ONLINE X-RAY ELEMENTAL ANALYSIS OF ORE AND OTHER BULKY MATERIALS

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Abstract

Online elemental Analysis directly at the material stream or at a bypass is enabled by a modified X-ray fluorescence technology. These analysers were originally used to determine the quality parameters of coal only: Proximate analysis and ash fusion as well as specific elements of the coal, including trace elements such as arsenic and mercury. In the meantime, this technology is applied to a large variety of materials to determine their constituents such as in ore and cement and in intermediates such as sinter mixtures, raw mix or converter dust.

Introduction

Indutech started in 1997 to develop an online elemental analyzer based on the X-ray fluorescence (XRF) technology. The analyzer is based on the energy-dispersive XRF technology, which is well known for laboratory devices. Material irradiated by X-rays is ionized: Electrons of the inner shell of the atom are extracted. Electrons of the outer shells fill the created gaps. Caused by this event a photon is emitted with an energy, which is characteristic for the emitting element. Energy-dispersive X-ray spectroscopy determines the energy of each photon and counts these events. The spectrum is obtained by plotting the number of events over the energy. This spectrum can be divided into background and characteristic lines. The intensity of a line, i.e. the peak area, is a measure for the concentration of the respective element. When determining the concentration, however, one has to take into account that characteristic photons may interact with other elements nearby. This interaction is called matrix effect, which can be compensated for by mathematical means. The characteristic energy of the atoms is in the low keV range. The atoms with a low atomic number emit photons with such low energies, that the absorption through the necessary windows and the air becomes large and therefore these elements cannot be measured with XRF. To reduce this effect, laboratory devices work with vacuum chambers, which allow to measure down to Boron with an atomic number of 5. Because of these low energies, only the surface is measured with XRF techniques, which must be representative for the whole material. For laboratory XRF measurements, an extensive sample preparation is necessary. The material is ground down in the µ-range and the powder is pressed to pills. XRF analyzers were used for process control, especially in the cement industry, but here usually modified laboratory devices were used and the samples were prepared automatically.

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Online X-ray Elemental Analysis

Indutech uses the energy-dispersive XRF method in a modified form. The patented technology of Indutech´s Online X-ray Elemental Analyzer OXEA® allows measurements at bulky material with a particle size of up to 10 - 50 mm, depending on the particle size distribution. Elements with an atomic number Z > 10 can be measured.

The technology was continuously improved. This results in the following features:

- excellent energy resolution and spectra quality.
- excellent detection limit and accuracy for low elements such as sodium and magnesium and for trace elements
- matrix compensation to achieve an excellent long-time stability of the calibration
- the Partial Least Square (PLS) regression method to simplify the calibration.
- a new XRF-based method for the ash determination to improve accuracy and long-term stability.

In the meantime further models of the OXEA® line are available, which allow online measurements of material with a particle size of up to 100 mm.

