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**REMOTE REAL-TIME ANALYSES OF PHOSPHATE
FINAL REPORT**

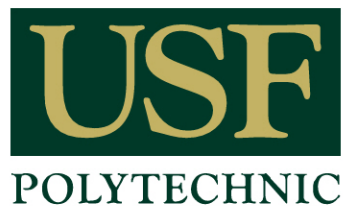
Prepared by

Laser Distance Spectrometry
Petach Tikva, Israel

in collaboration with

R Squared S, Inc.
Lakeland, FL

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FIPR Institute

February 2012

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Interim Executive Director
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G. Michael Lloyd, Jr.
Director of Research Programs

Research Directors

G. Michael Lloyd, Jr.
J. Patrick Zhang
Steven G. Richardson
Brian K. Birky

-Chemical Processing
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-Reclamation
-Public & Environmental Health

Publications Editor
Karen J. Stewart

Florida Industrial and Phosphate Research Institute
1855 West Main Street
Bartow, Florida 33830
(863) 534-7160
Fax: (863) 534-7165
<http://www.fipr.poly.usf.edu>

REMOTE REAL-TIME ANALYSES OF PHOSPHATE

FINAL REPORT

Michael Gaft
Principal Investigator

LASER DISTANCE SPECTROMETRY

11 Granit St.
Petach Tikva 49514
ISRAEL

Regis Stana

R SQUARED S, INC.
2214 Deerbrook Dr.
Lakeland, FL 33811

Prepared for

UNIVERSITY OF SOUTH FLORIDA POLYTECHNIC
FLORIDA INDUSTRIAL AND PHOSPHATE RESEARCH INSTITUTE
1855 West Main Street
Bartow, Florida 33830 USA

Project Manager: Dr. Patrick Zhang
FIPR Project Number: 07-04-075S

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

A decade-long research collaboration between Dr. Gaft of Laser Detect Systems of Israel and the FIPR Institute has resulted in the development and commercialization of the world's first on-line analyzer for wet minerals using the laser-induced breakdown spectroscopy (LIBS) technology. Although the original objective of the online LIBS analyzer was to determine dolomite content, much more has been accomplished. The commercialized analyzer not only gives dolomite readings with acceptable accuracy, but also analyzes or calculates contents of other important components such as BPL, CaO, minor element ratio (MER), Fe₂O₃, Al₂O₃ and Insol. Another nice feature of the analyzer is remote, wireless operation. Two Florida phosphate companies have each recently purchased a new analyzer, and some other phosphate and coal mining companies are in the process of acquiring this analyzer. According to an industry estimate, one installation of the LIBS analyzer at a phosphate beneficiation plant could bring an annual economic benefit of about \$3 million.

The application of ore evaluation in the exposed mine face and in the dragline bucket can increase reserves by including phosphate deposits with high Mg content from southern Florida in economically viable production. Because of selective excavation and dumping, most of the dolomite will be separated near the open pit, thus reducing ore transportation costs significantly. An additional advantage may be the lowering of energy use and flotation chemical consumption, because ore with excessive contaminants will be removed before expensive grinding and flotation processes.

The FIPR Institute and the Israeli research team have long set the goal of developing a LIBS-based analyzer for remote analysis of ores and overburden before these materials are dug out or in transit to the beneficiation plant. The many years of research and development of the online analyzer have laid a sound foundation for developing a remote LIBS, and the successful commercialization of the online LIBS ultimately boosted the confidence of the FIPR Board of Directors in funding research on remote LIBS.

Distant evaluation in the lab and field testing of a remote LIBS prototype demonstrated its feasibility for distant (from 5-25 m) real-time chemical analysis of phosphate minerals excavated by a dragline. Analytical data from the remote LIBS correlated well with laboratory analyses, giving a correlation coefficient of $R^2 = 0.915$ for P₂O₅ and 0.75 for MgO. Although the correlation coefficient for MgO is a bit low, it will be good enough to differentiate between the mine samples with high BPL with regard to their MgO content. It provides the following useful information: differentiation between overburden, matrix and bedrock; analysis of the P₂O₅ content; and analysis of MgO content in matrix samples. This technology has great potential for improving both mining and beneficiation efficiency.

ACKNOWLEDGEMENTS

We would like to express our gratitude to Dr. Chaucer Hwang of CF Industries for his contribution to this project.



ABSTRACT

LDS earlier constructed and produced an industrial LIBS Machine, which gives on-line analysis of Mg, Fe, Al, Si contents on a moving belt conveyer. It allows real-time shipping and discarding decisions based on sound analytical data. Two such machines are working in the Florida phosphate industry (CF Industries and Mosaic). The goal of this project was to prove the feasibility of a remote real-time analyzer on phosphate mine minerals before they are conveyed to the beneficiation plant. LDS constructed and successfully tested in real field conditions a remote LIBS (ReLIBS) unit capable of phosphate mine mineral analysis from a 5-25 m distance. The ReLIBS device proved the feasibility of distant real-time chemical analysis of phosphate minerals excavated by a dragline and provided differentiation between overburden, matrix and bottom; analysis of the P_2O_5 content; and analysis of MgO content in matrix samples. The optimal position for the device was found to be the washing pit where the matrix is piled prior to slurring for transportation to the beneficiation plant.

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EXECUTIVE SUMMARY

Low P_2O_5 content, high MgO content and variability of phosphate rock significantly affect the ability to efficiently digest the phosphate rock in a phosphoric acid production plant. The most significant variables are CaO, MgO, Fe_2O_3 and Al_2O_3 . Current practices require either the stockpiling of pebble product until quality control data from sampling become available, or making the shipping or discarding decision based on visual observations of the rock. This practice can result in the shipping of undesirable products to the chemical plant or the discarding of acceptable phosphate rock. One method to improve rock quality would be to continuously analyze the rock received by the production plant and then stack it in places on the pile with rock of similar composition. Then rock could then be retrieved from various places on the pile in order to keep its overall composition relatively constant. While this would significantly improve the problem with variability, it will only become practical when a continuous analyzer becomes available that can accurately and quickly provide the several analyses required on the rock as received without sample preparation. Online and automatic analysis allow phosphate producers to promptly detect changes in incoming materials, enabling them to take appropriate actions in the process streams.

Together with FIPR (now the FIPR Institute), LDS has already developed an on-line LIBS analyzer for the rock on a moving-belt conveyer. Two such machines are working in the Florida phosphate industry (CF Industries and Mosaic). Nevertheless, it will be even more effective to place the online analytical system on the first stage of the extraction process. The main opportunity is to use it for horizon control in open mining. Presently the samples are collected, transported to the laboratory, analyzed, and the data are transmitted back to the mine. This process is slow, error-prone, and does not allow real-time management of mining. Costs can be significantly reduced by 'in-situ' element analysis, enabling real-time selection of the highest-quality ore. The best way to solve this problem is to accurately define the indistinct top and bottom contacts between the overburden, apatite and dolomite layers and thereby accomplish crude dolomite separation by means of selective excavation. This may be done by horizon surface scanning using a LIDAR (Light Detection and Ranging) system for in-situ real-time phosphate-dolomite identification.

The goal of this project was to prove the feasibility of a remote real-time analyzer of phosphate mine minerals at the mine site, prior to their being conveyed to the beneficiation plant.

This project achieved the following:

- Theoretical assessment of the LIBS system for ore evaluation in an exposed mine face for dolomite-containing phosphate ores from Florida with a real-time scanning system;
- Theoretical evaluation of the parameters and preliminary configuration of the final product prototype;

- Construction and testing of the product prototype in laboratory scale;
- Optimization and correction of parameters according to laboratory tests;
- Feasibility testing of the product prototype in Florida for standoff detection in field conditions.

LDS constructed and successfully tested in real field conditions a remote LIBS (ReLIBS) prototype unit for the analysis of phosphate minerals from distances of 5 to 25 m. The ReLIBS device proved the feasibility of distant real-time chemical analysis of phosphate minerals excavated by a dragline and provided differentiation between overburden, matrix and bottom; evaluation of P_2O_5 contents; and evaluation of the MgO content in matrix samples. The optimal position for the device was found to be the washing pit where the matrix is piled prior to slurring for transportation to the beneficiation plant.

INTRODUCTION

BACKGROUND

Optical sensing techniques provide the capability of remotely monitoring and measuring different natural objects, specifically minerals, by directing a laser beam across a large atmospheric path to the target. These techniques are widely applicable due to the fact that the information is gained from the light recovered by a receptor which commonly measures either absorption or scattering of the probe beam, or fluorescence or Raman radiation emitted by the corresponding minerals and rocks (Gaft and others 2005). Our research proved that laser-induced time-resolved luminescence is not efficient in effectively separating the different minerals comprising Florida phosphate rocks. We also studied the Raman spectra of those minerals and arrived to the conclusion that Raman spectra are not suitable for the task. Laser-induced breakdown spectroscopy (LIBS) was found as the best technique to differentiate remotely between the relevant minerals. This was commercialized in a LIBS industrial machine, which is now being effectively used for online control of phosphate rock moving on conveyer belt. In this application, the phosphate rock is analyzed and all low quality rock is discarded effectively improving the quality of the rock used for the production of phosphoric acid. However, at this point in the mining process, a significant cost has been incurred for the production of the discarded rock. It would be more effective to put the online analytical system closer to the initial mining rather than on the conveyer. The first opportunity would be to use the analyzer to look at the mine face or as it is removed from the mine face. Presently samples can be collected, transported to the laboratory, analyzed, and the data 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. The best way to solve this problem may be to find indistinct top and bottom contacts between overburden, apatite and dolomite layers and thereby accomplish at least preliminary crude dolomite separation by means of selective excavation.

LITERATURE REVIEW

LIBS standoff mineralogical applications have been considered mostly for space tasks. The main reason is that elements' LIBS signals depend on atmospheric pressure and are approximately 2-4 times stronger on airless bodies, such as Mars and the Moon, than they are on earth. Nevertheless, even at atmospheric pressures standoff distances of 10-25 m have been achieved (Cremers and Radziemski 2006; Miziolek and others 2006; Sharma and others 2003). This development clearly indicates that LIBS sensors can be made rugged and compact, and can be excellent candidates for mining robotics applications. The excellent ability of LIBS to carry out remote sensing has been demonstrated in homeland security applications, where trace amounts of explosives at distances of up to 45 m using standoff LIBS have been detected and identified (Lopez-Moreno and others 2006; Gaft and Nagli 2006).

Our company, Laser Distance Spectrometry, is involved in industrial, specifically mining, applications. We have vast experience with LIBS of minerals, specifically with Florida phosphate rocks, coal, and potassium fertilizers (Gaft and others 2002; Gaft and Nagli 2004; Gaft and others 2007; Gaft and others 2008; Gaft and others 2009; Groisman and others 2010). Our cumulative experience gives us the means to evaluate the feasibility of remote LIBS analysis of phosphate rocks in open mine conditions.

To our knowledge, LIBS is not presently used by any company as a method for mineral remote sensing—neither generally, nor specifically for real-time analysis of phosphate ore with high dolomite content.

PURPOSE OF THE PROJECT

LDS was the first to propose, develop and introduce to the phosphate industry a LIBS device for mineral sorting on a moving-belt conveyer. The aim of the new project was:

- Theoretical evaluation and development of the prototype LIBS module for remote chemical analysis of phosphate rocks;
- Evaluation of the analytical abilities of such an approach and their usefulness for the technological process; and
- Evaluation of the optimal positioning of such a device.

METHODOLOGY

LASER-INDUCED BREAKDOWN SPECTROSCOPY

LIBS is a well-known laboratory technique commonly used for fast elemental analysis of materials. Its potential relies on the capability of high-power lasers to ablate a certain amount of material from a sample surface and the simplicity of the setup required to perform atomic emission spectrometry on the emitting plasma. Threshold irradiance to induce plasma formation is on the order of 10^9 W/cm² for most solids. This level is several orders of magnitude higher than those commonly employed by regular remote sensing techniques where the laser beam is directed unfocused towards the target [Laser Induced Luminescence (LIL), Raman]. Consequently, special care must be paid to tightly focus the beam in order not only to reach the plasma formation threshold, but to produce sufficiently bright plasma of analytical quality. This has only been attainable with the development of pulsed lasers capable of producing short pulses of high energy with high stability and low divergence. Additionally, in contrast with LIL and Raman spectroscopies where the analyzed spot may be relatively large, laser-produced plasma is a light source of a few millimeters. In addition, laser-induced plasmas are high-intensity radiating sources, usually an order of magnitude stronger than luminescence and, especially, Raman signals. The human eye can detect the emission from laser-induced plasma from a distance of several tens of meters in the daylight. As was already mentioned, the 10^8 - 10^9 W/cm² regime light interaction with matter is characterized by the formation of a high-temperature and electron-dense plasma, useful for determining the chemical species which constitute the original sample. Since laser-induced plasmas are pulsed sources, their excitation features are a function of time. During the first stages after plasma formation, the emission spectrum is dominated by an intense continuous emission background due to recombination and bremsstrahlung.* As plasma decays, the intensity of background and doubly ionized ions significantly decrease due to a decrease of temperature and electron density, and line emission due to single ionized and neutral species becomes detectable. Owing to the strict energy requirements of the plasma formation process, and occasionally to shielding of the laser radiation by the plasma, the amount of the ablated sample can be in the range of 10^{-9} - 10^{-6} g per pulse, depending on the characteristics of the laser source, the physical properties of the sample, and its surface state. In general, the ablated mass increases with pulse irradiance and sample temperature and decreases with surface reflectivity and the sample thermal conductivity and latent heat of fusion and vaporization. Detection limits achieved by the technique are commonly in the parts per million levels. The analysis principle for laser-induced plasmas is similar to those of other techniques based on atomic emission spectrometry. The plasma light is spectrally and time resolved to identify the light-emitting species. The execution of a measurement implies the integration of the signal corresponding to a line or group of lines of the elements of interest over a certain period of time. The quantity of the element is determined by building a calibration curve of the signal versus the concentration in samples of known composition.

*The electromagnetic radiation produced by the sudden retardation of a charged particle in an intense electric field (as of an atomic nucleus).

REMOTE UNIT DEVELOPMENT

Theoretical Evaluation

A typical LIBS standoff instrument is comprised of a laser; optical components for conditioning, guiding and focusing the beam; optical components for collecting and guiding the plasma light to a spectrograph; a detector; and, eventually, a delay generator (Figure 1). Further data processing is carried out on a computer. However, in a specific system such as this one, which is designed to conduct remote phosphate mineral analysis in open mine conditions, a number of considerations and decisions in the experimental approach and component selection must be made in order to make the system workable while at the same time, remaining relatively simple and of low cost.

