ONLINE X-RAY ELEMENTAL ANALYSIS OF COAL AND BULKY MINERALS

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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. This type of analysers was in the beginning only used to determine the quality parameters of coal: ash and sulphur content and in combination with a moisture meter the calorific value, volatiles as well as specific elements of the coal including trace elements as arsenic and mercury. In the meantime this technology is applied to a large variety of materials to determine their constituents as ore and cement and intermediates as sinter mixtures, raw mix or converter dust. Three application examples are presented.

Introduction

Indutech started in 1997 to develop an online coal analyzer based on the X-ray fluorescence (XRF) technology. The main topic was in the beginning to determine the ash- and sulfur content of coal.

At that time nuclear methods based on the dependence of the absorption coefficient of soft gamma rays were mainly used for ash determination. Transmission types (dual or triple energy) or backscatter types were used. With these methods the average atomic number of the material is measured. Because the elements, which appear in the coal, have a lower atomic number than the elements in the ash, such a system can be calibrated in ash content. However, this method is influenced by changes of the elemental composition of the ash, because hereby the average atomic number is changed in spite of a constant ash content. Especially a varying Iron and Calcium content is disturbing. E.g. a 1% change of the Iron content in the product disturbs the reading of the ash meter by about 8%. Also the natural gamma radiation is used, which correlates in some extent with the ash content. Here it is assumed, that the concentration of nuclear isotopes in the ash are constant. This is not always a valid assumption and therefore in some cases this method fails too. Of course, these methods determine the ash content only, not the sulphur content.

Contrary to these methods the PGNAA method allows to determine the complete elemental composition of the measured material. With the PGNAA method the nuclei of the atoms in the material are excited by fast neutrons, which are generated by a Californium source or by a neutron tube. The excited nuclei emit a

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characteristic gamma radiation, which lies in the MeV-range. Because of these high energies, the PGNAA method covers a large volume. Normally the available volume is smaller than the saturation volume. Therefore the measurement must be carried out on a bypass, where the volume is kept constant, or must be compensated for the varying volume. Furthermore, the material should be homogeneous, because material close to the detector has a higher measuring effect, than deeper layers. A compensation of this effect is difficult, especially, if the percentage of the different materials is varying. Also matrix effects occur with the PGNAA method and must be compensated. The volatile matter content and the calorific value can be determined only through modelling, since in both cases the chemical bond plays a decisive role, which cannot be determined by the PGNAA method. The half-life time of the mainly used californium source. is about 2 years. The source has to be renewed or refreshed within such a period. Therefore, the operating costs are rather high. The shielding effort is quite substantial as a result of the high energies and two different types of radiation. The approval procedure is therefore complex and time consuming too.

In addition to these analyzers Indutech developed an online Ash and Sulphur Analyzer 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. The created gaps are filled by electrons of the outer shells. 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 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 be 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 of 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 grinded down in the µ-range and the powder is pressed to pills. XRF analyzer were used for process control, especially in the cement industry, but here usually modified laboratory devices are used and the samples were prepared automatically.

Online X-ray Elemental Analysis

Indutech use 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 - 20 mm, depending on the particle size distribution. Elements with an atomic number $Z > 10$ can be measured. The short proximate analysis is carried out in large number of applications. In the meantime the volatile matter content and the complete elemental analysis of the ash including trace elements can be

determined. Based on this experience a method of type recognition was developed, which allows to distinguish between coal and other materials, as coke slag or petrol-coke. This method allows yet to distinguish between coal of different origin. This feature is requested especially by coking plants .

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. as sodium and magnesium and for trace elements
- matrix compensation to get an excellent longtime 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.

Since 2004 Indutech has started to expand the XRF technology to non-coal applications. In the meantime further models of the OXEA® line are available, which allow online measurements of material with a particle size of up to 50-80 mm.