Measuring Setup

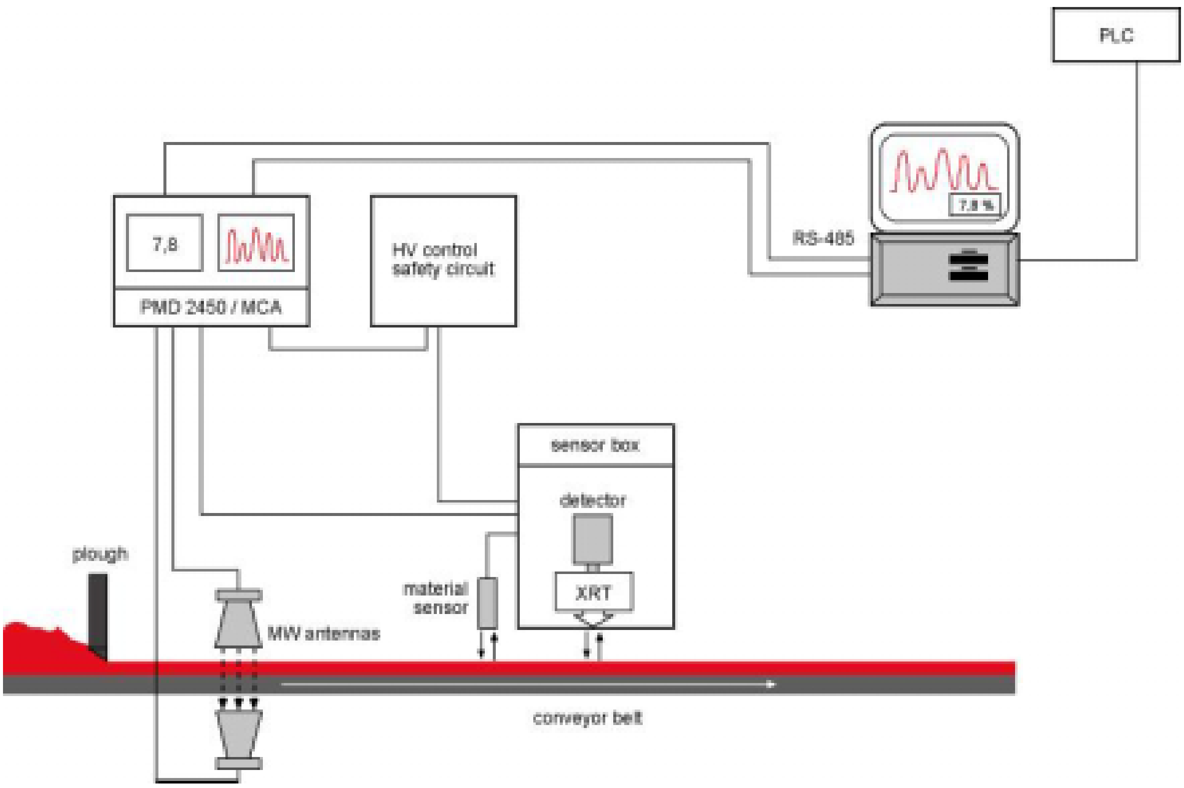

Fig. 1: Measuring principle of the OXEA®1000-line

The models of the OXEA® 1000-line are installed at a bypass belt or at the main belt. In Fig. 1, the measuring principle of the OXEA® 1000 line is shown as bypass installation. The plough generates a constant layer thickness and a flat surface. The Sensor Unit with X-ray tube and detector is installed over the conveyor belt. In the High Voltage Supply Box, the High Voltage for the X-ray tube is generated. Here the safety circuits are housed and the routing of several signals is located here. The detector signal is connected to the Multi-Channel Analyzer MCA. The material sensor detects the presence of material. If the belt is empty, the measurement is interrupted and with the patented electronic shutter, the X-ray tube is switched down in a safe state. The lifetime of the X-ray tube is hereby not reduced. Because the material is continuously moving, a large amount of material is measured, which enables a representative measurement without a sophisticated sample preparation. The microwave moisture meter PMD 2450 of Indutech is installed optionally. The output signals of the PMD 2450 and the MCA are connected to the PC over a serial interface). The PC can be connected to the PLC over Modbus, Profibus etc. to transfer the final results. Fig. 2 shows an OXEA® 3000 at a bypass belt.

Fig. 2: OXEA® at a bypass belt

To install the OXEA® at the main belt, it must be taken in account, that the load on the belt is not constant. To get a constant distance between the sensor and the material surface, the analyzer must automatically adjust its position, i.e. the sensor cannot be installed in a fixed position over the belt. A solution is the use of a sled. Fig. 3 shows an OXEA® 3000 installed at the main belt on a Sled. The sled is hanging on four supporting arms of the same length attached to the mounting frame. The supporting arms are hinged at both sides, the sled and the mounting frame. Hereby the sled is variable in the height and enforced to be parallel to the mounting frame and with proper alignment also parallel to the belt. If the belt is empty, the sled hangs above the belt, so the sled will never touch and damage the belt. The use of sleds is very popular to install sensors, which must be in contact with the material or which must have a constant distance to the surface of the material. The first time the author used such a sled was in 1979 to install a microwave resonator moisture meter on a conveyor belt. Sleds are available in different sizes.

