Online X-ray Elemental Analysis of Coal with a Particle Size of up to 50 mm

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ABSTRACT

X-ray Fluorescence Spectroscopy (XRF) Elemental Analysers have been successfully used in laboratories. Attempts have made to install this technology online but up until now the particle size has been limited to 10-12 mm. Other problems with accuracy and repeatability have limited the success of this technology. This paper will discuss how recent improvements in the technology have enabled the end users to accurately determine the ash, sulphur, volatiles, bulk density of coal and to detect impurities such as iron ore on the main belt. The analyzers are installed on a sled, which is sliding over the material. Two case studies will be presented. In one case the analyzer has been running on blended coal since 2004 in a closed loop to control the gas fuel consumption at a coking plant and it shows the long term stability and accuracy of the Online X-ray Elemental Analyzer technology. In the second case, the analyzer is installed at the received coal belt of a coking plant with a particle size up to 50mm. It is shown that, under these conditions, the material can be analyzed on the main belt without any reduction in accuracy and without mechanical problems. Additionally the origin of the received coal can be recognized by spectra comparison using the fingerprint method to control the correct stocking of the incoming coal.

INTRODUCTION

Today there are three large scale consumers of coal: Power stations, coking and gasification plants. In all these applications the processes can be improved by installing an online analyzer and implementing control strategies to gain higher efficiency and consistent quality of the final product. Only a small window of variation in feed coal is allowed in the coke plants. Therefore online measurement of a large variety of coal quality parameters is necessary. In addition to the knowledge of ash content, moisture content and calorific value other parameters such as volatiles, ash fusion point, slagging and fouling or the concentration of specific elements such as sulfur, sodium, chlorine, arsenic or mercury become important.

These parameters cannot be measured with simple online ash analyzers, which only measure the average atomic number. More information about the measured material is necessary. Currently only two technologies have enough information to fulfill these new requirements: The Prompt Gamma Neutron Activation Analysis (PGNAA) and the X-Ray Fluorescence (XRF) technique.

Development of this technology began in 1997. The task was to make the energy dispersive XRF technology, well known for laboratory instruments, suitable for online measurements and to measure the ash and sulfur content without strong nuclear sources, as used in PGNAA. A prototype of the patented technology [1] was installed at Detroit Edison´s Monroe Power Plant (USA) in January 1998 by a German-US-joint venture [2]. This prototype is still under power today. After the dissolution of the joint venture in 2002 InduTech has been continuously improving the technology with the following key features as goals for the Online X-ray Elemental Analyzer technology:

- Excellent energy resolution and lower limits of detection for elements such as sodium magnesium, aluminium and silica
- Stable calibration using matrix compensation methods resulting in long-term repeatability.
- Improved accuracy of the ash measurement based on a new XRF-based method for the ash determination
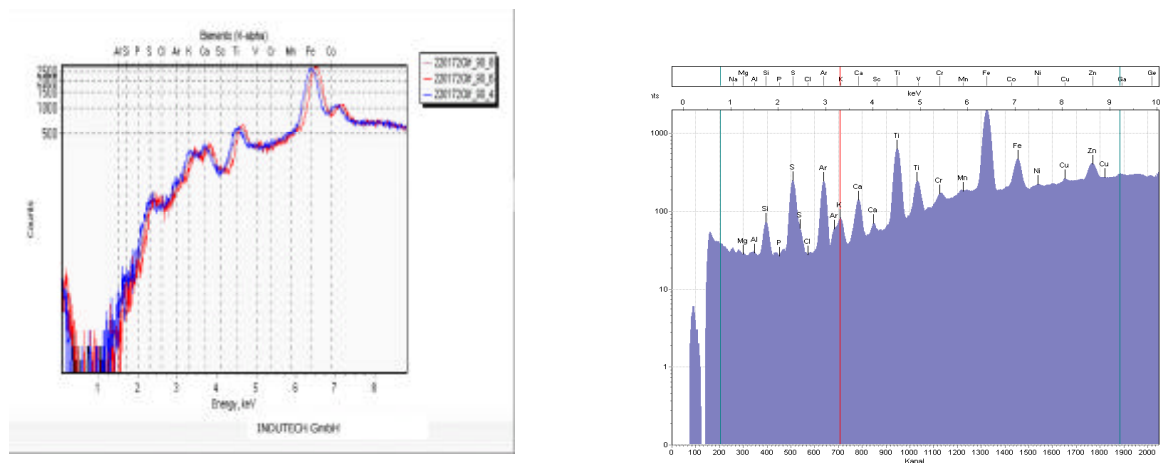

Fig 1: Comparison of spectra quality: Spectrum from 2001 (Duke Power Cliffside, USA) left and a 2003 Online X-ray Elemental Analyzer spectrum

Figure 1 compares spectra from 2001 with an Online X-ray Elemental Analyzer spectrum which has been available since 2003. In the left spectrum the low elements Al and Si, which are important for the ash determination, are completely missing. The resolution of sulfur is poor.

