Laser Induced Breakdown Spectroscopy (LIBS) Online Analyzer

- The pulsed 1064 nm Q-switched Nd:YAG laser, generates plasma which vaporizes a small amount of the sample.

- Excited electrons emit light in the optical range, providing very high spectral resolution and selectivity.

- Spectra are processed by custom-tailored algorithms in order to deliver analytical quantitative information for the relevant elements: Ag, Al, As, B, Ba, Be, C, Ca, Cr, Cu, Fe, K, Li, Mg, Mo, Na, P, Pb, S, Si, Sr, Ti, Zn.

- Major and minor elements are analyzed. Lowest detection limit is 0.02-0.1 % depending on the element and matrix.

- Limitation: Only the surface is analyzed, thus the application has to be selected where the surface statistically represents the volume.
• LIBS has several benefits, because the sample requires no special preparation, the process is relatively simple, fast and inexpensive.

• Not only that LIBS can be used to determine the elemental composition of any sample, and unlike certain different techniques, LIBS can also analyze liquids and gases.

• Even very hard materials are fair game for high energy lasers ability to produce plasma.

• But one of the greatest benefits of LIBS is its ability to provide information without destroying the sample.

• The laser removes less than a milligram of material, which is practically invisible.

• This makes LIBS an ideal solution for analyzing valuable items, such as paintings or archaeological artifacts, mining ores etc.
Laser Distance Spectrometry

Laser Induced Breakdown Spectroscopy
Mineral Online Analyzer
Typical Installation photos

Analyzing Minerals and Ores Online by LIBS – Safe and Simple
To improve the mining and production of minerals, chemicals and raw materials by means of Online laser-based analysis technologies.
In any industrial technology, variations of raw materials take place.

- Continues Lab analyses for 24/7 real-time process control is impossible.
- Periodical point measurements misses the variations of parameters.
- Averaged measurements over a long time period are not informative enough.

Therefore:
- If any mineral production processes are optimized to neutralize variations, the end result is decreased productivity and increased losses.
- Operators have no real time information about quality of material for immediate decision making such as – rejection of low grade material, batching/flotation control, sorting etc.

Real time data is often more important than very high accuracy point analysis, when the material being processed, has significant variations.
Benefits of the Online Analysis

**Without on-line analysis**

- **Mineral % in concentrate**
  - Recovery losses due to unnecessarily high quality

**Quality**
- Occasional loss of off-spec product or excessive refinement margin

**Waste**
- Potentially marketable product lost to tailings

**Reagents**
- Overdosing of reagents to assumed, mineral concentration to be on the 'safe side'

**Motivation**
- Little operator knowledge of the process

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**With on-line analysis**

- **Spec.**
  - Off-spec. product lost

**Quality**
- Product quality stabilized

**Waste**
- Product loss minimized

**Reagents**
- Wasteful overdosing avoided

**Motivation**
- Better understanding of process with heightened individual motivation
Benefits of the Online Analysis

- The main objective of on-line analysis is to have a much better control over the and **allow Immediate reaction when needed**.
- On-line analysis is complementary to laboratory analysis and geological predictions, it is automatic, and possible human error is significantly reduced.
- The higher the analysis frequency, the higher the frequency of the variations that can be controlled. In present practical applications the minimal frequency is 30 seconds.

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**Real time analysis** vs. **Lab - after 2-6 hours**
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Many known technologies are based on indirect information on useful or poisonous elements, such as luminescence, color, magnetic and so on.

LIBS enables direct elemental analysis, as XRF, PGNAA, Gamma ionizing techniques.

LIBS provides absolute safety for the personnel and environment. It is greatly simplifies the implementation of equipment by eliminating the need to obtain a license, maintain strict safety measures, and undergo periodical inspection.

XRF disadvantages: only finely granulated material (less than 10 mm) may be analyzed; not suitable for the light elements (elements from H to Na are not detected, Mg, non reliable detection).

PGNAA disadvantage: Gamma radioactive radiation risks.

Weight: starting at 3000 kg compared to 350 kg for LIBS; inability to analyze material quantities less than certain limit (100 mm height for coal) while LIBS has no such limitation.