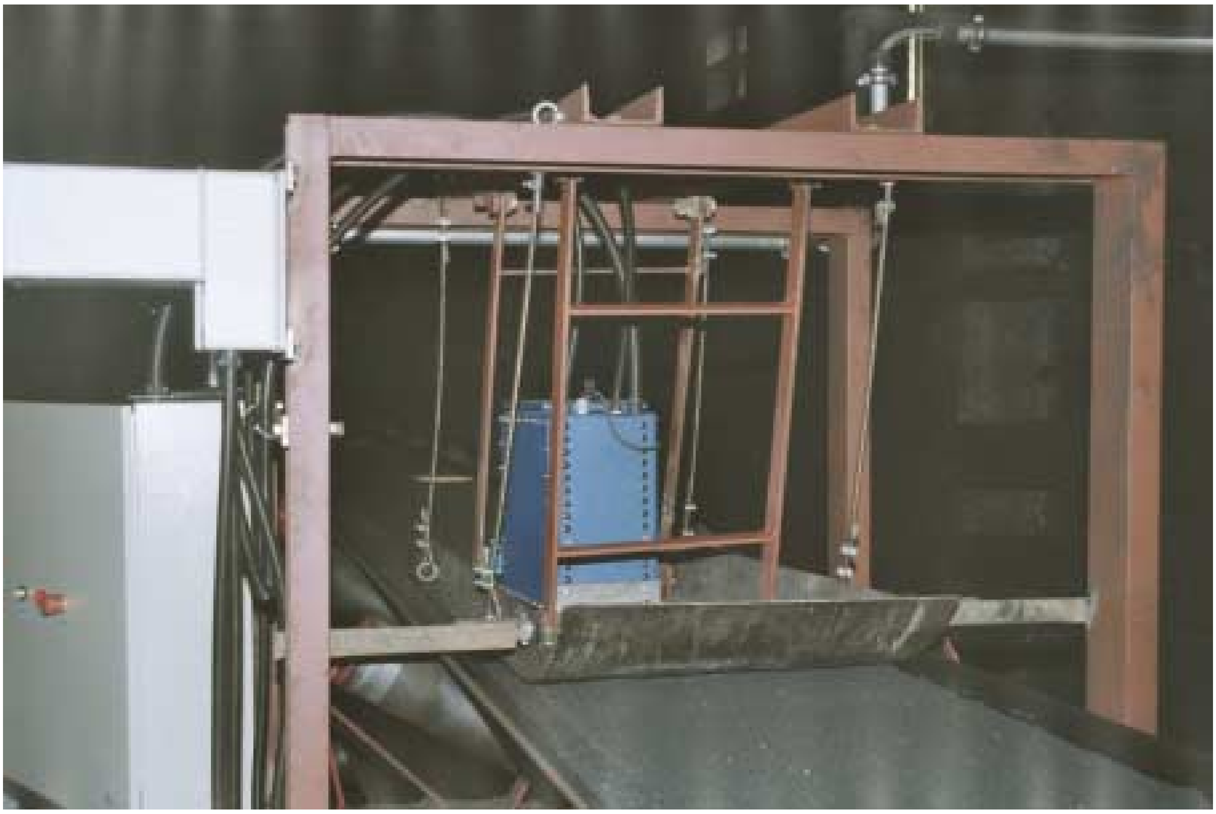

Fig. 3: OXEA® 3000 installed on a sled in a coking plant to determine the volatiles of the blended coal

Applications

Analysis of Magnesite ore

The magnesite ore is a raw material for the refractory industry. Therefore, impurities, which reduce the heat-resistance of the material, decrease the quality of the material. Especially Silicon must therefore be traced. An OXEA 3000® was installed at a bypass belt. The installation is shown in figure 2. The concentration of silicon is in the range 0-2% only. To improve the limit of detection and the accuracy of the system a Helium Flush was installed. Hereby the Si-peak is increased by a factor of about 2. Fig. 4 shows the spectrum. Because of the high resolution of the detector, all elements are detected without overlap, which makes the evaluation of the spectrum easy.