When the technology was first developed a bypass belt with a sampling system was required to maintain a particle size of 12 mm. Since its introduction, the technology has improved so the analyzer can also be installed on the main belt. The sensor is mounted on a sled, which is sliding on the material. This helps maintain a constant distance between the product and the analyzer. Once calibrated under these conditions the instrument will perform with excellent repeatability.

Following are the two case studies showing the use of this technology on the main belt of a coal process with varying size up to 50mm from a variety of sources, coal types and blend ratios.

DETERMINATION OF THE VOLITILE MATTER IN COAL [3, 4]

Offline Tests

In 2002, the voestalpine Stahl GmbH (Austria) wanted to know if, in addition to the short proximate analysis, the volatiles of the coal can be determined using XRF technology. If they could verify the amount of volatiles going into the coke oven, they could implement a control strategy to thermally control their coking ovens. Intensive investigations in laboratories showed that the information taken by XRF measurements is sufficient to develop a model for describing the volatiles. These tests were carried out on over 100 samples. Six types of 'as received coal', mainly coming from Czech Republic and Poland were investigated.
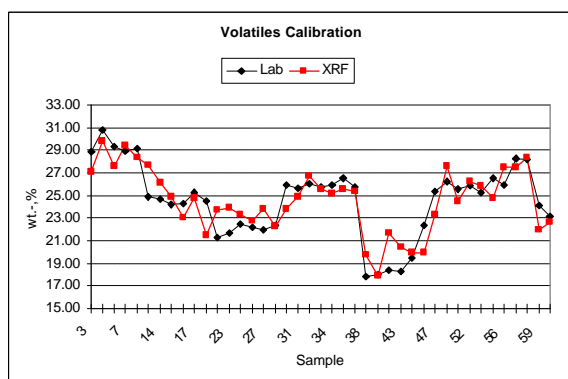

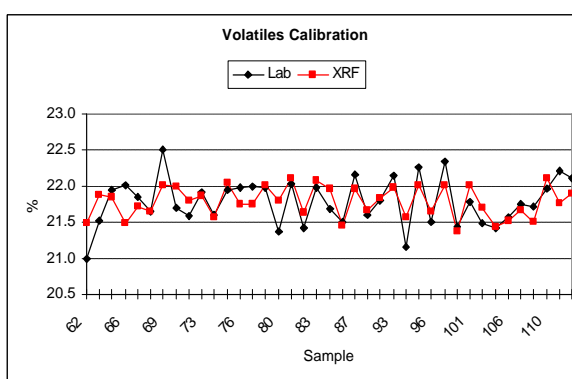Fig. 2: Volatiles of the received coal

Fig. 3: Volatiles of the blended coal

Using the model developed in the laboratory it was discovered that all 6 of these varying coal types could be calibrated into one calibration curve, as shown in fig. 2. The accuracy for the volatiles is 1.5 wt.-% at one sigma. This accuracy was found to be very acceptable to the coke plant.

The second group were samples of blended coking coal. This is the product, which voestalpine also wanted to measure. The results are shown in fig. 3. With a standard deviation of 0.25 wt.-%. It was determined the obtained accuracy is sufficient to control the gas fuel requirements of the coking process.

Online Installation and Results

Based on these results in 2003, an Online X-ray Elemental Analyzer was ordered and installed on a sled at the main belt transporting the blended coal from the blending facility to the coal piles. The load is 300 t/h, time of operation: 18 h/day, the belt speed is 2.3 m/s. The maximum particle size is less than 10 mm. The sled can swing its arms which are hinged at the sled as well as at the support frame. This allows the sled to move up and down on the material as the load varies. See Fig. 4.
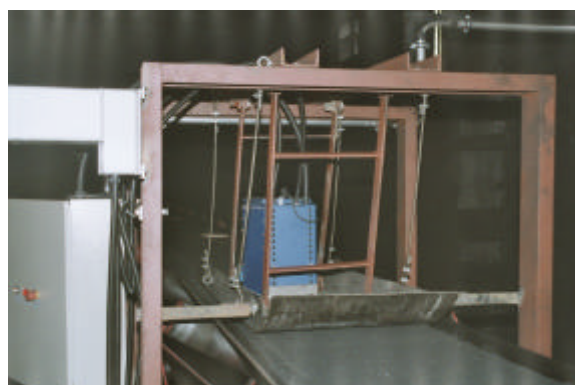

Fig. 4: Online X-ray Elemental Analyzer installed on a sled at a main belt

Fig. 5: Hinged plate to smooth the surface of the coal.