PGNAA advantage – volume and not surface analyzes.
Relevance of Surface LIBS Analysis

Since LIBS analyzes the surface only, it has to be applied on a surface which 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 (60-600m of conveyor belt run). For such mass, surface analysis is proven to be statistically relevant.

For powdered materials: (iron concentrate, sintering batch etc.) you need the following:
- Get material to the conveyor belt via averaging storage;
- Choose installation point after the mixing drums;
- You can mix the material by simple and inexpensive mechanical tools;

Bulk materials: Typically reach the conveyor belt after explosive/crushing processes, which are random in nature.

LIBS surface analysis relevance has been proved to be highly accurate by all current industrial installations, including sintering and refractory material industries which we shall later discuss in this presentation.
Economic efficiency is a result of higher quality/price of the final product after timely discharge of all off-grade ore, and extraction of high grade material.

Benefits of the Online Analysis
Higher Mg content increases consumption of sulfuric acid and reduces the filtration capacity resulting in low $P_2O_5$ recovery. Mg is contained in dolomite CaMg(CO$_3$). High dolomite zones are presently bypassed. Current practices require either stockpiling of pebble product until the quality control data from sampling become available, or making the shipping or discarding decision based on visual observations of the rock. It can result in shipping of bad products to the chemical plant or in discarding of acceptable pebbles.

Control screen of LIBS on-line analyzer: Mg, BPL(calcium phosphate), Fe, Si, Al.

The biggest benefit of LIBS on-line analysis consists in obtaining a real-time knowledge about rock variability (instead of an average one).

Thus, it is possible to discard the portions of rock with high MgO content.
Accuracy of On-line Analyzer
LIBS vs. Laboratory over 1 year period

- Accuracy requirements was determined according to how valuable is the online control for the technological task.
- Two percent MgO pebble content was considered as a decision point for “bad” rock discarding. 92.8% of the rock samples for which LIBS indicated a high percentage of MgO were later confirmed as such by laboratory measurements.
- If the accuracy of an on-line analyzer is not well understood, and as a result will prevent the implementation of LIBS as a controlling tool, it will eventually cause loss of process control, loss of product, and finally loss of money.
Economic Benefits

Evaluation of $ profit from removing high MgO rock from production

<table>
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<th></th>
<th>Rock now</th>
<th>Balance</th>
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<tbody>
<tr>
<td>Tons</td>
<td>2,000,000</td>
<td>1,900,000</td>
</tr>
<tr>
<td>Level of MgO</td>
<td>1</td>
<td>0.53</td>
</tr>
<tr>
<td>$Value/Ton</td>
<td>109.64</td>
<td>118.53</td>
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<tr>
<td>Total Value, $</td>
<td>219,280,000</td>
<td>225,207,000</td>
</tr>
<tr>
<td>Profit by Discarding</td>
<td></td>
<td>5,927,000</td>
</tr>
</tbody>
</table>

1. Assuming $100/ton for 65 BPL rock with 0.5% MgO
2. Research has shown that discarding 15% of low value rock (mainly dolomite) Will result in actual discarding of 72% of the MgO
Magnesite Group, Russia – CaO, Al₂O₃ and Fe₂O₃ Control in Raw Material - Case study

- First LIBS analyzer installed 1 year ago.
- Presently 3 analyzers are combined with mechanical separation device to operate as an automated sorter.
- 2 sorters have been specially produced for open mine conditions where temperatures plummets down to -50 °C during winter.

The LIBS analyzer is connected to a mechanical device, which based upon online data received from it, separates 20% of high quality raw material from material determined as a low quality and 10% of a low quality raw material from material determined as a high quality. As a result, additional high grade product was produced with a higher total uniformity and quality.
Metallurgy, Russia
NLMK - Novolipetsk Steel

- Application: on-line analysis of Fe and CaO.
- Task: Automated CaO dosage according to measured concentration.
- The Analyzer functions as an automatic CaO dispenser/controller
Coaltech Research associates is a collaborative research program formed by the major coal companies, Universities, CSIR, NUM to address the specific needs of the Coal Mining Industry in the Republic of South Africa. (RSA)

Coaltech research association RSA agreed to test an LIBS analyzer in accordance with International Standard order for on-line analyzers ISO 15239 in order to evaluate its potential. It was installed over the product conveyor at Optimum Colliery mining, where a Coalscan\textsuperscript{(R)} 9500X PGNAA (Prompt Gamma Neutron Activation Analysis) analyzer is in operation. Two-hourly samples were taken and analyzed by Optimum Culliery’s Lab routinely. Coalscan and the Lab analyses were used to provide a comparison readings obtained from both PGNAA and LIBS equipment. The outcome was positive:

- “The testing shows that LIBS analyzer operated in parallel with an on-line real-time PGNAA analyzer, LIBS Final results are statistically valid”.

