The History and Future of Nuclear Elemental Analyzers for Product Optimization in the Cement Industry

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Abstract

This paper takes a critical look at the use of nuclear elemental analyzers** for the manufacturing of cement- past, present and future. The paper begins with a brief historical tour of analyzers and then discusses in detail the strengths and trade-offs of current equipment, where they work, the value they deliver, and where they failed, concluding with a look at the latest development in the technology, and the future for nuclear elemental analysis in cement manufacturing control and cost reduction.

** Nuclear Elemental Analyzers as defined for the purposes of this paper includes those analyzers that measure, based on nuclear interactions, the individual elements of the periodic table. For example, Silicon, Iron, Calcium, Aluminum, Potassium, Titanium, etc…

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Performance of PGNA
Historical Applications
Strengths and weaknesses
The future – an exciting new application

Introduction

Cement commerce in most jurisdictions is based on proper characterization and performance of the shipped cement. Standards organizations, such as ASTM and AASHTO and local jurisdictions specify guidelines and procedures to state the quality of the shipped cement, using specific limits for many quality parameters. The need for process control and to monitor these parameters has necessitated widespread use of material sampling systems and lab analysis. Although nuclear elemental analyzers have yet to qualify as the basis for conducting commerce in cement they are now an accepted approach for real-time monitoring and control of processes to optimize the manufacturing process, resulting in delivered cement to specific contractual quality parameters.

Real-time monitoring and control as made available through nuclear elemental analyzers provides value through optimization of manufacturing of their product. Major and minor oxides can be optimized for pile construction, or through real-time proportioning for raw-mix control.   In both cases, cement producers can lengthen the life of reserves, optimize the use of raw materials, and reduce process costs and energy used.   Real-time monitoring can thus be of great value to many cement producers, adding profit directly to the bottom line. In some cases, the economic justification for real-time on-line analysis can be compelling, with some analyzers paying for themselves within a few months.

Despite the value provided by real-time elemental analysis, nuclear elemental bulk-material analyzers are not universally used in cement plants. The use of real-time monitoring had at times been limited by the high cost of the equipment, implementation difficulties, long-term cost of ownership and issues with the performance of the equipment. X-ray fluourescence remains the dominant method for quality assurance and post-mill process control (cement and raw mix).   However, in the area of on-line raw-mix proportioning control, nuclear PGNA analyzers are increasingly preferred by cement makers.

This paper will briefly review the use of nuclear elemental analyzers in the cement industry. The article will discuss the strengths and trade-offs of the current equipment, the latest developments in the technology, and how these developments will affect cement product optimization and cost reduction in the future.

A Brief History

A True Nuclear Elemental Analyzer

As a result of the pioneering work of Bob Stewart at the Bureau of Mines in the 1970's and further research under grants from the federal government and from EPRI in the 1970's and 1980's it became possible to introduce a commercially viable nuclear elemental analyzer in the mid-1980's.

The technology uses a technique known as prompt gamma neutron activation (PGNA). In this process a spontaneous fissioning nuclear source such as Californium 252 is used to bombard a sample to be analyzed with massive quantities of neutrons – several hundred thousand per second. In turn, the elemental atoms in the sample capture a large number of the incident neutrons. These atoms become unstable but quickly re-stabilize by emitting an array of gamma energies. Since each element emits a unique set of gamma energies, spectral analysis identifies which elements are in the material. As a true elemental analysis technology, it can measure on-line and in real time the quantities, expressed as oxides, of SiO_2, CaO, Al_2O_3, Fe_2O_3, TiO_2, MgO, K_2O, SO_3, as well as Chlorine, Nitrogen, and Hydrogen.

The first successful version of these instruments was "chute-type" analyzers that required a gravity-feed of the producer's crushed quarry materials from the top of the unit onto an exit conveyor underneath the unit.   The basic sticker price for these units was as much as $1.0M. With the costs of mounting the unit and getting the cement into and out of the unit taken into consideration, the total cost of ownership often topped $1.5M.   These first chute-type units in cement often had operational problems because of liner wear due to the abrasive sample material and material flow issues. After about 20 or so such units sold into the cement market the vendors, in collaboration with Holderbank and Lafarge, re-tooled and offered a belt-type unit to avoid the wear and flow problems.

1985 First chute-type nuclear elemental analyzer available commercially – first successful units placed in coal and cement

