

Optimising combustion with alternate fuels and monitoring with online XRD

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Abstract

Fuel costs constitute about one third of the total cost of producing cement, so any reduction in energy costs translates into very significant savings. Alternative fuels are usually lower in cost than regular fuels and can provide quantifiable benefits when they are used. The cement rotary kiln is an ideal processor for alternative fuel, however, alternative fuels provide certain challenges because they tend to have low and variable calorific value, their composition is variable and their supply may also be variable.

Burner technology can address many of the issues of alternative fuel firing by using modelling techniques to ensure that the burner generates rapid fuel and air mixing which ensures that combustion is efficient within the wide range of specifications for alternative fuels. The purpose of the burner is to ensure the fuel burns so that it provides the correct heating profile to form good clinker.

Optimisation of the burner will help overcome fuel variability but often alternate fuels change the temperature profile or burn on the bed, which affects the clinker forming reactions and hence clinker quality in addition to chemistry and phase changes they may generate.

Traditionally cement process control has been governed by the measurement of chemistry and free lime. Given optimal/ideal burning conditions and chemistry it is sufficient to monitor the chemistry and make the assumption that the clinking reactions have properly transformed the raw materials into clinker. In practice it is common to have variations in both chemistry and burning conditions. In particular, with the use of alternate fuels the burning conditions can be more variable, leading to variable clinker quality.

To ensure clinker quality, a continuous knowledge of quality is beneficial. That can be obtained by using a Continuous On-Stream Mineral Analyser, which directly measures the quality of clinker using proven X-ray diffraction (XRD) techniques. XRD analysis measures mineral content of clinker, such as C_3S , C_2S and free lime. This information indicates how well the clinker forms. If clinker quality starts to vary, the operators immediately become aware and are able to execute the required corrective measures in such a timely manner that clinker quality always remains acceptable.

To use alternative fuels a well designed burner is the first requirement. The burner must efficiently burn the fuel and also allow for good control. To know how to control the burner, while ensuring quality is maintained, an on-line clinker quality analyser, such as Continuous XRD is needed. This paper describes how a combination of modern burner design and on-line XRD quality control allows a plant to maximize its use of alternative fuel and cement production.

1. Introduction

This paper describes two proven technologies that can be used in tandem to maximize alternative fuel use in a cement kiln. One is burner design and the other is on-line mineral analysis using X-ray diffraction (XRD). Both technologies are established and in industrial use.

We start with a review of clinker formation in a kiln, discussing high temperatures and the energy to achieve these temperatures. With the impetus for this paper being alternative fuel use, a description of the principles for an optimum burner design are described and a brief description of some of the alternative fuels used in the cement manufacturing process. Due to their nature, alternative fuels cannot be fired like conventional fuels. They are variable in form and composition and this affects how they burn, the corresponding heat transfer, and hence clinker formation.

In order to monitor the effect of alternative fuel use, and ensure that clinker quality is maintained, continuous knowledge of the mineralogy of clinker is needed. Section 5 describes a Continuous XRD analyser that can provide this very information.

To conclude, Section 6 brings together these two technologies. It describes how continuous knowledge of clinker mineralogy and an optimized burner can maximize the amount of alternative fuel used in a kiln without jeopardizing the quality of the clinker produced.

2. Clinker Formation in a Kiln

Cement manufacture involves blending a raw mix of materials containing calcium, iron, aluminum, silicon and small amounts of other elements. The finely ground materials are heated and then cooled to form a clinker in a pyro-processing system. Upon heating the various compounds react to form a multi-phase crystalline system. The material is then rapidly cooled to freeze the crystalline structure.

The resulting clinker is then ground and mixed with gypsum to form cement. Where permitted, fillers such as limestone and pozzolanic materials may be added at this stage.

During the heating process the various compounds in the raw mix react to form calcium silicates, aluminates and ferrites. A multi phase system is formed. Figure 1 shows the temperatures at which the various minerals form. These reactions require a finite time at these temperatures. As such the material inside a cement kiln must undergo a heat up and cool down profile. In general, material is gradually heated up to clinkering temperature. In the clinkering zone the material heats rapidly and then cools rapidly on exit. If the heating and cooling are too slow, then the cement crystals become large and require more grinding energy. Figure 2 illustrates two hypothetical temperature profiles inside the kiln and the effects that they may have on the relative sizes of the clinker minerals.

