Industrial Online Raw Materials Analyzer Based on Laser-Induced Breakdown Spectroscopy

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From its inception, laser-induced breakdown spectroscopy (LIBS) has been recognized as a prospective tool for online process control. Nevertheless, it took considerable time and effort to transform this potential opportunity into application in a working industrial system, such as the mining industry, under real-life conditions and a 24/7 operating mode. There were three main attributes of LIBS to prove: its advantage over other online techniques, mainly prompt gamma neutron activation analysis and X-ray fluorescence; its ability to give relevant data despite its surface but not volume analytical abilities; and its ability to be sufficiently accurate for online process control needs. Comparison of the quantitative results gained from industrial installations of an LIBS analyzer with results of conventional analytical methods and, most importantly, the substantial improvement of the technological process effectiveness proved that LIBS is in fact an excellent technique for online process control in the mining industry.

Index Headings: Laser-induced breakdown spectroscopy; LIBS; Industrial production processes; Online; Mining; Metallurgy.

INTRODUCTION

In any industrial production process, there is variability in the raw materials. Periodic laboratory measurements miss the variation of batch parameters and do not allow online control of the production process. Thus, any mineral production process is optimized to defuse variations and minimize risks. In a real-life scenario, process control is frequently based on experience, visual evaluation, and intuition. Detecting material variations in real time enables refinement of the technological process for improvements in efficiency and profitability. Contemporary online analysis instruments are improving productivity and adding value to mineral resources worldwide by providing real-time process data that are automatic, continuous, rapid, and accurate.

A detailed description of laser-induced breakdown spectroscopy (LIBS) fundamentals has been published previously.\textsuperscript{1,2} To summarize here, when a focused pulse of light from a high-energy laser strikes an object, it creates a ball of plasma. The cooling plasma gives off an emission that is spectrally analyzed to determine the elemental composition of the sample. Breakdown spectroscopy as an analytical technique has many advantages under field conditions. The analysis process is fast, because it is done without sample preparation, and remote detection is possible. With the miniaturization of lasers and ruggedized gated charge-coupled device (CCD) spectrometers, field-portable instrumentation becomes achievable.\textsuperscript{3} Still, two other techniques have already been in wide use for online process control in the mining industry: X-ray fluorescence (XRF) and prompt gamma neutron activation analysis (PGNAA). Our first step toward introducing LIBS into online process control in the mining industry was to evaluate its advantages and disadvantages compared with XRF and PGNAA.

Considerable research has been devoted to exploring LIBS applications for bulk analysis of nonconducting materials; most close for our applications is cement.\textsuperscript{4,5} Nevertheless, examples of applications of LIBS online analyzers in the mining industry under continuous operating mode in actual industrial processes are not available to our knowledge. We have accumulated considerable laboratory experience with LIBS during past 15 years, but it is not clear how LIBS would function in real-time applications, e.g., in open mine conditions. The second task was to evaluate the possibility of extracting quantitative information that meets accepted mining industry standards.

Here, we present proof that LIBS is advantageous compared with other online techniques for real-time process control of raw materials, and we describe implementations of our system that are already realized in different branches of the mining industry worldwide.

LIBS IN COMPARISON WITH OTHER ONLINE TECHNIQUES

X-ray Fluorescence. X-ray fluorescence is produced by bombarding a sample with X-rays. As a result of the interaction, X-rays that are characteristic to the elements inside the sample are emitted and analyzed to determine the elements present within the sample. Low-energy X-rays enable relatively simple shielding and easy licensing. The main analytical disadvantage of an online, on-belt XRF analyzer is that it is not suitable for detection of light elements. It is claimed that elements starting from an atomic number (Z) $>13$, or even 11, may be measured in online mode.\textsuperscript{6,7} Nevertheless, according to our knowledge, actual industrial applications are known for elements starting from S with Z = 16. In contrast, LIBS technology does not suffer the inherent restriction of detecting elements because of their atomic weight and has sufficient analytical ability for online control of all of the periodic table elements. Finally, a laser, unlike XRF, does not create ionizing radiation.

