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LIBS MODULE FOR DOLOMITE CONTENT EVALUATION ON A CONVEYOR

FINAL REPORT

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LIBS MODULE FOR DOLOMITE CONTENT EVALUATION ON A CONVEYOR

FINAL REPORT

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

Dolomite (MgO) content is one of the major quality indicators for the phosphate pebble product. With the depletion of the higher-grade, easy-to-process Bone Valley deposits, the central Florida phosphate industry has moved into the lower-grade, more contaminated ore bodies in the Southern Extension. The phosphate deposits in the Southern Extension may be divided into two zones: an upper zone and a lower zone. The upper zone is readily processable using the current technology, but the lower zone is highly contaminated by dolomite. This makes it more critical to control the quality of the pebble product, particularly the MgO content. Current practices require either the stockpiling of the pebble product until quality data from sampling become available, or making the shipping or discarding decision based on visual observations of rock as it is being produced. Obviously, this practice can result in the shipping of undesirable products to the chemical plant or the discard of acceptable pebbles. A reliable rapid analytical method is the ultimate solution to this problem.

In-line analysis is also important for optimizing flotation. Currently the high-dolomite phosphate pebbles are either stockpiled as a waste or left in the ground together with the associated flotation feed. This practice will not last long, because it causes the loss of too much resource. No technology on the horizon is more feasible than the flotation process for processing dolomitic phosphate pebbles. To separate dolomite from phosphate in these pebbles by flotation, fine grinding is necessary. Flotation of high-dolomite phosphate with fine grinding is more expensive than floating siliceous phosphates. Therefore, process optimization will be more important for the Florida phosphate industry in order for it to stay competitive internationally. In-line or on-line analysis is essential for optimizing flotation of dolomitic phosphates.

The current project is the final phase of three in FIPR's effort to develop a laser-based analyzer for in-situ analysis of dolomite. During Phase 1, Dr. Gaft of LDS in Israel investigated both laser-induced luminescence and breakdown spectroscopy methods for real-time evaluation of dolomite content on a moving belt. It was concluded that LIBS was more feasible. Phase 2 focused on developing a robust prototype LIBS for real-time determination of MgO content on a moving pebble conveyor. The system was installed at the Four Corners mine and tested for a few weeks. The 26 data points collected indicated very good agreement between the LIBS results and those by conventional wet chemistry. However, long-duration testing of the analyzer was deemed necessary to establish confidence in the system for both the equipment designer and users.

Although the goal of Phase 3 was to design and test a LIBS module for dolomite evaluation on a conveyor, the project team has accomplished much more. The analyzer not only gives dolomite readings with acceptable accuracy, but also analyzes or calculates contents of other important components such as BPL, CaO, MER (minor

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element ratio), Fe_2O_3 , Al_2O_3 and Insol. Another nice feature of the analyzer is remote, wireless operation. Most importantly, the phosphate industry has found the analyzer to be extremely useful.

ABSTRACT

In an earlier project, LDS proved the feasibility of laser-induced breakdown spectroscopy (LIBS) technology for real-time online evaluation of dolomite content in phosphate rock on a moving belt conveyor and developed a prototype module for dolomite concentration evaluation in phosphates. The aim of the current project was the development of an industrialized LIBS module for online Mg, Fe, Al and Insol content evaluation in phosphate rock moving on a conveyor. As a result, we constructed and successfully tested for a period of nine months an industrialized LIBS module under actual field conditions. The comparison between LIBS and laboratory data was quite satisfactory. During the test period, continuously collected data showed the large variability in rock quality and the ability of technology to minimize this problem by discarding only a small portion of the pebble.

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EXECUTIVE SUMMARY

Among the deleterious materials in phosphate rock (iron as Fe_2O_3, aluminum as Al_2O_3, calcium as CaO, and magnesium as MgO), dolomite is the most troublesome. Dolomite causes higher consumption of sulfuric acids, reduces filtration capacity, and lowers the P_2O_5 recovery in fertilizer manufacturing. Therefore the MgO content is a very important index in evaluating the quality of the phosphate concentrate. In Florida, the MgO in final phosphate concentrate is usually required to be less than 1%.

The high-dolomite zones have been bypassed during mining operations because there is no technology available to process the high-dolomite pebble economically. It has been well recognized that the development of technically and economically feasible beneficiation technology to process dolomite pebbles is very important in order to improve the recovery of phosphate values, extend Florida phosphate reserves, and prolong the life of the Florida phosphate industry. This makes it more critical to control the quality of the pebble product, particularly the MgO content. Current practices require either stockpiling of pebble product until quality control data from sampling become available, or making the shipping or discarding decision based on visual observations of rock as it is being produced. Obviously, this practice can result in the shipping of undesirable products to the chemical plant or the discarding of acceptable pebbles. A reliable, instantaneous analytical method is the ultimate solution to this problem.

This Phase III project continues the previous two: "Laser-Induced Time-Resolved Luminescence for Evaluation of Phosphate with High Dolomite Contents," carried out in 2000-2001 (Gaft and Nagli 2002) and "Development of LIBS Module for Dolomite Concentration Evaluation in Phosphates," in 2002-2003 (Gaft and others 2005a). The feasibility of LIBS technology was proved for real-time online evaluation of dolomite content in phosphate rock on a moving belt conveyor and a prototype module for dolomite concentration evaluation in phosphates was developed. The aim of the current project was the development of a fully industrialized product prototype suitable for reliable, continuous, around-the-clock functioning that can be easily maintained and repaired. The development of a product prototype includes the redesign of the cradle mechanical construction in a way that enables maintenance without stopping the conveyor. Other issues in the development were a remote operation module and remote computer control.

The work was successfully carried out through the following stages:

- Redesign to upgrade prototype module to industrialized module
- Alpha site tests
- Long-term reliability and stability test under real field conditions

As a result, a fully industrialized LIBS sensing system was developed for online real-time Mg, Fe, Al and Insoluble content evaluation in phosphate ore transported on a conveyor belt. Evaluation of the ore was based on analyses of Mg, Fe, Al, Si and Ca

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lines. The LIBS module was successfully tested for nine months on the main conveyor at the CF Industries mine in Florida. An impressive correlation between the LIBS results and approximately 300 traditional laboratory analyses was achieved during the site test.

INTRODUCTION

BACKGROUND

Phosphate rock is one of the basic materials for fertilizers. U.S. phosphate production represents approximately one-third of the world's total, with about 70% of U.S. production coming from Florida. With the depletion of the low-dolomite, easy-to-process Bone Valley siliceous phosphate deposits, phosphate mining must move further south and southeast (the "Southern Extension") where the phosphate matrix becomes leaner in grade and high in dolomite. The phosphate deposits in the Southern Extension may be divided into two zones. The upper zone may be processed using current technology, while the lower one is highly contaminated by dolomite. Geological and mineralogical data show that about 50% of the phosphate resource would be wasted if the lower zone were bypassed in mining, and about 13% of the resource would be lost if the dolomite pebble in the lower zone were discarded (Gao and others 2002). This makes it very critical to control the quality of the pebble product, particularly the MgO content. A reliable, instantaneous analytical method is the ultimate solution to this problem.

LITERATURE REVIEW

The need for a high-capacity, low-cost method of removing waste products, prior to expensive milling and concentration processes, led to the development of radiometric sorting. It is based on the selective influence of different kinds of irradiation on the minerals, and results in the separation of coarse ores. Sorting is a unit operation whereby discrete pebbles or batches are analyzed within a fraction of a second for a characteristic that can distinguish between "accept" and "reject" fractions. The information is processed by a computer, which activates a mechanical device for actual sorting (Salter and Wyatt 1991; Gaft and others 2005a and b).

Currently, LIBS is used in several different fields of mineralogy: bulk analysis of geological samples (Gornushkin and others 2000; Suna and others 2000); determination of spatial distribution profiles of elements on the surfaces of mineral samples (Yoon and others 1997); automated quantitative analysis of phosphate ores (Rosenwasser and others 2001); and stand-off detection of minerals on planetary surfaces (Sharma and others 2003). Recently, more and more information has appeared on the excellent potential of LIBS for online analyses, especially in the recycling industry (Cremers and Radziemski 2006; Miziolek and others 2006).

PURPOSE OF THE PROJECT

LDS was the first to propose LIBS for mineral sorting on a moving-belt conveyor (Gaft and Nagli 2004). Later, Progression Inc. proposed online, real-time elemental analysis of minerals, ores, slurries, and aerosols based on laser-induced breakdown

spectroscopy (2005). In our Phase I and Phase II proposals, the feasibility of LIBS technology was proved for real-time online evaluation of dolomite content in phosphate rock on a moving belt conveyor and a prototype module for dolomite concentration evaluation in phosphates was developed. The goals of the current project were:

- Development of the fully industrialized LIBS module for reliable, continuous around-the-clock functioning, with easy maintenance and repair;
- Development of the cradle mechanical construction that enables maintenance without stopping the conveyor;
- Development of the remote operation module and remote computer control.

METHODOLOGY

REDESIGN TO UPGRADE PHASE II MODULE TO PHASE III MODULE

Laser Selection

The LIBS machine principally consists of a laser source, an optical system to focus the laser beam and to collect the emission light, a gated CCD spectrometer for emission detection and a computer for system managing, data analyses and decision-making. Based on previous project beta site test results, we selected and purchased a "Big Sky" Nd-YAG compact laser with energy power up to 50 mJ per pulse and a repetition rate up to 30 Hz. One of the problems detected during the previous field test was that the old laser could not accommodate temperatures higher than 30º C. and the thermal isolation of the machine was insufficient. The new laser is an industrial model with a working temperature of up to 45º C. and is much easier to use and to maintain.

Analytical Spectral Range Selection

LDS was asked by CF Industries to analyze Al and Fe as well as Mg. According to our accumulated experience, it is not possible to do this in the spectral range used in the previous model, namely 350-530 nm. In order to select a suitable spectral range, additional spectral experiments have been done using the experimental setup developed in the previous stage. Figure 1 shows the corresponding data for phosphate rock representative of the CF material. In order to use such a spectral range, we changed the glass optic in the previous model to a fused quartz optic. Also, a different spectrometer, AvaSpec 2048, was used for this spectral range and needed spectral resolution.
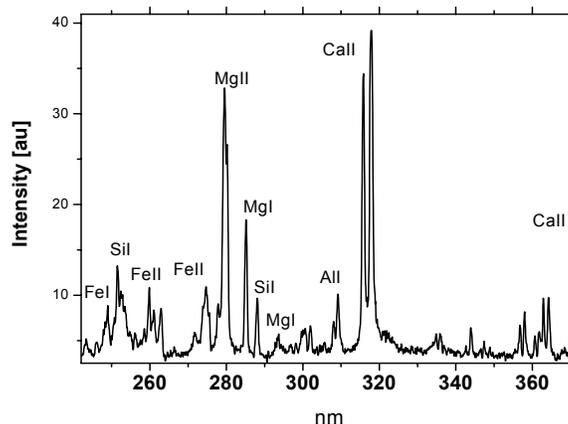
Figure 1. Breakdown Spectrum of Typical Phosphate Rock with Analytical Lines of Mg, Fe, Al, Si and Ca.

IMPROVEMENTS FOR BETTER USAGE AND MAINTENANCE

System Cooling

The side-mounted small air conditioner was replaced with a bigger, much stronger one, which sits on top of the system just above the laser. The walls are now temperature-isolated, and a sunroof was added to reduce sun radiation.

Dust Sealing

The system optical frame was redesigned so that it was now made of stainless steel and sealed. The optics section was also over-pressurized with air. The overall system is now better sealed.