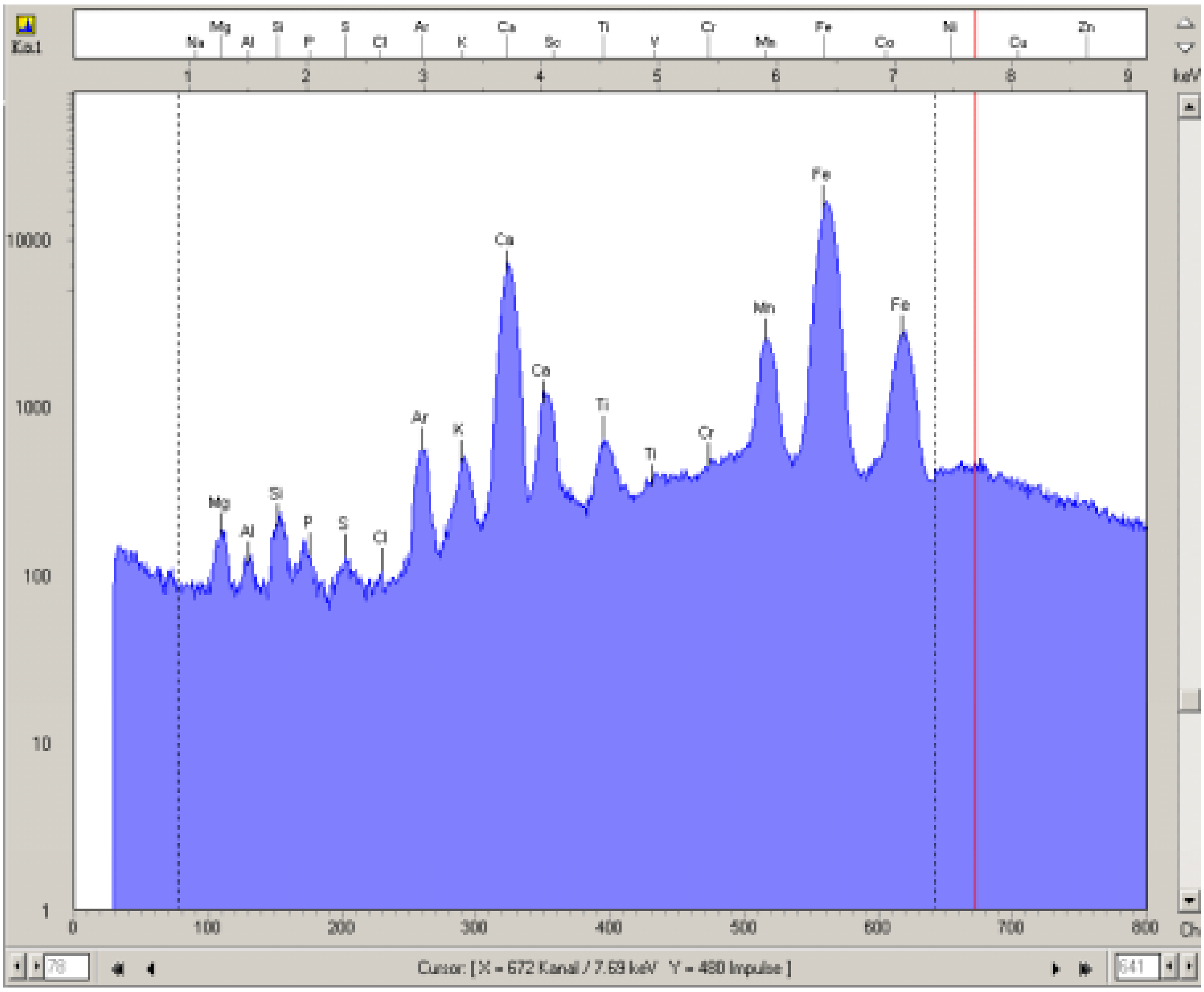

Fig. 4: Typical Spectrum of magnesite ore

The result of the Silicon calibration is shown in Fig. 5. The standard deviation is 0,073 wt.-% with a correlation coefficient of 0,986. Of course, further elements are evaluated too: Al, Ca, Ti, Mn and Fe.