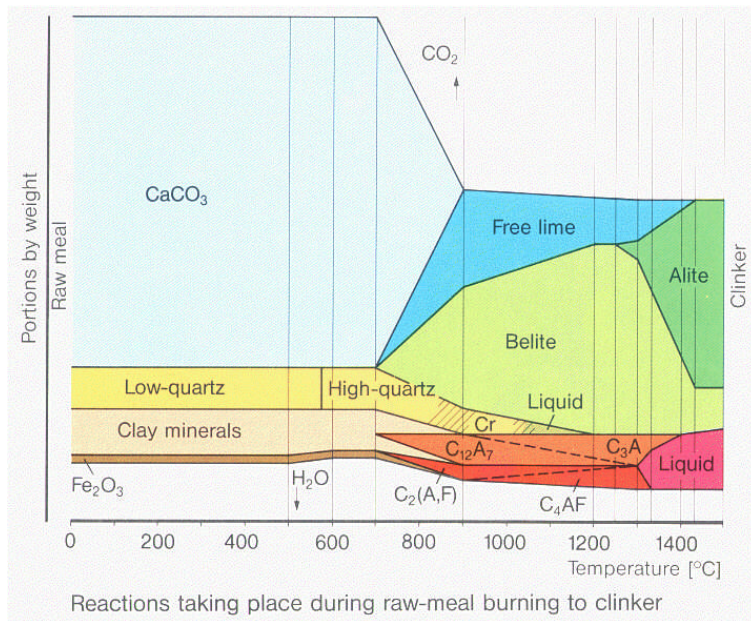


Figure 1: Clinker mineralogical changes with temperatures

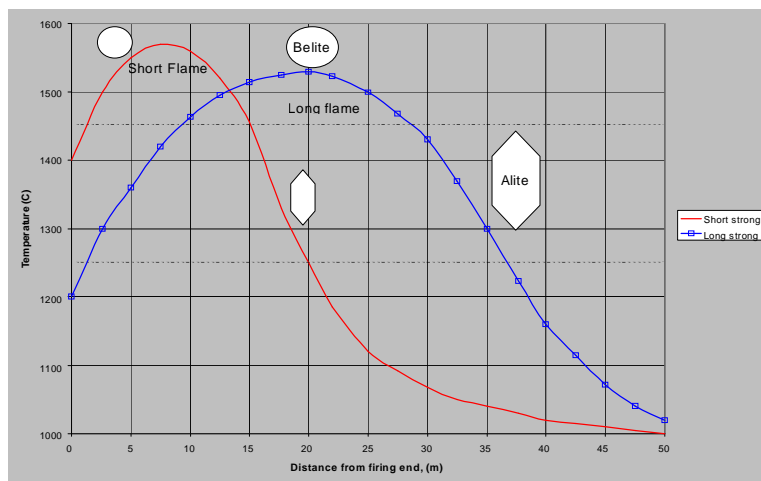


Figure 2: Effect of flame temperature profile on clinker minerals

Burning fuel provides the energy to achieve the temperatures needed for the clinkering reactions. The purpose of the pyro-processing system is then to facilitate heat transfer between the hot gases formed by burning the fuel, and the clinker material.

In calciner kiln systems the CO₂ is driven off the hot meal, which is then transported into a rotary kiln. In the kiln the raw meal is heated up to the temperatures needed to form the final clinker minerals. The burning zone in the kiln still remains the most critical section that determines clinker quality in terms of mineralogy and cementitious content.

3. Burner Design

The purpose of a kiln burner is to introduce fuel and air into a kiln, such that the fuel burns and releases heat to form clinker. In particular, the fuel must come into intimate contact with oxygen in the air, the combustion reaction has to occur efficiently and, finally, the desired heat profile must be released. At the same time, emissions such as CO, hydrocarbons and NO_x must be minimized, while the flame must not impinge on the kiln walls and damage refractory.

Burner design is further complicated by the harsh atmosphere inside a kiln. Flame temperatures are over 2,000°C and the gases have an extremely high dust load. Thus, the burner is subjected to heat as well as abrasion damage.

There are, therefore, two areas than need to be considered in effective burner design:

- Combustion and heat transfer design, to address the chemical reactions and heat transfer.
- Mechanical design, to ensure the integrity of the design in the harsh kiln atmosphere.

Combustion and Heat Transfer Design

The heat transfer needs of a kiln system are quite specific. A burner that is optimum in one kiln may be disastrous in another. Effective burner design requires an understanding of the various processes carried out in a kiln.

Fuel Combustion

Traditional fuels are gaseous (natural gas), liquid (oils) or solid (coal and coke). In many cement industries solid fuels predominate due to their economics.