Service and Maintenance

Two new openings were made, one where the laser is located and the other where the main optical elements sit. The first opening was done to make it easier to change the lamps in the laser source, while the second was made for optical adjustments, if needed.

The laser mount was redesigned so that the laser can be removed and remounted without subsequent optical alignment.

Optical redesign and production for the detection of additional elements (Al, Fe, Si), included the purchase of a new spectrometer, the production of a new lens holder, and the design and manufacture of new optical elements.

New system software was added for synchronization with both the new laser and spectrometer. LDS had to modify the DLL software for the spectral analysis to comply with the requirement that the system be capable of evaluating additional elements such as Al, Fe and Si. This program was already used to analyze the samples sent to LDS from the site.

ALPHA TESTS OF THE INDUSTRIALIZED APPARATUS IN CONDITIONS SIMULATING FIELD OPERATION

Mineralogical Composition of Phosphate Rocks

LDS analyzed six different samples of phosphate rock typically found in production at CF Industries, each with a different chemical composition. Based on the accompanying information, the main minerals in the samples should be apatite (or

francolite) and dolomite, with a small quantity of clays. The dolomite and apatite/francolite particles tend to be separate.

To check the samples, LDS used IR spectroscopy, which is quite efficient for the diagnostic testing of apatite, dolomite and clay. Representative samples were taken from each of the six batches, and several types of IR spectra were detected (Figure 2). According to these data, most pebbles were apatite or dolomite, with clays, calcite and mixtures of different minerals also present.
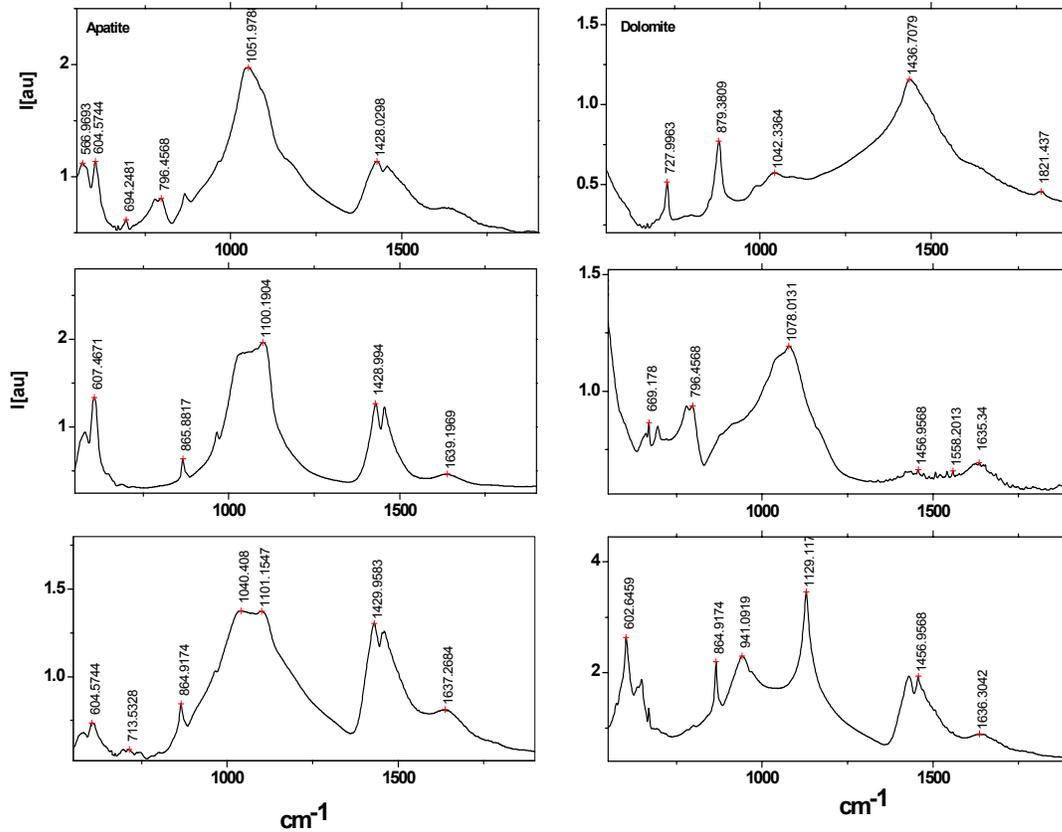
Figure 2. Representative IR Spectra of CF Phosphates.

A LIBS study of the representative samples revealed several spectral types, which may be confidently ascribed to different minerals present in phosphate rocks (Figure 3).

The studied rock was sorted into six groups by appearance:

1. White smooth – white or nearly white chalky, very smooth in texture.
2. Black – irregularly shaped, black or charcoal colored; often covered in tiny spots with a light material.
3. Light rough – sandy texture, off-white to beige shade.
4. Brown – upon closer inspection often mixed with black, irregularly shaped.

5. Smooth dark – usually rounded, often with a marble-like texture (not chalky, no pores evident); wide range of dark colors.
6. Dark rough – similar to light rough, but with a somewhat darker, mortar-like appearance.
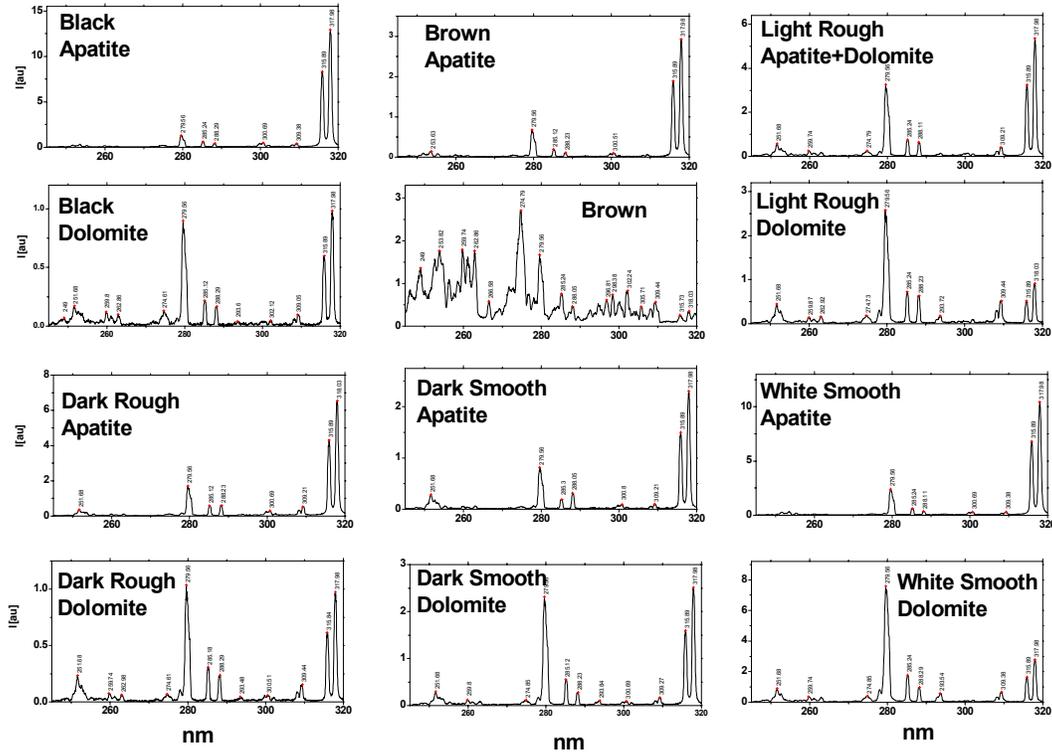
Figure 3. Representative LIBS of Different Stones in Phosphate Rocks (Batch 2).

Spectra were identified as apatite, dolomite or clay. The following criteria were used:

Apatite – The amplitude of the Mg line at 279.1 nm was a low fraction, well below half of the Ca line at 317.5 (the stronger line of the doublet).

Dolomite – These two lines were comparable in strength. Intermediate cases, indicating the possibility of an apatite/dolomite mixture, were noted.

Clay – The overall emission intensity is low and the relative intensities of Si, Al, Fe and Mg lines are strong compared to Ca lines.

Evaluation of Impurities Concentrations

Table 1 represents analytical data for the six different studied batches. Our task is to accomplish real-time online quantitative analyses of Mg, Fe and Al in phosphate rock on a moving belt conveyor. The major drawback of LIBS in industrial quantitative applications is related to the stability of the spectroscopic plasma signals, which undergo

considerable fluctuations that originate from the very nature of the breakdown emission. The laser intensity fluctuates within 1-5%, and the scattered light depends on the local matrix effects and on physical and chemical characteristics. The geometrical parameters also vary during the measurement due to the surface crater formation. Sample humidity variation as well as the atmospheric composition and even sample color also contribute to the observed signal fluctuations. Many models and techniques have been developed in order to overcome such problems. Usually, calibration curves are needed for the quantitative determination of the elements. They emerge from a number of reference samples with known elemental composition; a similar composition for the unknown sample is necessary. This requirement is acceptable for laboratory measurements, where reference and unknown samples can be embedded in the same matrix, but is a severe restriction for field operation. Thus, field experiments are usually limited to a semi-quantitative analysis in cases of highly variable or unknown rock compositions.

LDS chose a different approach, which is based on the determination of mineralogical composition. Because the average concentrations of impurities in each mineral are known, it may be possible to recalculate the content of elements based on minerals concentrations. Such an approach was successfully employed for Mg concentration evaluation during the Phase II project.

Table 1. Chemical Compositions of Typical Phosphate Rocks from CF.

Sample	BPL	Insol	Fe_2O_3	Al_2O_3	MgO	CaO/P_2O_5	CaO	P_2O_5
R2S #1	53.08	14.09	1.09	1.10	2.27	1.66	40.29	22.53
R2S #2	56.02	17.85	0.88	1.68	1.27	1.51	38.59	25.55
R2S #3	61.30	13.14	0.68	1.25	0.82	1.50	42.05	28.03
R2S #4	62.15	10.05	0.89	1.68	0.79	1.50	42.71	28.47
R2S #5	61.95	11.92	1.28	1.37	0.61	1.51	42.71	28.28
R2S #6	63.81	11.79	0.89	1.61	0.38	1.46	42.53	29.13

According to information received on the above batches, the dolomite contained all the MgO above about 0.3-0.4%. The apatite contained the majority of the iron and aluminum, a small percentage of the MgO (0.3-0.4%), and most of the P_2O_5. In order to check this, we analyzed the laboratory data from Table 1. The P_2O_5 content should give an estimate of the apatite concentration in a specific batch. Since the batch with the highest apatite content should have the lowest dolomite concentration, we expect to see an inverse relationship between P_2O_5 and MgO. Furthermore, the relationship between P_2O_5 and Fe_2O_3 and Al_2O_3 should be linear. Figure 4 represents the corresponding data based on chemical laboratory analyses. It may be clearly seen that such a relationship is absolutely correct for Mg content evaluation, reasonably correct for Al, while not relevant for Fe content evaluation.
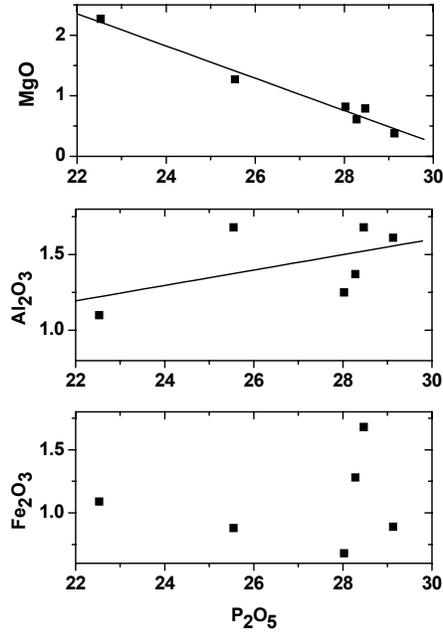
Figure 4. Correlation between P$_2$O$_5$ (Apatite) and Mg, Al and Fe Impurities Concentrations Based on Chemical Analyses (Table 1).

