On-line Measurements at Phosphate Chemical Plants

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Introduction

The driving factors behind process control include increased safety, improved product quality, and higher productivity. The intrinsic value of these factors is amplified by the economic benefits of 1) increased revenue as a result of higher production rates and product quality and 2) lower costs due to improved product recoveries, reduced raw material consumption, and more efficient use of labor.

Fundamentally, process control involves measuring process variables and taking control actions based on those measurements. In many industries, on-line control consists primarily of measurement and control of temperatures, pressures, and flows due to the limitations of on-line analytical techniques. Control of stream composition and product quality is often limited to periodic off-line measurements analyzed remotely in a production laboratory.

Instruments now exist that can measure phosphate levels and elemental composition of phosphate rock on-line at phosphate chemical plants and mines using either Nuclear Magnetic Resonance (NMR) or Laser Induced Breakdown Spectroscopy (LIBS). NMR has been a viable on-line process measurement for over 15 years, including several years in the phosphate industry. While the LIBS technique has been around for over 40 years, recent improvements in primary components, including lasers, spectrometers, and cameras, have made LIBS a viable process technology.

Whether control decisions are implemented by operators or distributed control systems (DCS), continuous measurements provide a tremendous opportunity for increasing profits in the phosphate industry.

Phosphate Industry Benefits

NMR at Chemical Plants

NMR has provided benefits to the phosphate mining industry for a number of years. The technology has been demonstrated to accurately measure phosphate content in on-line process configurations. Phosphoric acid plants and granulation plants can also realize a significant benefit from on-line phosphate measurements. Measurements of rock feed, phosphoric acid, filtrate, gypsum, and final products have the potential to provide economic value to phosphate chemical plants.

Intrinsic to the design of the NMR system are no moving parts and an unobstructed flow-through probe. Further, the components of the system that come in contact with the process can be made from a number of different materials of construction to resist corrosion and scaling.

Measurement of rock feed in either dry or slurry form can provide feed-forward control to the reactors. This feed-forward control can provide optimization of sulfuric acid consumption. Conversely, by measuring gypsum repulp, a plant could employ a feedback control scheme where phosphate levels in the gypsum repulp are measured.

Other potential measurement points of interest may be found around the filter, the evaporator circuit, or product acid storage. Measurements around the filtration system can provide near real-time data for filter optimization.

On-line NMR can create value to phosphate chemical plants by taking measurements in a variety of locations. These systems have been proven in the phosphate industry and can provide accurate, timely measurements of phosphate levels in dry rock, rock slurry, or acid.

NMR at Mining Operations

The data generated by the NMR allows the plant to monitor beneficiation process efficiencies as well as the quality of mine feeds in near real-time. Additionally, these measurements at the beneficiation plant provide the opportunity for optimization of plant control and reduction in the quantities of reagents used. Many existing sites currently rely primarily on operator experience or infrequent measurements for process monitoring. Therefore, the frequency and accuracy of NMR measurements allow for significant cost savings and efficiency improvements at mines, allowing for a rapid return on investment.

Using customized sampling systems, a plant may measure dry rock or rock slurry at the mine. Samples are taken automatically and fed to the NMR system where the measurements are taken. These results are communicated to the plants DCS system for closed loop or operator control. The instrument is capable of withstanding harsh and hazardous environments. Systems have been located in climates ranging from the Middle East to northern Scandinavia in corrosive and explosive environments.

At phosphate mines, the MagModule II™ can be set up to measure at a number of different sample points, some of which may include: rock reed, beneficiation feed, or beneficiation tails. The system may also be configured to alternately measure samples from different sample points. Thus, the flexibility of the system allows beneficiators to choose the location that provides the most value to their specific process and sample from multiple locations when needed.

LIBS Analysis

Laser Induced Breakdown Spectroscopy (LIBS), seeks to generate significant value for the phosphate industry. **progression**'s iPulse® brings LIBS on-line for use in the mining industry. This instrument may be mounted over a conveyor belt to directly measure elemental composition of phosphate rock and other minerals or it may be utilized for the measurement of slurries and liquid streams. Unlike NMR, LIBS provides a complete element profile. As a result, in addition to monitoring phosphorous, a mine or chemical plant also has the ability to measure magnesium,

calcium, aluminum, and other impurities in the phosphate rock.