1986 Ad appears for PGNA analyzer

1987 Initial units expensive – analyzer priced at $800K + $500K to

install

1988 Most of the initial market penetration is in coal segment

1989 A few installations yield payback in less than 12 months

1990 Two major vendors selling PGNA analyzers. Calibrations are

site specific – in coal there is trouble with multiple seams

1991 IEA Survey shows 30 PGNA chute-type units sold –

1992 Price/Performance Ratio makes many purchases hard to

justify

1993 Slurry Analyzer introduced for cement raw mix

1994 First belt-type version installed for cement

1995 Lab version of PGNA announced

1996 One main vendor dominates market with over 70% of sales

1997 Hybrid chute/belt unit introduced – vendors develop well

designed

factory calibration standards to allow for robust calibrations

that can

handle a wide variety of coal seams or variations in quarries

1998 Units begin to gain widespread acceptance – 30 to 40 sold per

year

much less nuclear source needed without sacrificing

performance

1999 New vendor lowers price tag significantly for cement – prices begin to come down – three major vendors

2000 Over 100 units sold – now 4 major vendors selling services

and products

2001 First belt version for coal introduced

2002 Low-cost belt version for coal introduced – units are built

using the latest

in computer technology – analyzers can be viewed via the

internet

2003 Version developed for partially cooled clinker – prices

continue to drop

2004 Affordable high performance, easy to install versions now available

2005 The technology has gained widespread acceptance although

there are still

occasional applications with poor results – these are usually

the result of

As the timeline shows above, the first commercially viable units were introduced in the mid 80's although the basic research was done in the 70's. This delay was in part because instrument manufacturers had to wait for the signal processing technologies to catch up. It took time for other technologies to advance enough to make it practical for instrument companies to utilize the technique for on-line, real-time determination of elements in a moving stream of material. In order for analyzers to acquire enough statistics in the measurement process they needed to convert incoming pulses into digital signals at the rate of several hundred thousand per second. Not until the mid 80's did computers and analogue to digital (A/D) converters exist that had the speed and capacity to process the incredible quantities of data involved in PGNA.

Over 20 years ago, a cement plant in Clarkdale, Arizona became the first cement producer in the world to purchase an on-line nuclear elemental analyzer for quality control of bulk materials. The purchase was necessitated by a complicated quarry and varying raw-material composition, and was installed upstream of the pre-blending piles with the goal of achieving a more consistent chemistry in the piles. In the company's Clarkdale, Ariz. plant, this goal was especially important since it had no corrective bins between the pre-blending piles and the raw mill; thus, the plant has to achieve the exact kiln feed chemistry it wants in these piles, just downstream of the crushers.

The unit was placed between the secondary crusher and the stockpiles, giving the operator a real-time view of each pile's cumulative chemistry.

Much of the pioneering work done at by this cement company led to the emergence of a version of the technology that mounts across producer's existing conveyor belts. Now there are five major providers of the technology – one in France and one in Australia, and three in San Diego, California. With sales beginning slowly in cement in 1984 and gradually increasing over the years, PGNA is becoming an accepted standard for on-line control of cement plant quality, with over 250 belt-type units sold around the world for cement-production applications.

All the current vendors offer on-line technology with associated software for raw-mix control/blending. In some cases the software is home grown and in others, the contracted supply includes third-party control software from vendors in the United States, Europe, and Canada.

Below are two examples of the belt technology:

Figure 1. This type unit completely surrounds the belt

Figure 2. A Version of the technology designed to mount on existing conveyor structure

How They Work

Basic Principles
When a bulk material such as cement is bombarded with thermal neutrons, (<1 electron volt neutron energy), from a Californium 252 nuclear source, many of the neutrons are captured by elemental atoms within the cement. When this happens the atom becomes temporarily unstable. In order to re-stabilize the atom sheds a spectrum of high-energy gamma rays. The specific energies of gamma rays given off are a unique set for each of the elements within the periodic table. This principle makes it possible to create a signal to enable the on-line elemental analysis of cement possible with PGNA.

Obtaining and Processing the Signal
In order to create an electronic signal used for the determination of the weight percent of the elements of interest within the cement the unique elemental signature gamma rays resulting from the capture of neutrons by elemental atoms are detected by a scintillating crystal such as Sodium Iodide (NaI). As the gamma rays penetrate the detector they deposit their energy as high-speed electrons within the crystal. These electrons create ionization, which can be detected as UV light pulses. The light pulses are in turn detected by photo-multiplier tubes (a vacuum tube electronic component operating at a high voltage, typically 500 to 1000 VDC) and turned into electrical pulses which are immediately amplified, shaped and then converted into digital signals, and collected into a spectrum over some predetermined period of time (typically one minute) which can then be processed by a computer at very high speeds.
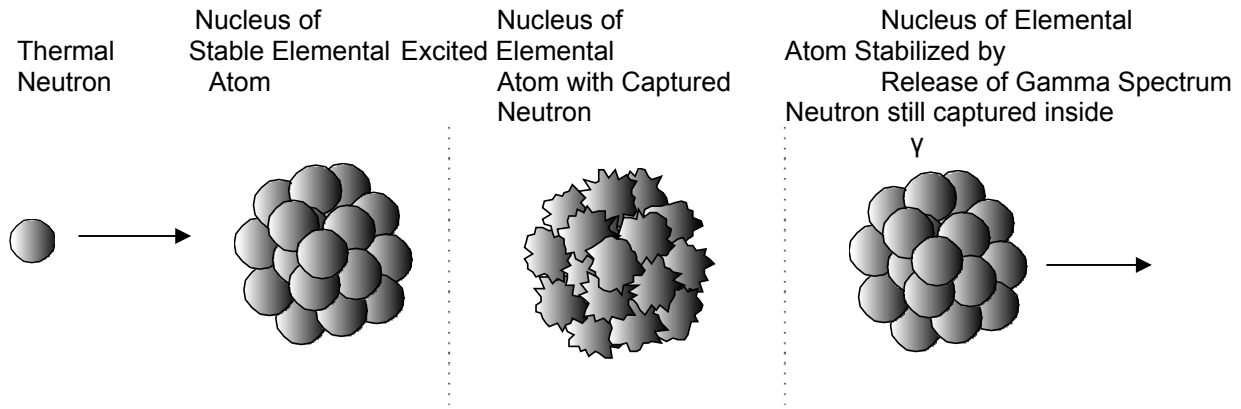
Figure 2. The Nuclear Physics of PGNAA

