SENSOR-BASED SORTING OF SPENT REFRACTORY BRICKS

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ABSTRACT

Refractory materials are essential for all high-temperature applications in industry. Depending on the position in the furnace and specific process requirements, refractories are produced from several raw materials, such as dolomite, magnesite, bauxite, graphite or chromite. Most of these raw materials are not rare but strict quality requirements limit the producers of refractories to only a few deposits in the world. Thus, raw material supply is a critical factor for the production of refractories and accounts for 40-50 % of the total costs of refractories.

A possible way to lower dependency on raw material supply is recycling of spent refractories. Main challenge in recycling is the separation of different brick types from each other and the removal of impurities, such as steel or slag. The European FP7 project REFRASORT aims to apply sensor-based sorting for separation of spent refractories. Sensor-based sorting is known from food industry, recycling and mineral processing and has proven its reliability. Nevertheless, some adjustments are necessary compared to applications in mineral processing because of other sensor-types and a higher number of products in one sorting step. This paper presents the results of feasibility tests for sensor-based sorting of refractories with near infrared spectroscopy and laser-induced breakdown spectroscopy (LIBS). Both sensors showed the potential to identify different brick types but the most promising results were obtained using LIBS technology.

KEYWORDS

Sensor-based sorting, recycling, refractories, LIBS

INTRODUCTION

Refractories are solid, ceramic products, which can sustain temperatures of more than 1500°C, without losing their stability or shape. Bricks of refractories have to withstand corrosion in contact with liquid steel or slag. Various high temperature applications, such as the production of glass, steel, copper or cement, require high quality refractories. The quality requirements of refractory bricks are strict, because small impurities can lower the thermal strength significantly.

Due to quality requirements of refractory products, raw materials for the production of refractories also have to meet strict qualities and are short in supply. For some of the used raw materials, the natural sources are limited to only a few regions or countries in the world. The costs for raw materials account for 40 – 50 % of the costs of refractories (Ducastel et al., 2015). Table 1 lists the most important raw material and their main source.

Table 1 – Important raw materials for refractories (Guéneguen, Hartenstein, & Fricke-Begemann, 2014)

Raw material	Formula	Melting point	Main source
Silica	SiO_2	1720°C	Global
Fireclay	$SiO_2 + Al_2O_3$	1100°C	Global
Alumina silicate	$SiO_2 + Al_2O_3$	1350°C	China
Alumina	Al_2O_3	2050°C	Synthetic
Zirconia	ZrO_2	2715°C	South Africa
Zircon	$ZrSiO_4$	1775°C	Australia
Chromite	$FeCr_2O_4$	2265°C	South Africa
Spinel	$MgAl_2O_4$	2135°C	Synthetic
Magnesia	MgO	2820°C	China
Sinter dolomite	$CaO + MgO$	2370°C	Europe/global
Graphite	C	3600°C	China

Due to the concentrated origin of some of the raw materials, the supply depends on a few countries and companies. As a result, producers of refractory are facing risks in terms of available qualities, quantities, and prices for required raw materials. One possible way of lowering the dependency on such a small number of suppliers is recycling. During operation, a certain proportion of each brick is consumed but the majority is still intact at the end of their life span. These bricks still meet the quality requirement and are only taken out to ensure a certain safety distance between the liquid steel and the vessel. If properly treated and sorted, used bricks can be used to substitute raw materials in the production of new refractories and thereby lower the dependency on primary raw materials.

CHALLENGES FOR RECYCLING OF REFRACTORIES

A major challenge in recycling of refractories is producing a clean fraction of a certain refractory type. Depending on the position of the brick and the conditions in the furnace, different types of refractories are used. In total eight different types of refractories were defined, which cover approximately 80-90 % of the bricks used in a steel mill. Separating these brick types and removing impurities, such as steel or slag, is essential for recycling of refractories.

The selected eight brick types can be divided in three main types and further subdivided into two and three sub types (see Figure 1). In this publication, the main types are named type A, B and C. Type A is based on magnesite and has a high MgO content. For type A, three sub types are defined with two types containing graphite and one type without graphite. Type B consists of dolomite and contains MgO and CaO. Here, two sub types are defined, one with graphite and one without graphite. Type C is based on different types of aluminum oxides with high Al_2O_3 and SiO_2 contents. For this type, three sub types without graphite can be defined.