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Prompt Gamma Neutron Activation Analysis. The physical principle of PGNAA systems is that neutron activation of the sample stimulates prompt gamma emission that is analyzed to determine what elements are present and their concentrations. PGNAA methodology has proven to be effective from analytical and technological standpoints, as it enables all relevant elements’ online determinations in a real-life scenario. The main problem is its potential health and environmental hazards and the necessity of meeting strict regulatory requirements. The real radiation dose rate is rather low, but not low enough to avoid the need for protective areas around the analyzer imposed by radiation protection authorities. For example, in Germany, a distance of at least 4 m to the analyzer is required to reduce the irradiation rate, because the dose rate is 4–26 times higher than Europe’s acceptable secure dose rate at the neutron source door.† There are additional problems with PGNAA outlined here. For example, the machine is very bulky (minimum weight is 3200 kg); and the radioactive source, $^{252}$Cf, is highly toxic and can be used for preparing dirty bombs, so very strict measures to avoid $^{252}$Cf theft must be taken. There also is high potential of personnel exposure during source replacement; thus, servicing can only be done by the analyzer’s supplier staff. The average service life of the source is 2.54 years, and it has to be replaced every two years. Continuous exposure to neutrons and gamma rays by the material on the stopped conveyor belt risks residual activation of the mineral or belt (metal lining). The system has to be transported under extreme safety conditions with high transportation cost. There are paperwork and import procedures (up to one year) for reprocessing a worn source. There is a gap under the belt and over the radioactive source; thus, continuously irradiated dust will be end up as highly activated nuclear waste whose cleaning may be a safety issue. And PGNAA entails difficult licensing, installation, and maintenance because of extensive radiation problems.

In contrast, the LIBS technology provides absolute safety for personnel and the environment. It simplifies the implementation of equipment by eliminating the need to obtain a license, maintain strict safety measures, and undergo inspections, all of which are required for neutron technologies. A mobile mode, where one system is used for several conveyers, is possible for LIBS, but not for a PGNAA unit. From an analytical point of view, PGNAA is characterized by relatively low sensitivity. According to our knowledge, a minimum thickness of material on the conveyor belt is needed, typically 100–150 mm, to make the effective analysis possible. For LIBS, a minimum thickness is the monolayer of the particles. The minimal signal accumulation time for PGNAA is typically 1–2 min, making fast process control impossible. For LIBS technology, the full spectral information is received in every single laser pulse, making short control time intervals possible; e.g., 20–30 s in one of our applications. There are several additional disadvantages of PGNAA compared with LIBS. PGNAA results depend on the weight of irradiated material, and industrial analytical scales have an accuracy of $\pm 10\%$, whereas the LIBS technology does not demand any additional measurement besides the spectroscopic measurements. The PGNAA measurement is strongly influenced by Fe and Cl thermal neutron capture from the analyzed material and the conveyor belt itself, whereas LIBS enables the measurement of any element in the presence of any other element.

An additional advantage of LIBS is that it is a laser-based technique; therefore, it is easily combined with other laser spectroscopy techniques, such as time-resolved luminescence and gated Raman. Specifically for the mining industry, such spectroscopic combination would enable analyses of both elements and minerals with characteristic luminescence or Raman signals, PGNAA and XRF can only analyze elements. A potential advantage of PGNAA in comparison with XRF and LIBS is its ability to measure not only the surface, but also the volume. The penetration depth of a laser beam is relatively shallow, no more than approximately 100–120 $\mu$m, with a single laser pulse burst depending on laser pulse energy and material properties, which is not comparable with material depth on a conveyor belt, changing from tenths of centimeters to several meters. So, on a moving belt conveyer, only the surface of the material is analyzed, but knowledge of the impurity concentrations of the volume also is needed. Moreover, only tiny spots on the particle surface are analyzed. Thus, the greatest challenge was to prove under ambient conditions of the material transported on a conveyor that it is possible to transform LIBS data into quantitative elemental content evaluations and that high-frequency sampling of surface chemistry is commensurate with the average of the total cross-section and length. It is clear that the LIBS analyzer has to be used on a surface that statistically represents the whole volume of the material. For industrial control, you need the data for certain time periods, from 30 s to 5 min (approximately 60–600 m of conveyor belt run). For such large quantities of sample, the surface in most cases is statistically relevant, because bulk materials typically get to the conveyor belt after explosive crushing processes that are random in nature. Its efficacy has been proven by many industrial installations of XRF, which is also of the surface analyzer type, and by our LIBS installations. According to our accumulated experience with powder materials, such as Fe concentrate and sintering batch, to get the surface representative of the volume you need the following: get material to the conveyor belt via averaging bunker, choose the installation point after the mixing drums, and mix the material by inexpensive mechanical tools. The applicability of LIBS surface analysis has been practically confirmed by all current industrial installations. INDUSTRIAL LIBS ANALYZER