Plasma Excitation

The laser source is the central component in any standoff laser-based system. For standoff LIBS applications in ambient conditions, the usual source is the first harmonic of an Nd-YAG laser ($\lambda=1064$ nm) with a 6-8 ns pulse duration and energy of 500-1500 mJ per pulse (Sallé and others 2007, Palanco and others 2004). Such lasers are relatively big and expensive, thus it was first necessary to determine if it was possible to achieve the project goal using a laser source with less energy per pulse. The Big Sky Nd-YAG laser source, which is used for the LDS industrial LIBS machine, was considered. It has an energy of 100 mJ/pulse and a 7 ns pulse duration, and a laser beam diameter and divergence of 4 mm and 1.5 mRad, respectively.

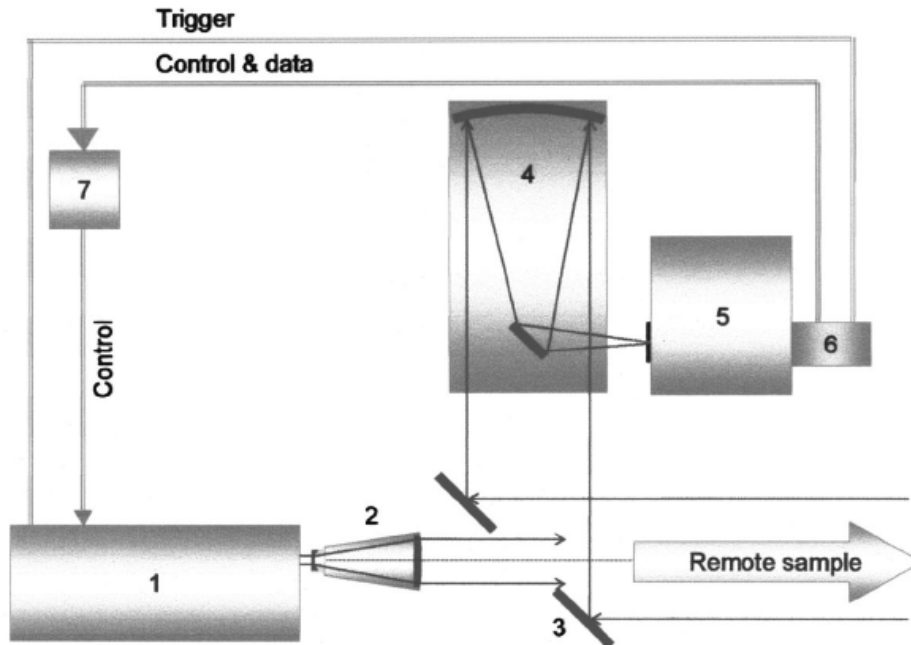


Figure 1. Principal Scheme of LIBS Standoff Instrument.

As a first step the power density was set at 2×10^9 W/cm². The calculation of the power density is based on a spot diameter of 3ω , which is the diameter that contains 98.5% of the power. To calculate the spot diameter ($3\omega_0$), the following equation was used:

$$\text{Power Density} = \frac{100 \times 10^{-3}}{7 \times 10^{-9}} \times \frac{4}{\pi D^2} \quad (1)$$

Then:

$$D = \left(\frac{100 \times 10^{-3} \times 4}{2 \times 10^9 \times 7 \times 10^{-9} \times \pi} \right)^{\frac{1}{2}} \quad (2)$$

and $D = 0.095$ cm = 0.1 cm. Therefore $\omega_0 = 0.318$ mm.

The relationship between the raw beam radius r (containing 86.5% of the beam) at the lens surface and the spot waist radius ω_0 at the object is given by:

$$\frac{\lambda}{\pi r} \times L \times M^2 = \omega_0 \quad (3)$$

where L is the distance from the lens to the object equal to 25 m, $M^2 = 2$ (quality parameter according to the laser manufacturer), $\lambda = 1064$ nm and $\omega_0 = 0.318$ mm. Based on these calculations, radius $r = 53.16$ mm. Therefore the minimum diameter of the lens has to be $3r = 159.5$ mm, or ~ 16 cm.

Optical System Geometry

Two different experimental approaches were explored: a biaxial setup, in which the interrogating laser beam travels through a different path than the returning plasma light, and a coaxial scheme in which the laser beam and the plasma emission share the same optical axis. It is more or less accepted that the coaxial scheme, although more complex in concept, enables a much simpler operation given that both light paths—laser and plasma collection—share the same optical axis. This approach was used in the LDS LIBS online analyzers. Consequently, the coaxial geometry was selected. Figure 2 represents the principal scheme.

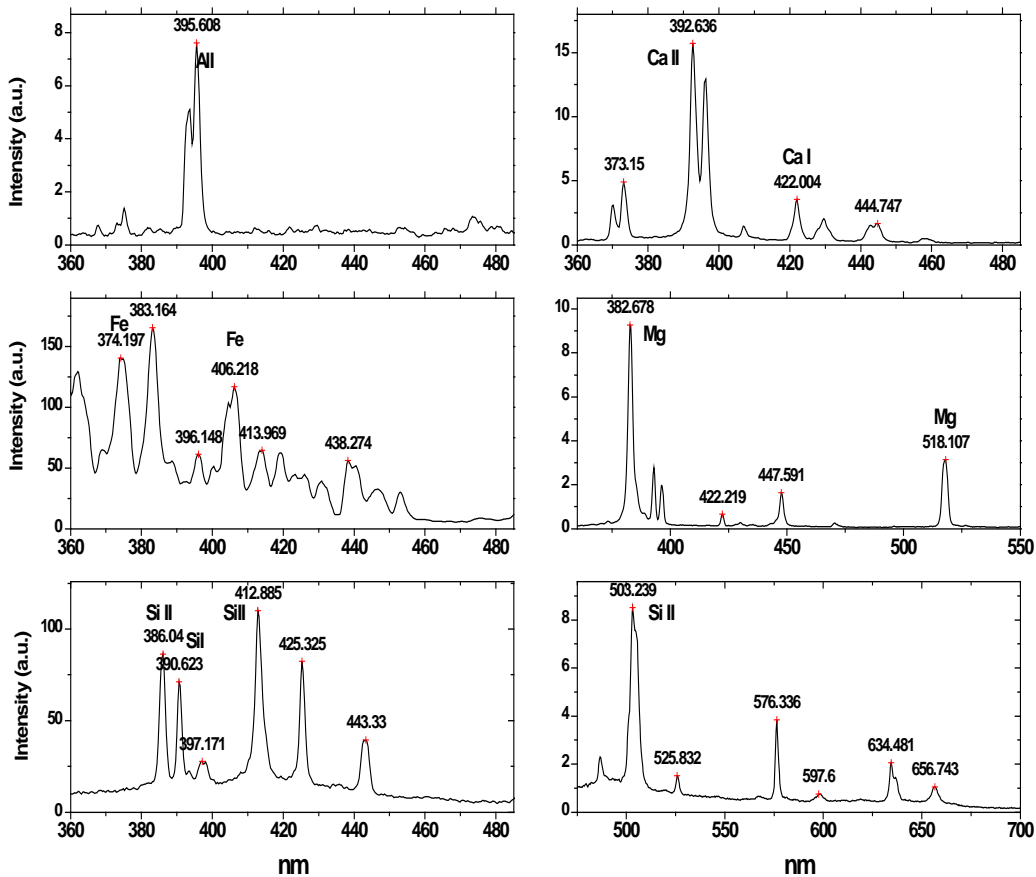


Figure 2. Breakdown Spectra of the Relevant Elements in the Visible Spectral Range.

Spectrometer Type

In the remote Raman system (Gaft and Nagli 2008) a very sensitive and expensive ICCD camera detection unit was used in order to detect the weak Raman signals. It is clear that breakdown emission is several orders of magnitude more intensive than Raman, making it possible to use a robust and inexpensive gated CCD camera, which is three orders of magnitude less sensitive than the ICCD device. In the LDS industrial LIBS machines an Avantes gated spectrometer is used, which is capable of changing the delay time starting from 50 ns and with a gate width of 2 ms. It is suitable for that specific application because the plasma area is shielded by a protective cover that is not transparent to sunlight. In the standoff application, sunlight represents a strong interference signal, which may be eliminated using a narrower detection gate width. Based upon LDS's experience, a gate width of 10 μ s is sufficient to eliminate this background interference.

Analytical Spectral Range

The analytical task is to differentiate between the following phosphate rock types: matrix, overburden, interburden and bottom. Those rock samples were collected from CF and Mosaic deposits. Table 1 represents the corresponding laboratory analytical data. The chemical elements relevant to the analysis of phosphate rocks are P, Ca, Mg, Al, Si, Fe. In our experience, the best analytical spectral range for the evaluation of all those elements is UV from 200 to 350 nm. A special UV optic is needed to work in this spectral range, which may be quite expensive if large lenses or mirrors are needed, which is common for standoff applications. For example, the plasma-emitting photon portion which reaches the telescope is $\cong (D/2)^2/2L^2$ (where D is the mirror diameter and $L = 25$ m). Thus for $D = 25$ cm, this portion will be approximately 0.001%.

Table 1. Laboratory Analytical Data on the Phosphate Rock Samples Studied.

N	Mine	CaO	BPL	MgO	Insol	Fe ₂ O ₃	Al ₂ O ₃	Company Designation	Analysis Designation
1	CF	5.49	7.65	0.64	85.45	0.78	2.54	Overburden	Overburden
2	CF	2	5.11	0.22	86.96	0.2	3.4	Overburden	Overburden
3	CF	18.75	17.61	4.74	51.1	0.99	1.76	Bottom	Bottom/Matrix
7	CF	4.74	6.31	0.93	84.13	1.01	1.56	Interburden	Interburden
8	CF	17.25	24.41	1.07	61.54	1.34	2.69	Matrix	Matrix
9	CF	20.44	24.87	2.57	54.37	0.73	1.01	Matrix	Matrix
10	CF	0.4	3.21	0.06	92.4	0.25	2.15	Matrix	Overburden
11	CF	3.41	4.98	0.91	83.59	3.06	2.34	Interburden	Interburden
12	CF	15.99	21.59	1.53	62.64	1.1	1.6	Bottom	Matrix
13	CF	0.15	0.26	0.01	97.44	0.05	0.11	Overburden	Overburden
14	CF	2.33	3.61	0.11	92.85	0.49	0.48	Overburden	Overburden
15	CF	13.5	20.17	0.35	69.71	1.26	1.18	Matrix	Matrix
16	Mos	13.27	8.79	0.24	69.64	0.83	1.34	Matrix	Matrix
17	Mos	10.42	7.44	0.25	72.33	0.85	2.43	Matrix	Matrix
18	Mos	17.66	11.73	0.26	61.21	0.86	1.43	Matrix	Matrix
19	Mos	16.66	7.01	4.94	49.75	2.57	2.28	Matrix	Matrix?
20	Mos	12.2	4.65	4.15	63.28	0.83	1.32	Matrix	Bottom
21	CF	0.25	0.31	0.04	97.65	0.07	0.15	Overburden	Overburden
22	CF	18.41	27.01	0.34	59.84	1.2	1.4	Matrix	Matrix
23	CF	10.32	11.58	2.15	69.69	1.06	1.77	Bottom	Matrix?
24	CF	1.37	2.71	0.06	92.6	0.28	1.13	Overburden	Overburden
25	CF	13.75	9.92	5.56	56.48	1.25	1.97	Bottom	Bottom
26	CF	18.63	18.31	4.85	49.85	1.05	1.54	Matrix	Matrix
27	CF	17.68	18.94	3.92	51.25	1.12	1.66	Bottom	Matrix
28	CF	4.13	6.25	0.84	80.89	1.18	2.14	Interburden	Interburden
29	CF	15.26	22.94	0.47	64.53	1.13	2.07	Matrix	Matrix

The most desirable means to accomplish the goal is to use the visible spectral range starting from approximately 370 nm. Table 2 shows the main analytical lines of all the relevant elements in the visible range. Figure 2 represents the corresponding spectra. It may be seen that all elements except P may be identified.

Table 2. Analytical Lines for Relevant Elements in the Visible Range.

Element	Visible Analytical Lines
Ca	393.4, 396.8, 422.7, 443.5, 445.7
Mg	516.7, 518.4
Al	394.4, 396.2
Si	504.1, 505.5
Fe	373.5, 374.6, 386.0, 404.6,
P	No

The preliminary analysis of the chemical laboratory data showed that the goal of remote rock type identification may be achieved without P detection. For example, the CaO/Insol ratio correlates well with BPL values (Figure 3). All nine samples with a BPL of more than 17% are clearly separated, but five samples with relatively low BPL levels are also characterized by high CaO/Insol ratios. However, four of these five samples are from the Mosaic mine. Re-analysis of these samples showed that the initial CaO analyses were in error. Excluding the erroneous results, there is a reasonably good correlation for the CF samples (Figure 4). In the following evaluations, the CaO/MgO ratio was used to differentiate rock with a high BPL and low MgO concentration (Figure 5). Thus it may be concluded that detection of Ca, Mg and Insol-related elements such as Si, Al and Fe, in the visible range, may be quite sufficient for remote matrix identification.

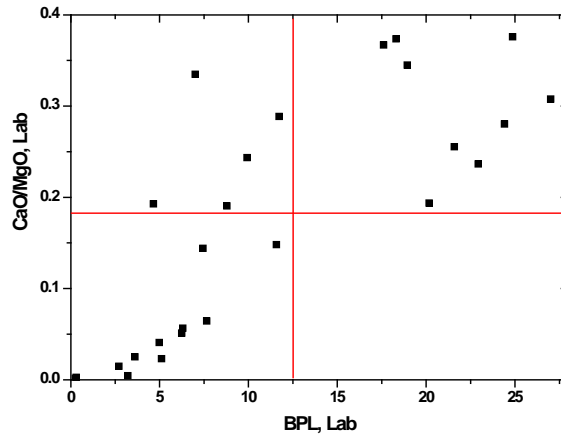


Figure 3. Correlation Between Laboratory CaO/MgO Ratio and BPL Content for CF and Mosaic Samples.

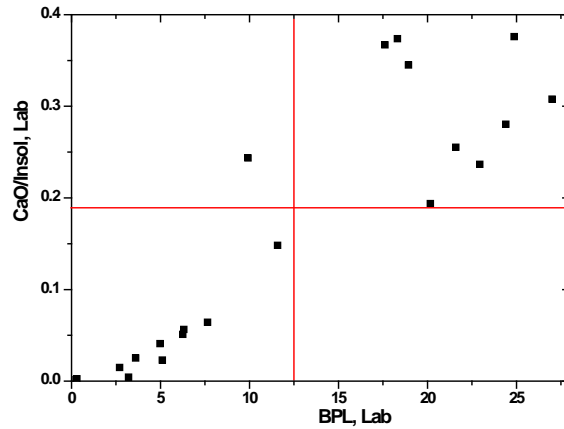


Figure 4. Correlation Between Laboratory CaO/Insol Ratio and BPL Content for CF Samples.