Measuring Setup

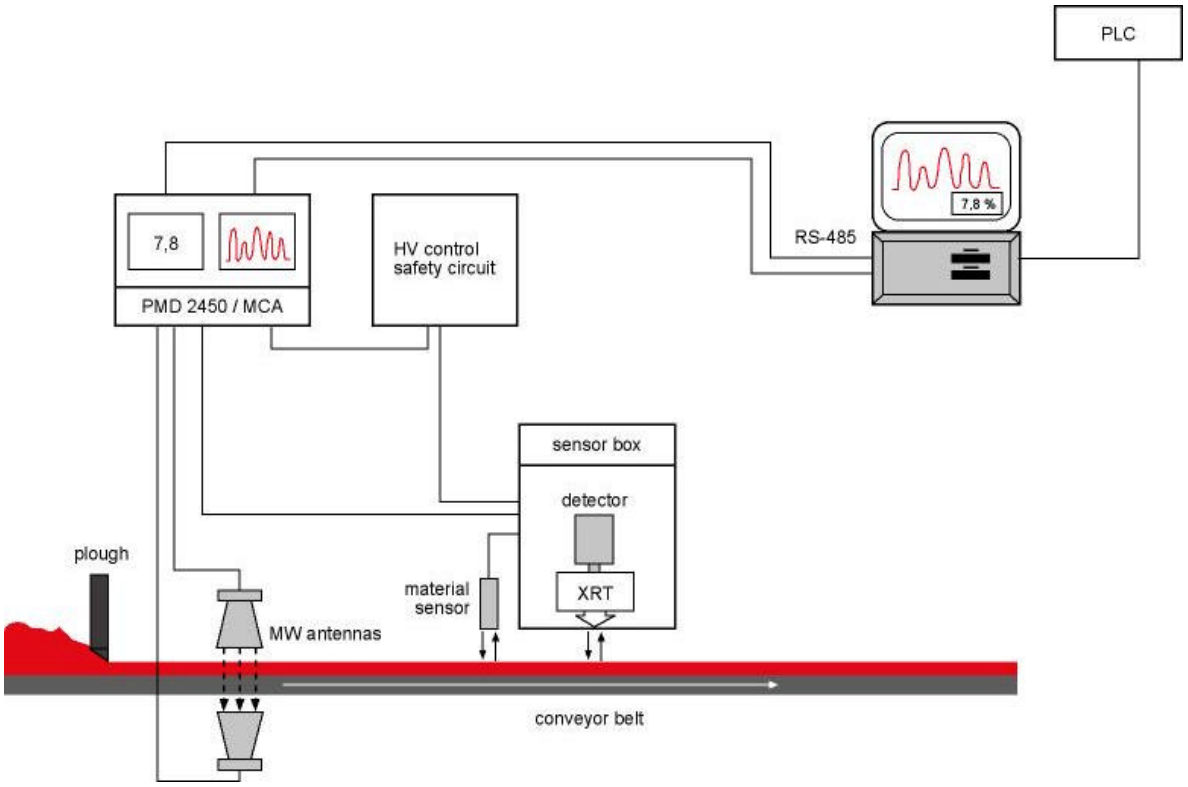

Fig. 1: Measuring principle of the OXEA®1000-line

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 flatten 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 also the safety circuits and the routing of several signals are done. The detector signal is connected to the Multi-Channel Analyzer MCA. The presence of material is detected by the material sensor. If the belt is empty, the measurement is interrupted and with the patented electronic shutter, the X-ray tube is switched off/down. 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.

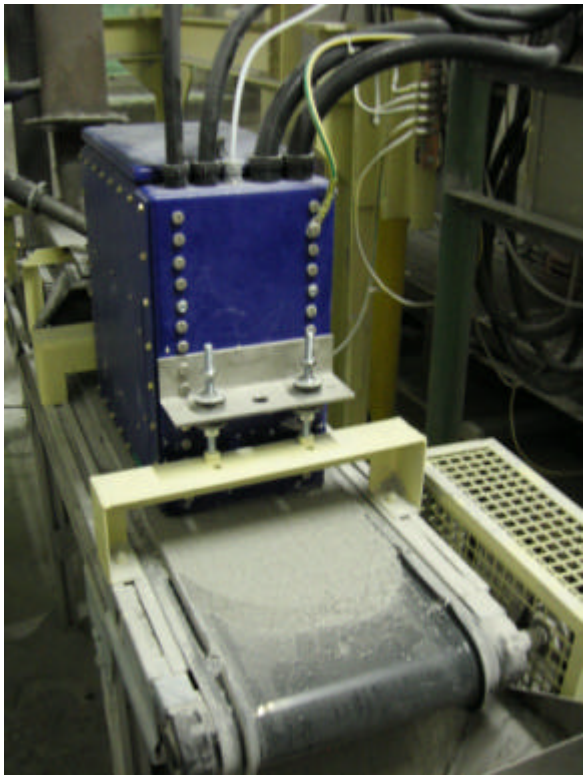

Fig. 2: OXEA® at a bypass belt

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 be automatically varying in 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 at four supporting arms of the same length at the mounting frame. The supporting ams 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 is hanging 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 use of such a sled by the author was in 1979 to install a microwave resonator moisture meter. Sleds in different sizes are available.