Processing the Spectrum
The resulting gamma-ray spectrum collected over a one-minute period is actually a distribution of all the incoming gamma-ray energy levels ranging from zero to ten Mev (Million electron volts). In cement applications anywhere from five to fifteen elements of interest are represented in the spectrum. A typical spectrum is shown below which over in one minute collects several million pulses.
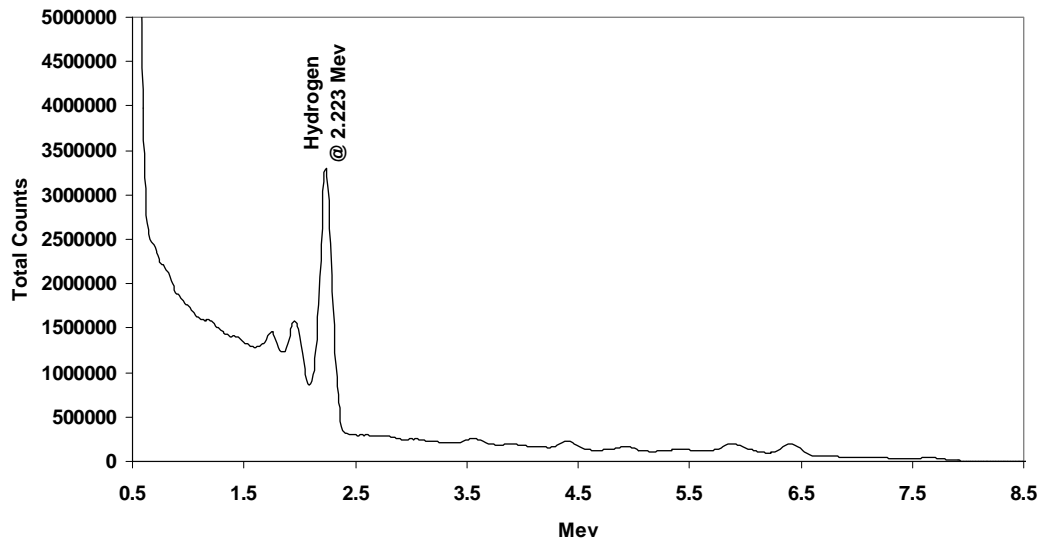
Typical PGNAA Gamma-Ray Spectra

Figure 3. A Typical Gamma Ray Spectrum – High and Low Energies
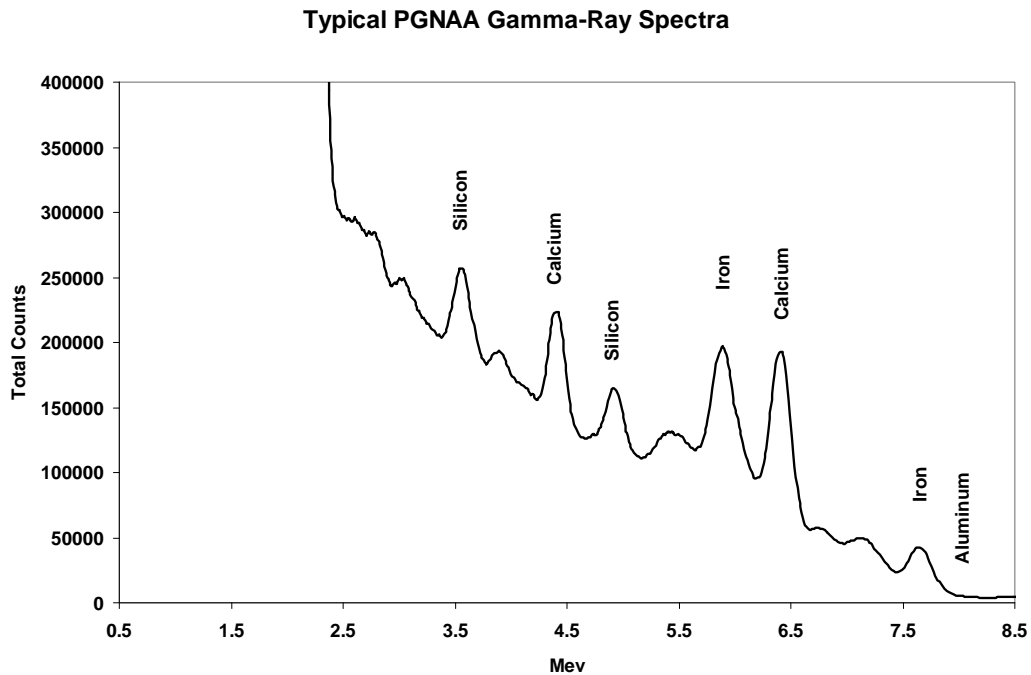
Typical PGNAA Gamma-Ray Spectra

Figure 4. A Typical Gamma Ray High Energy Spectrum

Intuition says that arriving at the weight percent of each element could be accomplished with a simple evaluation of the size of each of the peaks, which is not the case. The MLR approach takes into account the entire shape of all the elemental peaks. Most commonly, vendors use a full-spectrum analysis such as Library Least Squares that utilizes the instrument response to pure elements used as a library against which the incoming spectral data can be compared on a minute-by-minute basis. Typically a multiple linear regression technique is used which solves a linear matrix equation with matrix inverse math. With the high speed and data capacity of computers available today, the time required for this mathematical treatment (de-convolution of the spectra) of the data takes only seconds and becomes transparent to the end user. Prior to presentation of the final answers to the cement producer, the results of the multiple linear- regression are normalized with respect to each other.   The technology has made significant strides and now offers the marketplace impressive precisions and accuracies. **Today's analyzers calibrated in the factory with an orthogonal set of synthetic cement reference standards arrive at the site calibrated for the universe of possibilities in cement.** This means that the analyzers can be immune to changes in raw-material types particularly because the analysis is not susceptible to the mineralogic forms in materials.