In order to assure a smooth sliding sled the material stream does require some conditioning. This is done in 3 steps: First a plough fixed at a preset height removes the tops of the piles as they pass by on the main belt. Then two hinged plates smooth the surface. Figure 5 shows such a hinged plate.

The sled is mechanically engineered to ensure that it will always hang above the belt so if the belt is empty, the sled will never touch and damage the belt. Figure 6 shows the sled with the analyzer in empty state.

Fig. 6: Sled on empty belt

The presence of material is detected by a proximity switch which is located between the sled runners behind the analyzer. This will interrupt the measurement if the belt is empty or if it does not have enough material to analyze. Additionally, the proximity switch controls an electronic shutter which switches the X-ray tube to a safe state and thereby extending the lifetime of the tube. This also ensures that no radiation is transmitted to the environment, even if the belt is empty.

The Figures 7 through 10 compare the online results with laboratory assays for ash, volatiles, bulk density and sulphur, respectively.
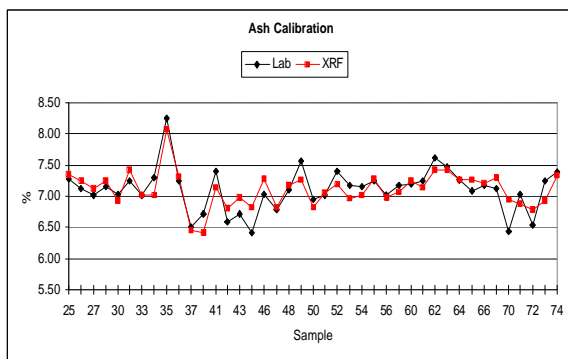
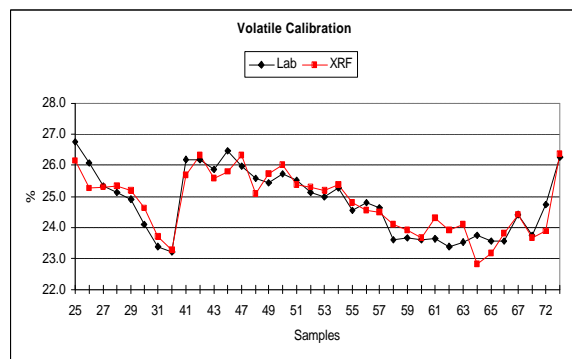

Fig. 7: Online measured ash content
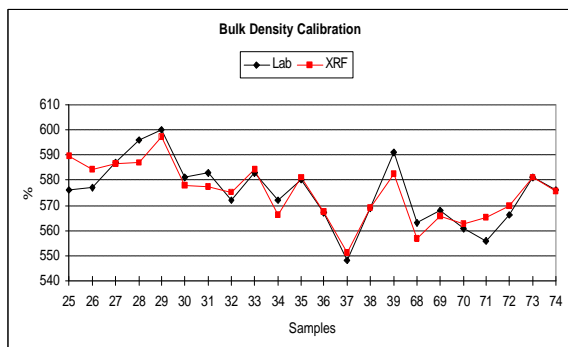

Fig. 8: Online measured volatiles

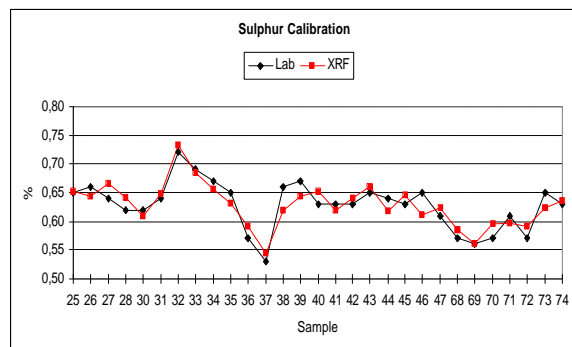Fig. 9: Online measured bulk density

Fig. 10: Online measured sulfur content

Table 1 shows the achieved accuracies of the online calibration for the most important parameters.

	Correlation	Std. Deviation
Ash	0.826	0.192 wt.-%
Volatiles	0.950	0.475 wt.-%
Bulk density	0.899	5.424 kg/m³
Sulfur	0.866	0.019 wt.-%