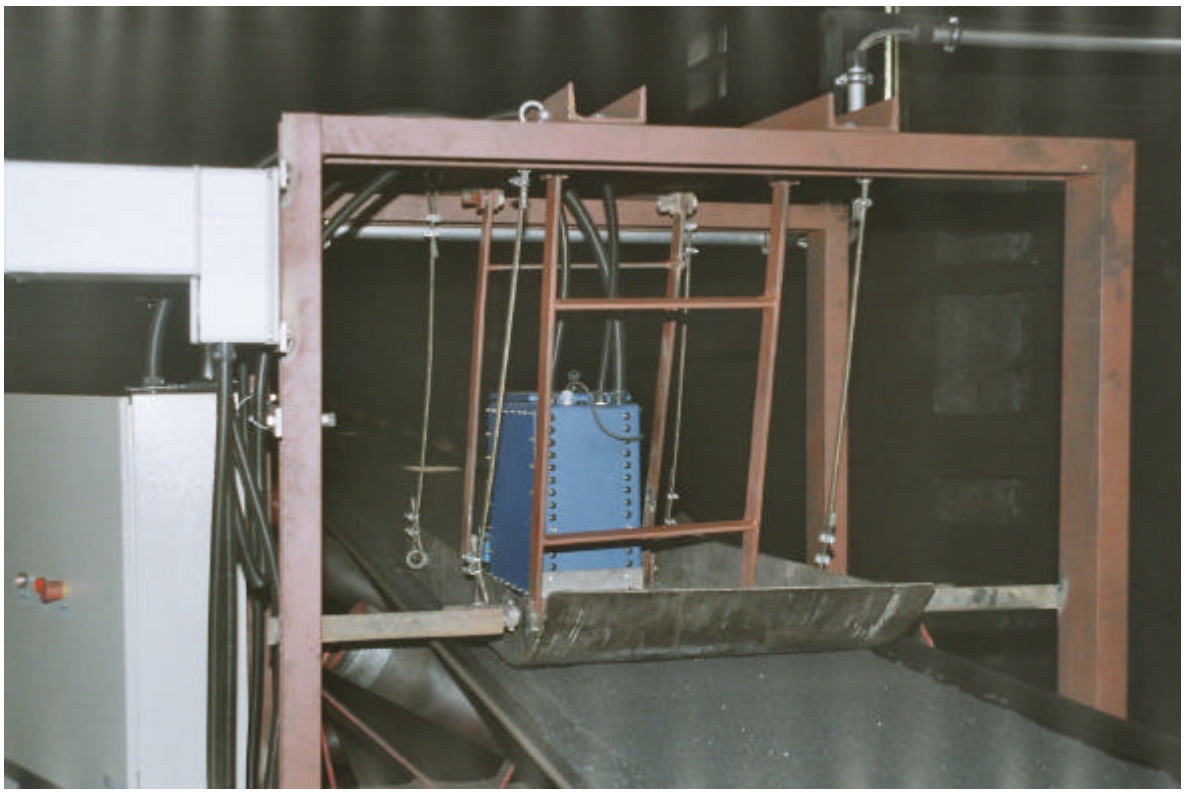

Fig.3: OXEA ® 3000 installed on a sled in a coking plant to determine the volatiles of the blended coal

Applications

Coking Plant

Indutech was contacted by a coking plant with the question, if in addition to the short proximate analysis also the volatiles can be determined for the thermal control of the coking ovens. Intensive investigations in Indutech´s laboratories were carried out at over 100 samples. It could be shown, that the information taken by XRF measurements is sufficient to develop a model for describing the volatiles, which is accurate enough to control the gas fuel requirement of the coking process.

