must guarantee its customers consistently high quality on a permanent basis. This idea can only be implemented if one standard is applied worldwide. On this note: one for all!