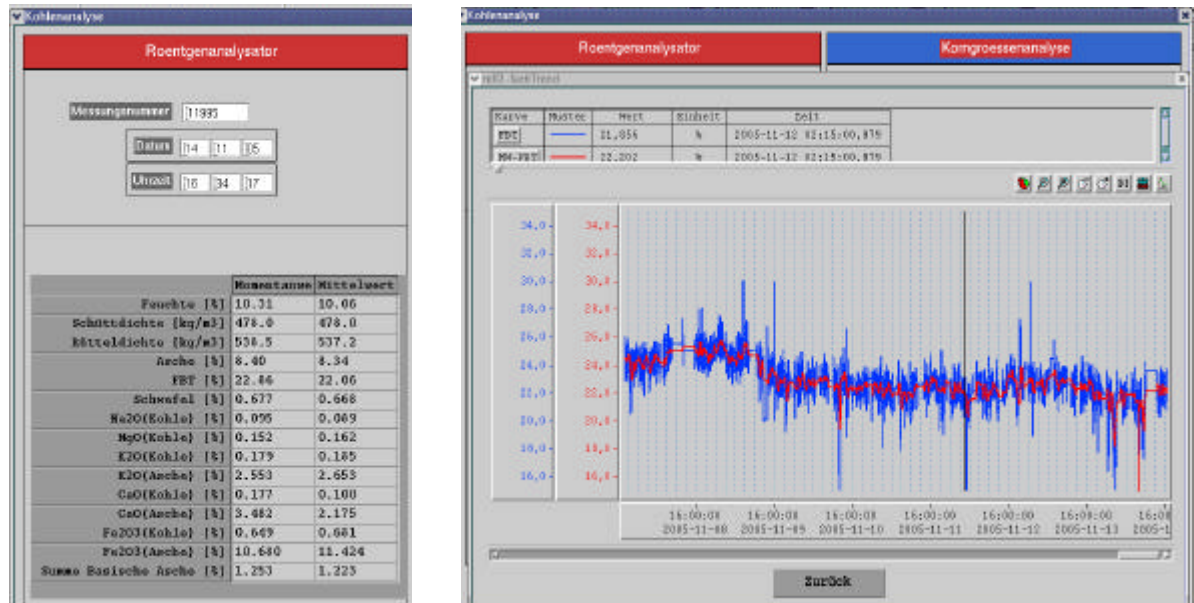Table 1: Results of the online calibration

Fig.11: Numerical and graphical display of the PLC in the control room with all readings given by the Online X-ray Elemental Analyzer

After the calibration, the analyzer was observed by the R&D group of voestalpine. The Online X-ray Elemental Analyzer results proved that the instrument was absolutely stable. 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. Fig.11 shows the alphanumerical and graphical visualization in the control room. The online test of the analyzer was successful and the volatiles were switched to a closed loop to control the gas fuel consumption of the coking oven.

Long-term Experience

The analyzer has been running for 5 years with normal maintenance and without any noteworthy problems. The stability of the calibration was continuously observed during this period. On the basis of daily samples the analyzer was found to be stable over this period, i.e. a recalibration was not necessary. Even after changing one of the coal types in the blend it was not necessary to recalibrate the system. However, in 2008 the recipe of the blending was completely changed and more types of coal were used.. Under these conditions it was necessary to recalibrate the analyzer. The samples were taken and the model for the volatiles was adapted to the new types of coal. The results were very similar when compared to the first calibration as shown in Table 2:

Parameter	Range	Correlation coefficient	Standard deviation
Ash	7.5 – 8.7 wt.-%	0.860	0.135 wt.-%
Volatiles	21 – 27 wt.-%	0.917	0.624 wt.-%
Bulk density	0.65 – 0.85 g/cm³	0.899	0.05424 g/cm³
Sulfur	0.57 – 0.71 wt.-%	0.765	0.025 wt.-%

Table 2: Results of the recalibration in 2008

This shows that the model to determine the volatiles is suitable for coking plants where over long periods the same types of coal are used. For other applications such as power stations, where types of coal are changed more frequently, the use of the model is restricted, because a recalibration is maybe necessary. In these instances the Spectrum Fingerprint method, described in case study 2, can be used to recognize the type of coal and automatically switch the calibration curve.

Availability

The service personnal of the coking plant maintain the analyzer. In the last 5 years the factory was only called twice for service. This demonstrates the high availability of the analyzer.

Advantages of Online Quality Control for the Coking Plant

Before the installation of the Online X-ray Elemental Analyzer the analysis of ash, sulfur, volatiles and bulk density were only performed once a day after sampling and lab analysis. Fluctuations of individual parameters in the course of a day could not be registered. The elemental composition of the ash was only determined once a month. An online moisture measurement was already installed, which is now integrated into the data acquisition of the analyzer.

With the installation of the Online X-ray Elemental Analyzer the volatiles can be determined continuously. The desired final temperature of the coke can be achieved with a low standard deviation, because the required gas fuel can be calculated more exactly. This control strategy reduces the consumption of energy and the investment for the Online X-ray Elemental Analyzer was amortized over a very short period of time. Furthermore, impurities such as Fe ore can be recognized and a reaction is possible to avoid the production of low quality coke. This results in a repeatable and consistent high quality coke product.