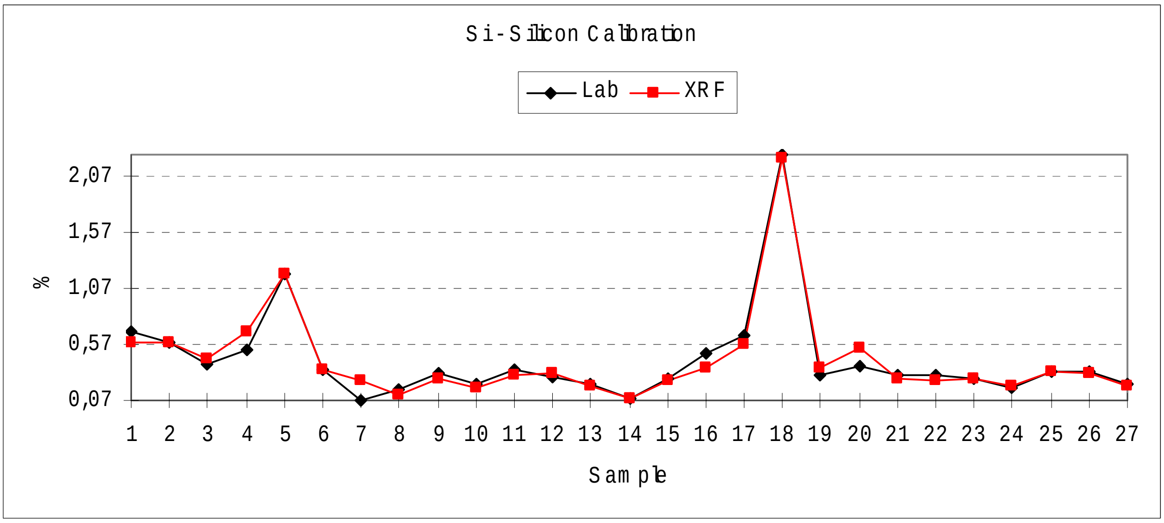

Fig. 5: Calibration of silicon in magnesite ore

The analyzer allows optimizing the classification of the material in different qualities. Hereby the quality of the product is improved and the amount of the higher qualities, which are sold at a higher price, is increased. The investment for the analyzer is amortized within shortest time.

Basicity of iron ore sinter mixture

The basicity of the iron ore sinter mixture is an important parameter for a proper function of the blast furnace. The basicity B4 is the ratio of the concentration of the basic and the acid elements:

$$B4 = \frac{CaO + MgO}{SiO_2 + Al_2O_3} \qquad (1)$$

Fig. 6 shows the installation of the sensor unit on the sled. The microwave horn antenna of the moisture meter is visible in the background. To calibrate the system, samples were manually taken from the running belt over a period of 3 minutes per sample. To calculate the B4 value, the 4 elements Mg, Al, Si and Ca must be measured. Additionally Manganese and iron are determined. Most critical is the measurement of Mg, because in general with XRF elements with such a low atomic number are difficult to measure. Fig. 7 shows the calibration of Mg as the element, which is most difficult to measure. Additionally the prediction according the “one leave out” method is determined to verify, that the calibration is stable. Fig. 8 shows the tracking plot for the B4-value.