Therefore, LIBS allows phosphate operations to better understand not only phosphate levels but also levels of impurities, which may impact the downstream processing of the phosphate. As a result, phosphate mines may benefit from a better understanding of the rock quality being produced while allowing for blending and sorting to meet rock quality requirements whereas phosphate chemical plants achieve a better understand of the effect of impurities on the process leading to improved control and cost savings.

Early Process NMR

NMR has been utilized as a commercial analytical technique since the early 1960s when Varian produced the first available NMR spectrometer for sale. Since then, the technology has been an enabler for a multitude of industrial and medical technology developments in areas such as polymers, synthetic resins, petrochemical products, and drug discovery.

The first on-line process NMR analyzers were produced in the late 1980s and early 1990s by Auburn International and Foxboro. These analyzers were targeted to edible foods, polyolefins, and petrochemicals and were large, cumbersome and expensive to install. Today, **progression** is producing third generation process NMR instruments which are a fraction of the size of prior instruments, easy to install and suitable for a wide array of industries.

Continued NMR Innovations and Improvement

The team at **progression** is dedicated to the continued advancement and development of process NMR technology. Since the first generation technology introduction more than 10 patents have been granted in the area of process NMR related to polymers and other

applications. These additional innovations have established the state-of-the-art third generation NMR for on-line analysis. As a result of electronic technology advances and re-engineering, the physical size (volume) of process NMR systems has been reduced by 89%. Central to the many recent advances that have taken place is the improved data analysis methodology. **progression** has made vast improvements using the patented data analysis methods for translating raw NMR spectra into valuable data.

Practical NMR Considerations

As is the case with most process analyzers, care must be taken with both sample presentation, or sampling, and the actual placement of the analyzer and attendant plant utility connections.

Sampling

progression typically provides sampling systems for each of our process NMR installations—these can be from conveyor belts or turbulent or laminar flow streams. With an installed base of over 100 process NMR systems, designs are available for most applications. Illustration 1 shows a sampling system from a turbulent flow line. It is designed to exclude "trash" from the sample line to minimize plant downtime due to plugging and to allow for easy, regular maintenance. The NMR analyzer is typically placed vertically below the sample point but within 25 meters of the sampling point itself.

*Illustration 1: Turbulent Flow Sampler
(Photo courtesy of Mosaic Corporation)*

Analyzer

The analyzer is contained in a NEMA 4 rated air-conditioned cabinet. Within the cabinet are the magnet, NMR spectrometer, NMR probe, and all associated logic and control equipment. A cutaway of the NMR system is detailed in Illustration 2.
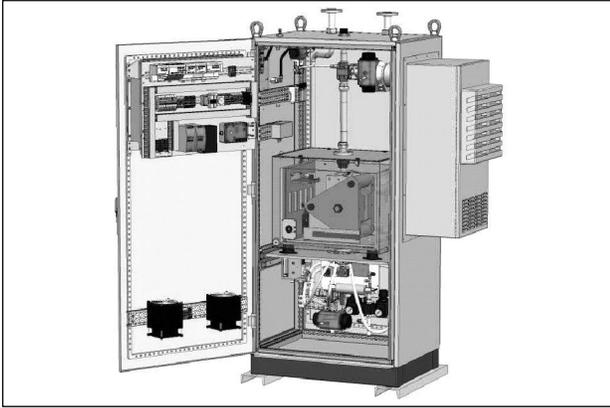

Illustration 2: Cutaway of **progression, inc**. MagModule II

Advances over the last several years have led to reduction in size of process NMR instruments of nearly 90%. Today, the MagModule II offered by **progression, inc**. is only 1.5 m^3 and with proper maintenance is capable of up-times greater than 97%. In addition due to the smaller size and rugged construction, these analyzers are available for placement in a wide variety of plant locations.