Laser Distance Spectrometry (Petah Tikva, Israel) was the first to propose using LIBS for online evaluation of bulk minerals on a moving conveyor belt. We developed the technology, built a machine, and proved its viability under field conditions for online analysis of different raw materials in the mining industry. Our industrial LIBS analyzer has dimensions of $150 \times 80 \times 130$ cm (Fig. 1), weighs 450 kg, and has a peak power consumption of
Plasma emission is produced at the mineral surface by a focused 1064 nm Q-switched Nd:YAG laser with energy of 20–100 mJ/pulse and a repetition rate of 1–20 Hz. A double-pulse LIBS module with two synchronized lasers is also operational, enabling higher sensitivity than the single-pulse unit. The laser flashlamp has a life of 50 million pulses, providing 3–9 months of continuous use at a frequency of 1–20 Hz in real-life scenarios. Changing the lamp is very easy, taking 10–15 min by a trained local technician, and the lamp has a replacement cost of less than US$1000. The nominal focal distance to the material is 35 cm and the depth of field is ±3 cm. If necessary, the minimal focal distance may be enlarged up to 95 cm. The height of the optical system is adjusted to maintain focus with changes in rock height in a range of ±15 cm, as detected by a height sensor above the moving belt. A special optical system is used for both laser beam focusing and plasma emission collection. A beam splitter is used to divert the returning plasma light to a lens that condenses it into an optical fiber, which guides it to the spectrometer. A robust CCD spectrometer was incorporated; it has a fixed grating and slit, both selected when ordering the spectrometer based on the needed spectral range and resolution. For present industrial online applications, we use the spectral range of 220–1100 nm, with a resolution of 0.1–0.5 nm. The vacuum ultraviolet (UV) spectral range from 190 nm was used under laboratory conditions for quantitative S analyses in ambient air.\textsuperscript{12}

An external trigger is applied to the spectrometer; a transistor-transistor logic output is available to trigger a pulsed laser. The delay before starting the measurement can be set in the software, starting from several nanoseconds. The spectrum is reported to the system computer that performs the analyses and controls the whole system. The system has sealed panels, shock absorbers, and an air conditioner, enabling it to operate outdoors in environmental conditions such as dust, rain, and extreme temperatures (−50 to +50 °C), and with mechanical vibrations. The optical system is additionally sealed and has positive air pressure. A dedicated cradle enables convenient service and maintenance at any time without conveyor stoppage. The system's modular design concept allows fast component replacement. The system software enables operation over the Internet from any remote computer, using a standard remote control program such as VNC Viewer\textsuperscript{TM} or pcAnywhere\textsuperscript{TM}, or a web-based service such as LogMeIn\textsuperscript{TM}.

**CHALLENGES IN TRANSFERRING LIBS FROM LABORATORY TO MINING**

Many challenges exist in transferring an LIBS system from the laboratory to the moving belt conveyor at a mine. The differences between these environments are numerous and consequential: uniform pellets versus variable sample forms; a fixed laser-to-sample distance versus a variable distance; stationary samples versus moving samples; averaging many pulses over the surface of a single sample to improve signal-to-noise ratio versus the possibility of only one pulse on a sample; uniform mineral composition versus variable composition; dry or uniformly wet samples versus varyingly wet samples; a hygienic clean room versus a dusty, harsh, and corrosive atmosphere; indoor air-conditioning versus heat and humidity; and highly trained technicians versus field operators. Moreover, many means of improving the analytical abilities of LIBS,
such as vacuum, buffer gases, picosecond and femtosecond lasers, and sensitive/intensified CCD cameras are not practical in a real-life scenario.