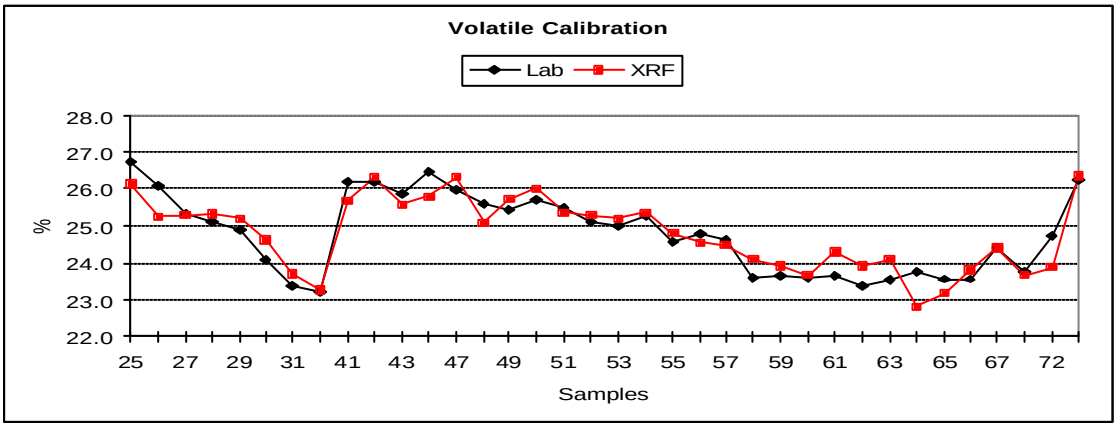

Fig. 4: Tracking plot of the volatiles

Based on these results OXEA® was installed in the plant.. The analyzer, shown in Fig. 3 is installed on a sled at the belt with the blended and mixed coal. A preparation of the material stream enables a smooth sliding of the sled. The load is 300 t/h, the time of operation is 18 h/day and the belt speed is 2.3 m/s. The particle size is less than 10 mm. After the installation samples were taken for the calibration. As example the calibration of the volatiles is given in Fig.4. Table 1 shows the obtained accuracy of the most important measured parameters.

	Corralation	Std. Deviation
Ash	0,826	0,192 wt.-%
Volatiles	0,950	0,475 wt.-%
Bulk density	0,899	0,0054 g/m³
Sulphur	0,866	0,019 Wt.-%

Tab.1: Results of the online calibration

The calibrated analyzer was observed by the R&D group of the plant.. During this final test period the signals of the analyzer were transferred to the PLC of the coking plant and visualized in the control room. The OXEA® worked absolutely stable. Consequently the volatile readings were switched in a closed loop to control the gas fuel consumption of the coking oven. The analyzer is now running satisfactorily since last 4 years. The model for the volatiles was approved as robust.

The online analysis has big advantages for controlling the coking process. With OXEA® the volatiles can continuously be monitored. The desired final temperature of the coke can be achieved with a low deviation, because the required gas fuel can be calculated more exactly. Furthermore impurities as ore can be recognized and a reaction is possible to avoid the production of a low quality coke.

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. 5 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 each sample. To calculate the B4 value, the 4 elements Mg, Al, Si and Ca must be measured. Additionally Manganese and iron is 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. 6 shows the calibration of magnesite as the element, which is most difficult to measure. Additionally the prediction according the one leaf out method is determined to verify, that the calibration is stable. Fig. 7 shows the tracking plot for the B4-value.