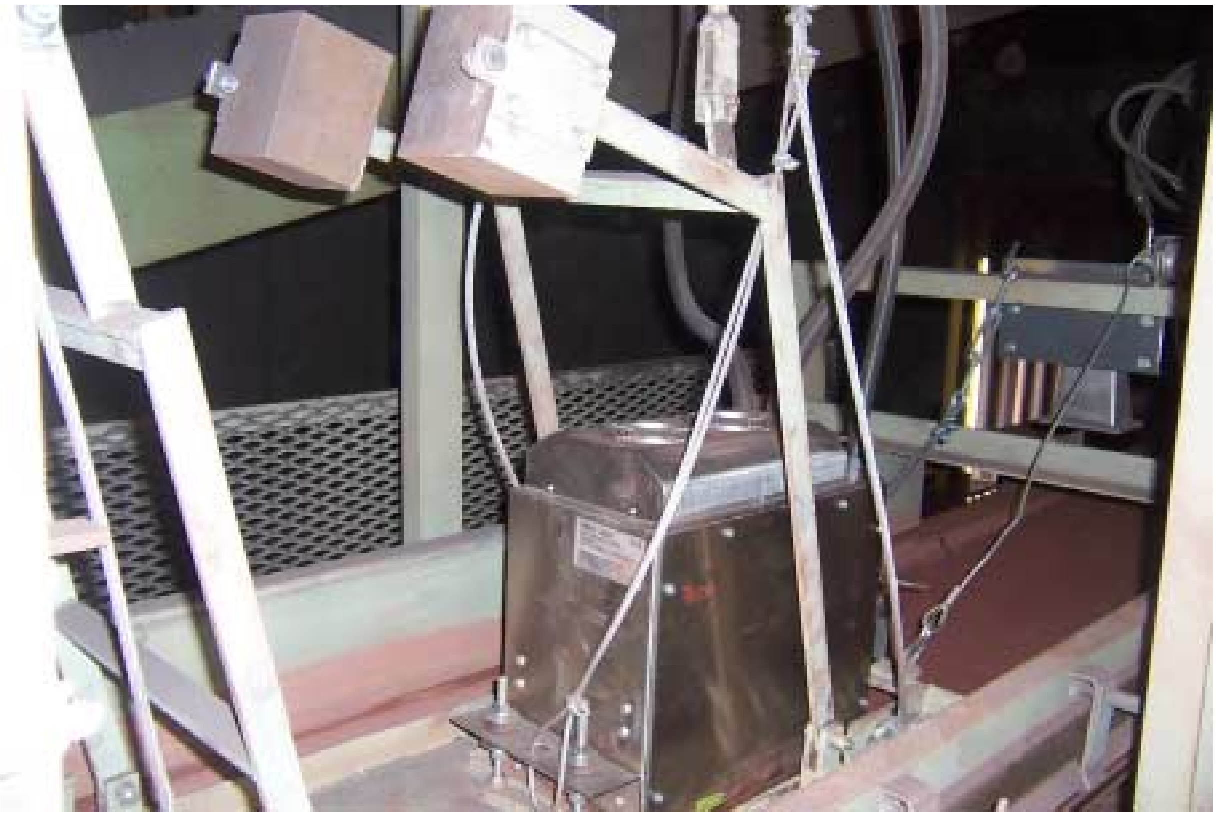

Fig. 6: Sled at the belt with sinter mixture

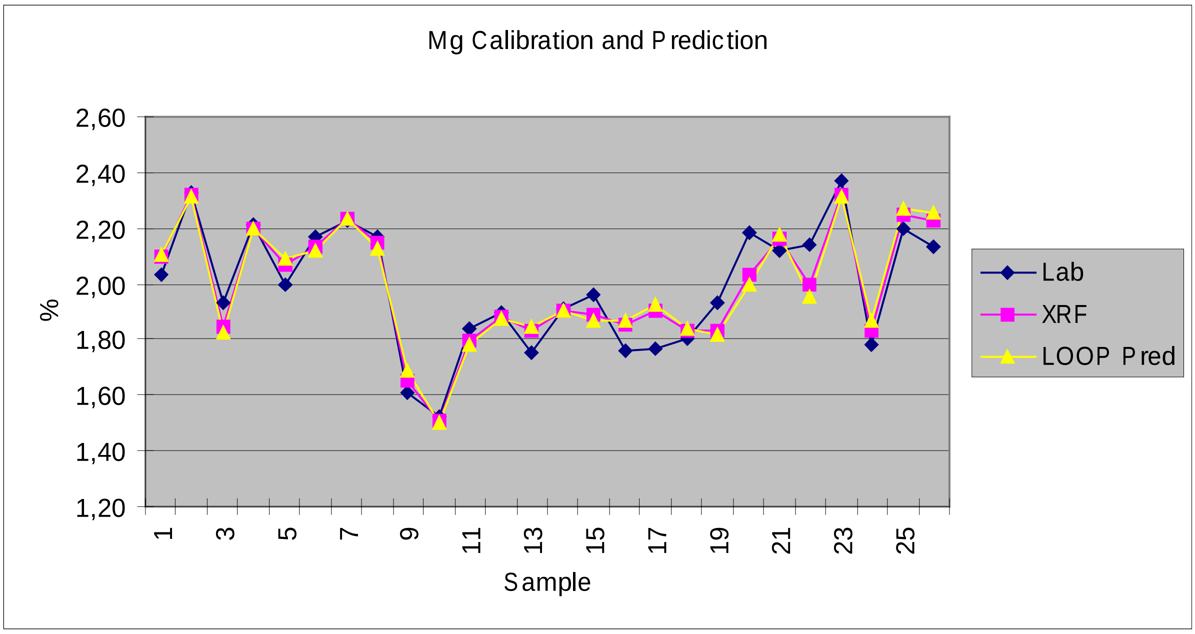

Fig. 7: Magnesite calibration and prediction of the sinter mixture

This installation and these tests were performed within a research project, which should compare OXEA® 3000 with a PGNAA analyzer. However, this comparison was not possible, because the supplier did not deliver the PGNAA analyzer.

The maximal particle size is less than 10 mm, which is excellent for a sled application. Agglomeration lumps with a diameter of up to 20 cm generated problems; however, these were solved by special scrapers.