**Plasma Research and Analytical Lines Selection.** In laboratory applications, the intensity of the LIBS emission depends on the concentration of the element, because other parameters remain more or less the same. In industrial applications, intensity is influenced by factors such as changes in laser-to-sample distance, different water content, and different matrixes. These factors strongly influence plasma parameters, and the intensities of specific spectral lines and ratios between them usually vary for the same element concentration. A good understanding of laser-induced plasma properties is vital for any industrial application. Thus, when evaluating any potential industrial task, much effort is invested in determining the best analytical lines to use.

With the very broad range of minerals and rocks, finding an analytical line is not a simple task. For example, the traditional approach for analytical LIBS is to take a delay time of 100–500 ns to quench the Bremsstrahlung emission. When working with low concentrations of certain elements, such as B, in the presence of much higher levels of Fe, the usual analytical lines of B I at 249.6 nm and B II at 345.1 nm, detected using such a delay time, were nearly totally obscured by Fe emission lines. Additional research revealed that a B III emission line that exists during first 50–100 ns of plasma life might be used for analysis. Besides B, many other elements, such as Fe, Pb, Ti, Al, and Zr, have highly ionized emitting ions. Moreover, during the first 50 ns of plasma life, we found Fraunhofer-type absorption lines that have the potential for direct and calibration-free analytical applications.

At the later phase of temporal plasma history, after long delay times, very important analytical information was revealed. For example, spectra from diatomic molecules of halogens and alkali earth elements were detected after a 25 μs delay; these spectra enable F and Cl detection much more easily than the traditional F I and Cl I ionic lines. After a delay of >100 μs, sometimes plasma-induced luminescence was detected; it is very effective for rare earth elements identification.

**Analytical Algorithm Development and Accuracy Evaluation.** To evaluate an LIBS potential for online analysis, samples with known concentrations of relevant elements are analyzed using a laboratory-scale conveyor and an LIBS analytical setup, imitating the industrial machine. Once the customer provides a detailed description of the technological task for the online stream analyzer, and we decide that it is feasible, the customer should procure and supply the representative samples of the material from the planned point of installation of the analyzer. This is essential for the initial calibration and evaluation of machine accuracy, development of the analytical algorithm, and modification of the instrumentation for the specific material according to technical tasks. This requires selecting samples of each material (every mineralogical type) so that they represent at least 20 different values of each measured parameter, for each prospective point of installation. These values should represent as uniformly as possible the whole variation range of the concentrations studied between the minimum and maximum values of the elements and should differ by not less than the laboratory error.

The influence of laser-to-sample distance, sample humidity, and matrix changes on the lines’ relative intensities was also studied. To compensate, at least partially, for these parameters’ influences, the laser-to-sample distance is controlled by a distance sensor, and a corresponding adjustment in optics height is made. The moisture content is controlled by LIBS data using the H I emission line and an additional device traditionally used for online humidity control. The specific mineral matrix also affects the analytical line intensity, and usually several different minerals are present on the conveyor. Matrix changes may be, in certain cases, compensated by adjustments in LIBS analysis that is dependent on mineral type. Thus, each mineral present

| TABLE I. Comparison of LIBS error to sampling/sample splitting/analytical error. |
|-----------------|-----------------|-----------------|
| Measurement     | Sample split/analytical, % | Two different samples, % | LIBS, % |
| Ferric oxide    | 0.07            | 0.10            | 0.16     |
| Aluminum oxide  | 0.09            | 0.08            | 0.20     |
| MgO             | 0.25            | 0.24            | 0.34     |
| Insoluble       | 0.87            | 1.48            | 1.70     |
| P₂O₅            | 1.81            | 2.34            | 2.36     |
| CaO             | 0.98            | 1.48            | 1.03     |

**FIG. 2.** Online breakdown spectra of apatite (a) and dolomite (b), the main minerals in Florida phosphate deposits.
in the specific rock is studied separately to find its individual breakdown spectrum for the sake of identification.