The NMR signal is affected by temperature. For that reason, compensating measures are built-in to the analyzer itself to neutralize the temperature effect. Figure 3 illustrates trends of BPL and ambient temperature for a 24 hour period in June 2004 for a location in central Florida.
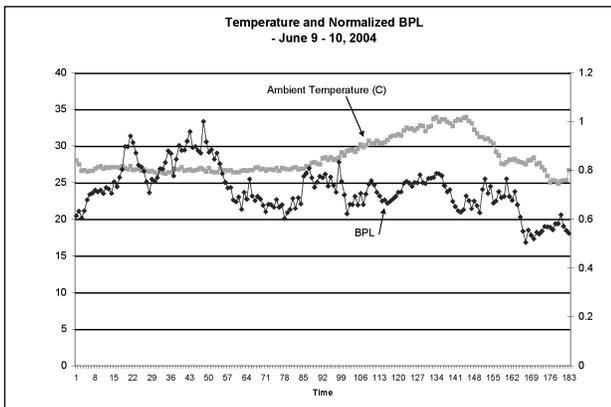

Figure 3: Trend of Normalized BPL and Ambient Temperature

Calibration

An NMR analyzer is typically calibrated against existing laboratory techniques over an analytical range of interest for a specified process stream. Figure 4 illustrates how this works in practice. Total error or standard deviation of the model can be explained by the following equation:

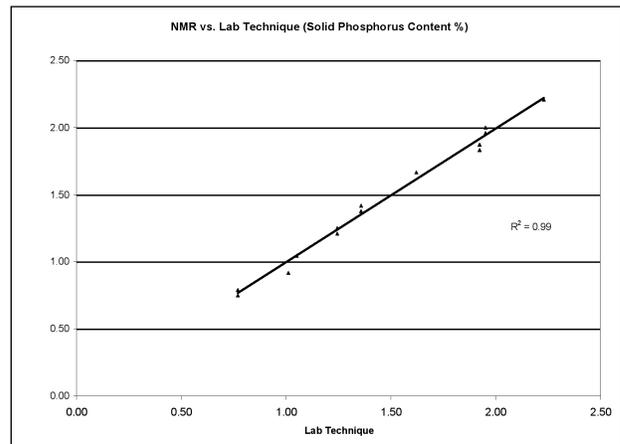$$Model\ std = \sqrt{NMRstd^2 + LABstd^2}$$

Figure 4: Calibration Example of Laboratory Data vs. NMR

Analytical Data

Once installed, process NMR data can be utilized to better control the process for increased recovery. Figure 5 below illustrates the data coming from an on-line NMR analyzer over a 10 day period in June 2004 on a feed stream to a float plant. All data has been normalized.
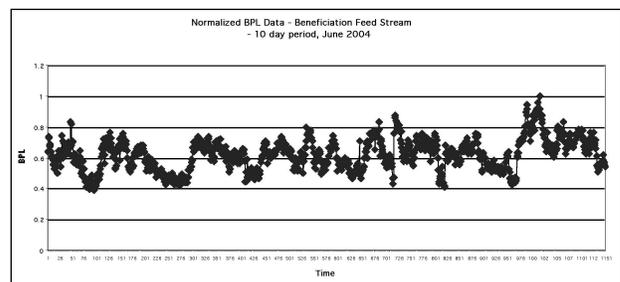

Figure 5: Normalized BPL Data on a float plant feed stream

Development of LIBS

The fundamental concepts underlying LIBS have been studied in various research institutions since the 1960s. Similar to ICP, LIBS is based on the creation of plasma; however, in LIBS, a high powered laser is used to create the plasma plume.

From the first observation of laser induced plasma in the early 1960s, LIBS has progressed significantly. Between 1964 and 1967, the first LIBS instruments were developed. Further research in the 1970s, focused on ablation, excitation, and spark observation. In the 1980s, work was done measuring hazardous vapors and interrogating steel in nuclear reactors. In the early 1990s, the focus of LIBS development changed to on-line mineral analysis, environmental monitoring, and material sorting.

Until recently, commercial applications of LIBS have been minimal due to limitations in the technologies of the underlying components. Recent improvements in lasers, spectrometers, and cameras have allowed for LIBS to be moved to its much anticipated place in process measurements.

Conclusion

Process measurements provide significant economic benefits to industrial processing facilities in every industry. On-line analyzers generate real-time feedback of stream composition. This information may be utilized for process optimization and enhanced control. These efficiencies result in numerous benefits including higher process efficiencies, reduced consumption of chemicals, and higher mineral recoveries.