INSTALLATION AT THE RECEIVING BELT OF THE ZKS COKING PLANT

The Task

In this second example, the Online X-ray Elemental Analyzer was installed at the main conveyor belt in the Zentralkokerei Saar (ZKS) coking plant (Germany). This belt transports the received coal coming from a domestic port or the railway discharging station to the stockpile or directly to the blending bed. The nominal particle size is up to 50 mm, but sometimes we observed a lot of larger lumps. The belt is also used to transport fine grained petrol coke. In addition to the ash and sulfur content and the elemental composition of the coal ash ZKS wants to distinguish between coals of different origin to control the management of the stockpiles and the blending bed. Impurities such as Fe ore need to be detected as well because they can influence resulting coke quality.

Special Conditions at ZKS

The first challenge of this application was the larger particle size of up to 50mm with a large percentage of oversized particles. When the Online X-ray Elemental Analyzer instrument was installed we found, that the larger particles are pressed in the material bed by the sled. This created a surface that was smooth enough for the Online X-ray Elemental Analyzer measurement (fig. 13). The results of this installation prove that the past limit of the maximal particle size being 10-12 mm can be overcome with this method and we can analyze directly on the main belt with coal that is up to 50mm providing that they can be compacted by the sled.
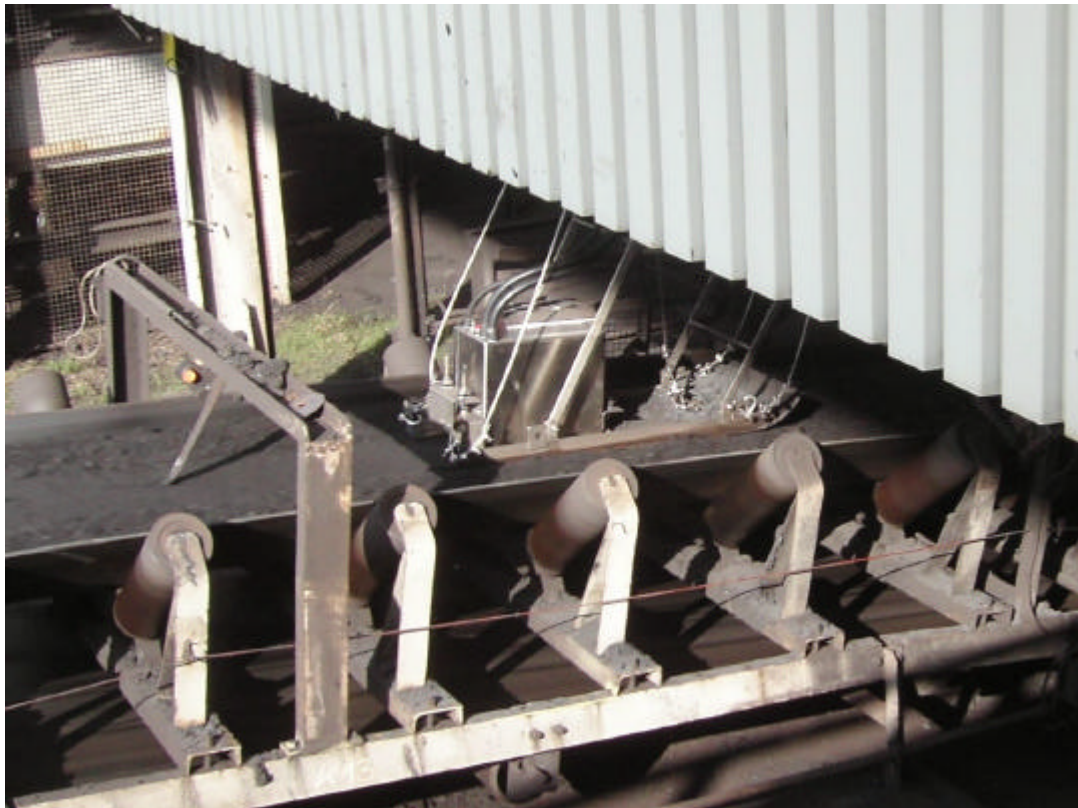
Fig. 12: Sled with Online X-ray Analyzer at the stacker belt

Fig. 12 Shows the analyzer at the stacker belt. The smoothed groove of the sled is easy to see with the large unpacked particles on either side of the track.
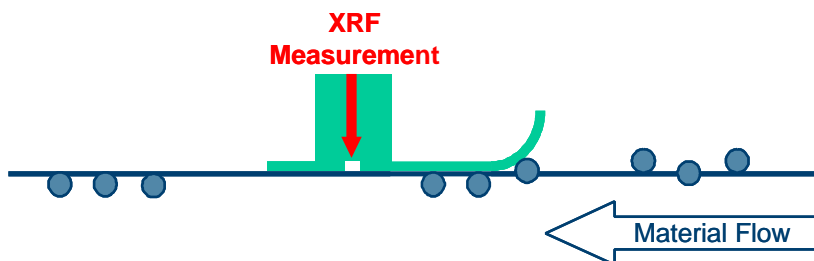

Fig. 13: Schematic illustration of the XRF on the sled pressing larger coal grains in the coal matrix.