It is clear that the absolute intensity of an emission line is inadequate; two different kinds of line ratios must be found: (1) those that are least insensitive to changes in plasma parameters, to provide a stable and accurate indication of element concentration levels; and (2) those that are relatively sensitive to plasma parameters, to use as plasma parameter indicators. Laboratory-scale LIBS analysis of samples enables determination of the optimal analytical lines and their ratiometric combinations. Analytical algorithms are developed to transform the spectra into concentration measurements. This transformation is done to minimize the absolute deviation between spectroscopically predicted and actual (laboratory) analysis of the samples.

The next development task is algorithm improvement as a result of industrial tests made with the LIBS analytical unit above the conveyor belt. The measuring device may be used for a purely analytical task where the main parameter is the highest possible accuracy. It is important to emphasize that an online analyzer is not a piece of laboratory equipment. Its value is not in the specific evaluation of a specific sample, but in the overall use of the analyzed properties to monitor quality levels, trends, and changes. Rock composition changes dramatically even during short periods of time; thus, even low-accuracy continuous measurements are substantially better than more accurate data that are much less representative. Thus, the immediate continuous nature of online analysis represents a decisive advantage for technological process control and the accuracy demand is determined by its usefulness for the resulting technology improvement.

Pure analytical accuracy may be determined by comparison with another analytical device measuring the same set of samples. To define the accuracy for online applications is not a trivial task, because the real determination has to be the comparison with another online analyzer that is measuring the same material. Nevertheless, this opportunity very rarely exists, so comparison with the existing offline technique—routine analyses of rock samples in the analytical laboratory—is important. It is clear that established laboratory analyses of specific samples are more accurate, whereas online

Fig. 3. Online breakdown spectra of P (a), Fe (b), Si (c), and Cu (d) in the spectral range of 212–255 nm.
analyses have a substantial advantage because of their continuous nature. Rock composition can change dramatically, and often there is a large change even over a few feet of deposit depth. Thus, even less accurate continuous measurements may be substantially better than more accurate data taken less frequently. In the work described below, LIBS average errors (differences between chemical analyses and LIBS values) are calculated for all evaluated elements and compared with the corresponding laboratory errors. However, there are many variables that could lead to distinctive errors in laboratory data, mainly sampling errors due to ineffective sampling stations, sample preparation errors, and sample analysis errors in the laboratory. Therefore, several tests were conducted to determine the sampling, analytical, and sample-splitting errors in LIBS and laboratory measurements of the same materials. In the first set of tests, the sample of phosphate rock collected was divided at the rotating splitter repeatedly, and the total sample was used in making up samples for the laboratory. Up to 10 smaller samples were prepared from the sample taken. These were submitted to the laboratory over several weeks and were not identified as duplicate samples. A second set of tests consisted of two people taking samples at the same time. These samples were submitted to the laboratory at the same time but were not identified as duplicate samples. Typically, the LIBS spectra collected on site were electronically sent to our company in Israel where they were correlated with laboratory data obtained from the same samples. It was usually found that the errors of the LIBS analyses are not significantly worse than the laboratory errors (Table 1). Thus, the immediate continuous nature of LIBS online control represents a decisive advantage.

Another issue is how to determine whether the accuracy is sufficient. Because our analyzer is intended for process control, the demand on the accuracy has to be optimized by technologists according to how valuable the result is for the task. Non-technologically justified demand on the accuracy of the online analyzer may prevent its implementation, with corresponding loss of process control and economy.