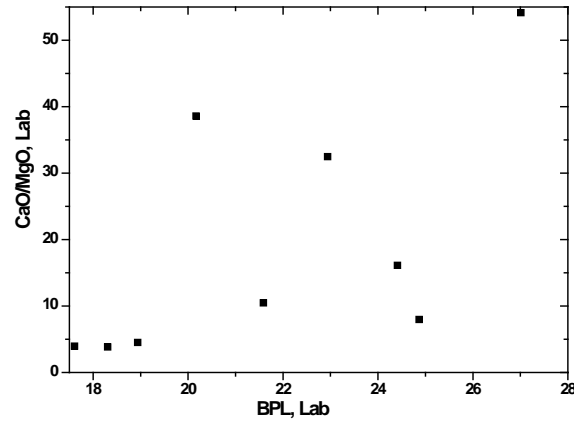


Figure 5. Separation of Rock Types with High BPL and Low MgO Levels According to Lab Data.

Remote Unit Specification

According to a theoretical evaluation of the ReLIBS system, the following specifications were selected (Table 3):

Table 3. System Specifications.

Laser Wavelength	1.064 μm
Energy per Pulse	100 mJ
Pulse Width	7 ns
Raw Beam Diameter	4 mm (assumed to be 3ω)
Laser M^2	< 3.0
Laser Equivalent Full Field Divergence	1.5 mRad (86.5% of the power)
Working Range	From 5 to 25 m continuous

Table 3 (Cont.). System Specifications.

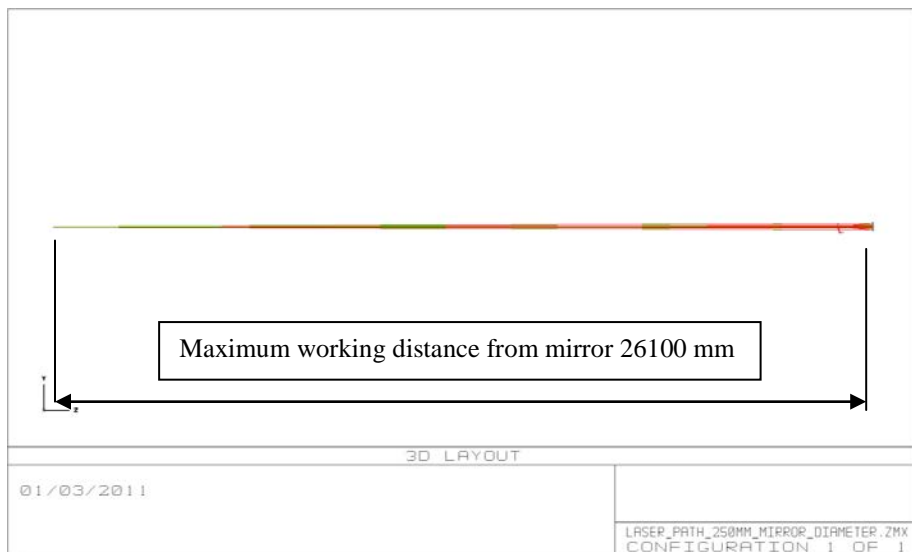
Power Density at 25m	$2 \times 10^9 \text{ W/cm}^2$
Mirror Diameter	300 mm
Overall Length of System	1100 mm
Collection Optics Wavelength	$380 < \lambda < 550 \text{ nm}$
Collection Optics Object Diameter	4.6 mm at 25 meters range
Collection Fiber Diameter	600 μm
Collection Numerical Aperture	0.041

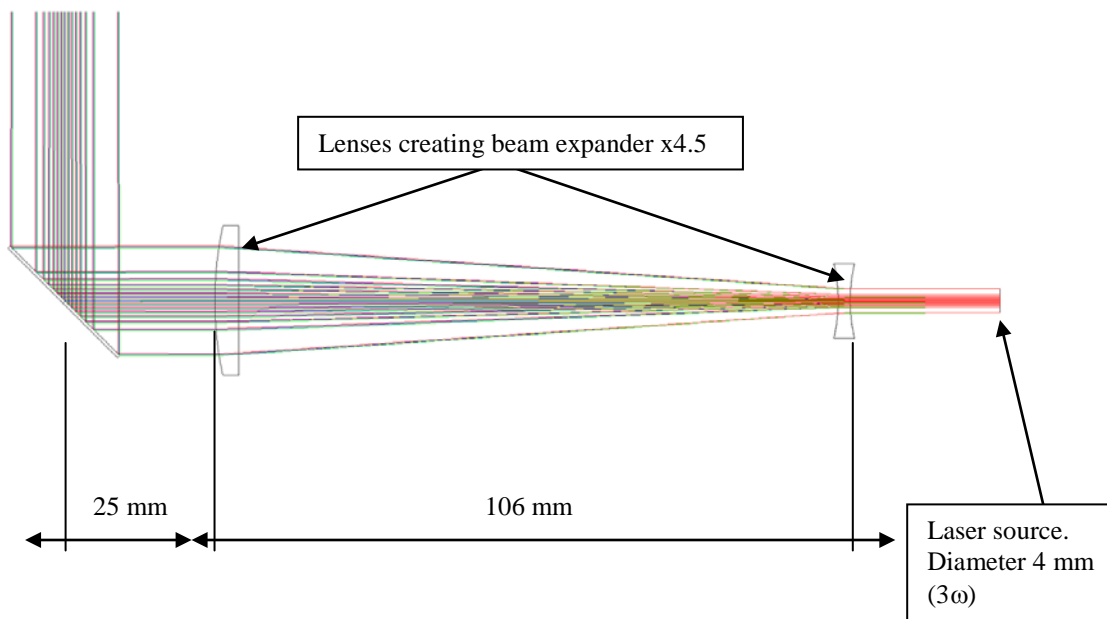
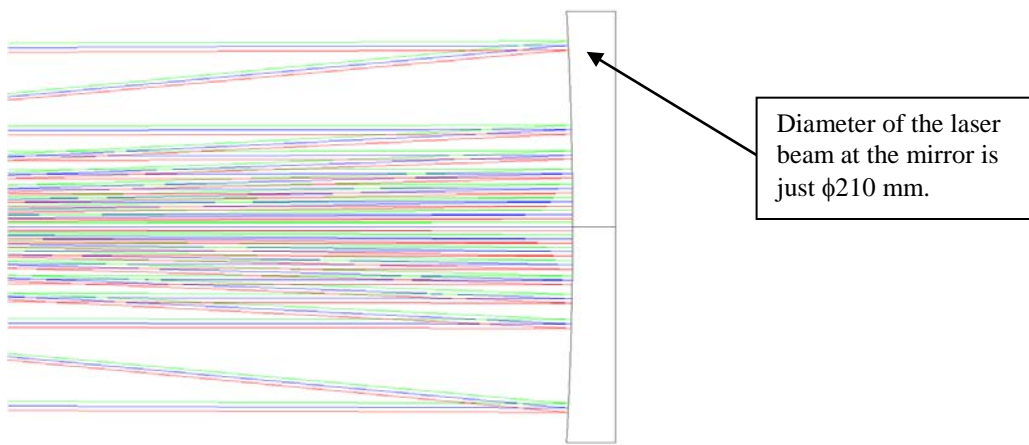
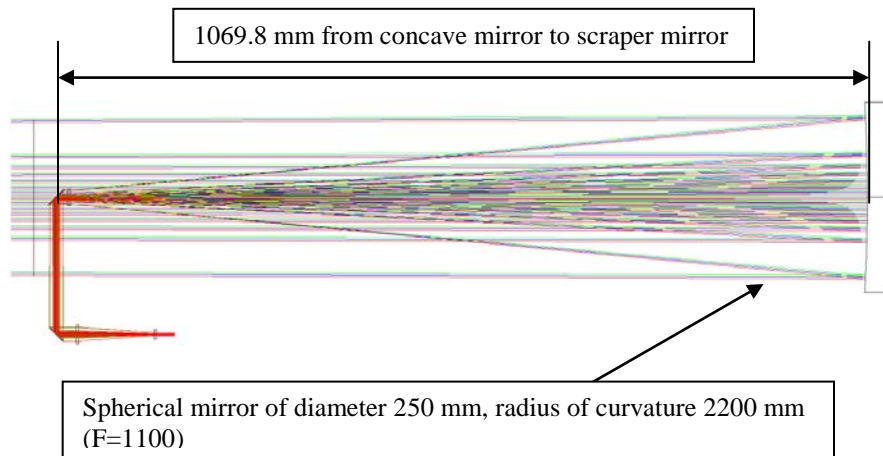
For the prototype system, the following main components were selected, checked and purchased:

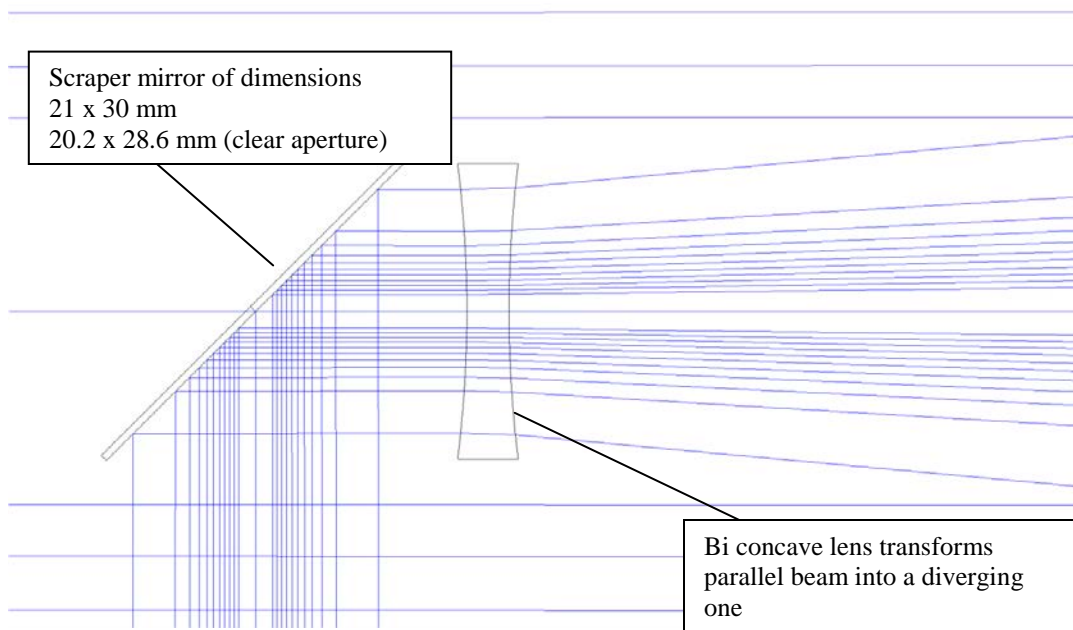
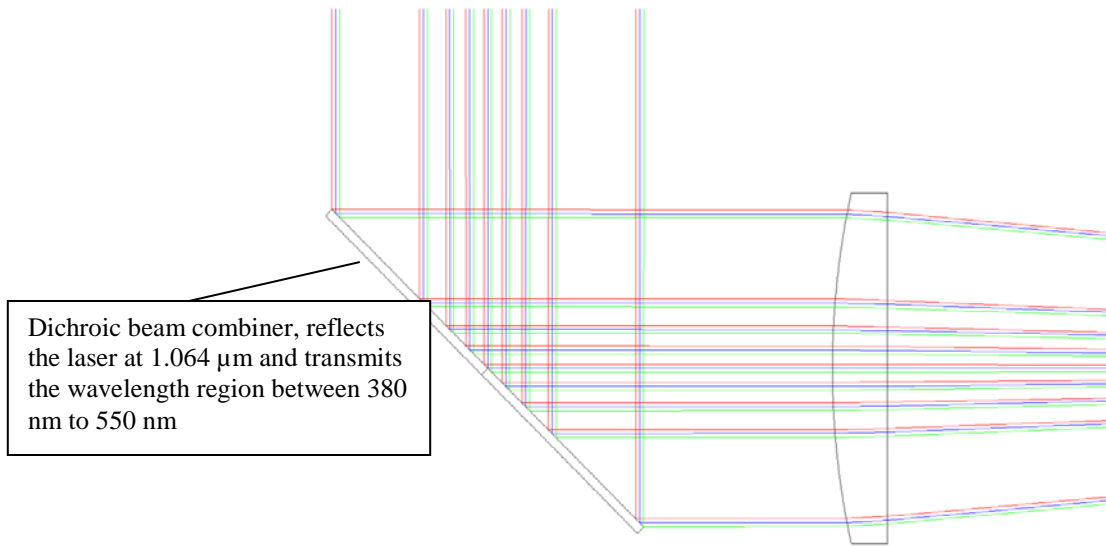
1. A Big Sky Nd-YAG laser source with energy per pulse of 100 mJ, pulse duration of 7 ns and frequency of 10 Hz. This specific laser source was specially checked by the producer in order to guarantee the needed beam quality parameter M^2 .
2. An AvaSpec-2048 industrial gated CCD spectrometer for the 385-525 nm spectral range with a changeable delay time from 100 ns and a fixed gate width of 10 μs for sunlight detection. Unfortunately, this spectrometer as received from its manufacturer had a defect which we were incapable of repairing before our departure for the field testing. Thus we had to use another Avantes spectrometer that had been used in our laboratory experiments; it had a minimal gate of 1 ms and twice the spectral resolution.