However, there were two other problems, which are very difficult to solve:

1. The material coming by trains are discharged to an underground bunker and from there transported on different conveyor belts with a more or less constant load. These are proper measuring conditions for Online X-ray Elemental Analyzer on the sled. However, the unloading of the barges is not buffered by a bunker. This material is directly loaded onto the belt by a continuous unloader. This causes tremendous variations of the load, which cannot be covered by the sled or even by additionally installed plates. Furthermore heavy vertical movements of the sled due to the load variation can damage the analyzer.

2. A second problem was observed during unloading of petroleum coke. The sled must be rather heavy to press the 50 mm particles in the material to obtain the necessary smooth surface for the analyzer. Therefore the sled sinks in the fine grained petrol coke and the measuring window is blocked immediately. The measurement of petrol coke is therefore not possible.

This means, that the analyzer can be used only if trains are discharged. This is sufficient to test the type recognition method, but the analyzer does not fulfill the requested requirements. Therefore the analyzer will now be installed at a bypass belt of a sampling system which is available. This will allow ZKS to measure all products. Some short term impurities might not be detectable however due to the run over on the belt between the two cuts of the sampler.

Type Recognition

The type recognition is based on differences in coal ash composition of various coal types (Figure 14) and realized by comparing the actual measured spectra with a set of spectra, which have been saved on the computer. Therefore the use of this method needs no sampling, but utilizes a learning process: If a new type of coal is used, spectra of this coal must be added to the stored set of spectra. The type recognition software calculates the probability of what type of coal it is seeing. If the coal just running over the belt is one of the coal types which is saved in the database the two most probable results are displayed on the screen with the percentage of probability. Of course, in addition to the recognition of the coal type also possible impurities are detected. This method is very helpful in coking plants or power stations, to check the incoming coal and to control the proper stocking and reclaiming to get a final blend with the needed quality and safety. This strategy can be refined to include an automatic selection of the coal type as it is being analyzed.
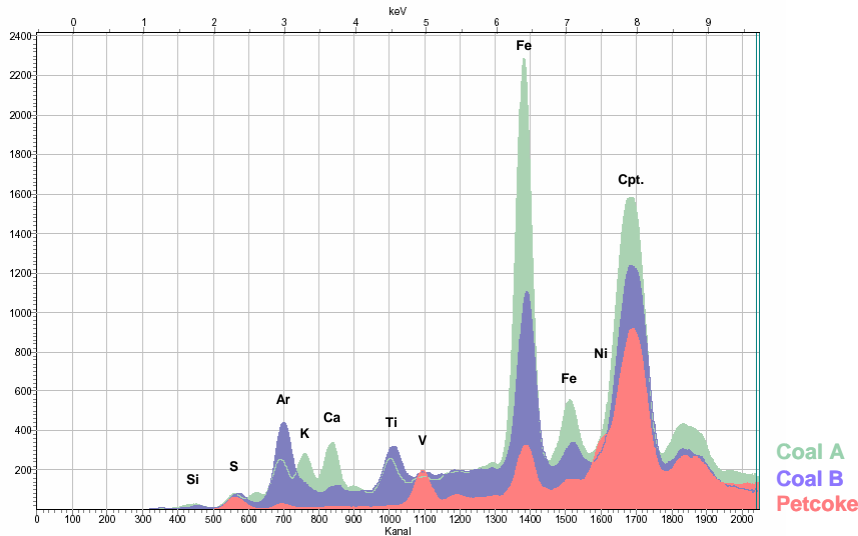
Fig. 14: Examples of typical coking coal and petroleum coke spectra

Fig. 15: Type recognition screen in the control room

The recognized type of coal is compared with the type of coal according the shipping documents and if there is a discrepancy, the belt is stopped and a detailed investigation is started. The Ca content curve shown in the upper part of Figure 15 is a good example for a local contamination from the unloading process. This Ca contamination would not be visible by analyzing the collective lab sample.

The performance of coal type recognition depends primarily on differences in their ash composition. This point has been checked before installing the system at ZKS by performing an offline study. Table 3 shows some results of the online type recognition, which confirms a high reliability of the method.