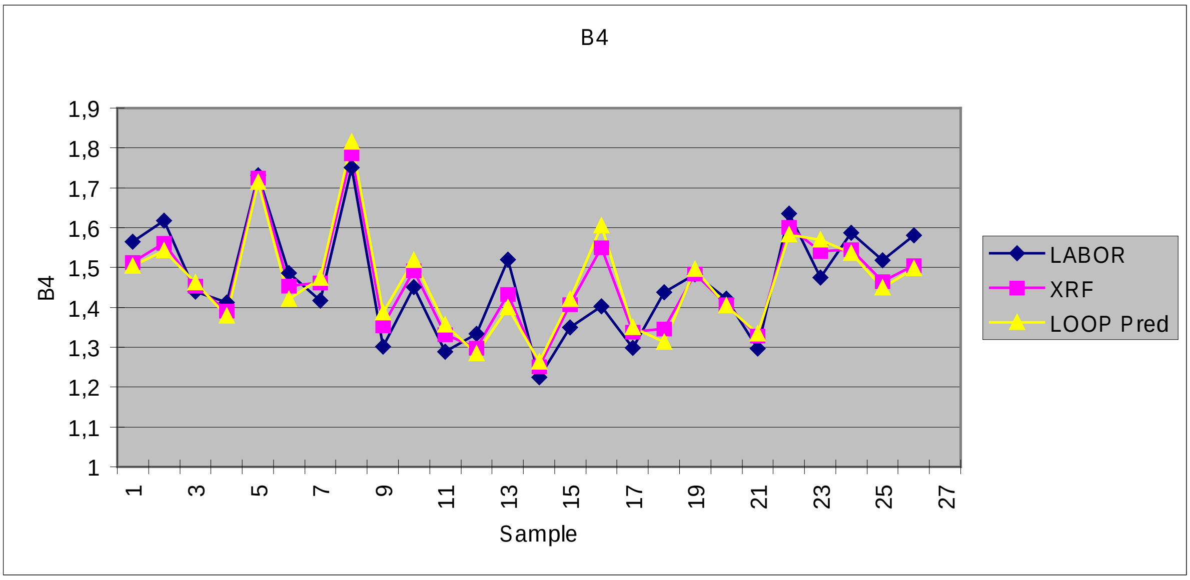

Fig. 8: B4 calibration and prediction of the Sinter mixture

Now the availability of the system is very high and the system is running under 24 hours / 7 days conditions. In the meantime, the test of OXEA® within the research project is successfully completed. The OXEA® 3000 is approved and the signal of the analyzer controls the blending of the sinter mixture in a closed loop.

Zinc measurement of converter dust

The dust, which is produced by the converter process of a steel plant, contains mainly iron, zinc and calcium. The zinc enters the process by zinc coated parts of the scrap in the furnace. If the zinc disturbs the furnace process, the material must be recycled. Depending on the zinc content different recycling methods must be applied. To select the proper recycling method it is necessary to measure the zinc content of the converter dust continuously. In the following, an online analyzer is described to determine the zinc content of the converter dust.

Fig. 9 shows the installation of the online zinc measurement. The material of several electrostatic filters is falling down in an oblique chute. A part of the material is collected by a turntable, which transports the material under the analyzer. A scraper is mounted before the analyzer, in order to produce a layer of constant thickness. After the measurement, a second scraper cleans the table. The material, which is removed from the turntable falls into a conveyor screw, which transports the material back to the main stream. The whole system is installed in a nitrogen atmosphere, because the unreduced iron and zinc would immediately burn in the presence of oxygen. The material temperature is up to 350°C. Furthermore, the turntable chamber is very dusty. Sophisticated engineering is required to manage the problems generated by these installation conditions. The project was performed in cooperation with the IfG Institute for Scientific instruments.

Fig. 9: Online Zinc measurement of converter dust

Before the OXEA analyzer was installed, the zinc measurement was carried out by a Libs (Laser induced burst Spectroscopy) Analyzer. Because of the high maintenance costs, Indutech was asked to replace the Libs-system by an XRF analyzer. As first step, an XRF system was installed parallel to the Libs Analyzer in 2004.