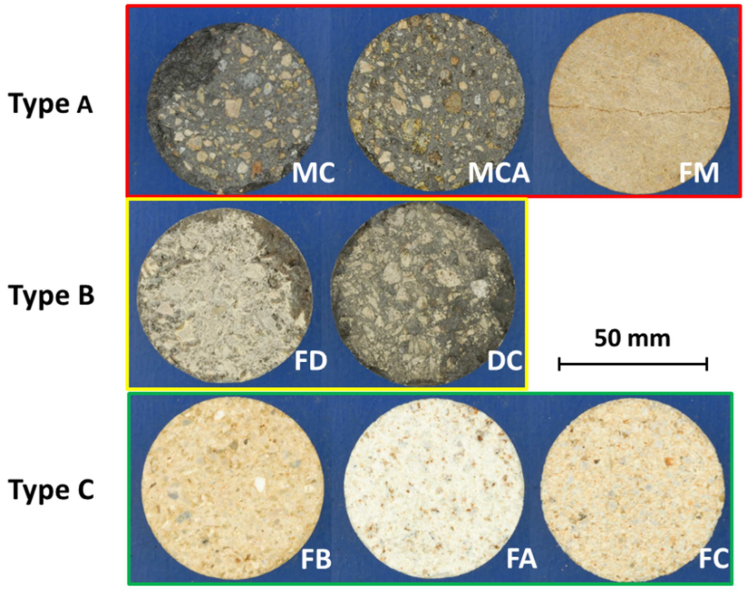

Figure 1 – Eight types of refractories

The spent refractories are usually brick-shaped or broken pieces of bricks in a size range from 60-300 mm. Preferably, they should be sorted in the given size and only crushed afterwards. Separating single particles at a coarse size fraction according to chemical properties could be accomplished by using sensor-based sorting (SBS). To enable SBS it is necessary to find a suitable sensor-type, which is able to identify the different brick types and impurities. An adaptation of conventional SBS is needed in terms of the required number of fractions. While normally only two fractions are produced by SBS, in this case up to nine fractions are necessary.

SENSOR-BASED SORTING (SBS)

Sensor-based sorting (SBS) is used as a collective term for all applications where particles are characterized by a sensor and subsequently separated by an amplified mechanical device. After preparation, the particles are presented to the sensor as they are transported on a conveyor belt or a chute. A sensor measures distinctive properties of each particle. Several sensors can be applied, such as optical, near infrared, X-ray transmission, X-ray fluorescence and metal detectors. The collected data undergo data processing, where a sorting decision is derived for each particle based on the measured values and a predefined calibration. The separation is done by compressed air or mechanical flaps. For all sensor-based sorters the process of sorting can be divided into the following sub processes (Knapp, Neubert, Schropp, & Wotruba, 2014):

- Material conditioning
- Feeding and presentation
- Detection and data processing
- Mechanical rejection

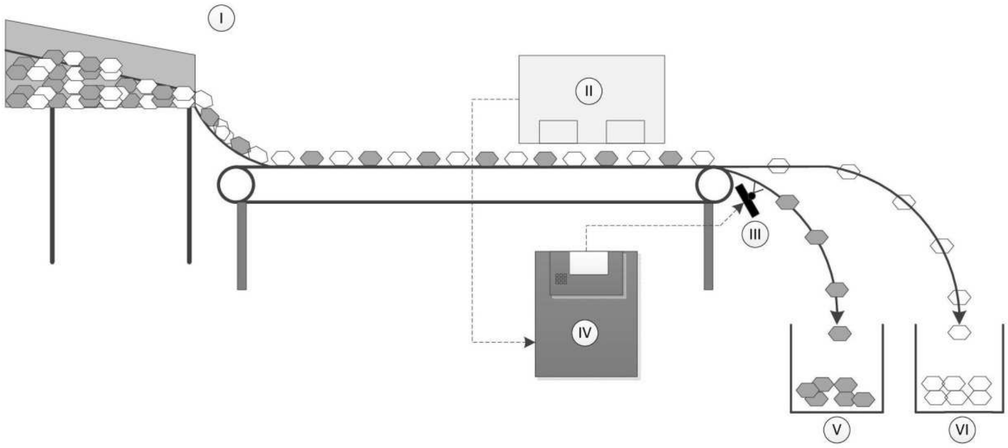

Figure 2 – Conveyor belt sorter: (I) conditioning, (II) emitter and detector, (III) separation unit, (IV) data processing, (V) & (VI) product streams (Knapp et al., 2014)