Figure 5 represents the correlations between apatite concentrations determined by LIBS and the content of Mg, Al and Fe in corresponding batches. It may be concluded that the correlation with Mg is good, is reasonable with Al, and is practically nonexistent with Fe. It is important to note that neither the LIBS nor the IR analyses revealed dolomite samples in batch number six, which agrees very well with a concentration of 0.38% MgO in this sample, since this is the exact concentration expected for pure apatite.
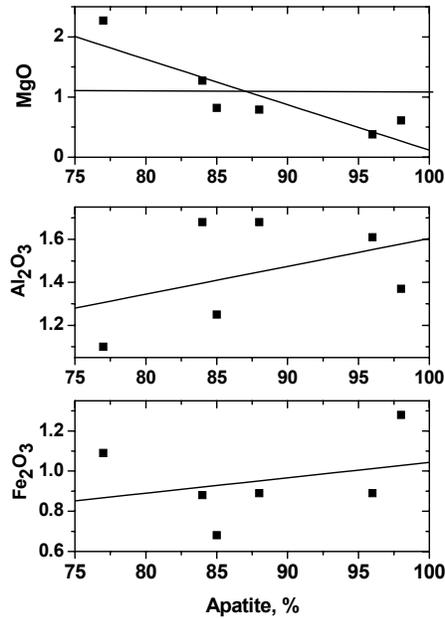
Note: the horizontal line represents the highest allowable MgO level.

Figure 5. Correlations Between Apatite Concentrations Determined by LIBS and Mg, Fe and Al in Corresponding Batches.

The poor correlation of apatite concentration with Fe content may be explained as follows: only part of the apatite pebbles contain elevated iron levels, while the share of such samples changes from batch to batch. To check this, we determined the relative number of pebbles with elevated Fe concentrations inside the apatite fraction. If the Fe line at 274.2 nm was relatively distinguishable, the corresponding pebble was counted as one containing elevated iron.

Figure 6 demonstrates the excellent correlation between iron concentration and the number of apatite pebbles with elevated emission intensity of Fe lines.
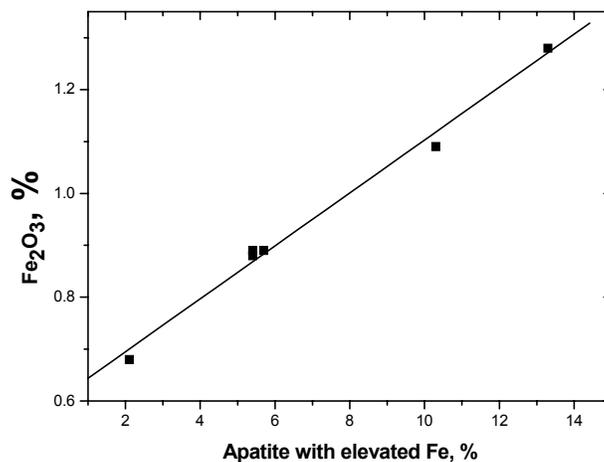

Figure 6. Linear Correlation between Fe_2O_3 Concentrations and Apatite Contents with Elevated Iron Contents.

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Development of the Analysis Software

The detection capabilities of the previous system were mainly for MgO and Ca analysis. It detected the percentage of MgO in the stones, indicating Go/No or Go according to a specified permitted MgO level. The spectrometer operated at the 370-530 nm range. In order to support the analysis and evaluation of additional elements such as Al and Fe, we modified the spectral range to 245-335 nm. New analysis software was needed to treat the UV spectrum and to meet the new demands. The new program included spectral analysis to obtain the intensity and integration of all relevant new peaks.

The results and conclusions from the different preliminary tests carried out in the lab were implemented in the spectral analysis program. In order to optimize the analysis, we had to carry out extensive tests in order to get the proper statistics and to improve the accuracy of evaluation.

In the spectral analysis software, we created parameters that will permit flexibility in the evaluation of data.

User Interface and Operational Software

As a result of extending the number of elements, there were some changes in the data presentation. In principle we left the main evaluation, which is the MgO % and the ability to define a limit for Go/No Go accordingly, as it was in the previous version. We have added presentation of the additional mineral elements. Since there are no specific requirements, the data is presented simply as numbers corresponding to relevant concentrations. However it can be modified according to customer needs.

There was no demand for external communication, but nevertheless we introduced the option for PC-Anywhere connector and software that can be operated if needed.

Software Implementation into the Product Prototype

The spectral analysis program is saved as a DLL. It enables changes according to results from the field in an easy way without the need to change and compile the main program. Since we have changed the output of the DLL, these changes are implemented also in the main program. The log file is also modified for presenting the additional elements.

LONG TERM STABILITY TEST

Installation

The LIBS unit was installed during the week of February 13, 2006, on the product pebble belt at the CF Hardee County mine. After initial calibration by technicians provided by LDS, the unit started operation on February 20th. Initially, the unit could only be operated locally. During the project, software was installed to operate the system from any remote computer using either VNC viewer or PC Anywhere software.

The CF mine produces relatively little pebble (20-40% of rock produced), with the +3 mesh fraction of this discarded. A requirement of the LIBS unit is to have at least 25 mm of rock on the belt. This is a safeguard so that the laser will not hit the belt and possibly cause damage. After a few days, it was apparent that the CF production did not typically give at least 25 mm of rock on the belt all day. After a few abortive attempts, sampling was fixed as 8-10 samples per week taken two or three times a week, during periods when there was adequate rock on the belt.

The pebble belt at CF operates at about 3 meters per second. It receives pebble from two separate screening systems. Each screening system is fed by a separate dragline operating in different areas of the mine.

Pebble Sampling Procedures

Samples of production pebble were obtained from the pebble product belt. The samples were coincident with the pebble that was examined by the LIBS unit. The sample procedure began by initiating the operation of the LIBS unit. At the start of the laser operation, a marker was placed on the belt to indicate the pebble surface where the LIBS unit began the detection sequence. The sampling point was on the pebble product conveyor belt approximately 45 meters downstream of the LIBS unit. As the marker passed the sample point, a series of grab samples was taken off the top surface layer of the pebble stream. When two draglines were operating, the top layer of pebble was from one dragline and the bottom layer was from the second dragline. Often there were significant differences in metallurgy between the two draglines' pebble products.

A large amount of care was taken to insure that the only pebble sampled was that which had been scanned by the LIBS unit. At the end of the LIBS detection sequence, a second marker was placed on the belt. When the marker passed the sampling point, the taking of grab samples was terminated. All of the grab samples from a single sampling period were combined into a single bulk sample.

Most of the time there are two layers of rock on the belt, and the LIBS unit can only analyze the top layer. CF personnel are planning to put in a device that will mix the two layers so that the LIBS looks at the average of both. When the rock is bad, they will

turn off the mixing device and see if the top layer is good or bad, and then throw away the bad layer.

In many instances, the single bulk sample from a single LIBS detection sequence consisted of a larger volume of material than what was required. At times, the volume approached fifteen liters of sample. In order to reduce the volume to about 1 liter of sample for the laboratory analysis, the "coning and quartering" technique was utilized. Coning and quartering is a metallurgical practice whereby a sample is poured onto a flat surface and allowed to form a cone. The cone is then flattened and divided into four equal quarters. Two opposite quarters are arbitrarily rejected, while the remaining two opposite quarters are saved as the sample. If one coning and quartering sequence does not sufficiently reduce the sample volume, the entire sequence is repeated until the desired sample volume is obtained. In all cases, the quantity of pebble sent to the lab was approximately 1 kilogram. The estimated number of rock particles was 5,000-10,000.

Measurement Procedure

Most of the data collected on the LIBS unit was at a laser pulse rate of 10 per second. The LIBS unit looks at the spectrum from each pulse and determines if there is adequate information in the observed spectrum. This does not happen with every pulse, since sometimes the laser can "hit" between large particles and the spectrophotometer is obscured. Sometimes the laser will hit a pocket of water, which will give a "blank" spectrum. The LIBS unit is designed to operate until a predetermined number of "good" spectra are collected. Then information from the spectrum is tabulated and presented on screen and in several tables. During all the test work, the digital record of each spectrum was collected in files, called "Scopes," and these were collected. This data was then analyzed to determine relationships between the analytical data obtained from the samples and the spectrum collected.

Analytical Data

Initially, the samples were analyzed for CaO, MgO, Fe_2O_3, Al_2O_3 and BPL. However in May, CF began experiencing problems with high-acid insoluble in the pebble. They asked that the LIBS unit also identify acid insoluble in the rock, so this was done for all samples after May 27th.

It is important to understand the analytical procedure for conducting analyses on phosphate rock. A ground sample of the rock is digested in aqua regia. A portion of the rock does not dissolve and is termed "acid insoluble," usually called just "Insol." While most of the Insol is silica, it also contains some aluminum (as a silicate) and minor amounts of other acid-insoluble minerals. However, the aqua regia does dissolve some of the silica in the rock, with the quantity dissolved somewhat depending on the digestion time and fineness of the ground rock. Therefore, the Insol is not a pure chemical species. However, a reasonable relationship between Insol and silica does exist.

The LIBS unit determines the quantity of each element in the observed rock. It determines the total iron, aluminum, magnesium, silica and calcium in the rock (the phosphorous spectrum is too weak to give meaningful results). As pointed out in the previous paragraph, at least some of the aluminum reports to the insoluble phase and is not detected in the laboratory analyses. If HF is added to the digestion acid, the soluble aluminum can increase as much as 50%. As such, the relationship between the LIBS value for aluminum and the analytical value for aluminum would not be expected to be as good as for magnesium, where very little of the magnesium reports to the insoluble fraction.