Coal A

Spectrum Number	1st Type	Probability %	2nd Type	Probability %
1	Coal A	96	Coal B	4
2	Coal A	100	Coal B	0
3	Coal A	99	Coal B	1
4	Coal A	99	Coal B	1
5	Coal A	99	Coal B	1
6	Coal A	98	Coal B	2
7	Coal A	99	Coal B	1
8	Coal A	98	Coal B	2
9	Coal A	99	Coal B	1
10	Coal A	99	Coal B	1
11	Coal A	100	Coal B	0
12	Coal A	100	Coal B	0
13	Coal A	95	Coal B	5
14	Coal A	100	Coal B	0
15	Coal A	100	Coal B	0
16	Coal A	99	Coal B	1
17	Coal A	99	Coal B	1
18	Coal A	98	Coal B	2
19	Coal A	100	Coal B	0
20	Coal A	99	Coal B	1
21	Coal A	99	Coal B	1
22	Coal A	100	Coal B	0
23	Coal A	99	Coal B	1
24	Coal A	99	Coal B	1
25	Coal A	99	Coal B	1
26	Coal A	98	Coal B	2
27	Coal A	100	Coal B	0
28	Coal A	99	Coal B	1
29	Coal A	99	Coal B	1
30	Coal A	98	Coal B	2
31	Coal A	100	Coal B	0
32	Coal A	99	Coal B	1
33	Coal A	98	Coal B	2
34	Coal A	98	Coal B	2
35	Coal A	100	Coal B	0
36	Coal A	98	Coal C	2
37	Coal A	99	Coal B	1
38	Coal A	98	Coal B	2
39	Coal A	99	Coal B	1
40	Coal A	95	Coal B	5

Coal C

Spectrum Number	1st Type	Probability %	2nd Type	Probability %
1	Coal C	100	Coal E	0
2	Coal C	100	Coal E	0
3	Coal C	100	Coal E	0
4	Coal C	100	Coal E	0
5	Coal C	78	Coal E	22
6	Coal C	100	Coal E	0
7	Coal C	70	Coal E	30
8	Coal C	100	Coal E	0
9	Coal C	100	Coal E	0
10	Coal C	100	Coal E	0
11	Coal C	100	Coal E	0
12	Coal C	100	Coal E	0
13	Coal C	100	Coal E	0
14	Coal C	100	Coal E	0
15	Coal C	100	Coal E	0
16	Coal C	100	Coal E	0
17	Coal C	77	Coal E	23
18	Coal C	90	Coal E	10
19	Coal C	100	Coal E	0
20	Coal C	100	Coal E	0
21	Coal C	100	Coal E	0
22	Coal C	100	Coal E	0
23	Coal C	100	Coal E	0
24	Coal C	100	Coal E	0
25	Coal C	100	Coal E	0
26	Coal C	100	Coal E	0
27	Coal C	100	Coal E	0
28	Coal C	100	Coal E	0
29	Coal C	93	Coal E	7
30	Coal C	88	Coal E	12
31	Coal C	100	Coal E	0
32	Coal C	95	Coal E	5
33	Coal C	100	Coal E	0
34	Coal C	100	Coal E	0
35	Coal C	100	Coal E	0
36	Coal C	100	Coal E	0
37	Coal C	100	Coal E	0
38	Coal C	100	Coal E	0
39	Coal C	93	Coal E	7
40	Coal C	100	Coal E	0

Coal E

Spectrum Number	1st Type	Probability %	2nd Type	Probability %
1	Coal E	100	Coal C	0
2	Coal E	84	Coal C	16
3	Coal E	86	Coal C	14
4	Coal E	85	Coal C	15
5	Coal E	90	Coal C	10
6	Coal E	54	Coal C	46
7	Coal E	100	Coal C	0
8	**Coal C**	68	Coal E	32
9	Coal E	100	Coal C	0
10	Coal E	100	Coal C	0
11	Coal E	100	Coal C	0
12	Coal E	82	Coal C	18
13	Coal E	100	Coal C	0
14	Coal E	100	Coal C	0
15	**Coal C**	51	Coal E	49
16	Coal E	100	Coal C	0
17	**Coal C**	74	Coal E	26
18	Coal E	100	Coal C	0
19	Coal E	100	Coal C	0
20	Coal E	72	Coal C	28
21	Coal E	100	Coal C	0
22	Coal E	100	Coal C	0
23	Coal E	100	Coal C	0
24	Coal E	81	Coal C	19
25	Coal E	100	Coal C	0
26	Coal E	75	Coal C	25
27	Coal E	60	Coal C	40
28	Coal E	100	Coal C	0
29	Coal E	71	Coal C	29
30	Coal E	100	Coal C	0
31	Coal E	77	Coal C	23
32	Coal E	100	Coal C	0
33	Coal E	78	Coal C	22
34	Coal E	100	Coal C	0
35	Coal E	100	Coal C	0
36	Coal E	100	Coal C	0
37	**Coal C**	94	Coal E	6
38	Coal E	66	Coal C	34
39	Coal E	63	Coal C	37
40	Coal E	100	Coal C	0

