



W H I T E P A P E R

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Subject: Excerpt from CALCIMA Technical Presentation:

Leveraging Gamma-Ray Emission Spectra Technology as an Effective Energy Efficiency Measure (EEM) at Dry-Kiln Portland-Cement Plants

It is interesting that indirect energy efficiency measures are sometimes the most effective. One such example is the savings of large amounts of energy *in the final step* of the cement-making process by using a fairly sophisticated technology *in the initial step* of the process. This technology, Gamma-Ray Emission Spectra is also referred to as *Prompt Gamma-Neutron Activation Analysis* (PGNAA) and is used to monitoring the composition of the quarried raw materials at a cement plant. How can this save energy throughout the many unit operations in a cement manufacturing plant?

At the heart of a cement plant is it's 'kiln'. From an engineering standpoint, a kiln is merely a (very simple) type of chemical reactor, characterized by high operating temperatures and low operating pressures. In at least one important respect, however, cement manufacturing is a very special case of a chemical process industry : over 99% of the mass of raw materials for this process are not purchased, but mined. Hence there is no upline supplier with whom to coordinate and implement quality control of these raw materials - they come directly from quarries and thus vary continually in composition. Hence the standard methods of controlling reactant composition are not possible to implement, yet the end product must still meet stringent engineering specifications. Quality control of cement, therefore, is both critical *and* complex:

In order to achieve some control over product quality, therefore, large quantities of these raw materials (limestone and lesser amounts of 'shales' - siliceous, aluminous, and ferrous ores) are

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W H I T E P A P E R

stored in silos and continually blended to reduce temporal variations in composition and ultimately achieve a kiln-inlet reactant composition that (A) will result in a cement with the intended properties (there are several main ‘types’ or compositions of cement, and many specialized varieties, all of which require slightly different reactant matrices), and (B) remains as consistent as possible over time. But raw material blending is confounded by the delay time in determining the composition of discrete samples taken from the storage- and blend-silo feed-systems. This means that the control room gets ‘snapshots’ of the raw-ore composition about ½ -1 hour after the material has been sent to silo / storage. In this time, approximately 100,000 to 300,000 lbs cement may be produced (before any control can be affected). When control-adjustments are finally made, the effective ‘time constant’ of the control is on the order of 20 to 45 minutes. And despite the fact that the plant personnel are skilled in overcoming this disadvantage, objective methods for reducing variations in raw material composition can directly reduce the ‘black art’ aspect to achieving tighter quality control, and hence have significant value.

Since the raw meal ‘mix’ (the “reactant matrix” in chemists’ terms) has a range of chemical properties depending upon the source of each component, and since the properties of the mix are not known on a real-time basis, in order to properly process the last ½ to 1 hour of throughput, the kiln firing process (conditions within the reactor vessel) must be set up to provide the minimum amount of specific energy required to actually facilitate the chemical reactions which form cement’s ‘active ingredients’ (‘tri-calcium and di-calcium silicates, called *Alite* /C3S and *Belite* / C2S respectively, the two components in the clinker which are responsible for the creation of calcium silicate hydrate, which allows the cement to ‘cure’ or harden by reacting with water), **as if its feed (raw meal) composition were somewhere between the last samples’ composition and a “worse case mix”**. This is the ‘black art’ of cement manufacture. In practice, it is simply accepted that this results in some degree of “over-firing” the *non-worse case* mixes – keeping the kiln temperatures sometimes hundreds of degrees higher than would be necessary, were the plant technicians to have real-time raw-meal composition information indicating / assuring that they were *not working with* the ‘worst-case’ raw meal composition.

The mass of extra fuel required to keep the kiln at these higher reaction–zone temperatures is significant, as are the attendant fuel costs and the additional combustion-gases emissions. Therefore reducing all these via technical improvements to the process is economically and ecologically beneficial regardless of ancillary effects.