MLR Example Calculation – Taking the Mystery out of PGNA

Step 1. The analyzer collects one minute worth of gamma data from the cement sample and prepares to perform a multiple linear regression (MLR) using its library of elements against the cement sample gamma spectra. See figure 5 below:
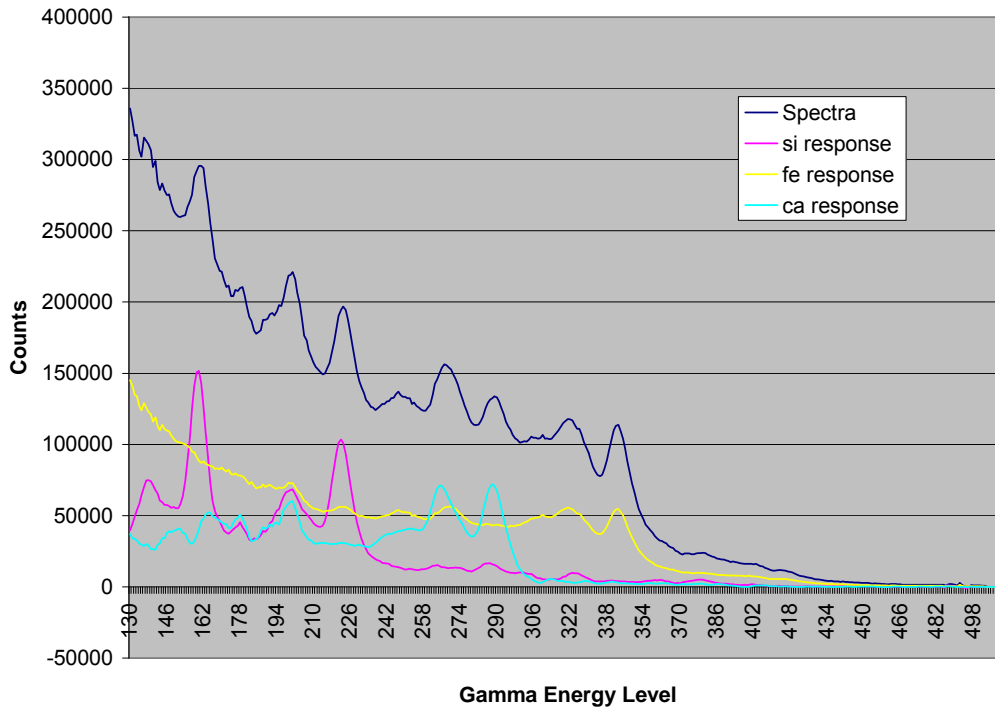
A PGNA Spectra and Elemental Responses

Figure 5. A Sample Signal Spectra, with Elemental Library Responses for Si, Fe, & Ca

Step 2. The analyzer computer performs a multiple linear regression. The regression software calculates the amount of each library response that will most nearly approximate the shape of the signal spectra when added together. See the results of the MLR in figure 6 below:

A Visual Comparison of Sample Spectra with MLR Results Using Si, Fe, and Ca
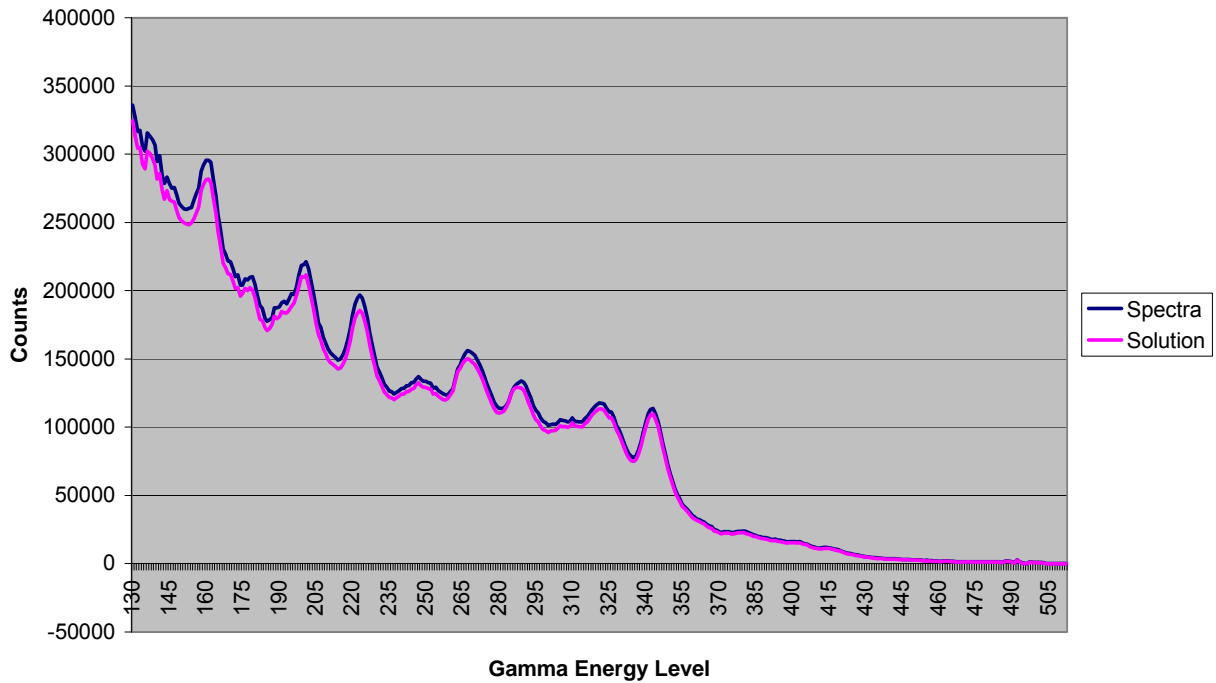