EXAMPLES OF LIBS ONLINE ANALYZERS INSTALLED IN MINING INDUSTRY

**Phosphate Deposits.** Industrial applications for online process control in the phosphate industry may be divided into two groups: control of poisonous impurities (mainly Mg) and content control of phosphorus pentoxide (P₂O₅) in raw materials and post-flotation concentrate. Figure 2 presents typical LIBS spectra of P-bearing apatite Ca₅(PO₄)₃F (Fig. 2a) and Mg-bearing dolomite (Ca,Mg)CO₃ (Fig. 2b). Using LIBS, it was a relatively simple application to detect online which portions of raw materials or concentrates were Mg and P enriched, and to make changes to the mining technology accordingly. As an example, pebble portions with elevated Mg were moved aside, and as a result its concentration in final pebble product was substantially lower and the corresponding price per ton higher. Subsequent laboratory control of the removed portions of the rock confirmed that nearly 93.0% of decision-making based on the LIBS online analyzer were correct. Another example is P₂O₅ control, where its high concentrations (20–30%) may be analyzed using P I emission lines near 255 nm (Fig. 3a). It is a more difficult task when relatively low P₂O₅ concentrations are accompanied by very high Fe content. The lines near 255 nm are not easy to use because they are nearly obscured by Fe I and Fe II emission lines. In such a case, spectral detection near 215 nm is preferred, because the emission line of P I is present, whereas the emissions from F and Si ions are relatively weak (Figs. 3b and 3c). In one specific case, the main interfering factor was the presence of Cu minerals with strong emission near 215.0 nm (Fig. 3d).

**Iron Sintering Mix Control and Composition Stabilization.** For an efficient sintering process, a constant and optimized basicity of raw mix without short- and long-term fluctuations is a must. Achieving real-time automatic process control without human factor influence requires online elemental composition data. Figure 4a presents the results of industrial LIBS unit test data, where laboratory calcium oxide (CaO) control data are compared with online analyzer readings. One hundred and forty samples were taken from conveyer belt and sent to laboratory for control analysis. The correlation coefficient (R²) = 0.88 was very high, with an average standard error of 0.31% mean absolute error or 7.3% mean relative error. It may be seen that online LIBS data

![Correlation between online LIBS and traditional laboratory data of the Fe sintering mix](image-url)
follow all trends in sintering mix chemical composition (Fig. 4b). The accuracy achieved by LIBS was considered as relevant for online process control, and the analyzer was incorporated in an automated factory supervisory control and data acquisition (SCADA) system that provides real-time access to data on the elemental composition of the Fe ore mix fed from storage to the sintering machine before dosing fluxes (limestone and dolomite).

The production capacity of the sinter plant is 14.5 million tons per year. The environment is extremely challenging: dusty, with wide temperature variations from −10 to +40 °C. The basicity level of sinter is 1.2 to 1.6 units, and the task is to keep the set parameter at the ±0.05 level. It is adjusted based on the chemical analysis of the Fe ore mix coming from the storage area by adding fluxes. CaO content in the Fe ore mix fluctuates significantly, due to poor blending and material segregation in the pile. The inconsistency is greatly increased by addition of 25–35 kg/ton of lime into the sinter pile. After successful pilot tests with the LIBS analyzer, the sintering technologists developed a system of automatic flux dozing based on communication of CaO content in the Fe ore mix from the online LIBS analyzer and making continuous automatic adjustment of the flux flow rate during subsequent proportioning, thereby reducing the fluctuations of the sinter basicity. The usual time interval for flux adjustment is 20–60 s.20

Implementation of the LIBS analyzer enabled several improvements: receiving and transmitting the data on chemical composition of Fe ore mix in automatic mode to the process control systems, to use them for online control of technological process; elimination of the human factor causing analysis errors, primarily related to sample collection and sample preparation procedures; decreased deviation of sinter basicity beyond the ±0.05 limit from 8–10% to 2–4%; and decreased coke consumption in the blast furnace process by 0.6–1.0 kg/ton Fe.

**Magnesite Crushed Ore Composition Control and Sorting.** At a crushing and concentration plant, an LIBS analyzer is used to grade the crushed ore fractions of up to 150 mm. Concentrations of Ca and Si determine

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*Fig. 5. Correlation between online LIBS and traditional laboratory data on Cu (a), CaO (b), SiO₂ (c), and S (d) for Cu-bearing ore.*
the material quality and depending on CaO and silicon dioxide (SiO₂) content in the portion of material passing along the conveyor during 60 s, the SCADA system, realizing control of the automatic gate on the basis of the operator’s order and data received from LIBS analyzer, determines where (to what bunker) this portion of the material should be directed. The accuracy and reliability of the analyzer’s readings were well confirmed in an application tasked with determining whether silicon oxide content exceeded the threshold value of 1.45% (corresponding to 2.9% after losses of 50.6% during burning for raw magnesite). The raw magnesite was graded into a bunker, and burning it yielded a batch of fired periclase (fireproof powder) with a silicon oxide content of 3%, the relative deviation between the analyzer’s readings and laboratory data was found to be <5%. Such deviation is not worse than the accuracy of the laboratory analyses themselves. By implementing the MAYA online analyzer, the capabilities to reject the 10–15% of material with noncorresponding parameters from the flow of qualitative raw magnesite and to extract an additional 10–30% volume of high-quality raw material from the flow of the medium-grade crushed magnesite were realized.21