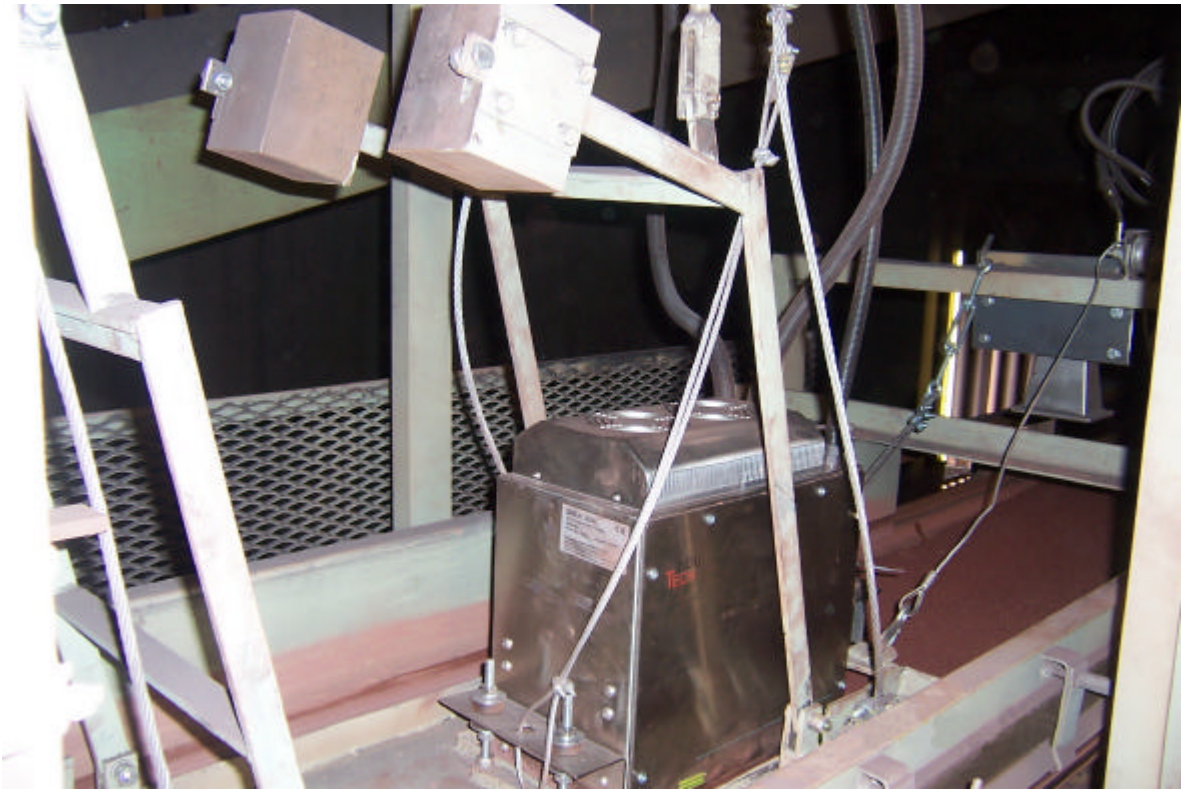

Fig. 5: Sled at the belt with sinter mixture

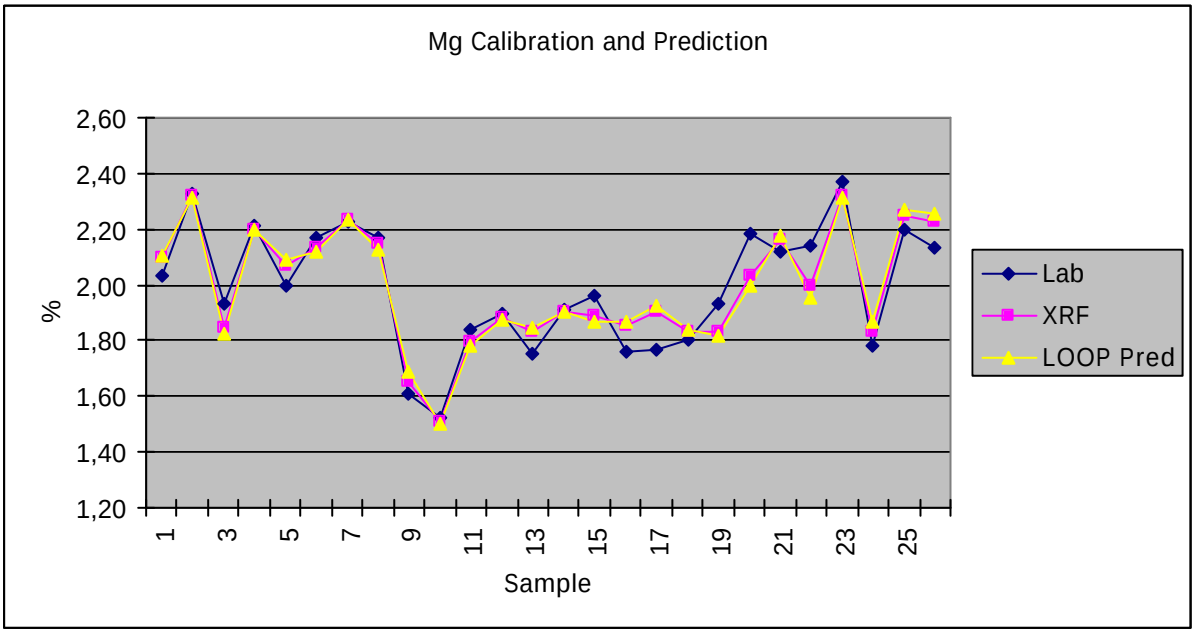

Fig.6: Magnesite calibration and prediction of the sinter mixture

This installation and these tests were performed with a research project. The sled is of course the easiest way to install the analyzer, but for an continuous use a bypass installation is to be prefered. The maximal particle size is less than 10 mm, which is good for a sled application, but because of agglomeration sometimes there are lumps with a diameter of up to 20 cm, which generate problems. Therefore the sled