Sampling/Analytical/Sample Splitting Error

The rock on the belt is the result of discrete "scoops" of matrix from the mine cut. There is very little mixing of rock in the screening system, so the rock composition can change dramatically between "scoops" and even within "scoops" as quite often there is a dramatic change in rock composition over even a few feet of depth. Figures 7-11 show the variability of the rock on the belt from three sets of sequential samples from the belt. It may be seen that even in a short sample time, the rock is changing and that how taking different samples on the belt can give different values.
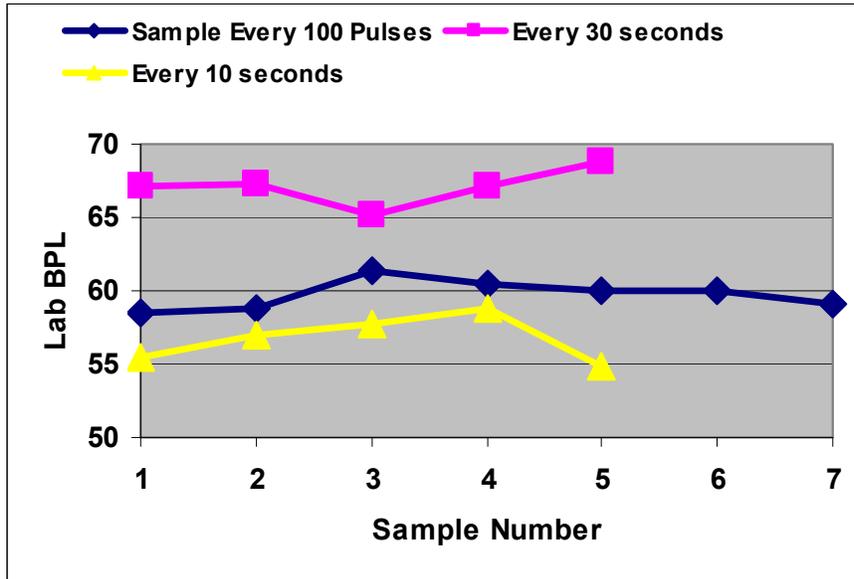
Figure 7. Lab BPL vs. Time for Sequential Samples Taken from the CF Pebble Belt.
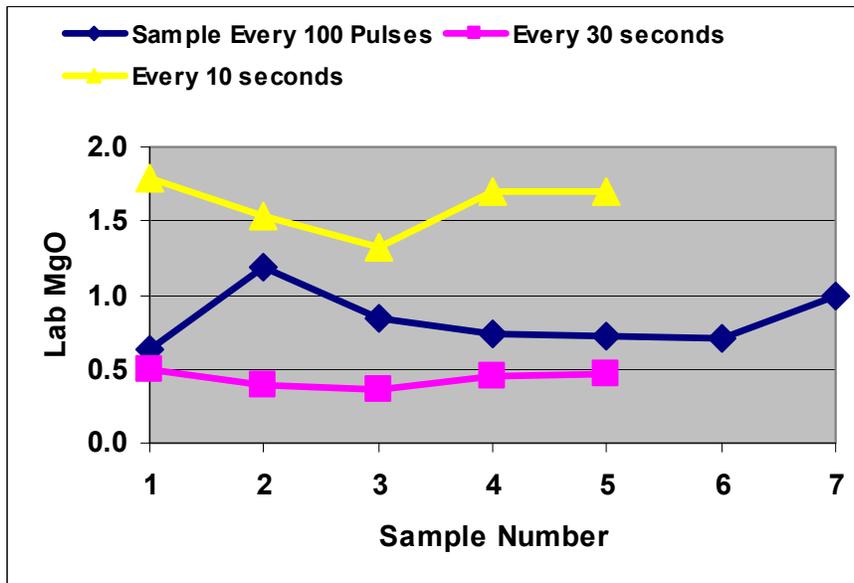

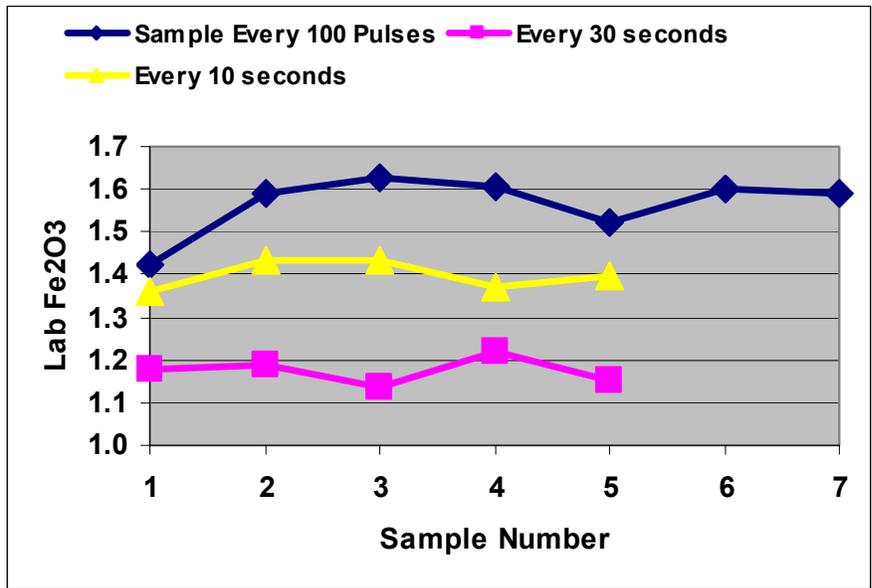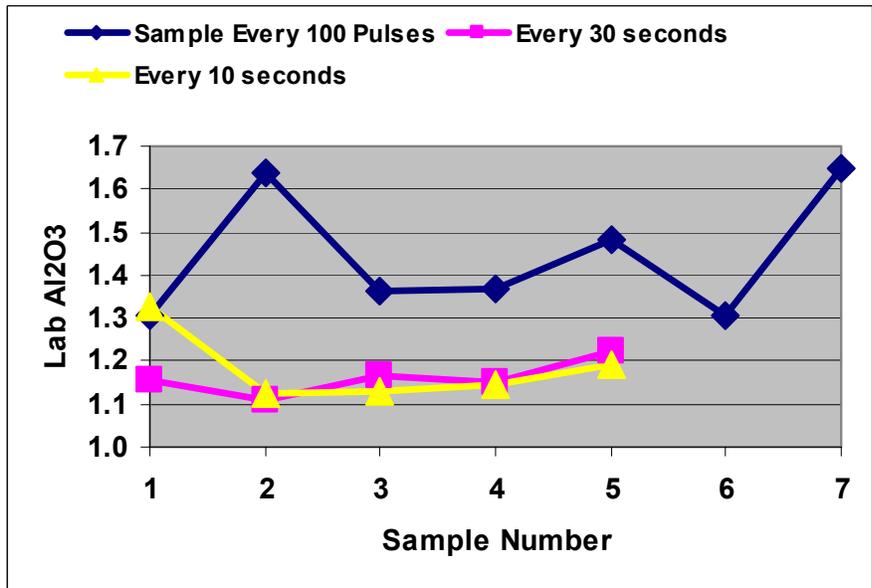**Figure 8. Lab MgO vs. Time for Sequential Samples Taken from the CF Pebble Belt.**

Figure 9. Lab Fe$_2$O$_3$ vs. Time for Sequential Samples Taken from the CF Pebble Belt.

Figure 10. Lab Al$_2$O$_3$ vs. Time for Sequential Samples Taken from the CF Pebble Belt.
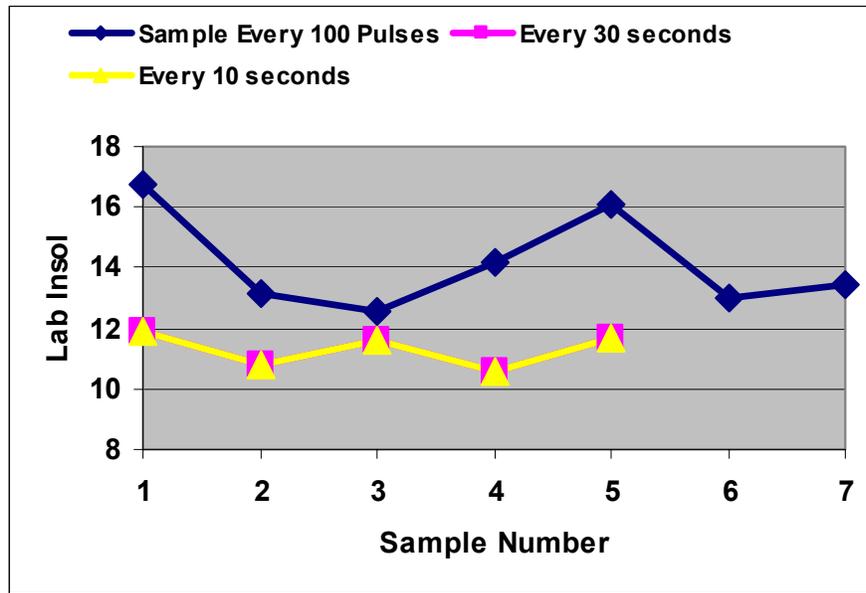
Figure 11. Lab Insoluble vs. Time for Sequential Samples Taken from the CF Pebble Belt.

A number of tests were conducted to determine the precision of the sampling, analytical, and sample splitting error. In the first set of tests, the sample of rock collected was coned and quartered repeatedly and the total sample was used in making up samples for the lab. Up to 10 samples were prepared from the sample taken. These were submitted to the lab over several weeks and were not identified as duplicate samples. A total of 32 analyses were performed on 5 separate sets of samples. The results of these tests will be given later in the report.

A second set of tests consisted of two people taking samples. One was at the normal sampling station while the other was at the LIBS unit. The sampler at the LIBS unit started sampling when the marker was thrown on the belt whereas the sampler at the sampler station started when the marker reached him. Both sampled for the same time period. These samples were submitted to the lab at the same time, but were not identified as duplicate samples. A total of 11 sets of duplicate samplings were taken. Again, the results of these tests will be given later in the report.

Relationships for LIBS Spectrum to Lab Chemical Analyses

The spectrum data collected was analyzed using one of several scope analyzers provided by LDS. The main scope analyzer looked at each spectrum and if it contained adequate spectra, decided if the spectrum was from apatite, dolomite, or clay. Figures 12-14 show typical spectrum for apatite, dolomite and clay.

Once a spectrum was identified, the areas under each of the peaks of interest (iron, aluminum, magnesium, calcium and silica) were integrated. The two strongest peaks were integrated for all elements and reported separately. The output from the program gave the number of spectrum that fell into each category (apatite, dolomite, clay and unidentified or weak) and the total area for each element for all the spectra in that category. It was important to summarize the data from the spectra in this manner since there is a significant difference in particle size for the three types of particles. In general, dolomite particles are larger than clay chips, which are larger than apatite particles, which are larger than clay particles.
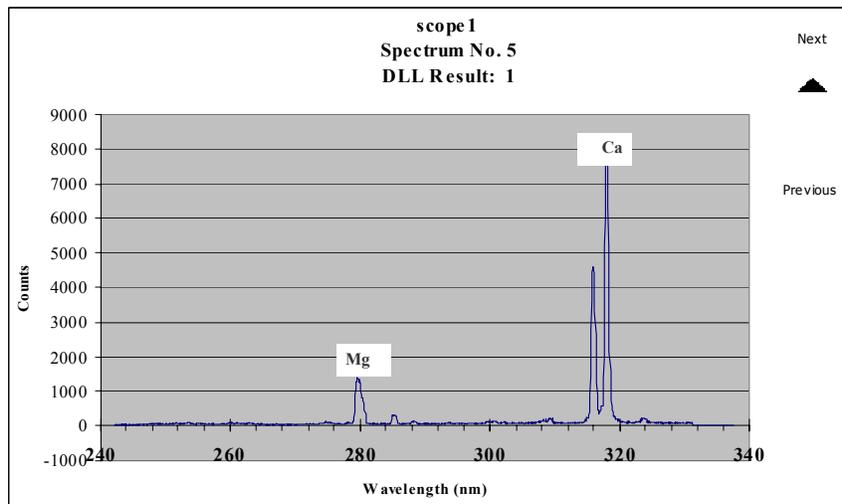

Figure 12. Typical Spectrum for Apatite.

A second scope analyzer did not break the spectrum down by mineral type, but simply integrated the area under each element for all spectra that were not considered as weak. This second scope analyzer was used only for samples of flotation feed (discussed later) where all the particles are about the same size.

The exact height (or area) of a spectrum associated with any element is not only associated with the concentration of that element. It is also affected by the quantity of moisture present in the sample, the distance from the laser (and spectrophotometer) to the sample and the focus point of the spectrophotometer within the plasma ball formed by the laser pulse.