Process NMR should be strongly considered for on-line phosphate measurement (P_2O_5 and BPL) at beneficiation and acid plants in a variety of streams. NMR calibrations are simple to perform and need little adjustment. The systems are rugged and the uptime of the instruments has been shown to be excellent. The data generated has proven to be extremely useful for increasing efficiencies.

NMR has several advantages over other analytical techniques when considering on-line phosphorus measurements:

❚ no sample preparation is required

❚ a more representative sample can be "looked at"

❚ the technique is non-destructive

❚ the sample can be returned to the process if desired

❚ uptime is excellent

LIBS is an extremely powerful optical technique, which recent advances in the technology have made viable for process environments. By using LIBS, mines and chemical plants can measure elemental concentrations of key components on-line in real time. LIBS can provide concentrations of P, Ca, Al, and Mg as well as other trace impurities. Improvements in the primary LIBS components including cameras and lasers have turned LIBS from a promising research technique to an invaluable process instrument for mines and mineral processors.

The benefits derived from these measurements allow for the realization of significant cost savings and profit enhancement. Overall, the migration from periodic off-line measurements to continuous on-line measurements can generate tremendous value for any processing company.

Appendix A: NMR Background

Basic NMR Theory

NMR systems make use of a physical phenomenon common to many atoms such as phosphorus, fluorine, and hydrogen. These atoms will resonate, or absorb energy at a particular frequency, when placed in a strong magnetic field. This resonance occurs because the nuclei of these atoms have weak magnetic properties, typically referred to as the nuclei's "spin". In a strong magnetic field, the simplest case dictates that the "spins" align themselves with two energy states: with or against the magnetic field of the NMR instrument. The resulting bulk magnetization vector is described by the Boltzmann distribution:

$$\frac{N_{upper}}{N_{lower}} = e^{\left[\frac{-\gamma B h}{kT}\right]}$$

where: N_{upper} = number of nuclei in the high energy state

N_{lower} = number of nuclei in the low energy state

γ = magnetogyroscopic ratio

B = external magnetic field (T)

h = Plank's constant (6.626176 x 10^{-34} Js)

k = Boltzmann's constant (1.380662 x 10^{-23} JK^{-1})

T = Sample temperature in Kelvin (K)

In the case of phosphorus at 30° Celsius (303.15 K) and a magnetic field strength of 0.47 Tesla the distribution would be calculated as:

$$\frac{N_{upper}}{N_{lower}} = e^{\left[\frac{(-10.8394 \times 10^{-7}\,rad/T \cdot s)(0.47T)(6.626176 \times 10^{-34}\,J \cdot s)}{(1.380662 \times 10^{-23}\,J/K)(303.15K)}\right]}$$

Where, the ratio of nuclei of the upper to lower energy states is 0.99999193457, or a slight excess in the lower energy state. In practical terms this means for every 5,000,000 spins there is a population difference of about 40 spins.

The population difference is inversely correlated with temperature and can be described by the Power law (see Figure A).
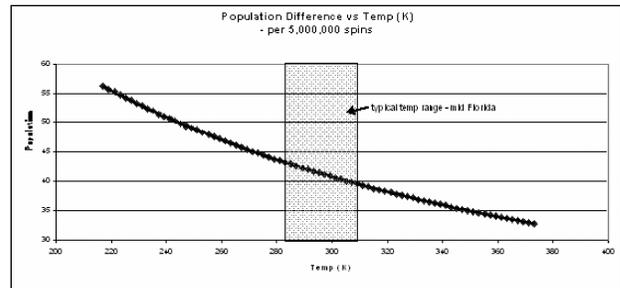

Figure A: Population Difference (per 5,000,000 spins)

This population distribution, like other spectroscopic techniques, has very important consequences. The signal intensity of any spectroscopic method depends largely on the population difference between the two energy levels involved. When a system is irradiated with a frequency, whose energy matches that separating the levels, transitions will be induced not only from the lower energy state to the higher state, but also in the reverse direction. Upward transitions absorb energy while downward transitions release energy. Because of this, the population difference gives rise to a net absorption or release of energy to observe.