DETAILED OPTICAL SYSTEM CONFIGURATION

Laser Path



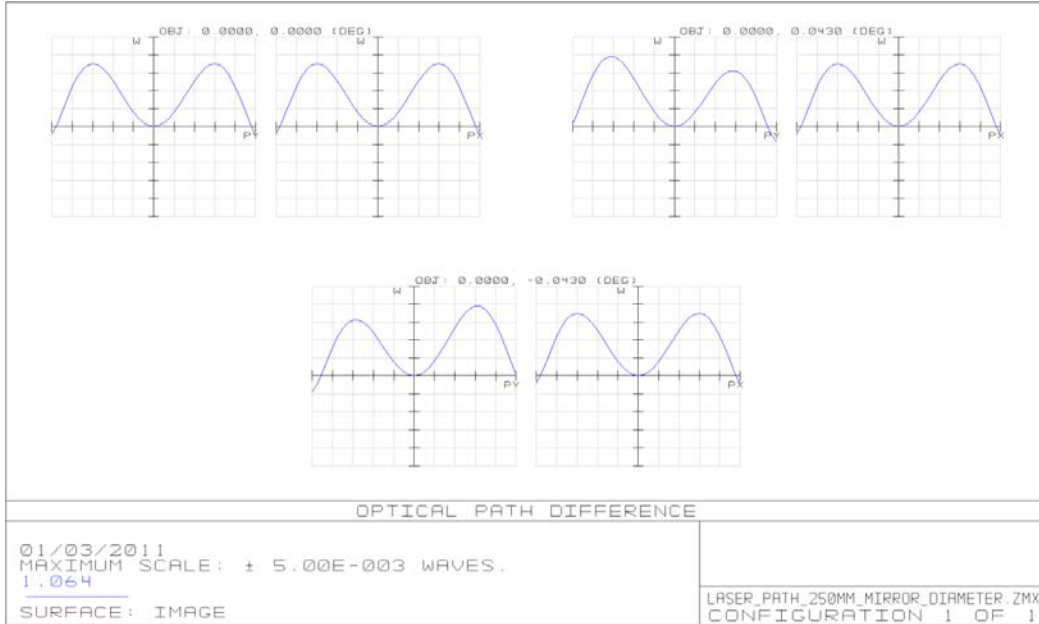




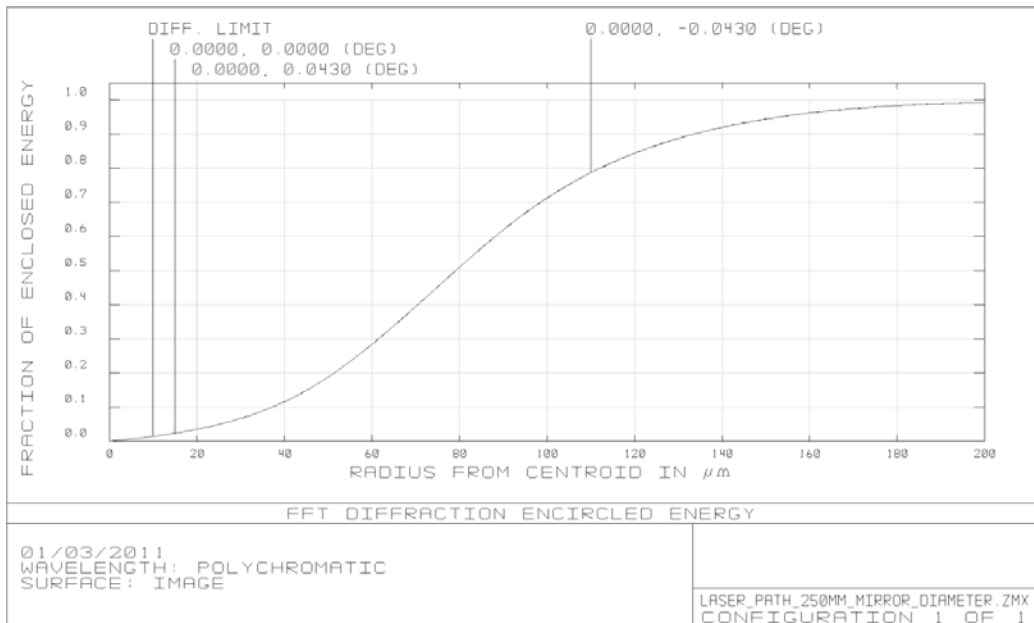
A diameter of 18 mm was chosen for the beam-expanded parallel beam. This is the 3ω diameter. The reason for such a large diameter is that the scraper mirror coating has to reflect both the laser at 1.064 μm and the collection beam in the wavelength region between 380 and 550 nm. It is evident that a dielectric coating is unsuitable and an enhanced aluminum coating is necessary. It is known that the damage threshold of enhanced aluminum is about 0.3 J/cm² for 20 ns pulses at 1.064 μm . By assuming the 100 mJ pulse energy and a 2ω diameter of 12 mm, then the energy density at the scraper mirror surface will be 0.0625 J/cm².

Nominal System Performance at 25 Meters

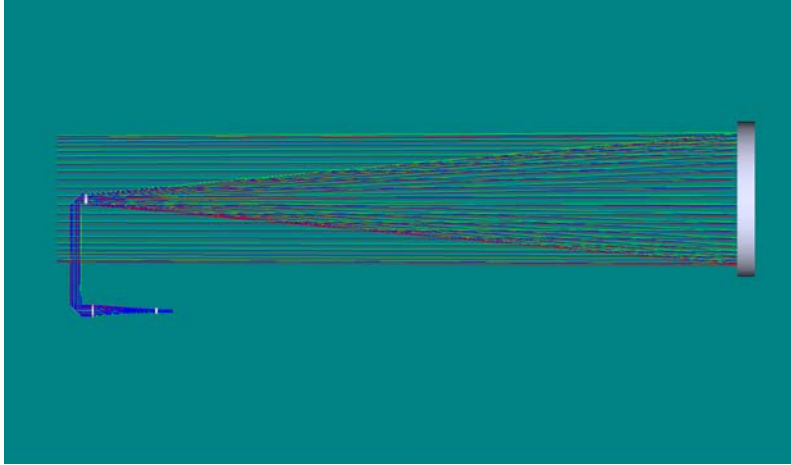
The graphs below show the OPD for the system at a working range of 25 meters. These curves are plotted assuming that there is no obscuration from the scraper mirror.



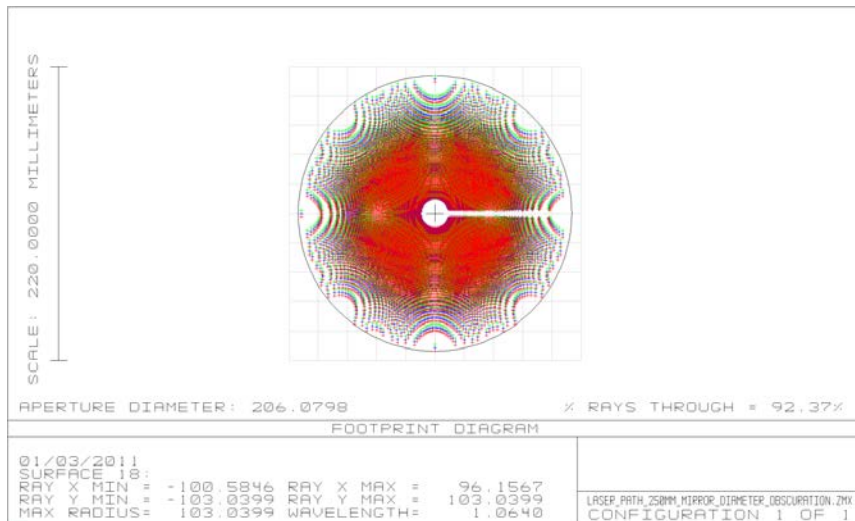
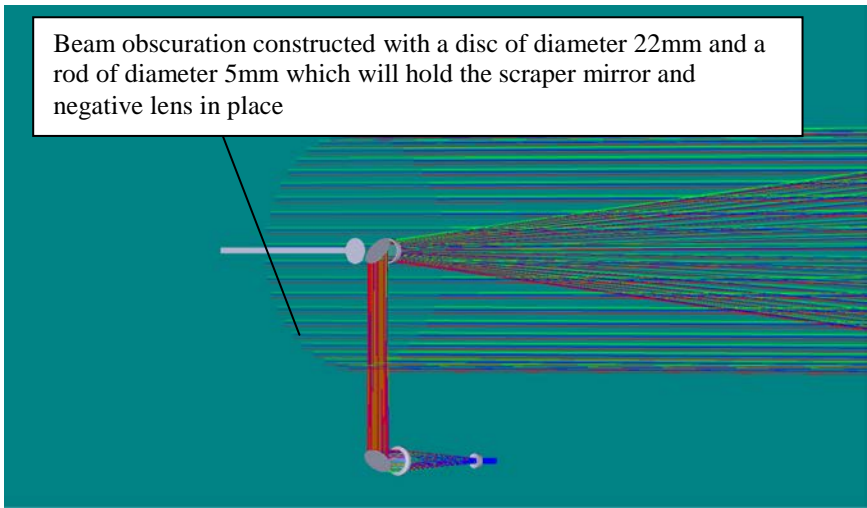
The wavefront distortion is extremely low and the system is well diffraction-limited.



Below are shown a model of the obscuration due to the scraper mirror and an estimation of the spot diameter.

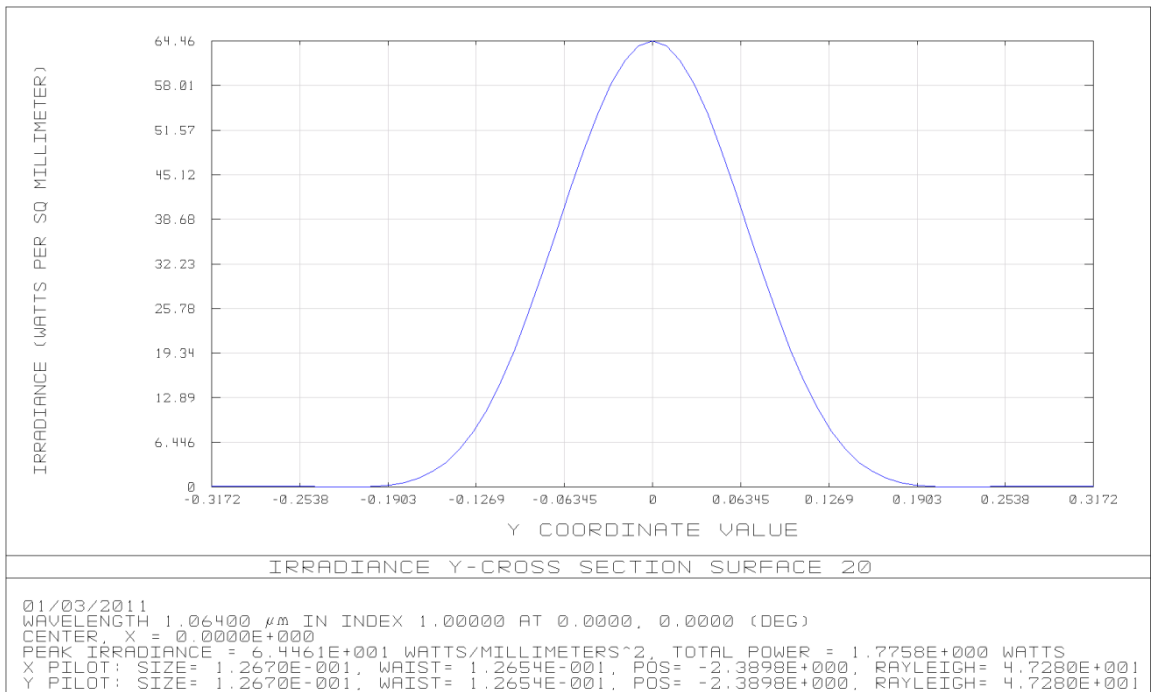
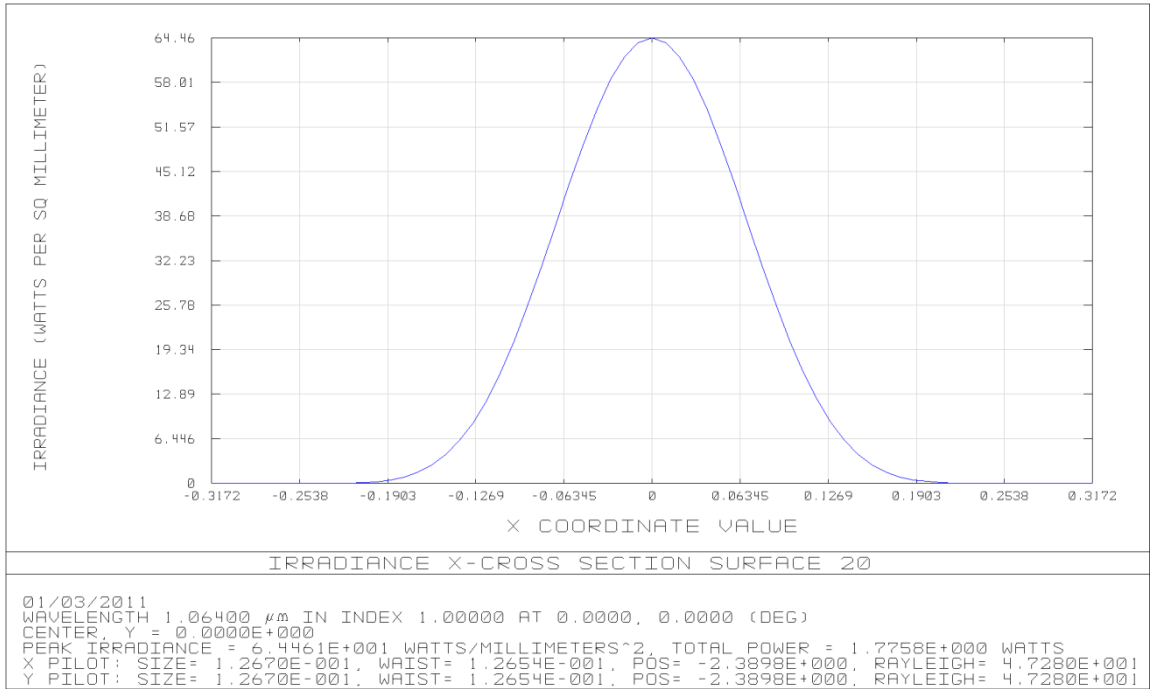


Beam obscuration constructed with a disc of diameter 22mm and a rod of diameter 5mm which will hold the scraper mirror and negative lens in place

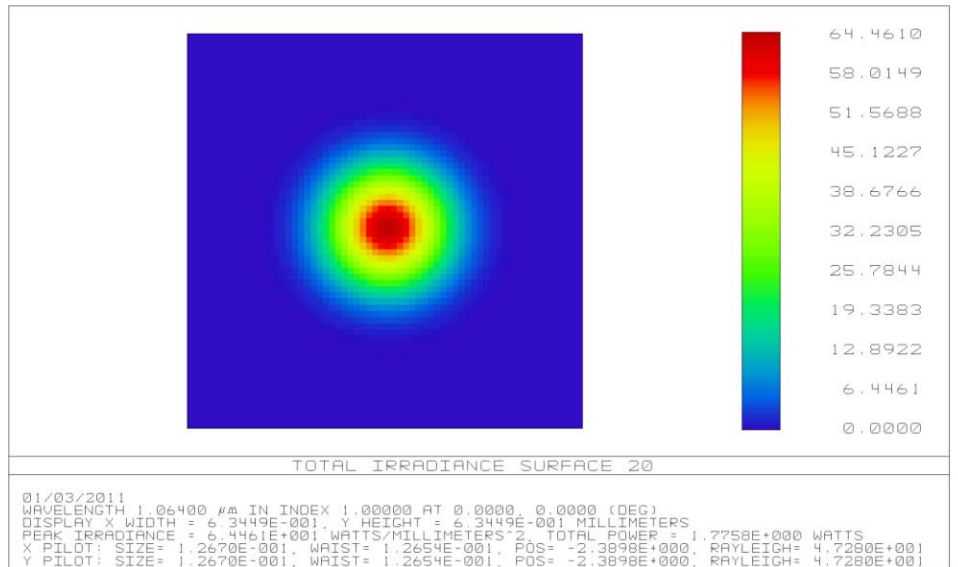


From the footprint diagram above we can see that the power loss due to the obscuration is 7.6%.