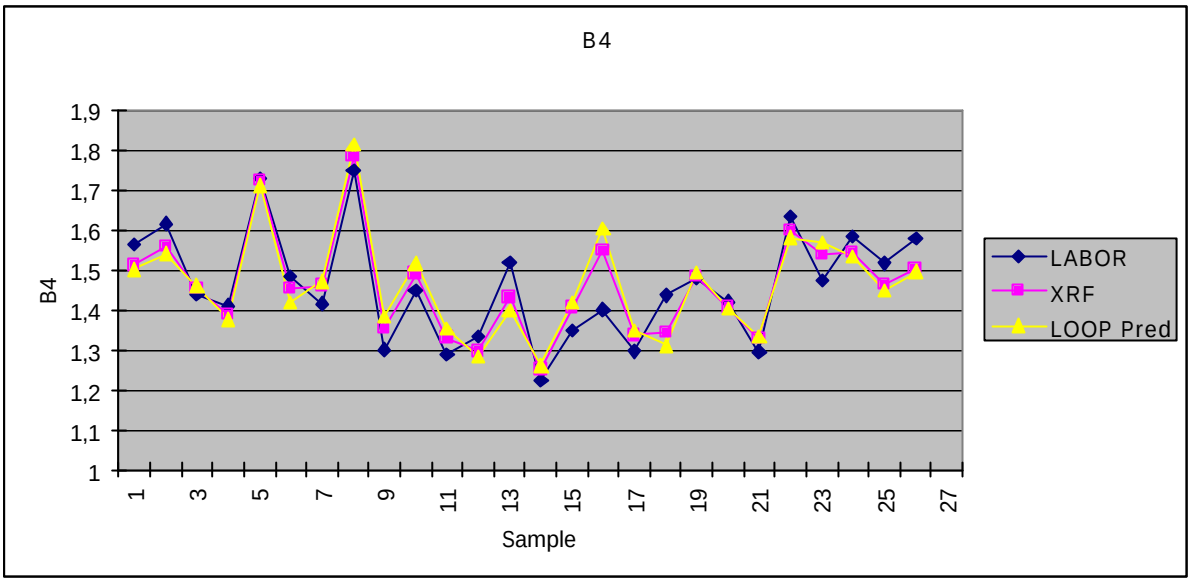

Fig.7: B4 calibration and prediction of the Sinter mixture

was in use only under observation. The preparation of the material stream was improved recently and now the availability of the system is tested under 24 hours / 7 days conditions. If the availability of these mechanical problems is to low, it is planned to install at a bypass belt for the analyzer.

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 comes into 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. 8 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. Before the analyzer is a scraper, which produce a layer of constant thickness. After the measurement the table is cleaned by a second scraper. The material, which is removed from the turntable falls in a conveyor screw, which transports the material back to the main stream. The whole system is under nitrogen atmosphere, because the unreduced iron and zinc will burn in the presence of oxygen immediately. The material temperature is up to 350°C. Furthermore the turntable chamber is very dusty. A sophisticated engineering is needed to manage the problems generated by these installation conditions. The project was performed in cooperation with the IfG Institute for Scientific instruments.

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 8: Online Zinc measurement of converter dust