Figure 2 illustrates the functional principle of a belt type sorter. The feed stream is divided into an accepted (V) and a rejected (VI) fraction. Usually, the smaller of the two fractions is rejected to reduce the consumption of compressed air. The process step of detection is crucial for the applicability of SBS. Only if a sensor is able to distinguish between different particle types, can SBS be applied.

METHODS

To test the technical applicability of SBS for the separation of spent refractory bricks, several sensors were tested for their ability to distinguish between different brick types. The tests were conducted with cylinders of virgin refractories of all eight defined types (see Figure 1). Three samples of each type were tested to lower the risk of outliers and proof the repeatability of the measurements. This paper presents the results of tests with near infrared spectroscopy (NIR) and laser-induced breakdown spectroscopy (LIBS).

Near Infrared Spectroscopy (NIR)

NIR uses differences in the reflection of radiation at wavelengths in the range of 780–2500 nm. NIR-active molecules are excited by this radiation, which results in molecular vibration and absorption of radiation at specific wavelengths. Minerals with NIR-active molecules cause characteristic absorption features and can be identified. Especially minerals with OH-groups, H_2O or CO_3-groups can be identified by NIR. (Robben, Knapp, & Wotruba, 2012)

NIR-sorters are applied mainly in the recycling and food industry but are also used for sorting of primary raw materials, such as talc, dolomite or calcite. Industrial sorters do not measure a complete spectrum but focus on a few wavelengths, which are distinctive for the specific sorting task. Because the distinctive wavelengths are not known for the tested refractories, a complete spectrum was measured for all refractory types with a desktop spectrometer.

Laser-Induced Breakdown Spectroscopy (LIBS)

LIBS uses a highly focused laser pulse to produce plasma on a samples surface. The spectrum of the resulting plasma is analyzed and gives information about the elemental composition of the measured material. This measurement technique is used for analytical purposes and for process control. Figure 3 shows the functional principle of a LIBS setup.

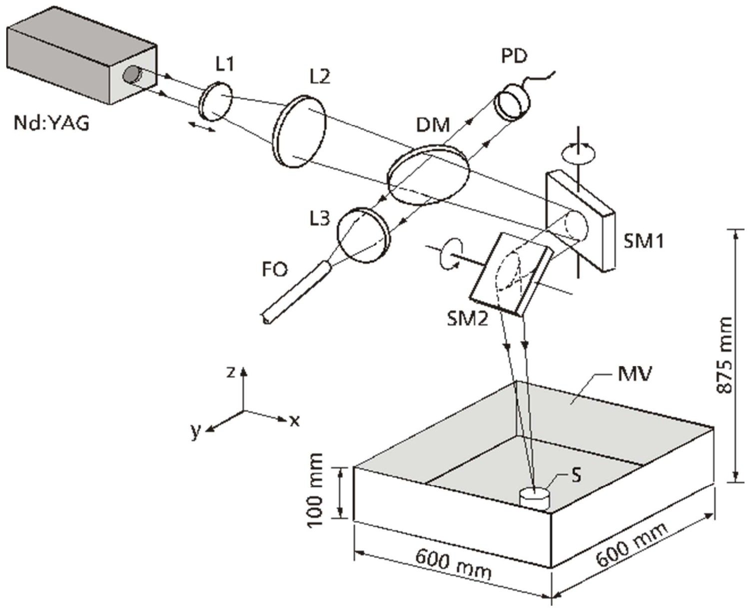

Figure 3 – Schematic drawing of the optical components of 3D scanning LIBS: L1 diverging lens, L2 two lens focusing system, DM dichroitic mirror, SM1,2 scanner mirrors, S sample, MV measuring volume, L3 focusing lens, FO optical fiber, PD photodiode.(Werheit, Fricke-Begemann, Gesing, & Noll, 2011)