The ratio of the spectra of various elements from the same sample is almost a constant, independent of the distance, moisture content or focus. Since the calcium in the pebble varies over a relatively small range, all other element spectra were compared in a ratio to the calcium spectrum.
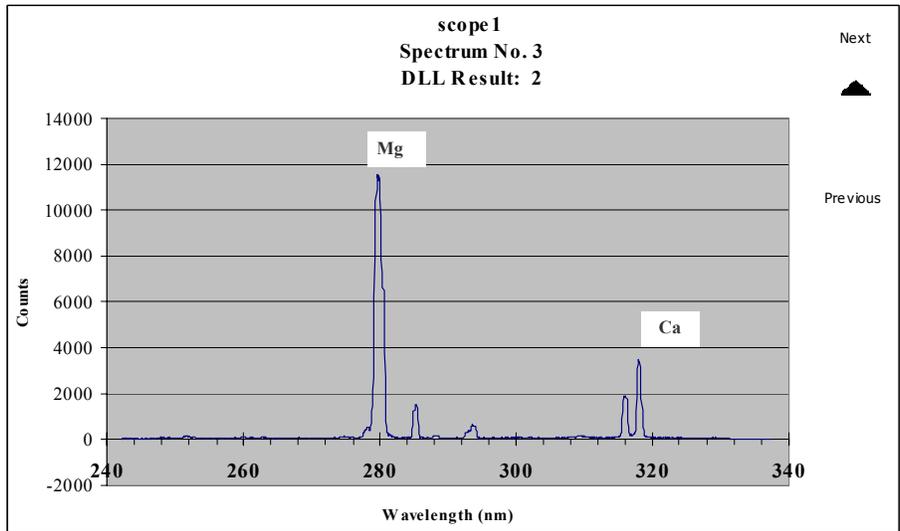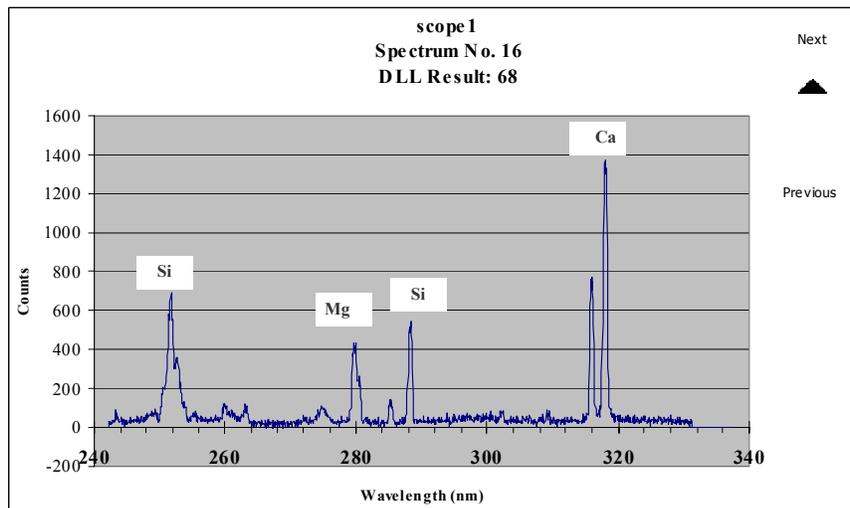
Figure 13. Typical Spectrum for Dolomite.

Figure 14. Typical Spectrum for Clay.

About halfway through the project, the data was quickly analyzed to determine the relationship between the data from the spectrum and the laboratory analyses. A more thorough data analysis was performed at the end of the test to improve the relations. Both give similar results with the differences generally being only a few hundredths of a percent for the analyses of interest.

During the initial tests it was thought that the scopes only collected the data from spectrum that had been identified. As such, the quantity of spectrum to be captured was set at a maximum of 1000 when a test run using 1000 pulses was used. When this data was analyzed, it became apparent that the scope contained the spectrum from all laser pulses and that the limit of 1000 spectrum meant that only a portion of the identified

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spectra were captured in the data. After the first two months, the number of laser pulses per test was reduced to 500, which meant that the data captured more nearly represented the data over the total sampling period. This meant that some of the data taken in the first 2 months (particularly when the rock was very wet or low on the belt) did not represent all of the spectra over the sampling period. In some cases, it was clear that only tests that captured a majority of the data should be used for the data analysis.

MgO Equation

The following equation was developed for the estimating the MgO content of phosphate pebble for the pebble belt at CF Industries. It was derived from the integration of the areas of the magnesium peak at 285.54 and the calcium peak at 317.978 nm:
MgO = 27.291x - 0.547, where:

x = [(Apatite Magnesium area + 4.2* Dolomite Magnesium area +0.1 * Clay Magnesium area)/(Apatite Calcium area + 4.2 * Dolomite Calcium area + 0.1 * Clay Calcium area). This equation was developed by trial and error to determine the constants 4.2 and 0.1 based on a best fit of the data. This makes sense, since dolomite is typically larger than apatite, which is larger than clay (combination of clay particles and clay chips). The relationships are shown for all data and only the data where we have captured at least 55% of the spectra for the sample (Figures 15 and 16).

The average difference between the LIBS predicted value and the lab value was 0.20 for all the data and 0.15 for only the data where at least 55% of the spectra were captured.
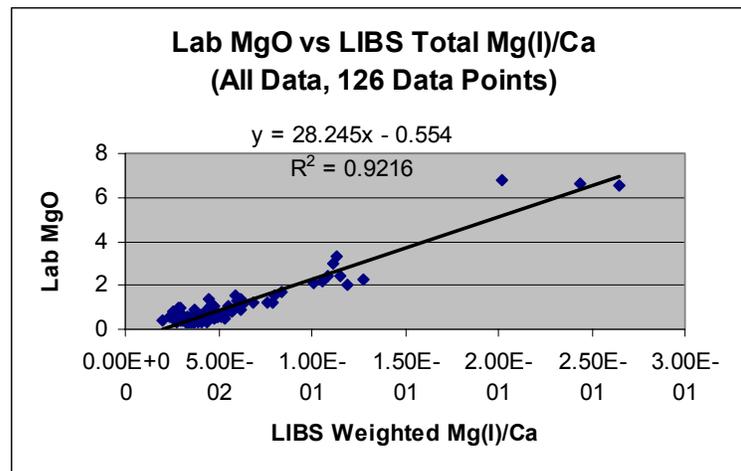

Figure 15. Relationship between Lab MgO and LIBS Weighted Mg/Ca for All Data.
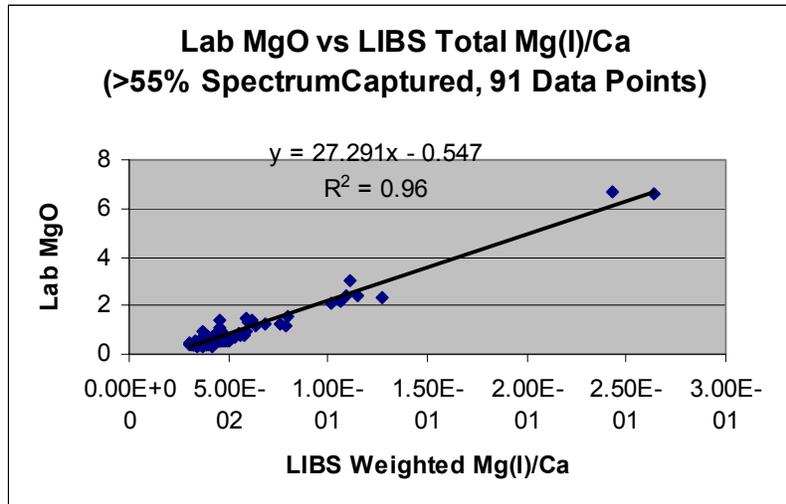
Figure 16. Relationship between Lab MgO and LIBS Weighted Mg/Ca for Data When >55% of the Spectrum Was Captured.

The final MgO relationship was derived from the integration of the areas of the magnesium peak at 285.54 and the calcium peak at 317.978 nm: MgO = the greater of 0.25 or 52.006x − 1.0577, where:

x = [(apatite iron area – 25 * number of apatite spectrum) + 0.90 * dolomite iron area + 70 * number of dolomite spectrum + 5.5 * clay iron area - 1750 * number of clay spectrum) / (apatite calcium area + 0.90 * dolomite calcium area + 5.5 * clay calcium area) (Figure 17).

These relationships were obtained by trial and error using essentially all the data collected including the multiple sample/analyses described earlier. The average difference between the lab analysis and LIBS value was 0.34.
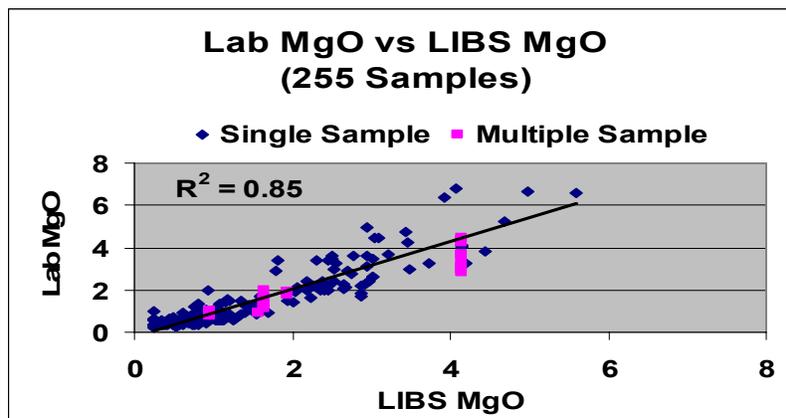

Figure 17. Relationship between Lab MgO and LIBS MgO, Based on the Previous Calculations.

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Al₂O₃ Equation

The following equation was developed for the estimating the Al_2O_3 content of phosphate pebble. It was derived from the integration of the areas of the aluminum peak at 309.607 and the calcium peak at 317.978 nm: $Al_2O_3 = 72.604x - 0.0223$, where:

x = [(apatite aluminum area – 31 * number of apatite spectrum) + 1.65 * dolomite aluminum area – 225 * number of dolomite spectrum + 1.5 * clay aluminum area + 940 * number of clay spectrum) / (apatite calcium area + 1.65 * dolomite calcium area + 1.5 * clay calcium area).

This equation was developed by trial and error to determine all the constants to give the best fit of the data (Figure 18). There was no improvement in the relationship by using only the samples with more than 55% of the spectra captured. However, 25 lab results were removed from the data set as they suggested that there was a lab error based on known relationships for phosphate rock.
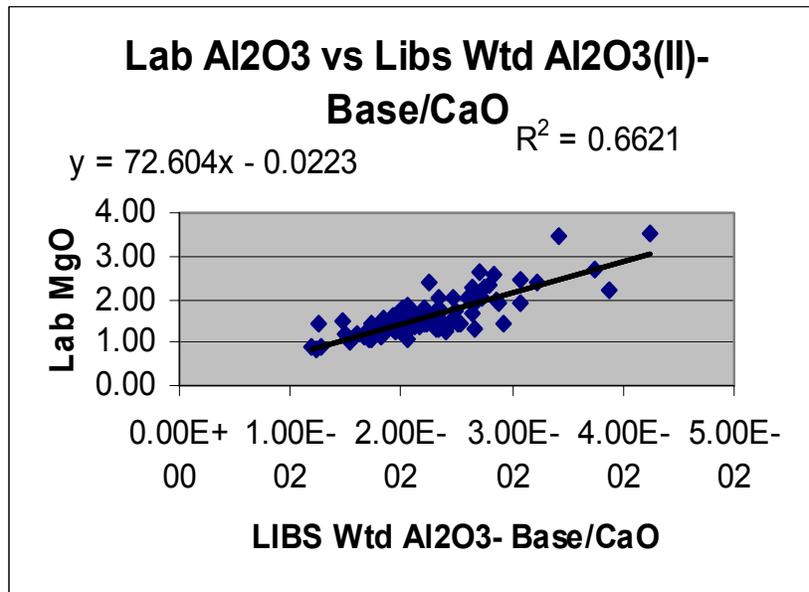

Figure 18. Relationship between Lab Al₂O₃ and LIBS Weighted Al/Ca for All Data.