Laser Beam Spot Diameter



The spot diameter containing 86.5% of the power is 256 μm.



The blue frame is 0.634 x 0.634 mm.

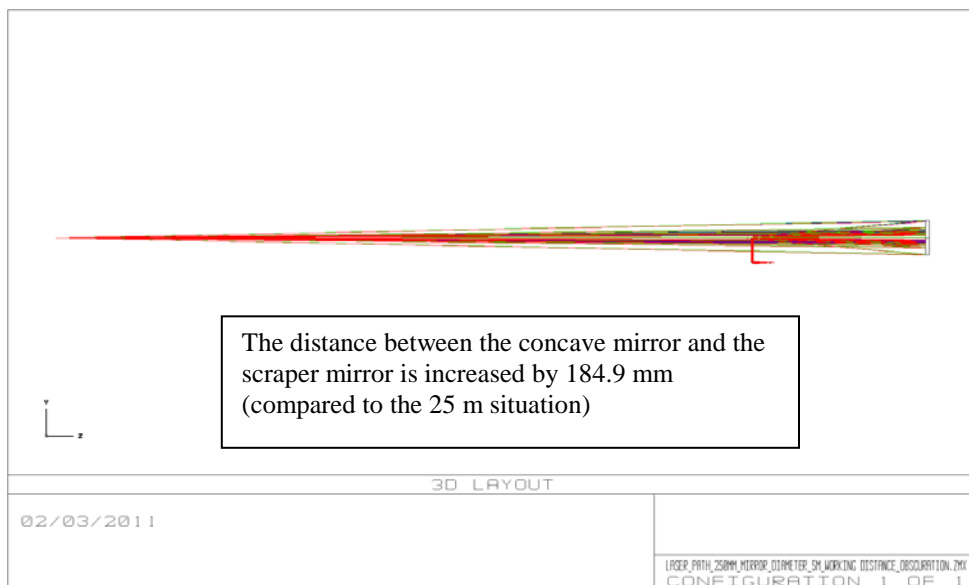
Assuming an M^2 of 2.0, then the full diameter spot will be $0.256 \times 1.5 \times 2 = 0.768$ mm.

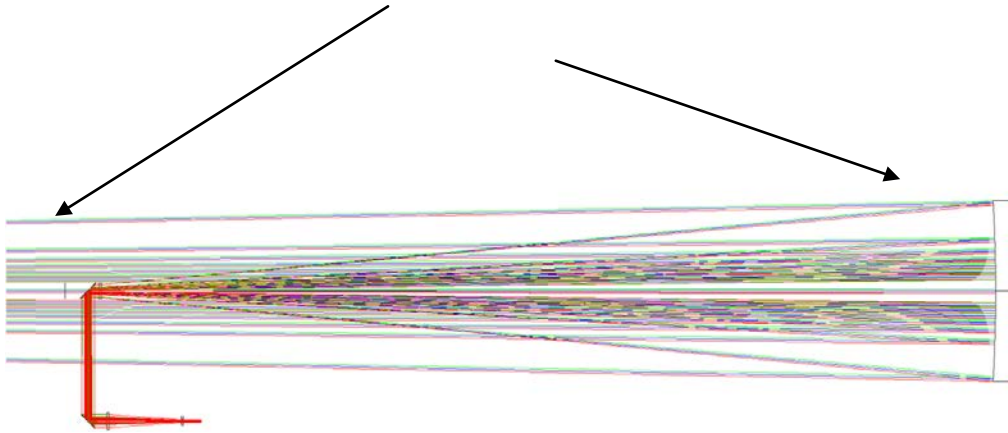
The power transfer is 92.4%, so the power density will be given by:

$$PowerDensity = \frac{0.924 \times 100 \times 10^{-3} \times 4}{\pi \times (0.0768)^2 \times 7 \times 10^{-9}}$$

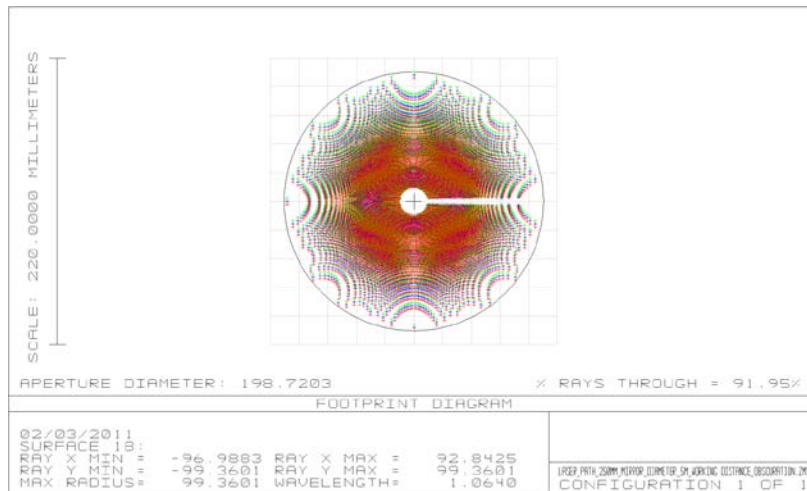
The worst case (lowest) power density is 2.85×10^9 W/cm².

Shorter Working Distance of 5 Meters



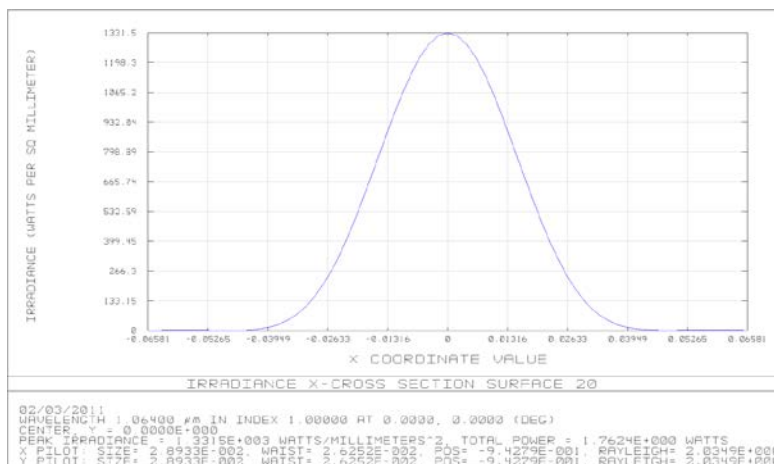


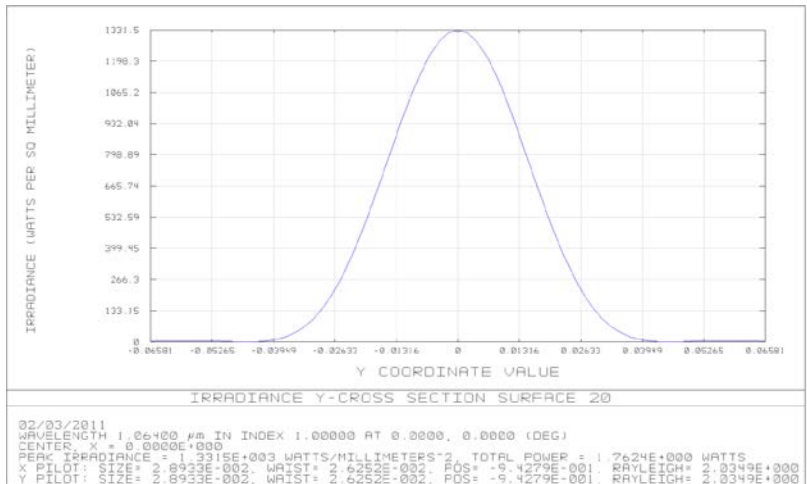
Below is the footprint of the rays just past the obscuration plane:



The power loss for this working distance is 8.0%.

Shown below is the spot diameter for this situation:





The spot diameter containing 86.5% of the power is 56 μm. Assuming an M^2 of 2.0, then the full diameter spot will be $0.056 \times 1.5 \times 2 = 0.168$ mm.

The power transfer is 92.0%, so the power density will be given by :

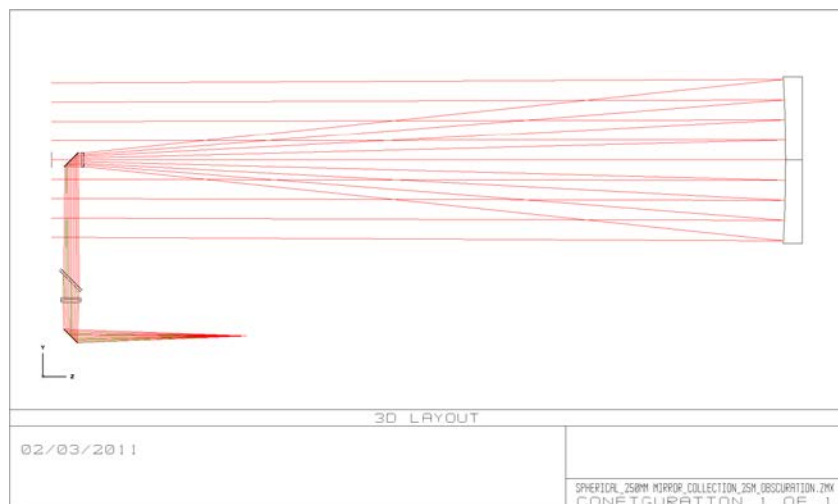
$$PowerDensity = \frac{0.92 \times 100 \times 10^{-3} \times 4}{\pi \times (0.0168)^2 \times 7 \times 10^{-9}}$$

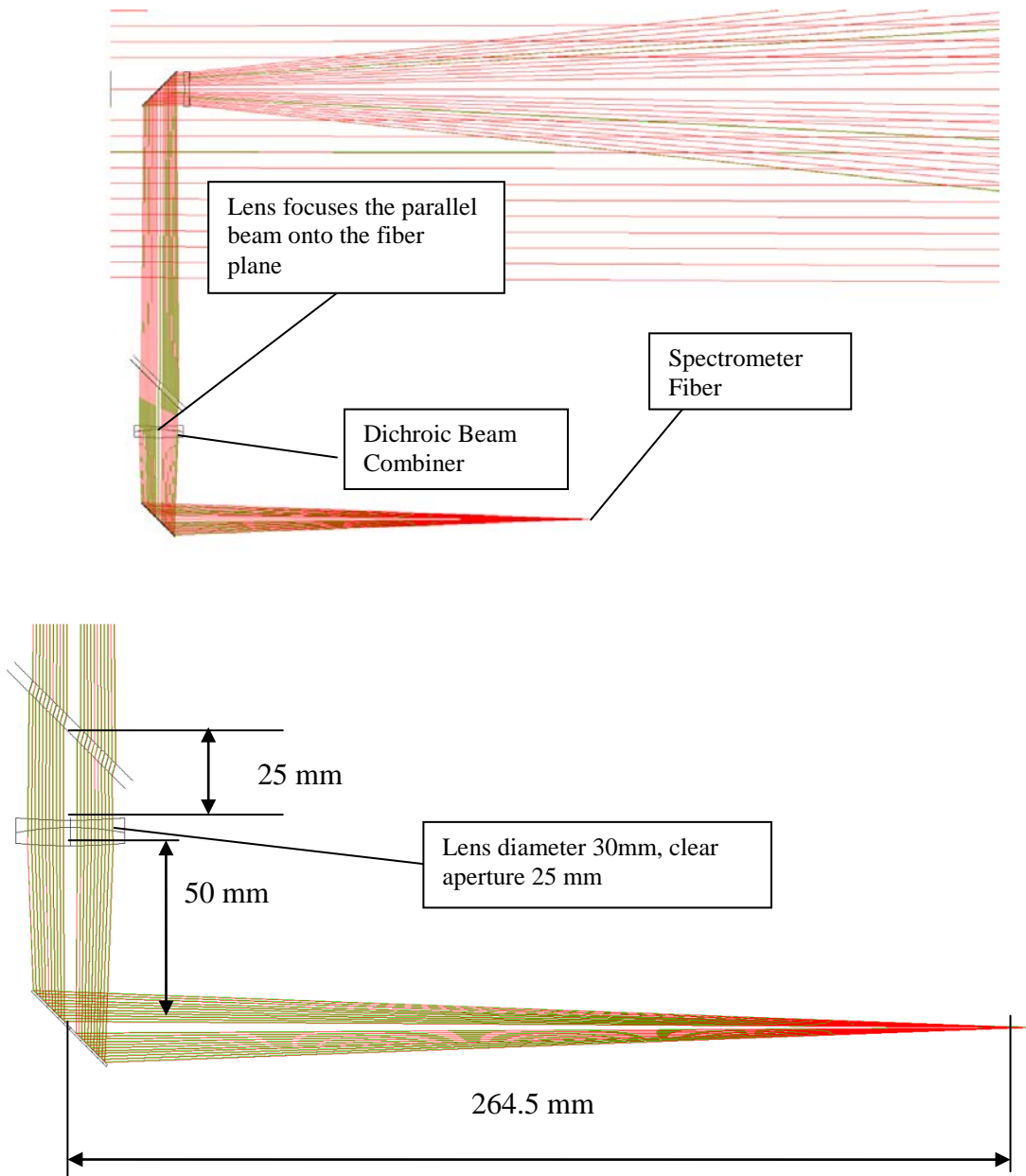
The worst case (lowest) power density at this working distance is 5.9×10^{10} W/cm².

Collection Path

The lens that focuses the collection path beam into the fiber has a numerical aperture of 0.0357. Then we can calculate the magnification of the system and the effective object size for a fiber diameter of 600 μm.