Figure 6. The MLR results have been applied to the Elemental Response Library and shown here graphically juxtaposed with the original Sample Gamma Spectra. Below is the Output of the MLR program:

MLR Output:

	Gain
Silicon:	0.596
Iron:	1.936
Calcium:	0.498
Overall Offset:	-199.800

These multipliers (gains shown above), returned by the Multiple Linear Regression evaluation of the data determine the levels of each element present in the sample and are therefore used to report to the cement producer the levels of the various elements in the cement.

Performance of PGNA

Expected Performance
The technology has evolved to the point that most vendors offer comparable guarantees, with each based on an hour by hour accuracy and a static precision based on groups of 10-minute averages of results.

The table below shows the theoretical range of sensitivity for each of the elements in the periodic table for a PGNA instrument, from which guarantees are derived:

Table 1. Expected PGNA Sensitivity to Elements of Interest*	
Sensitivity in Weight % **	Elements
<0.01%	Cl,Sc,Ti,Ni,Cd,Hg,Sm,Gd,Dy,Ho
0.01-0.1%	S,V,Cr,Mn,Fe,Co,Cu,Rh,Ag,In,Hf,Ir,Au,Nd,Eu,Er,Yb,H
0.1-0.3%	N,Na,Al,Si,K,Ca,Ga,Se,Y,Cs,La,W,Re,Os,Pt,Pr,Tm
0.3-1.0%	Li,Be,Mg,P,Zn,As,Mo,Te,I,Ta,Pb,Ce,Tb,Lu,Th,U
1.0-3.0%	C,Ge,Br,Sr,Zr,Ru,Pd,Sb,Tl
>3.0%	Other Elements
* Note: Table taken from "On-Line Prompt Gamma Neutron Activation Analyzers, Published in the Process/Industrial Instrument and Controls Handbook, Editor-Gregory K. McMillan, Fifth Edition, McGraw Hill, 1999. ** Three sigma detection limit in 10 minutes within an elementary simple rock matrix, ≥150mm thick	

For the cement manufacturing, the following table shows typical results for oxides commonly reported. The higher the inverse ratio with the Coefficient of Variation (relative standard deviation) the more apt the system, analyzer+control software, to have good control.

Oxide	Typical 10-min stdev	Typ Raw-mix average	1/COV
SiO2	0.2	14	70
Al2O3	0.2	3.3	17
Fe2O3	0.05	2.1	42
CaO	0.25	44	176
MgO	0.25	3*	12
LOI**	0.35	34	97
SO3	0.1	0.4	4
K2O	0.05	0.4	8
Na2O	0.1	0.1	1
TiO2	0.02	0.2	10
P2O5	0.5	0.5*	1
MnO2	0.02	0.05	3
Cl	0.005	0.015	3

* Where near normal limit of quantity in clinkerable raw mix
** Not measured directly, a calculated value

The relative control capability is best with the major oxides of Ca, Si and Fe. Alumina is relatively weaker but still possible to control in raw-mix. For stockyard pre-homogenization pile building, examples exist where cement plants control both major oxides and minor oxides
with inverse COV as low as 1 (due to averaging effects). Raw-mix control of oxides with inverse COV of 3 could be possible with suitable filtering.

Historical Applications in the Cement Industry

The Four Major Uses of the Technology

To date PGNA technology has been used exclusively on the front-end of processes in cement plants with four major applications as shown in the graphic below:

Nuclear Elemental Analyzers (PGNA) In Cement
The 4 Major Historical Applications
3 New/Potential Applications