The average difference between the LIBS predicted value and the lab value was 0.20 for all the data (after removal of 25 questionable lab results) and 0.26 when all the data is used. There is no reasonable basis for the weighting factors of 1.65 and 1.5 for the dolomite and clay fractions, particularly the weighting factor of 1.5 for the clay fraction. The weighting factors of -31, -225 and +940 suggest an average base line correction. It is possible that if the baseline correction is measured and made for each spectrum, the relationship will improve and the weighting factors for each rock type will be closer to those seen for the MgO relationship.

The following final equation was developed for the estimating the Al_2O_3 content of phosphate pebble for the pebble belt at CF Industries. It is derived from the integration of the areas of the aluminum peak at 309.607 and the calcium peak at 317.978 nm: $Al_2O_3 = 68.281x - 0.0223$, where:

x = [(Apatite Aluminum area – 54 * number of apatite spectrum) + 2.16 * dolomite aluminum area – 210 * number of dolomite spectrum + 2.7 * clay aluminum area + 1550 * number of clay spectrum) / (apatite calcium area + 2.16 * dolomite calcium area + 2.7 * clay calcium area (Figure 19).
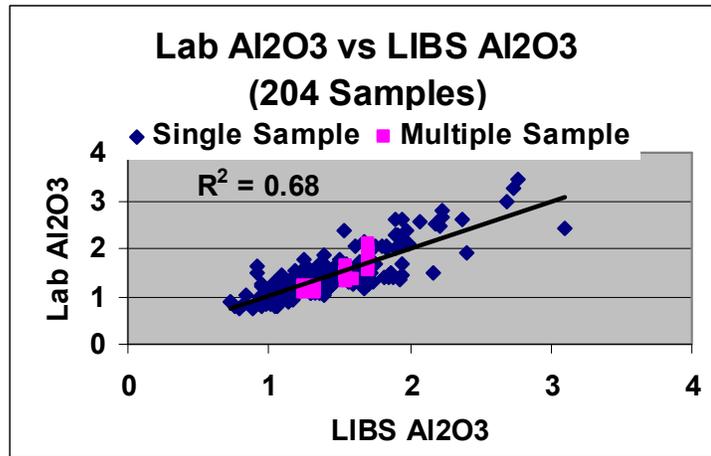

Figure 19. Relation between Lab Al_2O_3 and LIBS Al_2O_3, Based on the Previous Calculations.

This equation was developed by trial and error to determine all the constants to give the best fit of the data. There was a significant improvement in the relationship by using only the samples with more than 55% of the spectra captured. In addition, 17 lab results were removed from the data set, as they suggested that there was a lab error based on known relationships for phosphate rock.

Fe_2O_3 Equation

The following equation was developed for the estimating the Fe_2O_3 content of phosphate pebble. It was derived from the integration of the areas of the iron peak at 274.667 and the calcium peak at 317.978 nm: $Fe_2O_3 = 41.119x + 0.4049$, where:

x = [(Apatite Iron area – 49 * number of apatite spectrum) + 0.50 * dolomite iron area + 135 * number of dolomite spectrum + 0.1 * clay iron area - 1380 * number of clay spectrum) / (apatite calcium area + 0.50 * dolomite calcium area + 0.1 * clay calcium area).

This equation was developed by trial and error to determine all the constants to give the best fit of the data. There was a significant improvement in the relationship by using only the samples with more than 55% of the spectra captured (Figure 20).
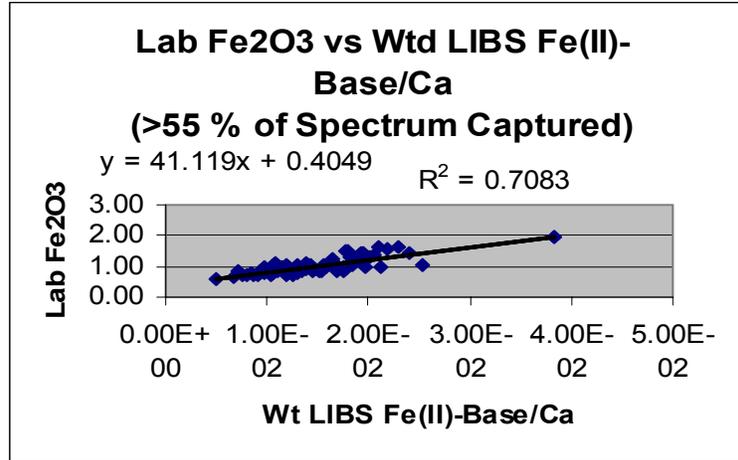

Figure 20. Relationship between Lab Fe$_2$O$_3$ and LIBS weighted Fe/Ca.

The average difference between the LIBS-predicted value and the lab value was 0.17 for all the data and 0.11 for only the data where greater than 55% of the spectrum was captured. While the weighting factor for clay of 0.1 (suggesting average smaller size) is similar to that found for the MgO relationship, the weighting factor for dolomite of only 0.5 is significantly smaller that the 4.2 found for the MgO relationship.

The weighting factors of -49, +135 and -1380 suggest an average baseline correction. It is possible that if the baseline correction is measured and made for each spectrum, the relationship will improve and the weighting factors for each rock type will be closer to those seen for the MgO relationship.

The following final equation was developed for the estimating the Fe$_2$O$_3$ content of phosphate pebble. It is derived from the integration of the areas of the iron peak at 274.667 and the calcium peak at 317.978 nm, Fe$_2$O$_3$ = 25.57x + 0.6565, where:

x = [(apatite iron area – 14 * number of apatite spectrum) + 0.16 * dolomite iron area + 500 * number of dolomite spectrum + 2.3 * clay iron area - 3000 * number of clay spectrum) / (apatite calcium area + 0.16 * dolomite calcium area + 2.3 * clay calcium area) (Figure 21).
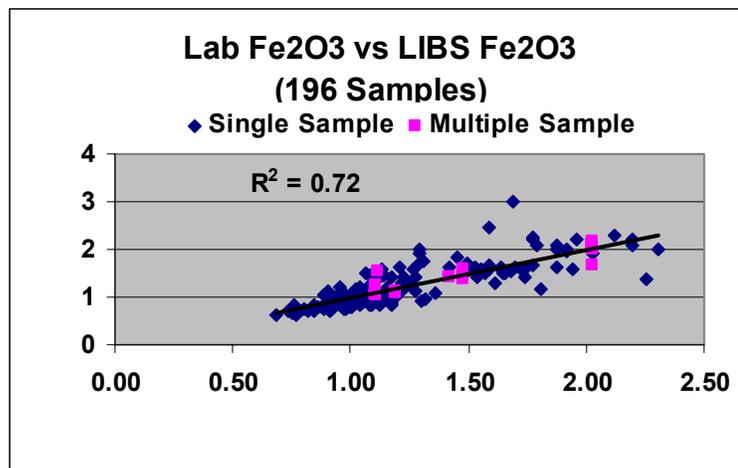
Figure 21. Relationship Between Lab Fe$_2$O$_3$ and LIBS Fe$_2$O$_3$, Based on the Previous Calculations.

The average difference between the LIBS predicted value and the lab value is 0.20. This equation was developed by trial and error to determine all the constants to give the best fit of the data. There was a significant improvement in the relationship by using only the samples with more than 55% of the spectra captured. The average difference between the LIBS predicted value and the lab value is 0.16.

Acid Insoluble Equation

The following equation was developed for the estimating the acid insoluble content of phosphate pebble. It was derived from the integration of the areas of the silica peak at 288.285 and the calcium peak at 317.978. Since there were only a few analyses of acid insoluble at this time, the integrated spectrum was not differentiated by rock type. Insoluble = 217.56x + 5.9852, where:

x = ratio of the total areas of silica to calcium (Figure 22). This relationship was based on only a few data points (21). The average difference between the LIBS predicted value and the lab acid insoluble was 1.46.
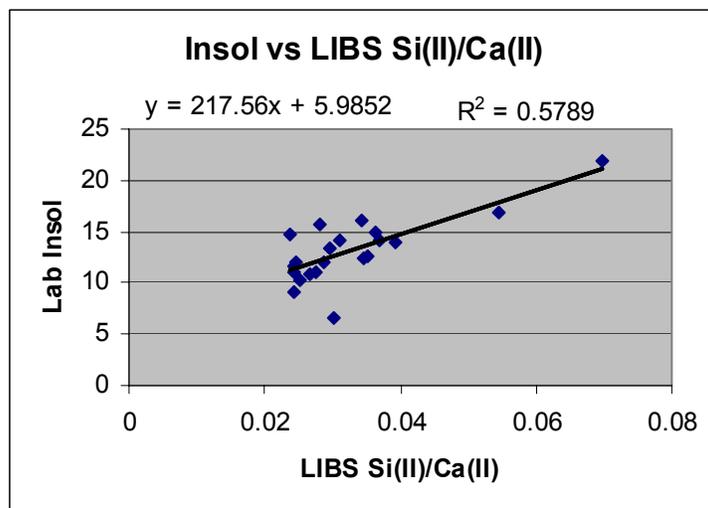
Figure 22. Relationship Between Lab Insoluble and LIBS Si/Ca for All Data.

The following final equation has been developed for the estimating the acid insoluble content of phosphate pebble. It is derived from the integration of the areas of the silica peak at 288.285 and the calcium peak at 317.978 nm: Acid insoluble = $266.19x$ + 5.7711, where:

x = [(apatite iron area – 78 * number of apatite spectrum) + 2.19 * dolomite iron area - 212 * number of dolomite spectrum + 0.4 * clay iron area + 5600 * number of clay spectrum) / (apatite calcium area + 2.19 * dolomite calcium area + 0.4 * clay calcium area) (Figure 23).

This equation was developed by trial and error to determine all the constants to give the best fit of the data. There was no significant improvement in the relationship by using only the samples with more than 55% of the spectra captured since there were very few with less than 55% captured when the acid insoluble data was available. The average difference between the LIBS predicted value and the lab value is 1.70.
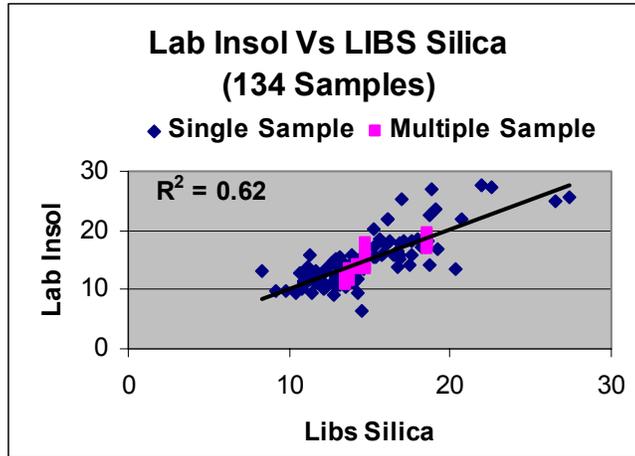
Figure 23. Relationship Between Lab Insoluble and LIBS Silica, Based on the Previous Calculations.