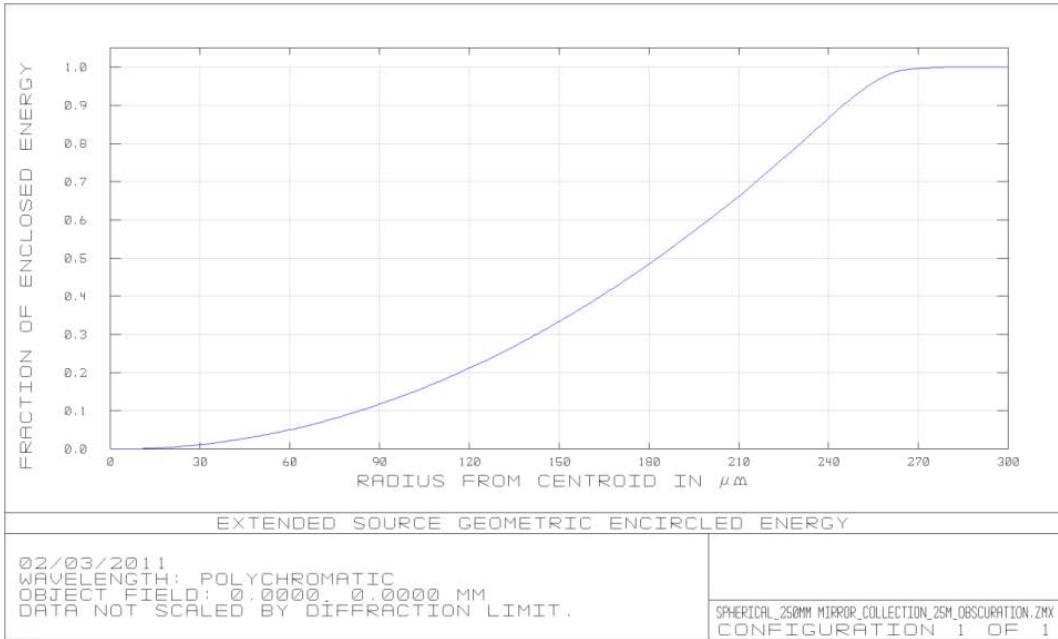
25-Meter Distance



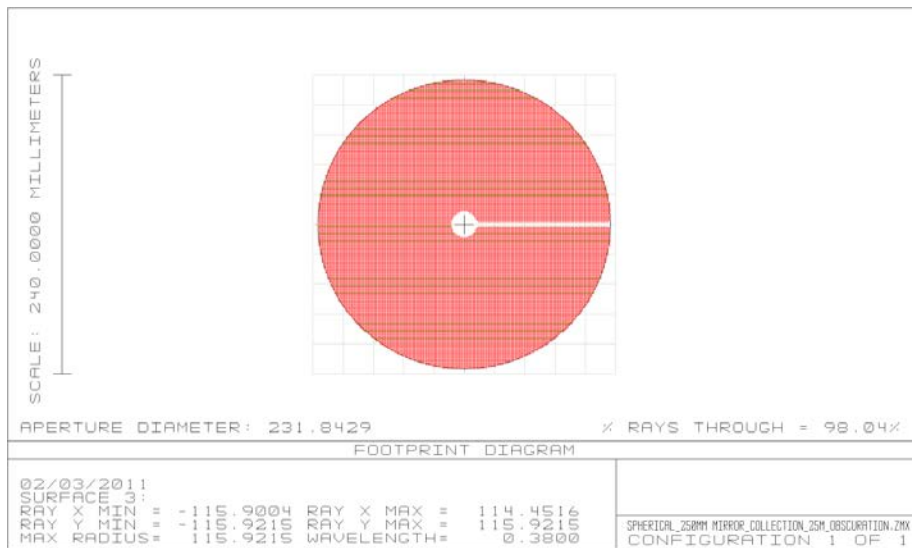


The numerical aperture of the beam into the fiber is 0.0357. The magnification of the system for the 25 m working distance is 0.1297. Therefore an object diameter of 1 mm will take up 0.1297 mm at the fiber plane. Alternatively, a 600 μm fiber will “see” an object of 4.63 mm.

Below is the extended source encircled energy plot for an object of 4mm diameter.



As can be clearly seen, the image of this 4 mm diameter object is 540 μm.

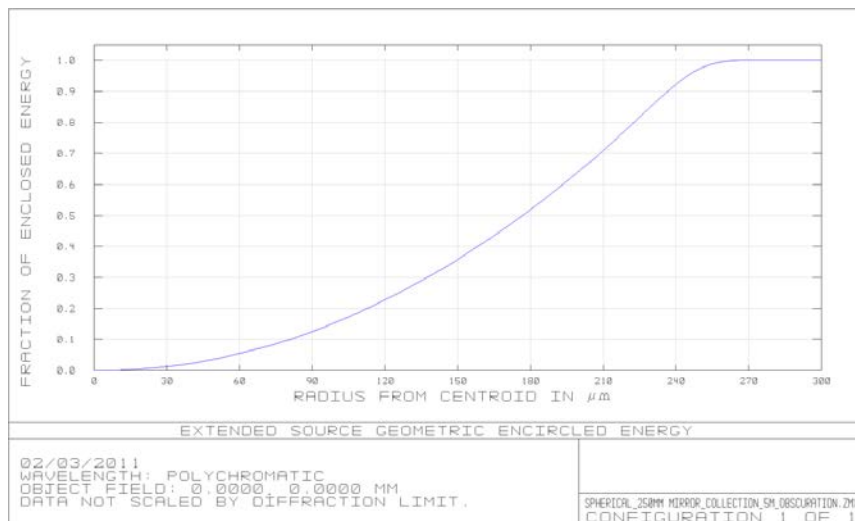


The obscuration blocks 2% of the power.

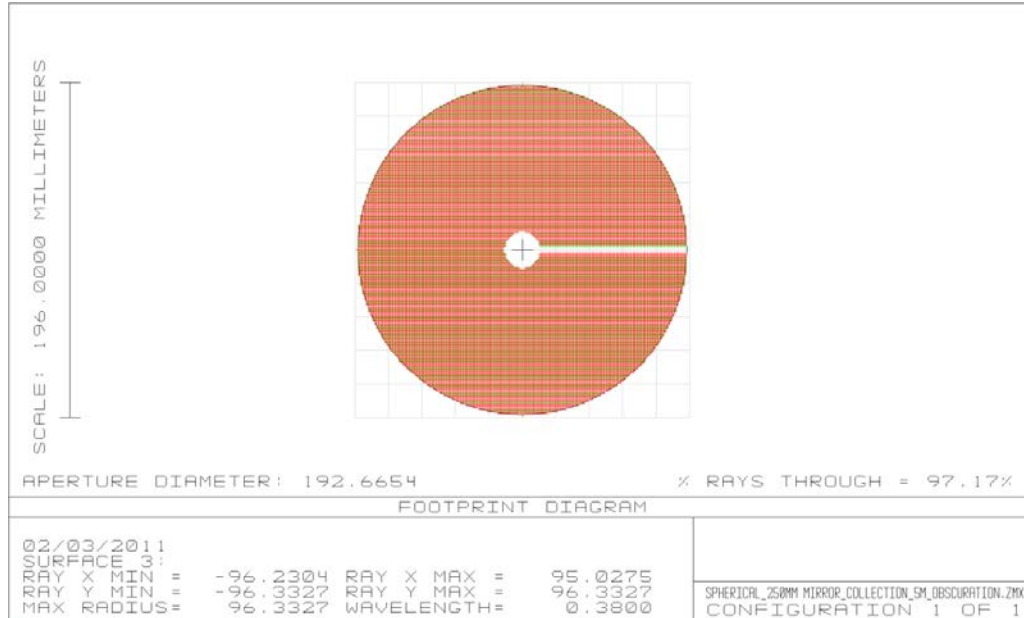
5-Meter Distance



The numerical aperture of the beam into the fiber is 0.0307. The magnification of the system for the 5 m working distance is 0.6253. Therefore an object diameter of 0.4 mm will take up 0.25 mm at the fiber plane. Alternatively, a 600 μm fiber will “see” an object of 0.96 mm. Below is the extended source encircled energy plot for an object of 0.8 mm diameter.



The image diameter is 520 μm .



The obscuration blocks 2.8 % of the power.

Analytical Algorithm Development

Remote Detection of LIBS from a Distance of 10 Meters in the Laboratory– Telescopic Detection

In the first stage of the project, before the development of the remote unit, we tested the system's capability in laboratory conditions using mine samples received from Florida. At this stage, we were not capable of creating plasma distantly, but we did have the telescopic detection system developed by LDS for remote Raman detection of explosive materials. This system is somewhat similar to those for remote LIBS detection. Thus we created plasma on the phosphate mine samples using a laser from a distance of 1 m, but the plasma detection was made from a distance of 10 m. In our experience, such an approach enables a reasonable simulation of a real-life scenario for the use of the ReLIBS system.

Figure 6 presents representative spectra received by this experimental setup from CF mine samples. It should be noted that those spectra were detected using a relatively simple and inexpensive AvaSpec spectrometer, similar to those used in the LDS online analyzers. The telescopic system developed specifically for the ReLIBS has to be more effective than the system used in the present experiments. Thus we determined that LIBS detection from longer distances of up to 25-30 m will be possible.

Figure 7 presents the preliminary results of ReLIBS analysis for differentiation between the CF mine samples with low- and high-BPL contents. It may be seen that the correlations are similar to those based on laboratory analysis data (Figure 4). Thus ReLIBS data correspond well with laboratory ones. The next stage was to evaluate the accuracy of MgO determination by ReLIBS. Figure 8 presents a comparison between the CaO/MgO ratio determined by ReLIBS and in the laboratory for the samples with low Fe, Si and Al. It may be seen that the correlation is quite reasonable. Figure 9 presents the differentiation for low- and high-MgO rocks with high BPL levels. The results are similar to those received from the laboratory analysis (Figure 5). Thus it may be concluded that ReLIBS will achieve this goal also.

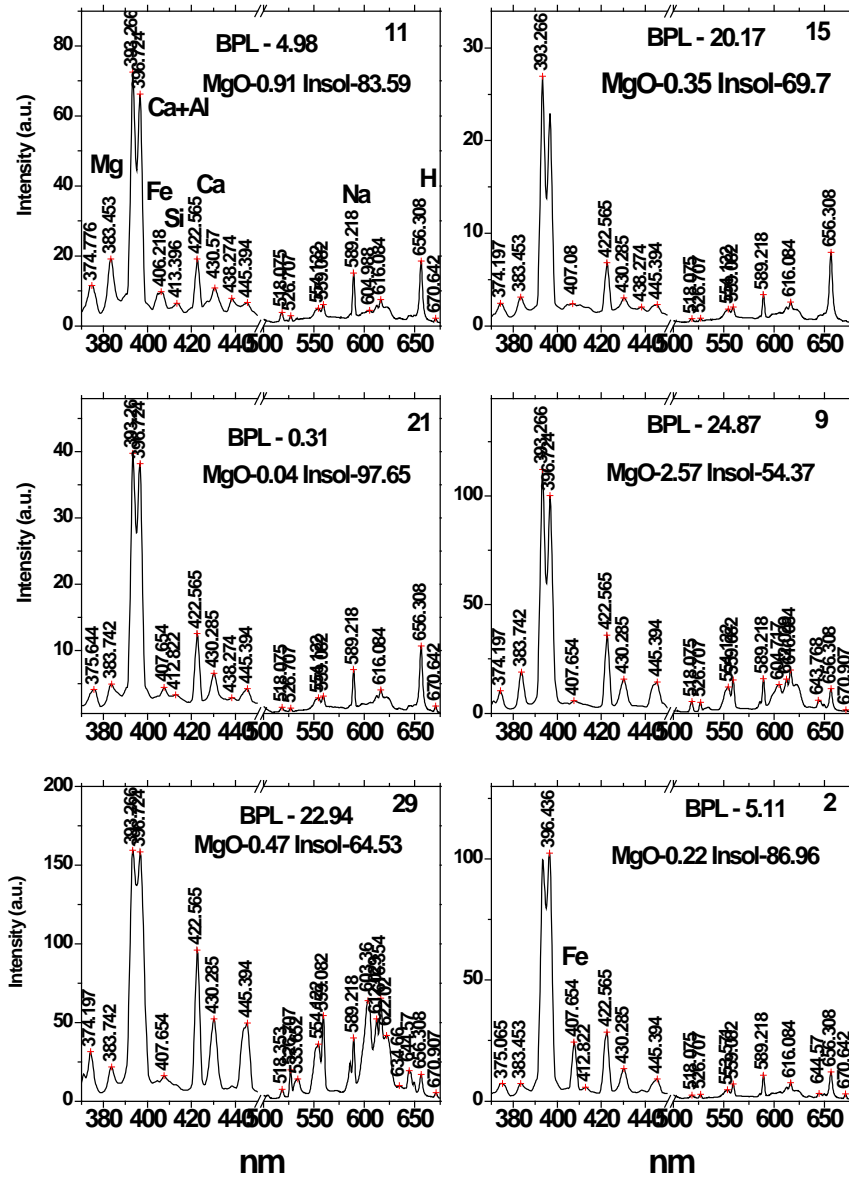


Figure 6. Representative Remote LIBS Spectra in Visible Range of Phosphate Mine Samples, CF Industries, Florida (see sample numbers and corresponding info in Table 1).

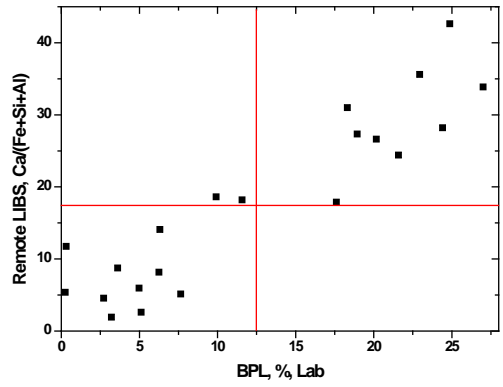


Figure 7. Correlation Between Remote LIBS CaO/Insol and BPL Content for CF Industries Mine Samples.

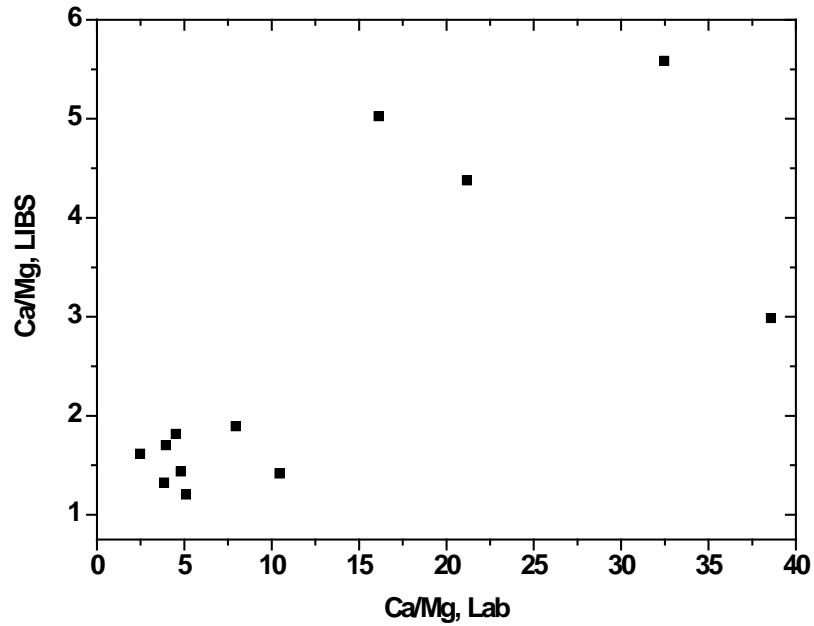


Figure 8. Correlation Between Remote LIBS CaO/MgO and Laboratory CaO/MgO for CF Industries Mine Samples.