1&2 Raw Material Sorting and
Prehomo Pile Building

3 Raw Mix Control - Blending

4 Raw Meal Control

1 Kiln Fuel Analysis

2 On-line Clinker Analysis
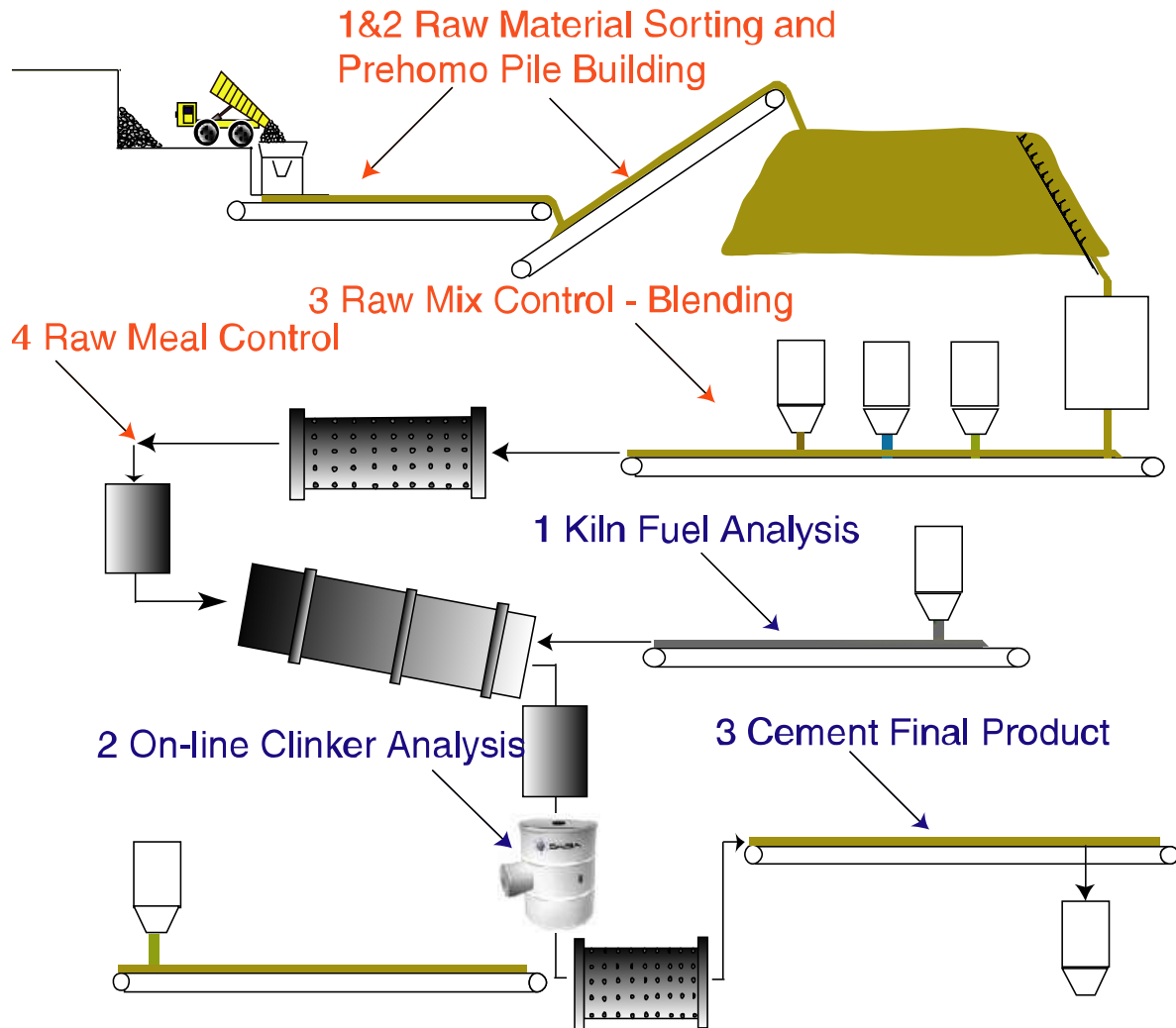
3 Cement Final Product

Figure 7. Historical and New PGNA Applications in Cement

Sales tend to be about 50% for raw mix control, 40% for pile building, 5% for sorting raw materials as they come out of the quarry, and 5% for raw meal control.   On-line XRF is often proposed in the market for the on-line analysis of raw meal as it comes out of the raw mill, but users face challenges from susceptibility to mineralogical and particle-size effects and equipment reliability.

The Strengths and Weaknesses

Weaknesses

Although PGNAA is a true elemental analysis technique capable of delivering minute-by-minute analysis of a moving stream of bulk material it has some important limitations that system designers must deal with and that producers should take into consideration before purchasing a system for use at a quarry, material stockyard, or cement plant.

The following list provides a look at limitations to be considered by analyzer designers and potential buyers:

1. Inter-element dependence. Because the extraction of the elemental information from the gamma-ray spectrum is done at once for all the elements an opportunity exists for some of the stronger elemental signals to influence or, dominate the weaker signals. For example, some elements like Al can be strongly influenced by Fe. *Mitigation: analyzer designers are improving the resolution of spectral capture, but in any event the guarantee specifies the net analytical performance.*
2. The element Oxygen cannot be detected by a PGNAA system that uses thermal neutrons, such as those supplied by the Cf252 neutron source. *Mitigation: cement material analysis does not require an oxygen analysis, however, a nuclear cement elemental analyzer using a neutron generator with the associated fast neutrons can measure Oxygen. These systems are usually bulkier and more expensive if fully shielded because of the associated neutron generator (high-energy neutrons).*
3. Some elements like MgO have a much smaller neutron cross section and therefore deliver performance which may not add value to an operation with an MgO control issue. *Mitigation: the vendor's guarantees must fit with the intended application.*
4. Calibration checks and adjustments have to be done on site with static reference standards and can be time consuming. *Mitigation: the project plan should allow the needed belt availability time during the commissioning period*
5. It does not add value to producers who are looking for elemental quantities too close to the detection limit. Mitigation: see 1 and 3, above.
6. Accuracy and precision are both subject to measurement protocols (averaging time) and for accuracy, the basis of comparison. *Mitigation: clear contractual definitions and due consideration of the sampling and accuracy of the reference method*
7. By contrast with XRF, the lower count rates demand longer count accumulation intervals to get comparable precision. *Mitigation: The control loop has the appropriate filtering or data accumulation interval.*
8. Certain combinations of varying material moisture contents and geometrical arrangement of layers on the conveyor belt can cause problems with dynamic accuracy. *Mitigation: appropriate project conception and possibly mechanical modifications to the conveying system.*
9. As opposed to the low-mass surface measurement with XRF, PGNA needs substantial mass for good precision in some situations the belt or sample in question needs to be increased in terms of mass presented to the analyzer. *Mitigation: modify belt speed, variable speed drive if better belt-loading uniformity is needed for the application.*

Strengths

Below is a look at the list of strengths for the technology:

1. PGNA looks at the entire sample on a nuclear level, accumulating hundreds of thousands of events per second to determine the composition of the entire stream. *Outcome: the analysis used for control includes no sampling errors.*
2. PGNA does a true elemental measurement of the material with no influence of particle size or mineralogy. *Outcome: the cement plant can obtain process data from any material after the primary crusher, cement plants have largely abandoned the use of sampling towers and raw-mix control increasingly takes place ahead of the raw mill.*

3. The penetrating nature of neutrons and resultant gamma rays means that the analysis zone can have nearly perfect uniformity of sensitivity from top to bottom and side to side with no effect of material particle size. *Outcome: many material streams can be analyzed with little or no engineering modification to the conveyance.*
4. With on-line, real-time information, rapid process control can be achieved for individual elements as well as calculated parameters such as LSF, C3S, etc…*Outcome: the control loop using the on-line information, with little delay time from the actuators (e.g., feeders) can correctly respond to more rapid chemical variations than previously possible.*
5. With proper attention and maintenance, the systems tend to have stable accuracy and precision. *Outcome: less time is required for the plant operator to perform analytical adjustments.*
6. The equipment has no or almost no moving parts and this technology has proven to be robust, reliable and consistent in the industrial environment. Some systems in use today have been in constant use for over 15 years. *Outcome: the life-cycle ownership cost becomes lower; the plant has a stable operating mode.*
7. The systems are increasingly easy to install in the field. *Outcome: the total project cost has dropped even faster than the purchase price of the analyzers.*

Weakness/Strength Summary
The list of weaknesses cannot be ignored or treated lightly but in most cases the analyzer design and project application engineering can minimize any adverse effects. Some of the weaknesses might preclude the use of the technology in some applications. However, as evidenced by the 250+ systems shipped to date and their continued use, the cement industry has found useful application of this technology for raw-material and raw-mix analysis. In these cases the producer is able to play to the strengths of the technology. Many of these applications have been great successes, adding significant dollars to the owner's bottom line.

Recent Developments and the Future
Recent Important Developments
One of the most recent developments of interest for the technology is the use of PGNA for the first time in the downstream area of the process. Under a special development purchase order from a major cement producer a unique analyzer has been developed that measures sulfur and potassium in partially-cooled clinker as it comes out of the kiln. The theory behind the application has to do with the common correlation in many kilns between the retention of sulfur or potassium in clinker and the burning conditions in the kiln.