BPL Equation

The spectrum from phosphorus is quite weak. As such, it is not feasible to use it to estimate the BPL content of the pebble. However, the rock BPL can be calculated from the following equation:

$BPL = 77.82 - 1.60 * LIBS\ Fe_2O_3 - 2.97 * LIBS\ Al_2O_3 - 5.17 * LIBS\ MgO - 0.50 * LIBS\ Insol.$

The average difference from this calculated number and the lab analysis is 1.01. This relationship was based on only the 21 sample sets where all the analyses were run.

The rock final BPL can be calculated from the following equation:

$BPL = 74.610 - 2.656 * LIBS\ Fe_2O_3 - 1.168 * LIBS\ Al_2O_3 - 6.679 * LIBS\ MgO - 0.405 * LIBS\ insoluble$ (Figure 24).
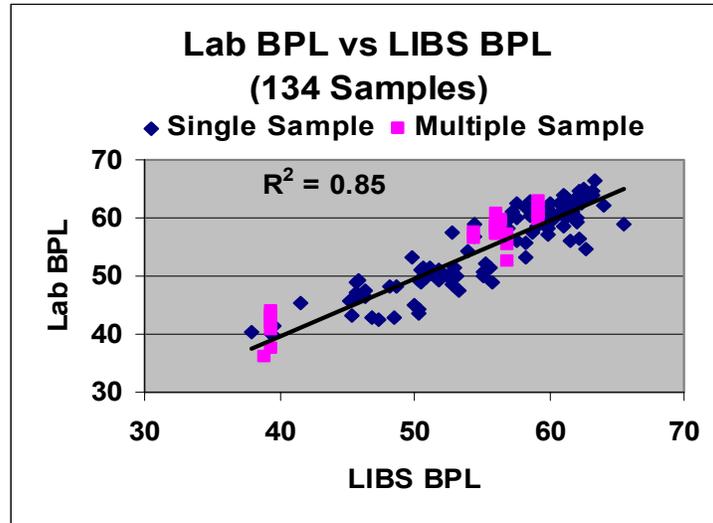
Figure 24. Relationship Between Lab BPL and BPL Calculated from LIBS Data.

The relationship is based on all the data available (limited by number of acid insoluble analyses). The average difference from this calculated BPL and the lab analysis is 2.36.

MER Equation

The MER is calculated from the following equation:

MER = 2.185 * (LIBS Fe_2O_3 + LIBS Al_2O_3 + LIBS MgO) / LIBS Calculated BPL

The average difference from this calculated number and the one based on lab analysis is 0.011, based only on the 21 sample sets where all the analyses were run.

The final MER is calculated from the following equation:

MER = 2.185 * (LIBS Fe_2O_3 + LIBS Al_2O_3 + LIBS MgO) / LIBS Calculated BPL (Figure 25).
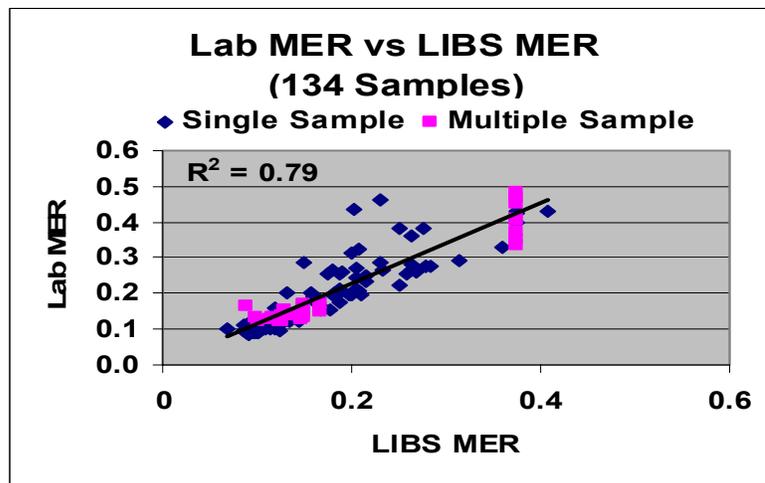
Figure 25. Relationship Between MER Calculated from Lab Analyses and MER Calculated from LIBS Data.

Again, the relationship is based on all the data available (limited by the number of acid insoluble analyses). The average difference from this calculated number and the one based on lab analysis is 0.029.

CaO Relationship

Since all other spectrum information was compared to the calcium spectrum to remove the effects of moisture, distance and focus, it could not be used to determine the CaO concentration in the rock. However, a relationship does exist between the CaO in the rock and the BPL, Fe_2O_3, Al_2O_3 and MgO in the rock. The relationship is:

$CaO = 6.6+1.33*LIBS$ $Fe_2O_3-0.84*LIBS$ $Al_2O_3 + 3.91*LIBS$ $MgO +0.76*LIBS$ BPL (Figure 26).
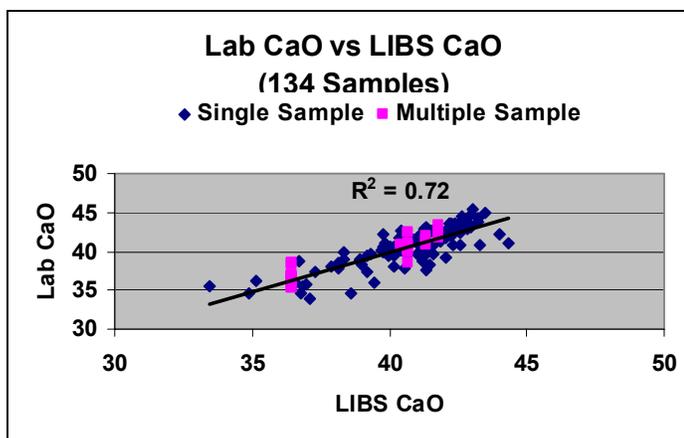
Figure 26. Relationship Between CaO from Lab Analyses and CaO Calculated from LIBS Data.

Again, the relationship is based on all the data available (limited by number of acid insoluble analyses). The average difference from this calculated number and the one based on lab analysis is 1.03.

Comparison of LIBS Error to Sampling/Sample Splitting/Analytical Error

Table 2 shows the relative difference in agreement for the LIBS data compared to measurements of Sampling/Analytical/Sample Splitting Error.

Table 2. Comparison of LIBS Error to Sampling/Sample Splitting/Analytical Error.

Measurement	Sample Split/Analytical Error		LIBS
	Sample 1	Sample 2	
Fe_2O_3	0.07	0.10	0.16
Al_2O_3	0.09	0.08	0.20
MgO	0.25	0.24	0.34
Insol	0.87	1.48	1.70
BPL	1.81	2.34	2.36
MER	0.022	0.016	0.029
CaO	0.98	1.48	1.03

As can be seen, the errors of the LIBS analyses are not significantly worse than the measurements of sample splitting/analytical error or the error introduced by two different samplers.

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Flotation Plant Sampling and Analyses

Samples were obtained from multiple locations within the flotation plant. These samples included rougher flotation feed, rougher flotation concentrate, rougher flotation tails, amine flotation concentrate and amine flotation tails. The rougher flotation concentrate is considered to be metallurgically equal to the amine flotation feed.

The rougher flotation feed was sampled at the rougher feed hydrocyclone by obtaining a grab sample of the hydrocyclone underflow. The rougher flotation concentrate was obtained by taking a grab sample of the rougher flotation cell overflow lip. The rougher flotation tailings sample was obtained by taking a grab sample from the rougher flotation cell underflow discharge box.

The amine flotation cell concentrate was obtained by taking a grab sample from the amine flotation cell underflow discharge box. The amine tailings sample was obtained by taking a grab sample of the amine flotation cell overflow lip.

The samples were thoroughly mixed and split. The one split was used for a chemical analysis and the other for presentation to the LIBS unit.

The flotation plant samples were dewatered and presented to the LIBS unit for analysis. The samples were moist when the LIBS unit performed its analysis. A separate study of dry versus moist sample presentation was also conducted.

A sample presentation device was constructed from wood that allowed for both activation of the ultrasonic focusing system and containment of the flotation plant samples for examination by the LIBS unit. The sample presentation device was designed such that incremental adjustments could be made to the vertical distance that the sample was below the laser and the detector, as well as infinite longitudinal and transverse movement relative to the laser and the detector.

The sample under analysis was randomly moved, relative to the laser impact point, by moving the sample presentation device in the longitudinal and transverse directions relative to LIBS unit and the belt. This was done while maintaining a constant vertical distance from the LIBS unit. Testing was also conducted at various vertical distances below the laser and the detector.

A total of 20 samples were presented to the LIBS unit on two different testing days (9 samples on one day and 11 other samples on another day). Data were collected for 500 laser pulses. Only the spectrum from the calcium peak at 317.978 nm and silica peak at 251.681 nm were used to determine if there was a relationship with the laboratory-measured BPL. Figure 27 shows the results.
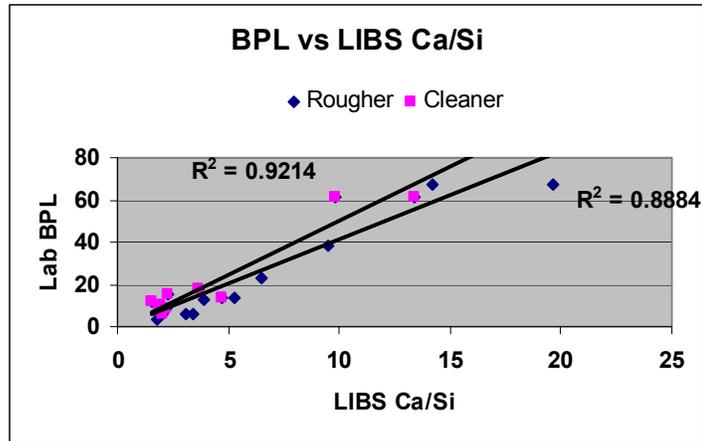
BPL vs LIBS Ca/Si

Figure 27. Lab BPL vs. LIBS Ca/Si for Flotation Feed Samples.

As can be seen, there is good correlation between the LIBS data and the analytical analyses, with somewhat different correlations for the rougher and cleaner samples. While this shows promise, many more samples would have to be run to determine the real accuracy of LIBS on feed samples.

Effect of Distance, Laser Focus and Water Content

During Phase II of this project, we studied the effect of distance, laser focus, and water content on samples from the Four Corners mine. At that point, we were interested only in Mg analysis and our aim was to identify the pebble as apatite or dolomite. It was found that if the sample was out of focus, the difference between apatite and dolomite remained, and even became more pronounced.

Now, in Phase III, the situation is different. Additional elements, such as Fe and Al, are being analyzed, and the problem needs further attention. Figure 28 represents the data showing Mg and Al behavior as a function of sample-laser distance and of laser energy. Unfortunately, Fe is not included. It may be seen that the apatite spectrum was practically the same, while in dolomite we see that the relative Mg intensity is slightly higher in focus and Al intensity is substantially more out of focus.
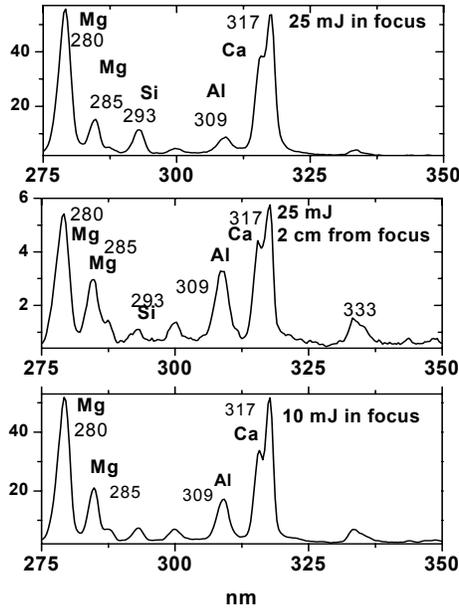
Figure 28. Dolomite Spectrum as a Function of Laser-Sample Distance and of Laser Energy.