With LIBS, the collected data are of high quality, allowing a quantitative measurement of chemical elements in the sample. A downside of LIBS however is the small measurement spot of about 1 mm^2. As a result, any analysis is only true for the measured spot. Because one measurement can be done in far less than a second, several measurements per sample are possible. Thus, the influence of the small measurement spot can be reduced by increasing the number of measurements per sample. During the feasibility tests, samples were measured ten times each to derive an average chemical composition of the samples. This would be done in a similar manner in an industrial application.

RESULTS

This section describes the results of feasibility test work to assess the technical applicability of sensor-based sorting of refractory bricks. Both, NIR and LIBS technology were tested. All tests were performed with cylinders of virgin refractories of different types. For most of the measurements three cylinders of each type were analyzed.

Near Infrared Spectroscopy (NIR)

The obtained NIR-spectra showed only few characteristic absorption features. In fact, only the dolomite-based samples of type B showed a clear absorption feature at 1412 nm. Absorption features in this range of the spectra are most likely caused by presence of water in the sample. Thus, the NIR-data indicate that the bricks of type B have higher water content than the other tested brick types. The higher water content might be due to the hygroscopic nature of fired dolomite.

In an industrial recycling application, the spent refractory bricks are taken out of the furnace, transported to the recycling company and sorted within a few days mostly by hand. When taken out of the furnace, the bricks should not contain any water due to the high temperature in the furnace. To use the water-absorption feature as a sorting criterion, it is necessary to prove that the water content increases in less than a few days. To do so, a spent dolomite-based brick was heated to 500°C for one hour to remove any present water. Afterwards, NIR-spectra of the same brick were taken in regular intervals. The resulting spectra are displayed in Figure 4.