Table 3: Some examples of type recognition results

Calibration of the analyzer

In addition to the type recognition the analyzer is calibrated for ash content and ash components as MgO, Al_2O_3, SiO_2, P_2O_5, S, Cl, K_2O, CaO, TiO_2, V_2O_5, Mn_3O_4, Fe_2O_3, NiO and ZnO. These measurements are based on the average values of coal ash from unloaded trains. The samples are taken and divided by the automatic sampling system and analyzed by ZKS Lab using XRF methods as well. The calibration is done with a common calibration for all types of coal. Figure 16 and table 4 show selected results.
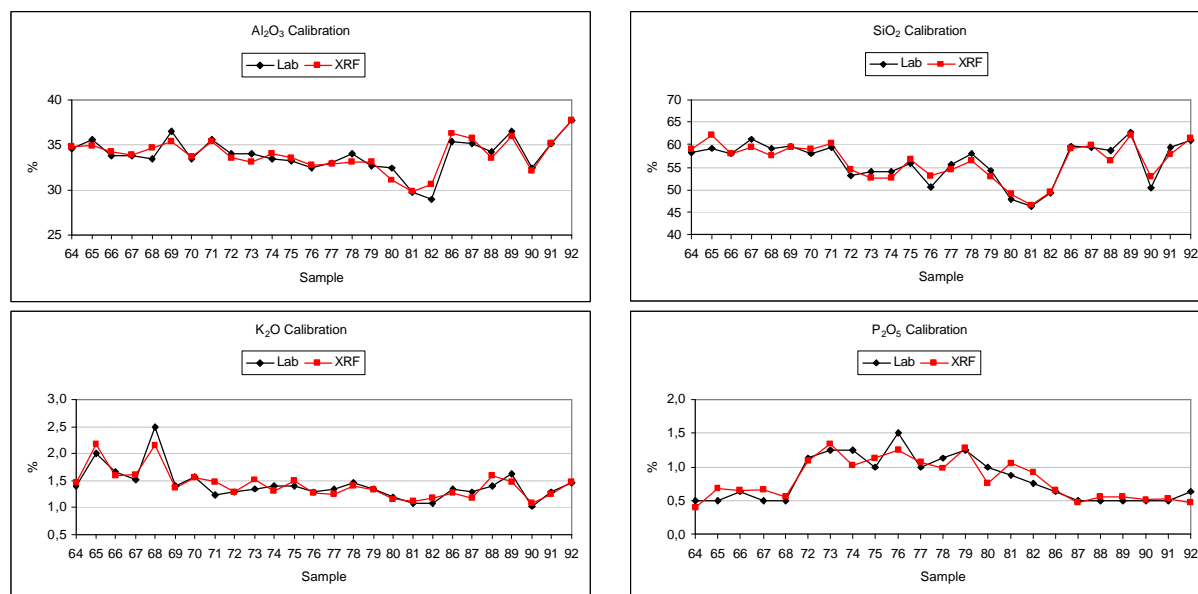

Fig. 16: Online calibration of some ash components of the received coals

	Correlation	Standard Deviation (wt. _% in Coal Ash)
Al_2O_3	0.926	0.683
SiO_2	0.947	1.372
K_2O	0.907	0.078
P_2O_5	0.910	0.033

Table 4: Correlation and standard deviation of the online calibration

Non Coal Applications

These two examples show that the Online X-ray Elemental Analyzer is well suited for several coal applications. This online XRF technology has also been successfully used in non-coal applications such as the determination of the silicon content of magnesite ore, the zinc content of converter dust at temperatures of up to 350°C or the determination of the basicity of sinter mixture in a steel plant, which is calculated from the concentration of the elements Mg, Al, Si and Ca. This shows the wide range of applications of the online XRF technology.

SUMMARY

Online XRF analysis will accurately determine the quality of the received coal and blended coal for coke production by accurately determining the ash and sulfur content, the volatiles and the bulk density. In addition to these parameters, the elemental composition of the material is evaluated to detect impurities such as Fe ore.

The analyzer can be installed at a bypass belt or at the main belt with varying load. In this case the analyzer is installed on a sled, which is sliding over the material. It could be shown, that in this configuration a particle size of up to 50 mm can be analyzed with excellent accuracy and repeatability without any mechanical problems.

The analyzer for the blended coal was installed in 2003/ 2004 and has been running continuously without major problems and has an uptime availability of over 95%. The model for the volatiles is very stable and a recalibration is necessary only if the types of coal are changed. The achieved accuracy allows the use of the readings of the analyzer in a closed loop to calculate the gas fuel consumption for the coking process. Because of the saved energy, the analyzer is amortized within a short period of time.

The measurement of the as received coal also allows the recognition of the type of coal by using the spectrum as a fingerprint. This is used to control the correct stocking of the coal, which is a precondition for correct blending. The type recognition works reliably to a high degree of accuracy and the selection of the type of coal being analyzed can be automated using this fingerprint method.

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