To study this point, large pieces of dolomite and apatite were collected from the scrap pebble belt. Several of these were presented to the LIBS machine at distances ranging from 70 to 145 mm, focus offsets of +7 and -7 mm, and "as is" and soaked with water. Data were collected for 100 laser pulses and the LIBS unit calculated the iron, aluminum, etc. There were significant differences in the analyses (the samples were not pure and probably there were differences in the composition within each sample). However, regression of the data showed no significant effect of distance, focus or moisture content of the rock for any of the LIBS analyses.

Use of LIBS by CF Industries

The LIBS unit was operated continuously from Sept 12-16, 2006. The unit operated at 10 pulses per second for the first two days, and at 5 pulses per second for the last two days. During this time CF only operated the beneficiation plant from 9 PM to 12 PM the next day. The draglines continued to strip overburden during the off-hours. As a result, the rock level on the belt was much higher than normal, allowing for almost continuous operation of the LIBS unit. Figures 29-34 show the data captured by the LIBS unit. During this time period, the LIBS unit provided 814 sets of analyses.

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Figure 29. MgO vs. Time During Continuous Run, Sept. 12-16, 2006.

Figure 30. Al$_2$O$_3$ vs. Time During Continuous Run, Sept. 12-16, 2006.

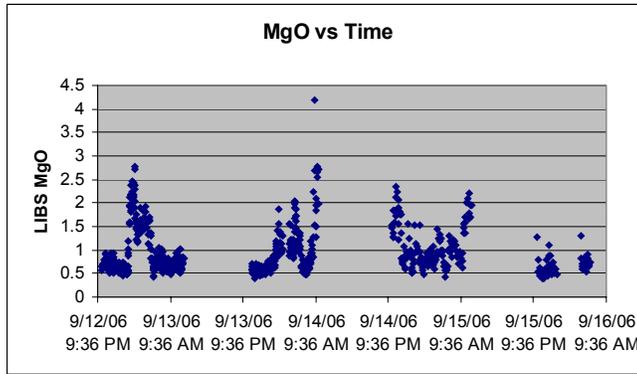**Figure 31. Fe$_2$O$_3$ vs. Time During Continuous Run, Sept. 12-16, 2006.**

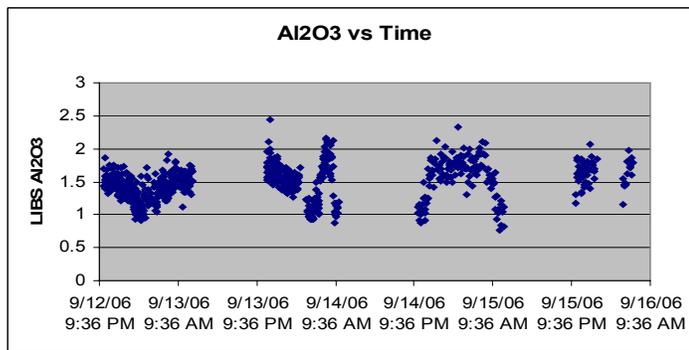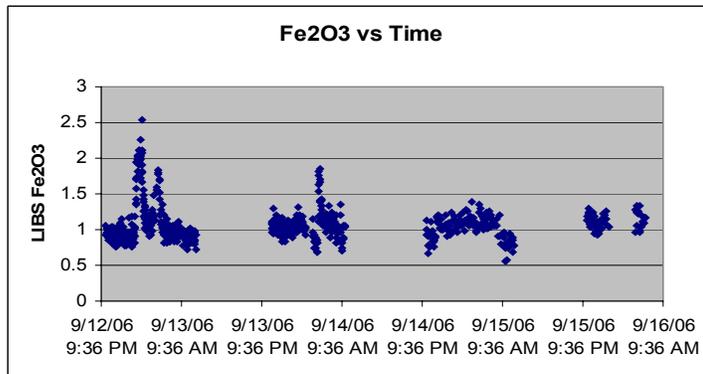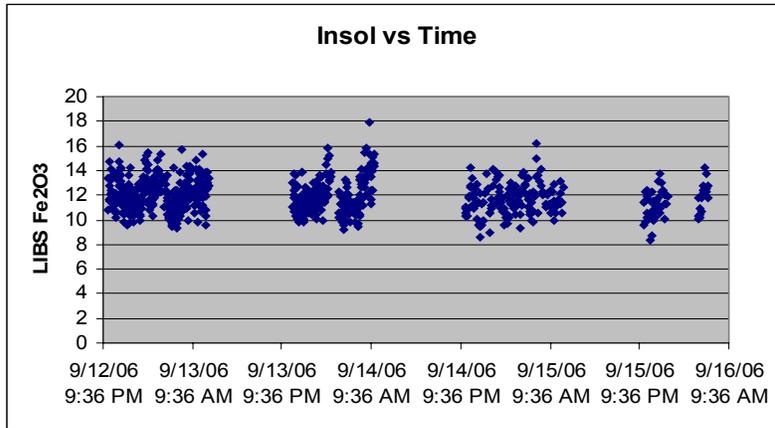**Figure 32. Insoluble vs. Time During Continuous Run, Sept. 12-16, 2006.**
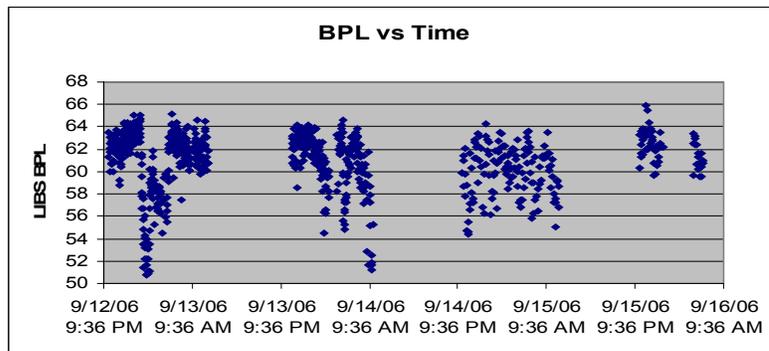

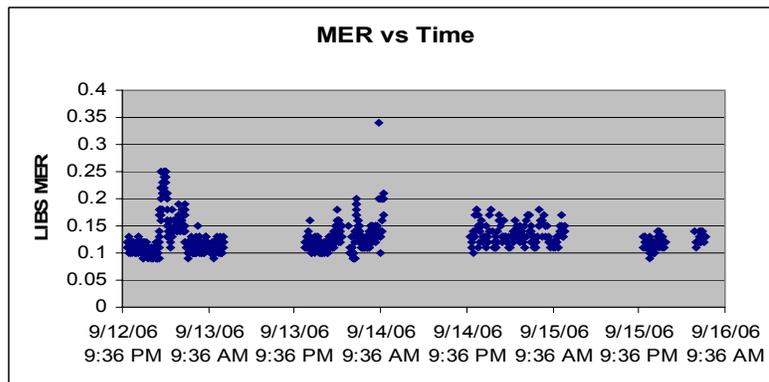**Figure 33. BPL vs. Time During Continuous Run, Sept. 12-16, 2006.**

Figure 34. MER vs. Time During Continuous Run, Sept. 12-16, 2006.

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CF has been using these data to discard rock at times by criteria that they have developed. Table 3 shows how the rock quality would be affected if rock were discarded based on the MER of the rock during this time.

Table 3. Effect on Rock Quality If It Is Discarded Based on MER (Sept. 12-16, 2006).

MER Cutoff	MgO	MER	Al_2O_3	Fe_2O_3	Insol	BPL	% Rock Discarded
0.4	0.933	0.1267	1.506	1.062	11.81	60.92	0.00
0.3	0.930	0.1265	1.507	1.061	11.81	60.93	0.10
0.25	0.922	0.1259	1.509	1.056	11.80	60.98	0.59
0.2	0.888	0.1237	1.517	1.038	11.75	61.19	3.05
0.19	0.884	0.1234	1.519	1.036	11.74	61.21	3.44
0.18	0.867	0.1224	1.521	1.029	11.72	61.31	5.21
0.17	0.847	0.1210	1.522	1.023	11.68	61.45	7.76
0.16	0.827	0.1195	1.516	1.017	11.61	61.61	11.30
0.15	0.788	0.1173	1.516	1.011	11.55	61.85	17.19

Table 4 shows similar data for the time period of September 19th to October 1st. During this time, the LIBS unit provided 1,194 sets of analyses.

Table 4. Effect on Rock Quality If It Is Discarded Based on MER (Sept. 19-Oct. 1, 2006).

MER Cutoff	MgO	MER	Al_2O_3	Fe_2O_3	Insol	BPL	% Rock Discarded
0.4	1.048	0.1251	1.352	1.049	11.85	60.78	0
0.3	1.048	0.1251	1.352	1.049	11.85	60.78	0
0.25	1.046	0.1249	1.351	1.049	11.84	60.80	0.17
0.2	1.031	0.1238	1.350	1.043	11.81	60.90	1.42
0.19	1.023	0.1231	1.349	1.039	11.78	60.97	2.43
0.18	1.012	0.1222	1.347	1.034	11.75	61.06	3.94
0.17	0.985	0.1204	1.346	1.026	11.70	61.24	7.45
0.16	0.955	0.1180	1.339	1.013	11.62	61.47	12.65
0.15	0.920	0.1147	1.325	0.990	11.51	61.79	20.94

While the effects here are relatively small for this short operating period, they do show that the unit is capable of continuous use and the data can be used to develop cutoff criteria for discarding rock. Obviously, almost any criteria utilizing the available analyses can be used for discarding rock.

CONCLUSIONS AND RECOMMENDATIONS

Data from the system, as well as samples of rock on the belt, were collected several times a week from February 20th to August 29th, 2006. The rock samples were analyzed for BPL, CaO, MgO, Fe_2O_3, Al_2O_3 and (periodically) Insol. Approximately 300 samples were collected during continuous and static tests. Relationships were developed between the observed LIBS spectrum and the chemical analyses.

The relationships showed an average error (difference between chemical analysis and LIBS value) of 0.34 for MgO, (range of 0.22-6.81), 0.16 for Fe_2O_3 (range of 0.54-3.00), 0.20 for Al_2O_3 (range of 0.76-4.89), 1.70 for Insol (range of 6.53-27.67), 2.36 for BPL (range of 29.4-68.76) and 0.029 for MER (range of 0.084-0.54). For comparison, measurements of sampling/analytical/sample splitting errors were 0.24 for MgO, 0.10 for Fe_2O_3, 0.08 for Al_2O_3, 1.48 for Insol, 2.34 for BPL and 0.16 for MER.

Static tests were also conducted on flotation feed, tails and concentrate samples. These gave an average error of 3.17 for BPL (range 3.02-67.61).

During the test period, there were no mechanical problems with the system. However, several software problems were encountered. Most of these were fixed during the test period or shortly after. Also, several modifications were made to the operating screen to better present the data.

During the test period, continuous data were collected during several long (>10 hr) time periods. These data showed the large variability in rock quality and the ability to significantly improve the rock quality by discarding a small portion of the pebble.

Properly applied, LIBS can give real-time, rapid, accurate analyses of phosphate pebble on a moving belt. LIBS can help mining operations improve rock quality. The LDS system is mechanically reliable in the "phosphate environment."

It is recommended that further tests be run on flotation feed samples.

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