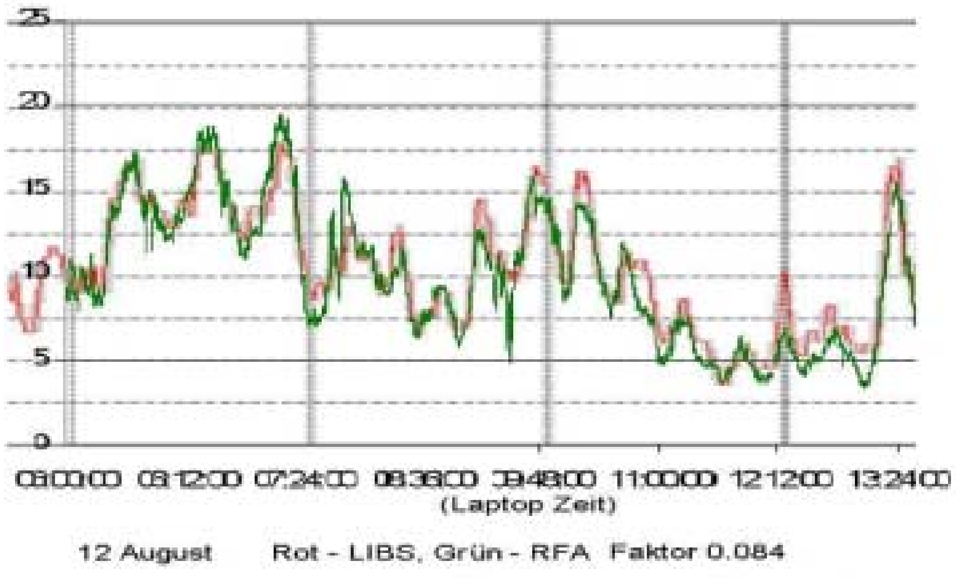

Fig. 10: Comparison of Libs- and XRF- analyzer

Fig. 10 shows, that the XRF-analyzer (green and the Libs-analyzer (red) are running very synchronously. After this successful test, the online analyzer was installed in 2005/2006.

From the experience with Libs, it was known that the material is very inhomogeneous. Therefore, it is nearly impossible to get representative samples from the running material stream. Therefore, the

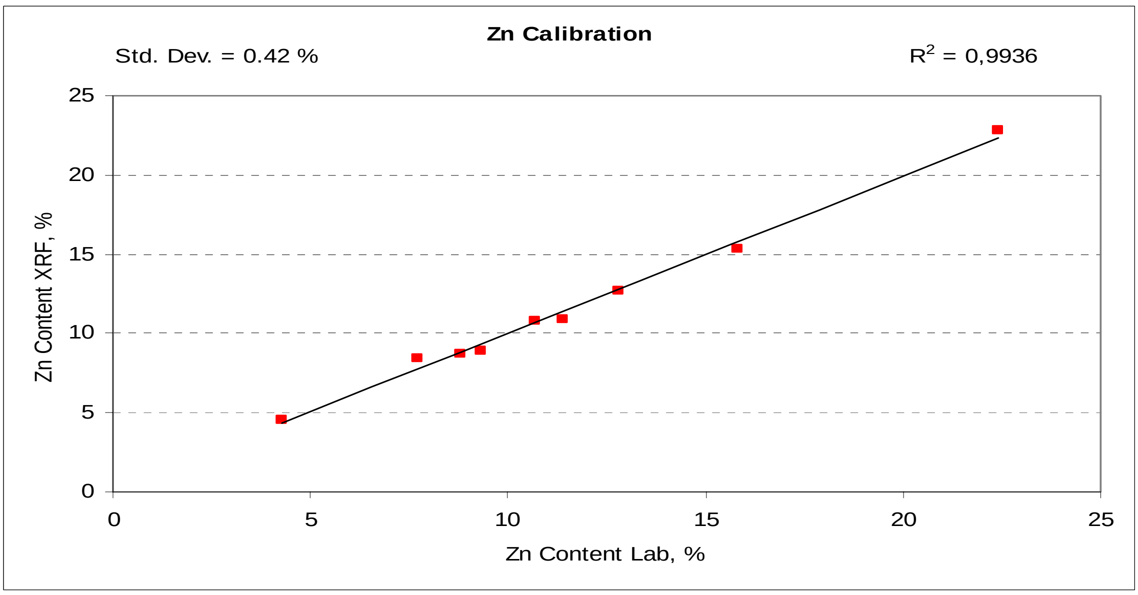

Fig. 11: Zinc Calibration for the OXEA 3000 at converter dust.

turntable is equipped with a lock, which allows to place pressed tablets under the analyzer. In one step three tablets can be measured. It was found, that, in spite of the strong density difference between the dust and the tablets these measurements can be used for calibration. Fig 11 shows the high performance of the calibration with the tablets.

The Analyzer is connected to the PLC via a Profibus signal. The system is in use since February 2006. Since July 2006 the system is running in a closed loop to control the sorting of the converter dust in three classes depending on the zinc content.

Conclusion

Online X-ray elemental analysis is an ideal method to determine the constituents of materials. In all examples the accuracy availability and reliability of the analyzer is high enough to control the process in a closed loop. A large range of different applications is possible. In all cases, the customer calculated the amortization period of the analyzer: In general, the amortization period is noticeable shorter than 3 years, in some cases a few months only. This underlines the benefit of the OXEA® analyzer.