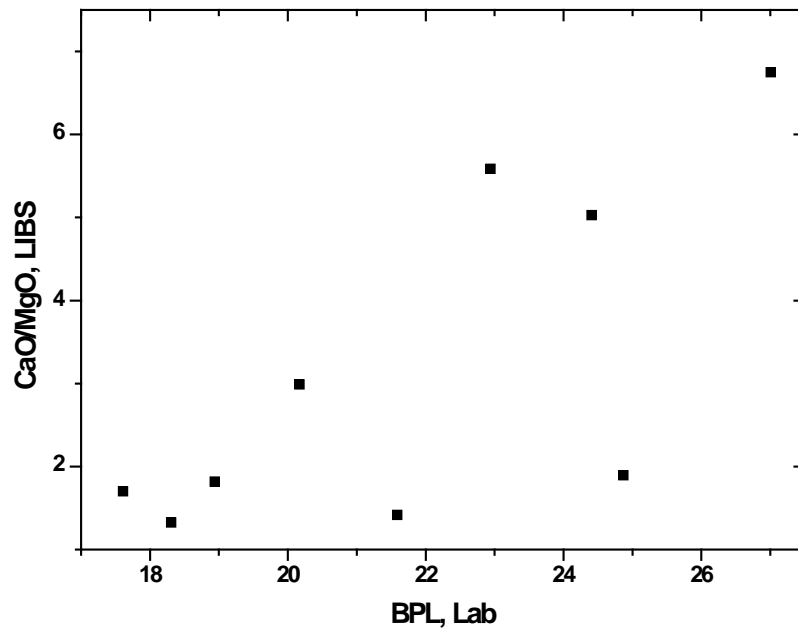


Figure 9. Separation of Rock Types with High BPL and Low MgO Levels According to Remote LIBS Data.

Remote Detection of LIBS from a Distance of 16 Meters in the Laboratory with ReLIBS Unit

The second-stage goal was to analyze phosphate rocks from Florida using the ReLIBS unit from different distances. Mostly it was done from a distance of 16 m, which is the largest space achievable inside our laboratory. Experiments from a distance of 25 m were accomplished outside the lab, but were of short duration because of concerns about eye safety.

Figure 10 presents breakdown spectra of different pure minerals, which contain elements important for the analysis of phosphate rocks, using ReLIBS from a distance of 16 m. The plasma was successfully created from this distance and it may be seen that lines characteristic for all relevant elements are detected. Figure 11 presents typical spectra received from different CF mine samples using ReLIBS. Starting from approximately BPL = 10 and higher, Ca emission lines dominate the spectrum. With lower BPL contents, the relative intensity of Al, Fe and Si lines becomes higher. An unusual line was detected at 453.3 nm which may not be ascribed based on pure elements data (Figure 10). According to its spectral characteristics, it may be preliminarily ascribed to Ti.

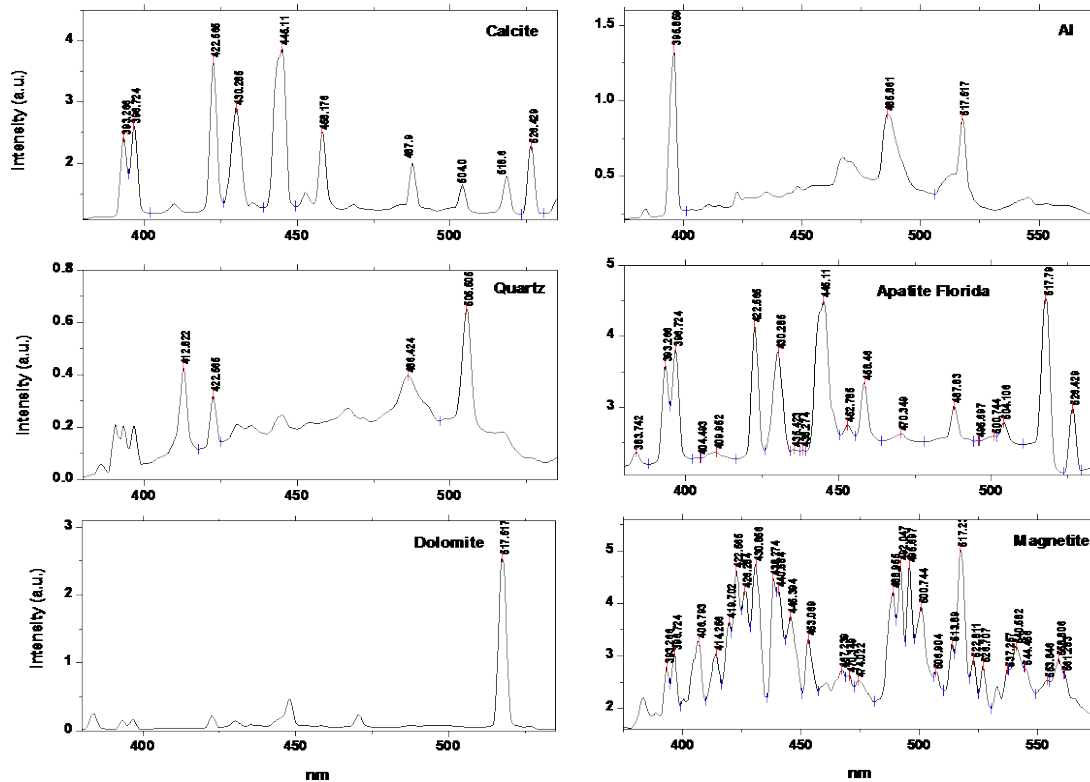


Figure 10. Breakdown Spectra of Different Minerals Relevant for Phosphate Rocks by ReLIBS from a Distance of 16 Meters.

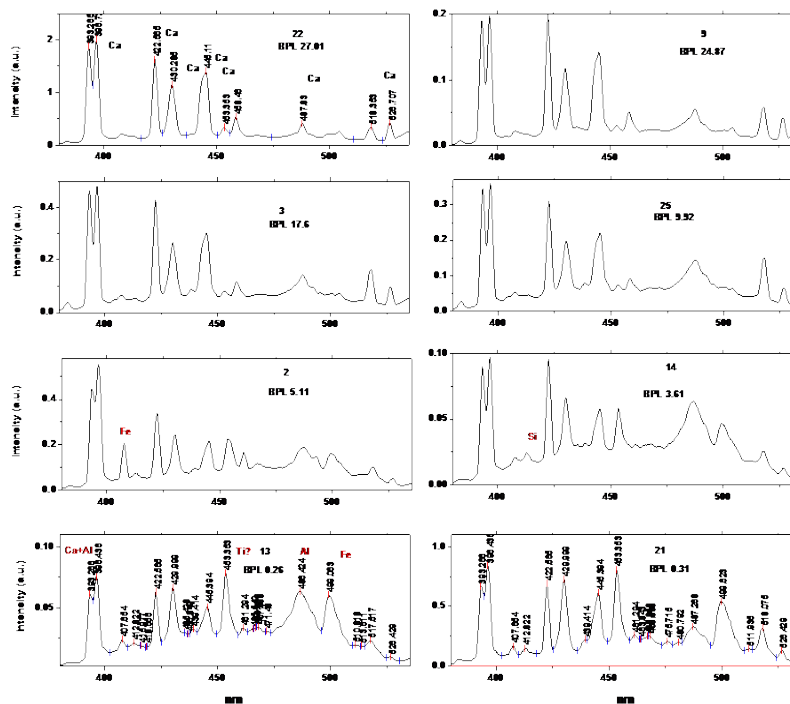


Figure 11. Representative Remote LIBS Spectra of Phosphate Mine Samples, CF Industries, Florida (see sample numbers and corresponding info in Table 1).

Figure 12 presents the results of ReLIBS analysis for differentiation between the CF Industries mine samples with low- and high-BPL contents from a distance of 16 m. Correlation is very good with $R^2 = 0.915$. Thus ReLIBS is capable of differentiating between mine samples with low, intermediate, and high BPL.

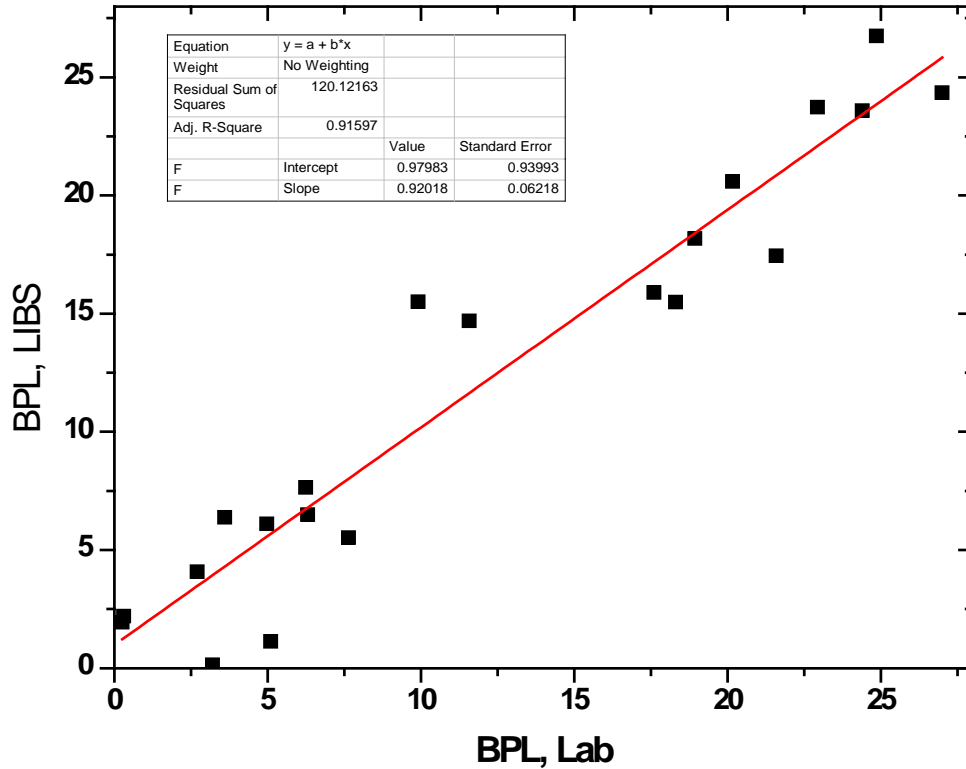


Figure 12. Correlation Between Remote LIBS CaO/Insol and BPL Content for CF Industries Mine Samples.

The next objective was to evaluate the accuracy of MgO determination by ReLIBS. Figure 13 represents a comparison between MgO determined by ReLIBS and in the laboratory for mine samples with high BPL levels. The correlation is worse as related to BPL with $R^2 = 0.75$, but it will be sufficient to differentiate between high-BPL mine samples with regard to their MgO content.

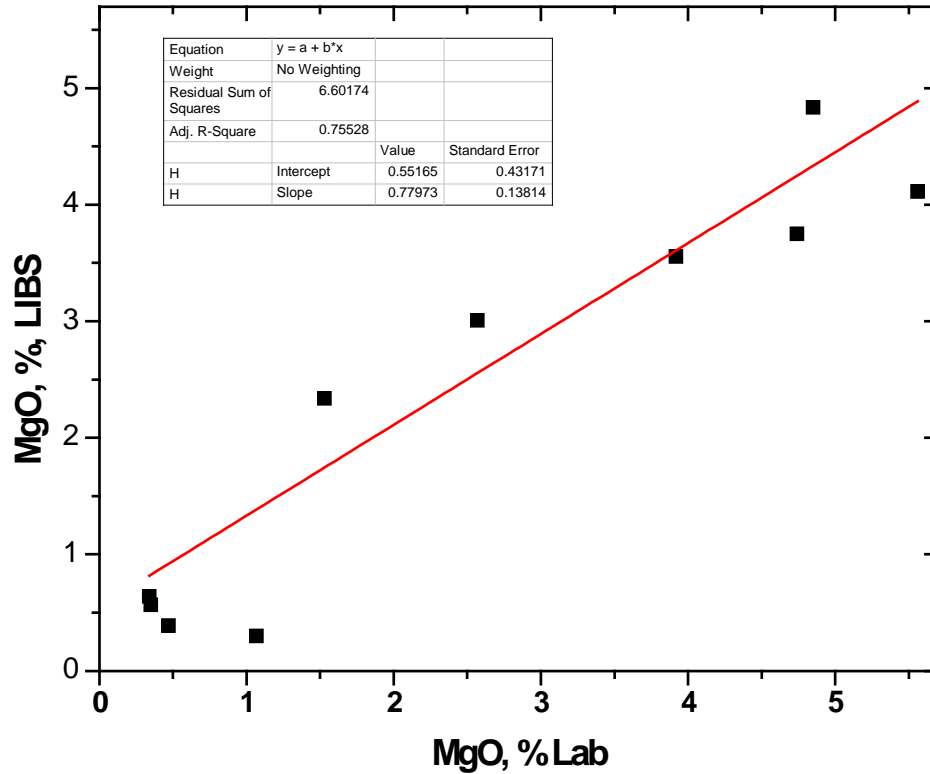


Figure 13. Correlation Between ReLIBS and Laboratory MgO for CF Industries Mine Samples with High BPL.

Remote Detection of LIBS from Distances of 10-25 Meters Under Field Conditions with ReLIBS Unit

Figure 14 shows the ReLIBS unit under field conditions (CF Industries, Florida). The system sustained the transportation well and was assembled in approximately 1.5 hours. It should be noted that in the feasibility stage the unit was not equipped with air conditioning and special dust protection systems, which are part of the LDS above-belt LIBS units. Nevertheless, it worked well under ambient conditions.

During the first testing stage, the dragline operator put three piles of different mine samples, overburden, matrix and bottom, on the ground. Those piles were then subjected to ReLIBS analysis from distances of 10-25 m using the test unit. It was found that plasma was well created by the remote unit from all the studied distances. Figure 15 presents typical breakdown spectra received from those piles. The detected intensity of the signals' dependence on the distance (R) corresponded well to the $1/R^2$ law. For example, the intensity from a 20 m distance is four times lower than that from a 10 m distance. The spectral types are quite similar to those detected under laboratory conditions. Namely, matrix is characterized by Ca emission lines, while overburden and bottom emission spectra contain strong lines of Al, Fe, Mg and Si. Thus the goal of remote identification of those mine sample types was successfully achieved.



Figure 14. Remote LIBS Unit During Test Under Field Conditions, CF Industries, Florida.