The estimated cost-recovery period for the project was not more than six months from its commissioning, due to the separation of more expensive high-quality products without damage to the existing mass production and due to timely correction of quality of fired magnesite used in subsequent production stages and for shipment to customers. The operating experience of the analyzers demonstrates that they could be used for composition evaluation at crushing and concentration complexes, at the ore output location, and for primary grading of the ore materials and inspection of the finished products.

Potash Quality Control. The main task for LIBS online analysis in potash quality control is Na impurity evaluation.22 It is essential in the production of high-quality potash, in which the highest acceptable Na concentration is 2%. Potassium and Na are difficult to analyze, especially at high concentrations, because of their strong resonance lines self-absorption.1 To overcome this, different K and Na lines and their ratios have been checked in single pulse and double pulse modes with different delay and gate times; the optimal algorithm exhibits good correlation with real analytical data in high-quality potassium chloride product, with Na concentrations of up to 4%.

APPLICATIONS PROVEN FEASIBLE BY LABORATORY-SCALE LIBS ANALYZER

Copper Ores Online Quality Control. Copper ores quality control is usually needed for several tasks. Breakdown UV spectra of Cu-bearing ore in online mode show clear analytical lines of major and minor elements, such as Cu, Ca, Si, Fe, Mg, and Zn. Sulfur analysis in online mode is a challenging task, but for concentrations in the 15–30% range, it may be done using S 1 analytical lines in the 920–925 nm spectral range. In this specific case, online control of Cu (Fig. 5a), Ca (Fig. 5b), Si (Fig. 5c), and S (Fig. 5d) was the task, and laboratory-scale tests gave R² values in the 0.9–0.96 range for all of these elements. Another important task is online control of Mo impurity in Cu-bearing ore. An online LIBS analyzer enables definite detection of even trace Mo concentrations in the hundreds of parts per million range. Correlation coefficients with laboratory data R² of Cu (Fig. 6a), Mo (Fig. 6b), and Fe (Fig. 6c) are in 0.92–0.98 range, promising the possibility of process control in industrial online LIBS application.

Nickel Ores Online Quality Control. The first example is Ni- and Cu-bearing ore requiring online control of both elements’ content. Both Cu and Ni are definitely identified by an online LIBS analyzer. Correlation between laboratory data on Cu (Figs. 7a and 7b) and Ni (Figs. 7c and 7d) and laboratory-scale LIBS tests for two different fractions with R² in the 0.89–0.94 range promise the possibility of process control in industrial online LIBS application. In another task, the Fe/Ni concentration ratio (Fig. 8a) and magnesium oxide (MgO) content (Fig. 8b) were the aims of online analyses, and the correlation between laboratory data and laboratory-scale LIBS conveyor tests gave R² values of 0.97 and 0.94, respectively.
POTENTIAL APPLICATION FOR INDIVIDUAL LUMP SORTING

All of the above-mentioned applications are examples of batch sorting, in which different portions of rock are analyzed and separated based on their chemical composition. In subsequent mineral processing, bulk ores undergo crushing and successive classification by size. The overall processing is much more efficient if effective sorting of individual pieces is inserted earlier into the cycle. This can be achieved by sorting of individual lump pieces (size in centimeters) according to their quality before the grinding stage, splitting the stream into concentrate, waste and intermediate products.\textsuperscript{10,23}

A LIBS sorter integrated into a lump conveyer should have the following units: a mechanical feeder; a frontal tracking system that determines the position and height of each incoming, individual piece to be analyzed; a LIBS instrument containing the laser source; a rapid autofo-cusing system for the laser beam; optics; and spectrometers with detectors.\textsuperscript{4} The main issue in LIBS lump sorting of minerals is its throughput. Because LIBS sorting is based upon plasma analyses generated on relatively small areas by a focused laser beam, the crucial point is how many pulses are needed for a piece of rock with certain size and weight to get a definite answer about its grade (i.e., whether it is concentrate, waste, or an intermediate product).