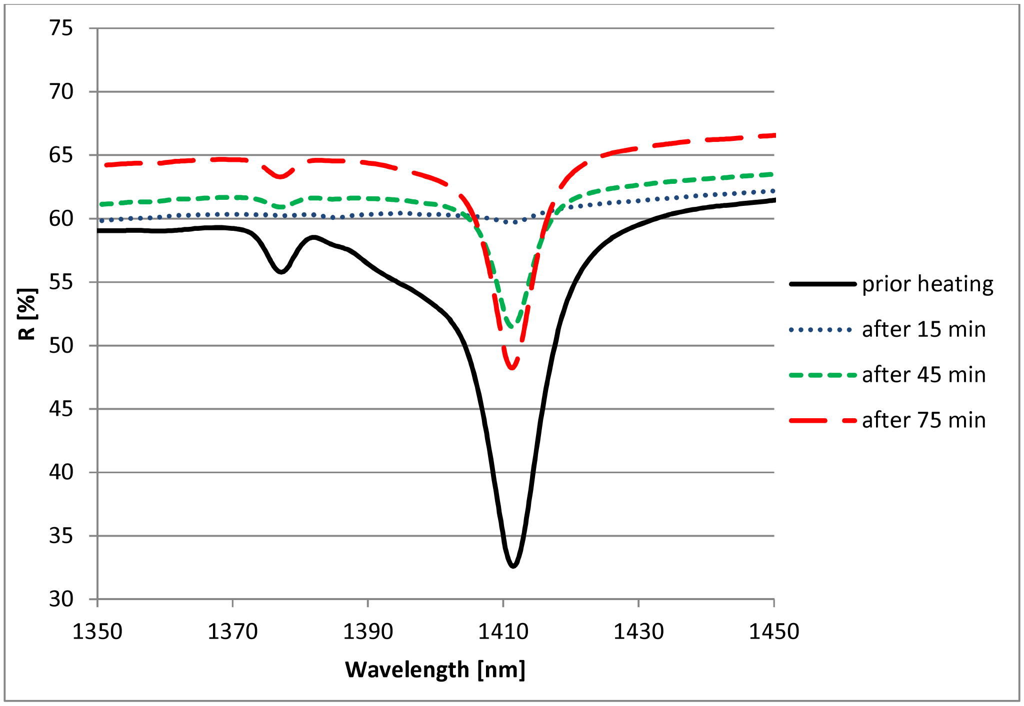

Figure 4 – NIR-spectra of a doloma-based refractory before and after heating

The blue dotted line in Figure 4 shows that no characteristic water absorption feature was detected directly after heating. However, it has shown that a decreasing NIR-reflection at a wavelength of 1,412 nm quickly develops. Already 45 minutes after heating a decreasing absorption is clearly measureable. As it takes at least a day to get the bricks out of the furnace and through the recycling plant, the feature would be strong enough to be used as sorting criteria by the time the brick arrives at the sorting plant. Nonetheless, because NIR-spectroscopy is only able to identify one type of bricks, it is not an ideal solution.

Laser Induced Breakdown Spectroscopy (LIBS)

The LIBS-based test work has demonstrated that it is possible to produce plasma on the sample's surface, which can be analyzed for material characterization. Ten measurements were conducted on each brick to reduce the influence of only one small measurement spot. Figure 5 shows an exemplary refractory sample while the plasma is produced.

Published by the Canadian Institute of Mining, Metallurgy and Petroleum

Figure 5 – Refractory sample with plasma from the LIBS-system

In the measured LIBS-spectra, several spectral features were identified, which correspond with different elements, such as Ca, Mg, and Al. The mean values and standard deviations were calculated for each sample. By calculating the overlapping of the Gaussian distributions of the eight refractory types, the identification correctness can be estimated for each class against all of the other seven classes (Table 2). It can be seen that the identification of the three main classes can be done with an accuracy of more than 99 %. For some of the eight sub-types, the correctness is lower but always above 90 %. The values in the table are mirrored along the diagonal axis, because symetric Gaussian distributions were used for calculation.

Table 2 – Identification correctness for the eight refractory types by LIBS measurement (Connemann et al., 2016)

Refractory Type	MC A	MCA A	FM A	FD B	DC B	FB C	FA C	FC C
MC		97.9 %	96.0 %	99.9 %	99.8 %	99.9 %	99.9 %	99.9 %
MCA	97.9 %		98.1 %	99.9 %	99.9 %	99.9 %	99.9 %	99.9 %
FM	96.0 %	98.1 %		99.9 %	99.9 %	99.9 %	99.9 %	99.9 %
FD	99.9 %	99.9 %	99.9 %		94.3 %	99.9 %	99.9 %	99.9 %
DC	99.8 %	99.9 %	99.9 %	94.3 %		99.9 %	99.9 %	99.9 %
FB	99.9 %	99.9 %	99.9 %	99.9 %	99.9 %		99.0 %	93.6 %
FA	99.9 %	99.9 %	99.9 %	99.9 %	99.9 %	99.0 %		92.0 %
FC	99.9 %	99.9 %	99.9 %	99.9 %	99.9 %	93.6 %	92.0 %	

CONCLUSIONS

Refractories are a vital part of any high-temperature application. The most important factor for quality and price of refractory products is the quality of necessarry raw materials. Recycling can help to lower the dependency on raw material suppliers and allows to diversify the sources of raw materials. Currently, most spent refractories are either dumped or recycled into low value applications whereas only a small amount is recycled into refractories again. Sensor-based sorting holds the potential to produce fractions of high purity, which can be used for the production of fresh refractories.

The tests with NIR-spectroscopy revealed the potential to identify the doloma-based refractories based on their water content. The doloma-based bricks are of such hygroscopic nature that the water feature can be measured already one hour after beeing taken out of the furnace. Nevertheless, NIR-spectroscopy is only able to identify doloma-based bricks so that additional sensor types become necessary.

The LIBS-technology was capable of identifying the three main types of refractories reliably. Futhermore, it was possible to identify the different sub-types of the Al-based type C at high accuracy. Therefore, LIBS is the prefered sensor type to enable a sensor-based sorting of spent refractory bricks. Maybe, complemetary sensors can be used to enhance the results of the LIBS-system so that even more refractory types can be identified.

ACKNOWLEDGMENTS

The REFRASORT project has received funding from the European Union’s Seventh Program for research, technological development and demonstration under grant agreement No 603809.

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