In this first application, the analyzer is receiving a partial stream of the partially cooled clinker as extracted from a reciprocating grate cooler. The project is not complete, but initial data is encouraging. Below is a photo of the actual analyzer as installed at the plant:
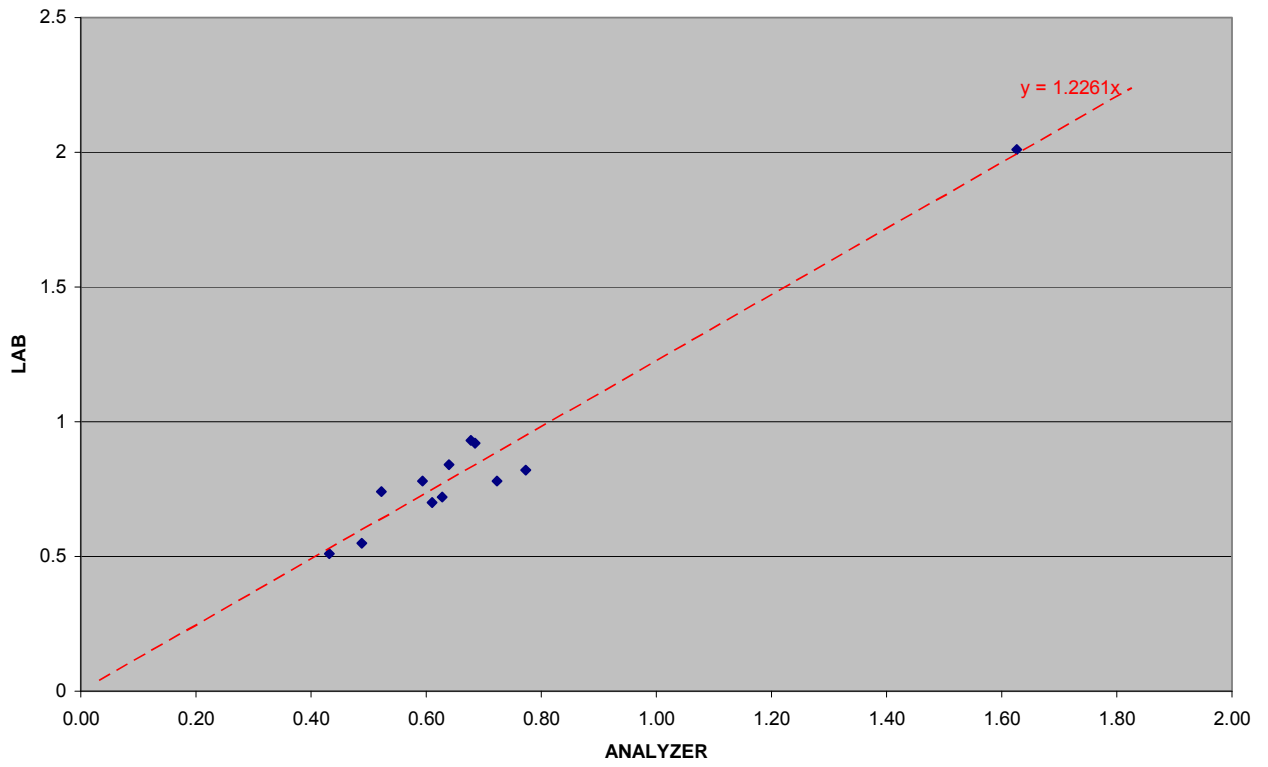
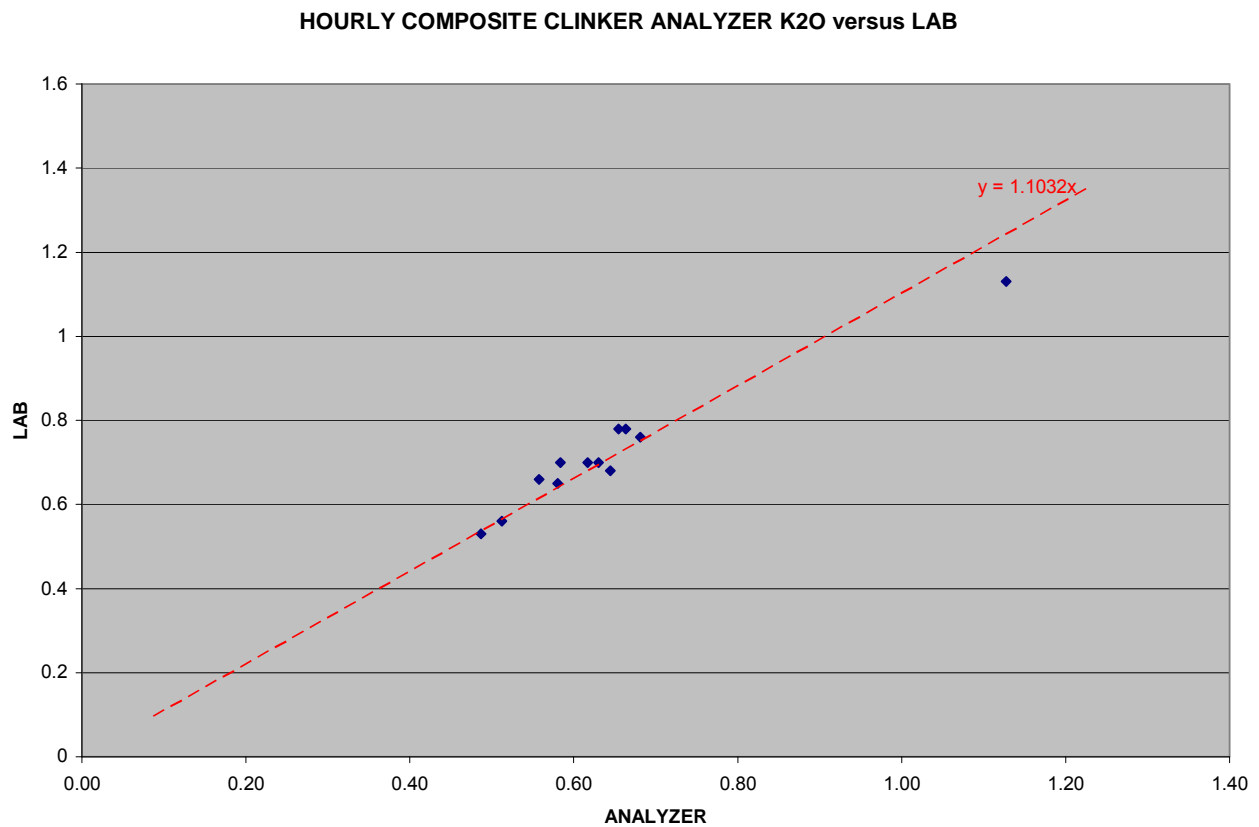Figure 8. A New PGNA Application – Analyzing Partially Cooled Clinker

Below is some of the initial performance data taken on the unit for SO3 and K2O.

SO3 XY-Plot
[Standard error = 0.08%]

HOURLY COMPOSITE CLINKER ANALYZER SO3 VERSUS LAB

K2O XY-Plot
[Standard error = 0.05%]

HOURLY COMPOSITE CLINKER ANALYZER K2O versus LAB

One disappointment in the project has been the inconvenience of dynamic calibrations. The long-term goal of this project would be to input the information into the plant kiln-control software to improve kiln stability and the consistency of the clinker product.

The Future
Great advances have been made in PGNAA performance in the last 20 years but the best is yet to come. In the past PGNA analyzers have been large, expensive to buy, expensive to maintain, with some important limitations in performance. In the future the units will be smaller, and should be more affordable with further improvements in performance. Performance will continue to improve with increasing ability to do trace elements such as Na and K. The nuclear sources needed to deliver the necessary performance will become smaller and smaller. As the technology continues to prove itself at more and more sites, it is

anticipated that it will be used in closed-loop software control applications in other areas of the cement plant. In this area the cement industry is ahead of other industries such as Coal.

With regards to calibrations, the units still require calibration adjustments on site but the ultimate goal of some manufacturers is to create a universal calibration with the unit working right out of the box when on site. This is an ambitious goal but there is at least a theoretical basis for such a dream. The universal calibration is probably several years away. In the past unsuccessful (in terms of market penetration) attempts were made to utilize a static sample, lab-scale version of the technology at various sites in a cement operation. This will probably be successful in the future.

In summary, the PGNAA technology has proven itself and if it delivers on the promise of the future, it may eventually find its way into other areas of the cement plant. This has been predicted before but with recent developments in technology it appears to be gathering momentum. Time will tell.

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