One example we studied is an Mn-Fe ore that has to be sorted piece by piece based on Mn concentration. An online LIBS analyzer enables to definitely detect the characteristic Mn and Fe emission lines with 50 mJ Nd : YAG laser (1064 nm) excitation. Correlation between online-determined and laboratory data of Mn and Fe concentrations (Figs. 9a and 9b) enables division of the individual lumps into waste (0–10\% Mn), intermediate product (10–30\% Mn), and concentrate (>40\% Mn). To evaluate the lump sorting industrial potential of LIBS, we determined how many analytical laser pulses are needed for proper Mn content evaluation and sorting according to predefined categories. The results demonstrated that an analysis made by five laser pulses had approximately 75\% accuracy to identify the correct grade for high and low grades of Mn-bearing lumps of 3–5 cm size. Three laser pulses gave the correct result 70–73\% at the time. Five laser pulses were selected as a reasonable number for each analysis of a lump-sorting
task as a compromise between sorting speed and analytical precision. For example, with a 200 Hz repetition rate, 40 lumps of 3–5 cm size may be analyzed per second: 144 000 per hour, which translates into 43.2 tonnes per hour (tph). Using two such lasers the throughput may be increased up to approximately 90 tph, which is quite acceptable for such applications.

POTENTIAL APPLICATION FOR REMOTE SENSING

Presently, LIBS industrial machines are effectively used for online control of minerals and rock moving on a conveyor belt. It would be even more effective to situate the online analytical system in the first stages of the mining extraction process even before the conveyor. LIBS stand-off mineralogical applications have been previously considered, and it was proved that effective information may be obtained at distances of 10–25 m.24,25 The earliest opportunity to use a stand-off analyzer is to scan the mine face from a distance of between 10 and 30 m for results about the grade of rock. Now, the samples are excavated, transported to the laboratory, analyzed, and then the data are transmitted back to the mine. This process is slow, error prone, and does not allow real-time management of mining. Mining costs can be significantly reduced by in situ element analysis, enabling real-time selection of the highest-grade ore.

Eleven phosphate rock samples analyzed by the remote unit from a 15–25 m distance were subjected to laboratory analysis to determine the main and impurity element concentrations. The analytical algorithm we developed gave good prediction of P2O5 content for this sampling (Fig. 10a). The linearity with $R^2 = 0.95$ is extremely good for the rocks differentiation task where all five matrix samples have been confidently identified. Another important task is remote evaluation of MgO impurities in those matrix rocks. Figure 10b presents the correlation between remote LIBS and laboratory data, demonstrating linearity with $R^2 = 0.90$. Thus, it may be concluded that remote LIBS is a promising tool for real-time analysis of rocks excavated by dragline machines for identification of matrix rocks with low MgO contents.

But where is a remote LIBS unit best situated? For field tests, the washing pit location was selected, where the dragline operator puts the excavated matrix for its transformation for pre-slurry and transportation for beneficiation.26 The advantages of such position are evident:

1. To the drag line operator, information is practically in real time, only one basket later compared to the information coming from a unit mounted on drag line machine
2. The distance from the LIBS analyzer and the rock is approximately 15–20 m, which is in the range of existing machine
3. The geometrical form of the excavated matrix is

![Fig. 8. Correlation between online LIBS and traditional laboratory data on Fe/Ni ratio (a) and MgO (b) for Ni-bearing ore.](image1)

![Fig. 9. Correlation between online LIBS and traditional laboratory data on Fe (a) and Mn (b).](image2)
Laboratory-scale dynamic tests proved LIBS ability for online process control in the Cu and Ni industries. In addition to over-belt analyzers, a remote LIBS unit was developed and field tested as capable of analyzing rock grade from a distance of 10–25 m.

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