When radio frequency (RF) energy is applied at exactly the right frequency to a sample in a magnetic field, resonance occurs, and the vector, or "spin", flips from one state to the other. As the spins are flipping, they absorb and then radiate energy. The exact frequency of the spin flips identifies the kind of atom involved (phosphorus, fluorine, etc) and the amplitude of the signal indicates quantity. NMR is one of the few non-destructive analytical techniques available for specific, elemental analysis and is able to measure bulk samples like phosphate pebble, slurries such as beneficiation plant feed and tails, and liquids.

Practically speaking, after the RF pulse is applied to the sample, a specific delay time is utilized before collecting the released energy from the sample. The resultant signal is referred to as a Free Induction Decay (FID) and an example is illustrated in Figure B.
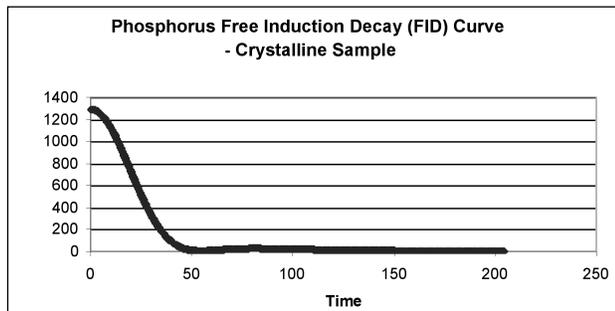

Figure B: Phosphorus FID Example

A complete process NMR instrument is comprised of five basic components: magnet, probe, spectrometer, housing, and control software. Permanent magnet based NMR instruments utilize a permanent magnet typically made from a rare-earth composition such as Samarium Cobalt (SmCo) or Neodymium Iron Boron (NdFeB). Other choices are Alnico, Ceramic or Ferrite. For a typical phosphorus process installation, the magnet strength is 0.47 Tesla which corresponds to nominal resonance frequency of 8.096 MHz for phosphorus.

NMR vs. Other Analytical Techniques

While NMR is not considered to be as sensitive an analytical technique as perhaps, UV-VIS, NMR has the unique ability to "look" at a very large sample as illustrated in Figure C without any sample preparation. It is also a non-destructive technique as well.
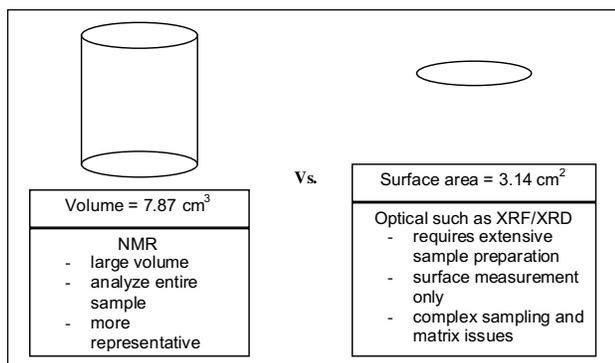

Figure C: Comparison of NMR with Optical Techniques

Appendix B: LIBS Background

In its simplest form, a LIBS system consists of a laser, a spectrometer, and a CCD camera. iPulse® uses one or two neodymium yttrium garnet (Nd:YAG) lasers generating up to 200mJ of energy to produce a plasma plume on or in the process stream of interest. An optical spectrometer is used to analyze the plasma plume for specific elemental analysis after a suitable time delay. Spectral analysis of these atomic emissions yields a fingerprint of the atomic species present in the sample. For greater sensitivity, the system may be configured with a second laser, which selectively excites atoms within the plasma plume. This technique, known as LIF, can lower detection limits by an order of magnitude.

LIBS is effectively non-destructive as the quantity of material consumed during each measurement is a few micrograms. Further, despite the production of plasma, the temperature change in the un-vaporized material is negligible.

LIBS	ICP
On-line capability	Laboratory only
No sample preparation	Samples dissolved and atomized
Effectively non-destructive	Relatively large sample required
High special resolution	Relatively low special resolution
Can measure solids, liquids, and gases	Measures aerosols only

Table 1: Comparison of LIBS and ICP courtesy of INEEL