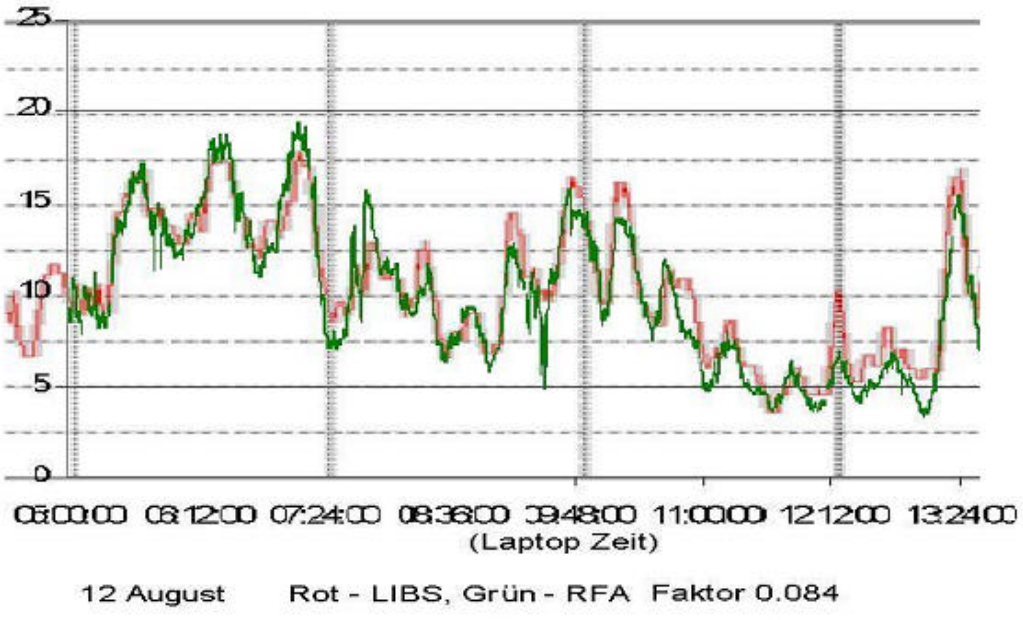

Fig 9: Comparison of Libs- and XRF- analyzer

Fig. 9 shows, that the XRF- and the Libs-analyzer are running very synchronously. After this successful test the online analyzer was installed in 2006.

From the experience with Libs was known, that the material is very inhomogeneous. Therefore it is nearly impossible to get representative samples from the running material stream. Therefore the turntable is equipped with a lock, which allows to put 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 10 shows the high performance of the calibration with the tablets.

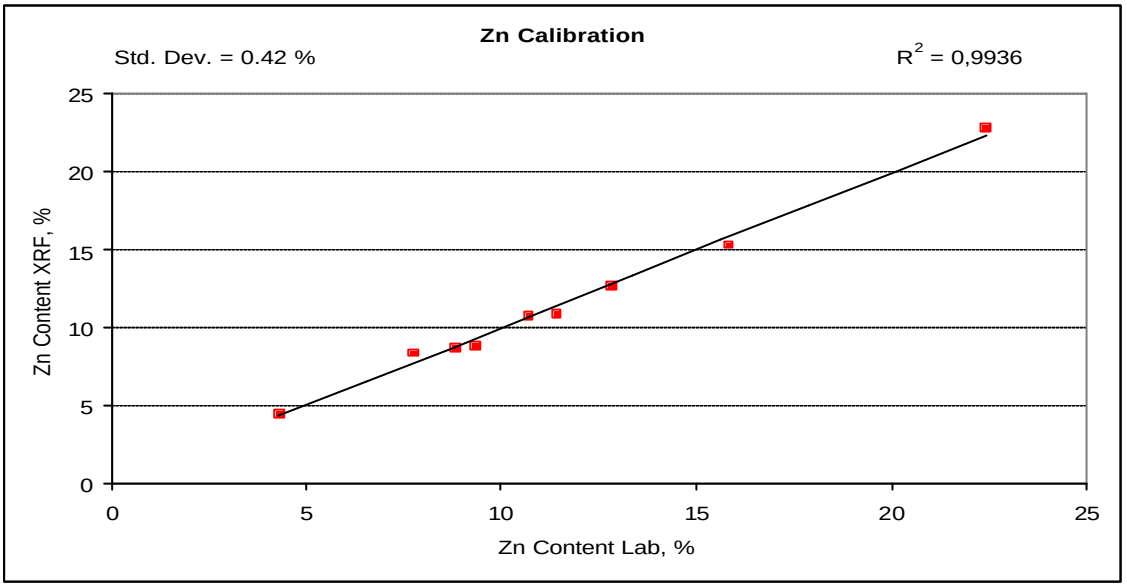

Fig.10: Zinc Calibration for the OXEA 3000 at converter dust.

The Analyzer is connected to the PLC over a Profibus. 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 analysis is an ideal method to determine the constituents of materials. The short proximate analysis and the complete constituents of the ash of coal including trace elements and several parameter, which are derived from this information, as volatiles and the origin of the coal can be determined. A large range of non-coal applications is possible and realised . In all cases the customer had calculated the amortization period of the analyzer: In general, the amortization period is noticeable shorter than 3 years. This underlines the benefit of the analyzer.