The next step was to evaluate the ability for more detailed differentiation between rock samples. Twelve samples analyzed by the ReLIBS unit were analyzed in the laboratory to determine the concentrations of main and impurity elements (Table 4). Three matrix samples were taken from the eastern part of the mine, with another three matrix, three overburden and three bottom samples taken from the western part of the mine. Figure 16 presents the corresponding calibration curve. The developed analytical algorithm gave a good prediction of P_2O_5 for eleven of the twelve samples. The linearity

coefficient $R^2 = 0.95$ was extremely good. One matrix sample was strongly out of this correlation and the reason for this was not understood. Another important task is remote evaluation of MgO impurities in matrix. Figure 17 presents the corresponding correlation between ReLIBS and laboratory data demonstrating a very good linearity coefficient of 0.93. Thus it may be concluded that ReLIBS is a promising tool for real-time analyses of the materials excavated by draglines.

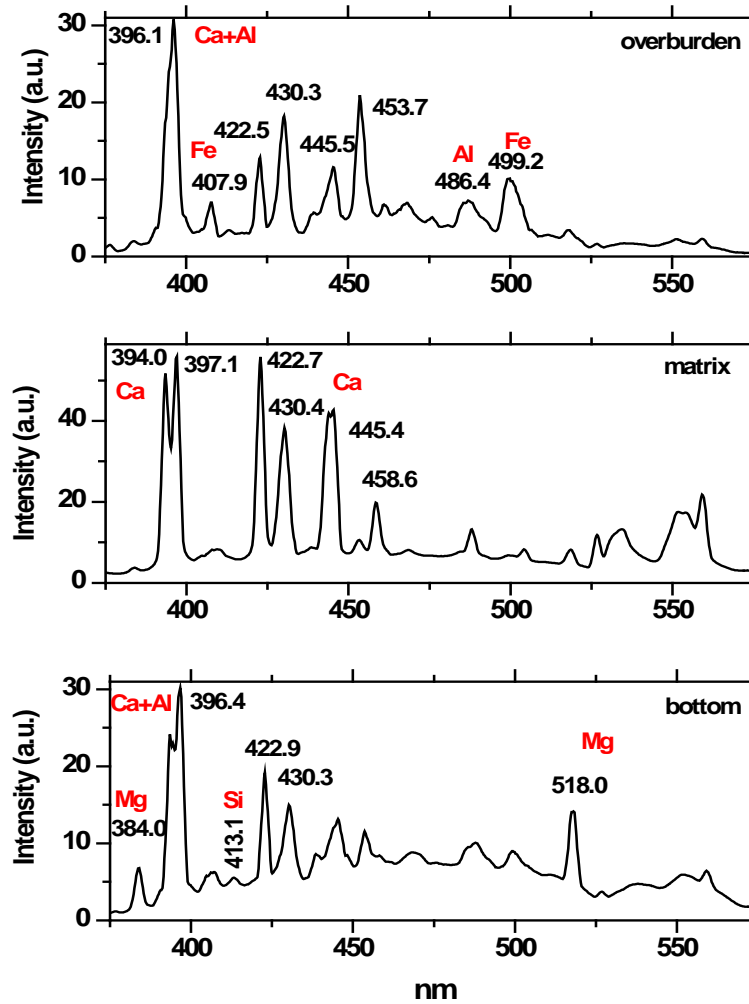


Figure 15. Typical Breakdown Spectra of Different Mine Samples Detected in Field Conditions by ReLIBS Unit from a Distance of 20 Meters.

Table 4. Chemical Compositions of Twelve Samples Distantly Analyzed by the ReLIBS Unit.

Sample	P ₂ O ₅	Insol	Fe ₂ O ₃	Al ₂ O ₃	MgO	MER	CaO
Matrix.16.9_1	10.64	64.19	0.67	5.21	0.57	0.6	12.96
Matrix.16.9_2	14.81	51.46	0.77	4.78	0.62	0.4	20.26
Matrix.16.9_3	16.94	46.38	0.79	3.56	0.56	0.3	24.36
Matrix.20.9_1	9.42	68.47	0.62	2.72	0.23	0.4	13.16
Matrix.20.9_2	9.55	67.67	0.66	5.07	0.14	0.6	11.41
Matrix.20.9_3	10.84	61.98	0.88	6.05	0.18	0.7	13.48
Bottom 20.9_1	3	88.44	0.29	0.65	0.3	0.4	4.67
Bottom 20.9_2	0.69	96.35	0.09	0.17	0.11	0.5	1.11
Bottom 20.9_3	3.7	82.56	0.51	2.63	0.53	1	5.86
Overburden1	3.2	86.65	0.96	1.37	0.55	0.9	4.89
Overburden2	3.47	84.24	1.15	1.62	0.58	1	5.31
Overburden3	3.27	85.78	1.07	1.35	0.5	0.9	4.97

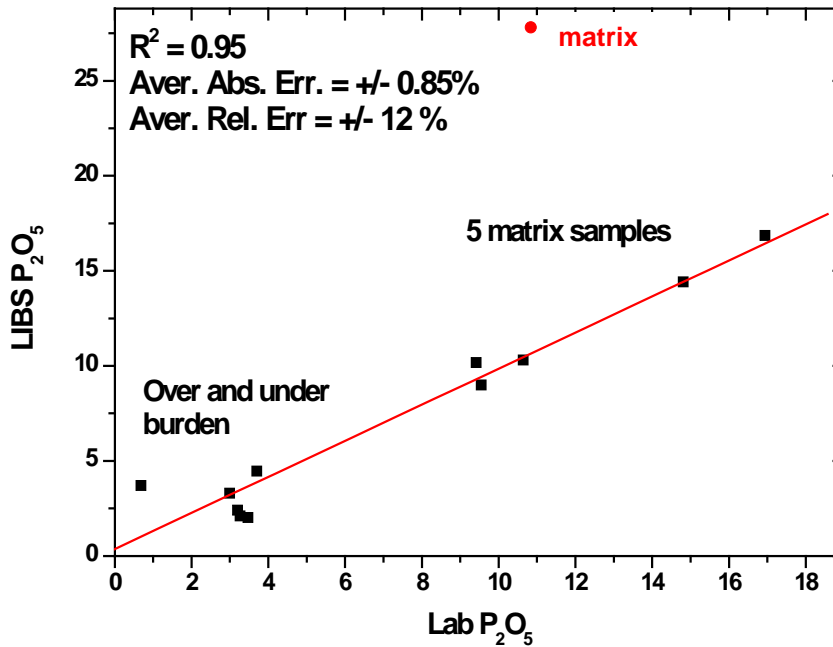


Figure 16. Correlation Between ReLIBS and Laboratory Data for P₂O₅ in Different Rock Types.

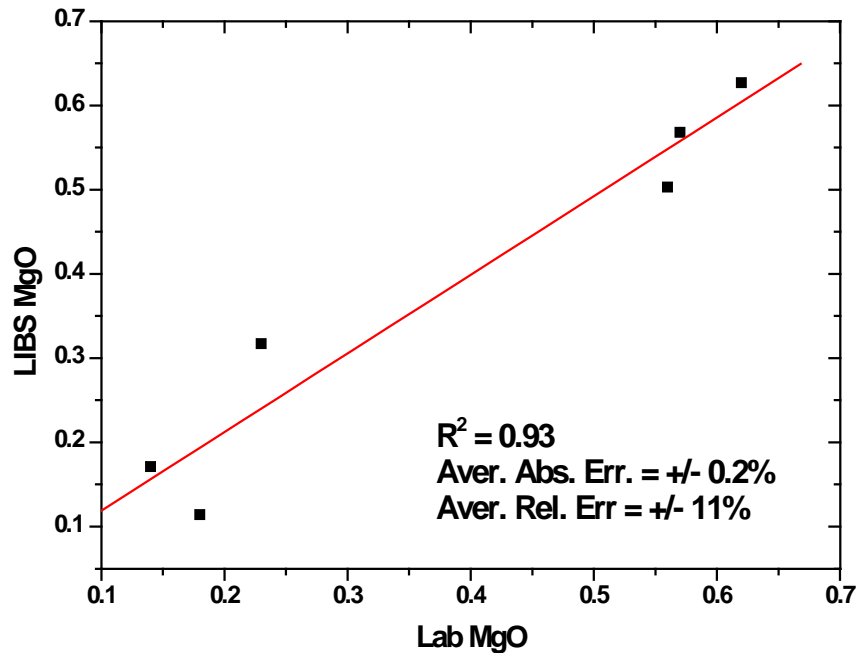


Figure 17. Correlation Between ReLIBS and Laboratory Data for MgO in Matrix Samples.

FUTURE IMPROVEMENTS IN DEVICE DESIGN

From what was learned from the field experiments, the following changes must be made in order to improve the device’s performance.

The spectrometer used was not optimal. The gating time of 1 ms is too long to totally eliminate the strong sunlight emission and when it strikes directly on the target the broad spectral band interferes with plasma emission. In order to remove this interference, gating time has to be shortened to 10-100 μ s. The main elements involved in the analytical algorithm are Ca, Mg, Fe, Si and Al. All those elements are much easier to detect in UV rather than in the visible spectrum. According to our cumulative experience, a 240-320 nm range will be optimal for this specific task. The spectral resolution will be twice that of the present spectrometers. All these requirements may be easily incorporated into a future device.

The present laser has 100 mJ/pulse energy and 10 Hz frequency. In order to minimize the analysis time, the frequency must be higher, perhaps as high as 100 Hz. The possibility of 200 mJ/pulse energy has to be considered. The Big Sky compact and ruggedized CFR 200 Nd-YAG laser with 200 mJ/pulse energy and 100 Hz frequency may be a good candidate for such a system.

The profile change is relatively large, and the device has to be equipped with a distance measuring device and the ability to rearrange the optical system in accordance with the changing distance between the device and target.

THE SEARCH FOR AN OPTIMAL SITE FOR THE ReLIBS UNIT

The main task of the ReLIBS analyzer is for “horizon control” in open mining. Presently the dragline operators are advised by field geologists on what to mine based on information from drill cores and visual observation. Nevertheless, such information may be erroneous. This generally results in at least some inclusion of overburden or base material in with the phosphate matrix or, alternatively, casts matrix aside with the overburden or leaves it in the mine cut. For example, in one of the tests, 56 samples of overburden, matrix, and bed according to drill cores were collected from 7 mines and analyzed. Out of the 51 samples which were clearly analyzed as “Mine” or “No Mine,” only 75% were correct. Compared to what was actually being mined, “correct” mining would have increased production by 9% and reduced MgO by 50%. However, actual mining was being controlled by the dragline operators. What if a geologist had been present? The same 56 samples were viewed by five geologists and characterized as being “Mine” or “No Mine.” The average accuracy was 79% (73-84%). All five geologists got the right answer on 31 of the samples and the wrong answer on 3 of the samples. Both the dragline operators and geologists were mining matrix containing as low as 2% BPL or with an MgO over 8%. Both the dragline operators and geologists were leaving overburden or bedrock containing over 30% BPL and less than 0.2% MgO. It is not always possible to physically see the difference between matrix and non-matrix. At one mine, samples of overburden, matrix and bedrock at each dragline were taken each day. Several hundred samples were taken depending on the criteria used. The accuracy of what was being mined (compared to what should have been mined) was 70-85%.

It is evident that the impact of correct mining is to increase production and improve quality. But where is the best location for the ReLIBS unit? In our original proposal it was supposed that the best place was on the dragline with the task of scanning the surface, and then based on the results, deciding what or where to mine (Figure 18). Such an opportunity is very attractive, but its practical realization is quite a challenge. The main reasons are the unsteady platform of the dragline, and long and variable distances to the mine cut.

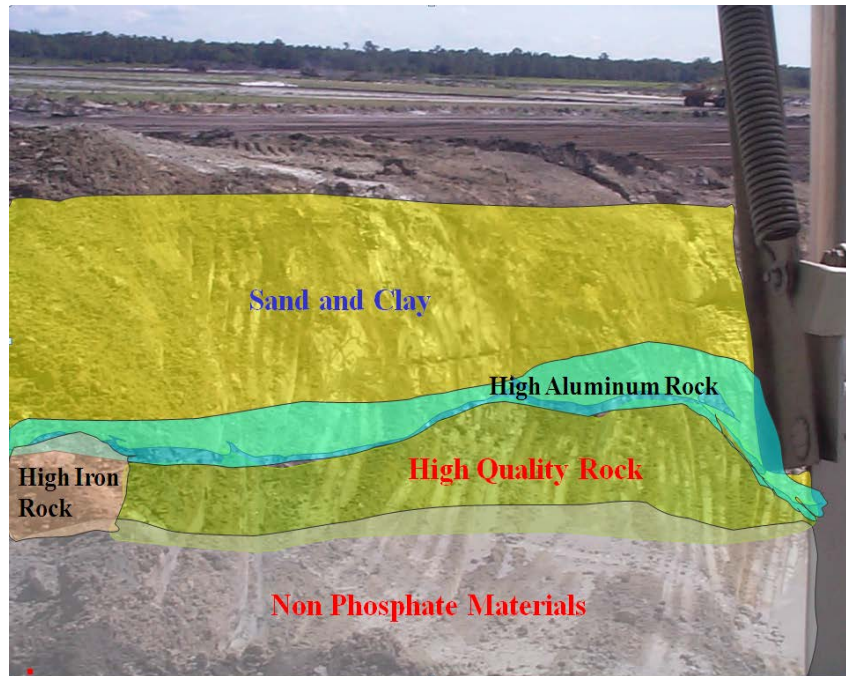


Figure 18. Potential Application of the ReLIBS Unit to Give the Dragline Operator the Ability of Selective Excavation.

As a result of the present field test, another device position was found and tested. It was the pit where the dragline operator puts the excavated matrix. At the pit the matrix material is sluiced with water to provide a slurry for pipeline transportation to the beneficiation plant (Figure 19). The advantages of such a position are evident:



Figure 19. ReLIBS Unit Situated at the Washing Pit Site Facing Matrix Rock Delivered by the Dragline.

- The information for the dragline operator is practically real-time; only one bucket later compared to the information from the unit mounted on the dragline;
- The distance is approximately 15-20 m, which is in the range of the existing machine;
- The distance is substantially less variable compared to the actual mine cut;
- The safety issue is substantially less severe because no one is allowed near the pit.

The only potential problem may be some delays in the matrix sluicing process, because this has to be stopped for a certain time to accomplish the scanning process. Nevertheless, according to our preliminary results this time will be relatively short, less than 1 min, when using a laser source with 100 Hz frequency. Besides, not every bucket has to be analyzed, only those in unclear excavating zones.

CONCLUSIONS

1. The ReLIBS device proved the feasibility of distant real-time chemical analysis of phosphate minerals excavated by the dragline and provided:

- (a) Differentiation between overburden, matrix and bottom;
- (b) Evaluation of P_2O_5 content;
- (c) Evaluation of MgO content in matrix samples.

2. The optimal position for the device was found to be the washing pit where the matrix is piled prior to slurring for transportation to the beneficiation plant.

3. The industrial device has to be equipped with a laser source with 200 mJ/pulse of energy and 100 Hz frequency. The optical module and spectrometer have to be suitable for a 240-320 nm spectral range and the spectrometer gating time has to be less than 100 μ s.

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