W H I T E P A P E R

Moreover, and more to the point here, there are significant secondary effects as well. The aforementioned “over firing” of the kiln reactant-mix can result in undesirable properties of the reaction product, called clinker, exiting the kiln. (Clinker is basically the cement product -- minus a small amount of additives -- but it exits the kiln in the form of near-spherical ‘nuggets’, usually about 5/8” in diameter, so it has to be ground to a very fine ‘powder’ before it can be useful as cement. This work is done in grinding mills, called ‘finish mills’ in the cement industry.) The finish milling system in a cement plant is basically the final step: the chemical reactions have all been effected, and the clinker is milled / ground, basically from 5/8” in diameter to particles somewhere in the neighborhood of ~200-300 microns in ‘diameter’ (these particles are not round). Clinker is also quite hard, averaging about 13.5 on the ‘Bond’ scale (limestone, by comparison, has about a 9.0 Bond value). Thus it is significantly harder than the main raw material for cement, and therefore requires commensurately greater specific energies to grind, especially to the small particle sizes required for cement to meet its strength tests and other specs. As a result, energy savings potential in the Finish Mills of cement plants are immense.

Generally the main effect of this ‘over-firing’ is to render the clinker ‘nuggets’ (1) less porous and (2) more crystalline in nature, and thus significantly harder which make it more energy-intensive to grind, or ‘mill’ the clinker to the required fineness for any given cement specification:

1. The less porous microstructure is caused in part by a higher Fe^{++} / Fe^{+++} ratio as a result of creating reducing conditions in the reaction zone.
2. The more crystalline nature of the clinker is caused by the creation of crystals of the active ingredients (‘Alite’ and ‘Belite’) which are actually larger than the average final particle size dictated by the finished-cement Blaine spec (m^2/kg). This means that, in addition to breaking up amorphous material, the milling operation must *overcome crystal lattice energies*, significantly increasing the specific milling energy requirements

So better control over the raw material composition at a cement plant could theoretically reduce the energy required to grind the clinker into the fine powder required for cement to have the



W H I T E P A P E R

surface-area-to-mass ratio required to be used in making concrete, and that is exactly what has been done at many cement plants in recent years: A Gamma Neutron Analyzer uses gamma-ray emission spectra to generate on-line quantitative elemental analyses of the (continual) flow of quarry feed to the quarry storage of a cement plant, thus replacing the manual sample-and-test procedures previously used by all plants. By providing continual, real-time feedback on quarry-rock composition, the GNA ultimately allows the plant control scheme to significantly reduce the standard deviation in the composition of the raw meal. This, in turn, has several beneficial effects, a few of which are:

- To significantly decrease the overall use of kiln-fuel per ton of clinker manufactured (and hence the amount of greenhouse gases emitted). Note also that while this is not directly saving kW on the grid, there is also a measureable effect on electrical energy consumption due to this decrease in fuel (coke, coal, Tires, etc.) fed to the kiln, since the motors which run the grinders, conveyors, and blowers, etc. for these fuels need now deliver less fuel. This results in annual load decreases, creating opportunities for real electrical energy savings.
- To lower the *average* kiln hot-zone temperature necessary for the creation of the required amount of alite (endothermic rxn, requires lots of heat)
- To make it easier to keep enough free-lime in the clinker (hotter reaction zones reduce free-lime below the optimal concentration of ~1 – 1.5% by wt)

So in addition to enhancing product quality, these effects combine to lower the overall *hardness* of the clinker, making it significantly easier to grind in the finish mills.

Therefore, the largest single electrical energy-consuming system, and **final unit operation in the plant** -- the 'Finish Milling' of the clinker (and small quantities of additives) into very fine particles which are then sold as cement -- experiences a significant decrease (often over 8 %) in specific electrical energy consumption (consumption per ton of product produced) as a result of a small **unit operation added to the front-end** of the plant. This can often translate into saving tens of millions of kilowatt-hours each year at each plant in which this technology is leveraged.

In the last few years, Onsite Energy has focused much attention on, and made considerable progress implementing and successfully completing PGNA and other Energy Efficiency (EE) projects within the cement manufacturing industry. Often, the electrical power and energy

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W H I T E P A P E R

savings actually achieved are large, commensurate with the magnitude of the power consumption of the plants themselves. Though such process-modification EE projects can be driven by the customers' desire for continuous quality improvement as well as for energy efficiency, the utility-funded incentives available specifically as a result of the energy savings which accompany the projects often significantly increase the ROI / decrease the payback periods of such projects, thus affecting the projects' CAPEX priority within the customer's corporate structure. Once the financial benefits tied strictly to the energy savings aspect of a major project are calculated and figured into the overall financial 'picture', the customer can make more informed CAPEX decisions and ultimately benefit their fiscal bottom line as well as become part of the solution to decrease the load on California's electrical grid and plant emissions.

Reprints of this white paper can be obtained by contacting:

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