Copper Bearing Ores, Peru

Good correlation between LIBS and Lab for copper both for high and low Cu levels

Good correlation between LIBS and Lab for silver both for high and low Ag levels

Good correlation between LIBS and Lab for arsenic
Copper Bearing Ores, Chile (CODELCO)

Copper and Molybdenum emission lines are easily detected and may be used for online quantitative analysis.

Good correlation between online LIBS and Lab data for Cu and Mo
The main task is carbonate control, which consists of calcite (Ca) and partly dolomite (Mg) minerals.

Sample A4 is different from all others by high relative intensity of Ca and C emission lines. It indicates the high carbonate content.
The samples were analyzed at the analytical laboratory of Israel Geological Survey (Jerusalem) for C, Ca and Si in copper ore. Then, based on the spectral data, calibration curves were calculated.
Cu, Fe, Mo, C, Si, Mg, Ca and Al lines can be clearly detected. Comparison of the two samples shows content differences between them:

- “Alimentacion linea 3” sample contains higher Cu, Fe and Mo concentration.
- “Relave Final sample” contains higher Ca, Si, Mg and Al than Alimentacion 3 sample.

Spectral analysis of 2 samples with the most different content:

1. Alimentacion linea 3 (black)
2. Relave Final (red).
Good correlation between chemical lab and laser (LIBS) analyses are received for Cu, Fe and Mo.

- All the required elements, Cu, Fe and Mo, could be clearly analyzed by continuous on-line LIBS system.
- High analysis precision and good correlation were received for all analyzed elements.
Copper Bearing Ores, Chile (Esperanza)

Quality analysis of 2 samples:
1. Baja Pirita (black)
2. Alta Pirita (red)

- Cu, Fe, Mo, C, Si, Mg, Ca and Al lines can be clearly detected.

- Although the samples have only small content differences, spectral comparison of the two samples is definitely able to show them.
Copper Bearing Ores, Ural, Russia

Very good correlation between LIBS and Lab for all relevant elements, such as Cu, S, Si, Ca

Cu, LIBS vs. Cu, Lab
- $R^2 = 0.97$
- Absolute Err. = ± 0.56%
- Relative Err. = ± 4.3%
- St. Deviation = ± 0.28%

S, LIBS vs. S, Lab
- $R^2 = 0.95$
- Absolute Err. = ± 0.69%
- Relative Err. = ± 2.36%

SiO$_2$, LIBS vs. SiO$_2$, Lab
- $R^2 = 0.83$
- Absolute Err. = ± 1.63%
- Relative Err. = ± 9.4%
- St. Deviation = ± 1.2%

CaO, LIBS vs. CaO, Lab
- $R^2 = 0.83$
- Absolute Err. = ± 0.28%
- Relative Err. = ± 12%
- St. Deviation = ± 0.3%
Drilling core samples – Cu-Zn ore

Copper and zinc lines are easily detected and may be used for online quantitative analysis.

Good correlation between online LIBS and online XRF data for Cu and Zn.
Conclusions

LIBS proved to be an excellent, cost effective choice as an on line production tool in all mining operations:

- Suitable for major and minor elements, including light elements.
- Without radioactive sources or X-rays emissions.
- Relatively small weight (450 kg) and compact (1.5 x 0.8 x 1.3 m).
- Solid particles slurry and gases may be analyzed.
- Online control of:
  - Minor elements, such as Mo, As, Ag (when more than 100-200 ppm)
  - Carbonates using C, Ca and Mg
  - Clays using Si, Al, Mg, Fe
  - Major elements, such as Cu, Fe, S
- Other potential applications tested in dynamic laboratory conditions are volatiles control in coal, fillers control in cement, and Ni, Pb, Zn, Mn, B, rare-earth elements and optical quartz deposits.
• Muchas gracias por su atención