Coal is the most commonly used solid fuel and is often supplemented with alternate fuels such as petroleum coke. The coke has higher calorific value but usually comes with an excess of sulfur which can cause buildup problems in the kiln or cyclones. Careful burner design can allow higher rates of petroleum coke firing and yield significant savings. Some plants have been able to increase coke from 40% to 100% because the sulfur is combined into the clinker and, therefore, does not accumulate in the process.

Natural gas is a convenient fuel, it is clean, easy to handle and there is no working capital in stock piles or tanks. The major drawback with gas is its low flame luminosity, which is much lower than that of oil or solid fuel. Gas flames have low emissivity and this in

turn reduces the amount of radiation heat transfer, $Q_{rad} \propto \varepsilon(T_A^4 - T_B^4)$. Figure 3 shows the heat release profile for a burner firing gas and oil (a coal flame will have a profile similar to oil). The heat release profile produced by a typical gas flame is not ideal for clinker formation. However, efficient burner design can compensate for this.

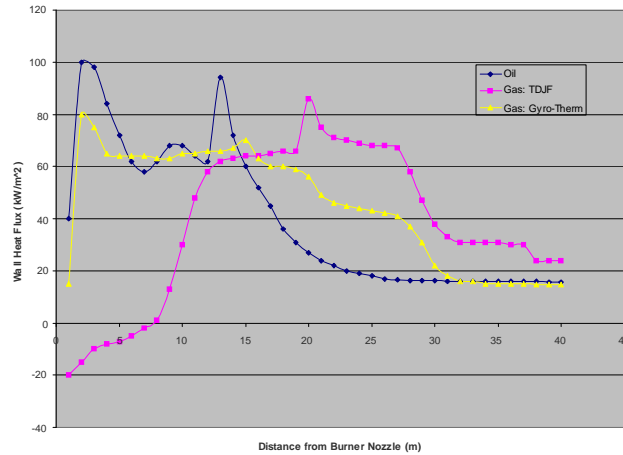


Figure 3: Heat release profile of various burners. Blue line is a typical oil flame and pink line is typical gas. Yellow line is a gas fired FCT *Gyro-Therm* burner.

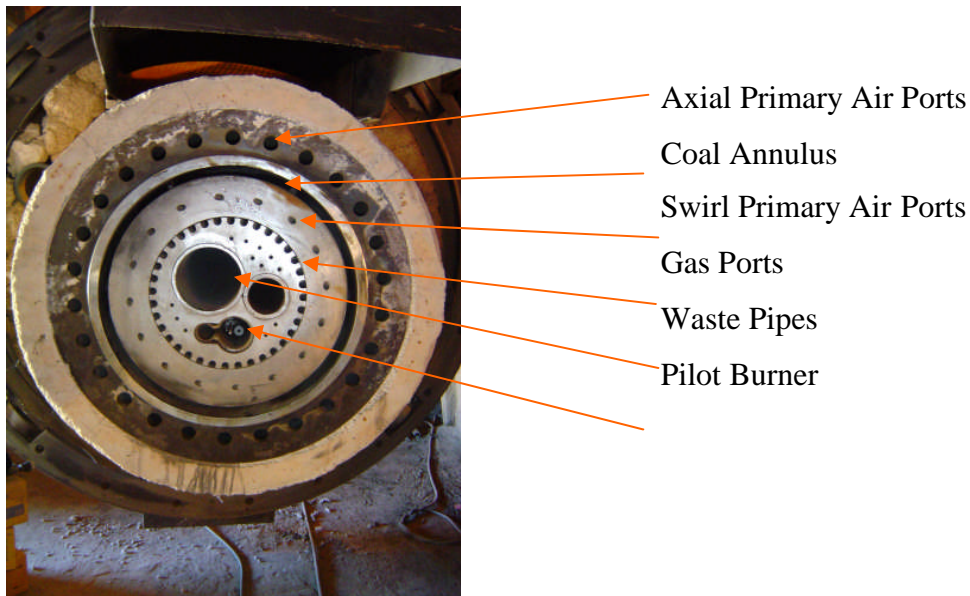


Figure 4: A typical multi fuel burner nozzle

Gas is introduced through a nozzle, typically of multiple ports. The size of the ports is based on the gas flow and available gas pressure. Figure 4 shows a typical FCT *Turbo-Jet* multi-fuel burner nozzle with circular gas ports.

It is possible to enhance the heat transfer from a gas flame by using a special nozzle. The technology utilizes an FCT *Gyro-Therm* nozzle (see Figure 5), where the gas exits the nozzle in a stirring motion. This different mixing environment creates a flame with a much higher emissivity resulting in a heat transfer profile that is more suitable for clinker

manufacture. Where gas is the primary fuel, an FCT *Gyro-Therm* burner provides the best heat release profile.

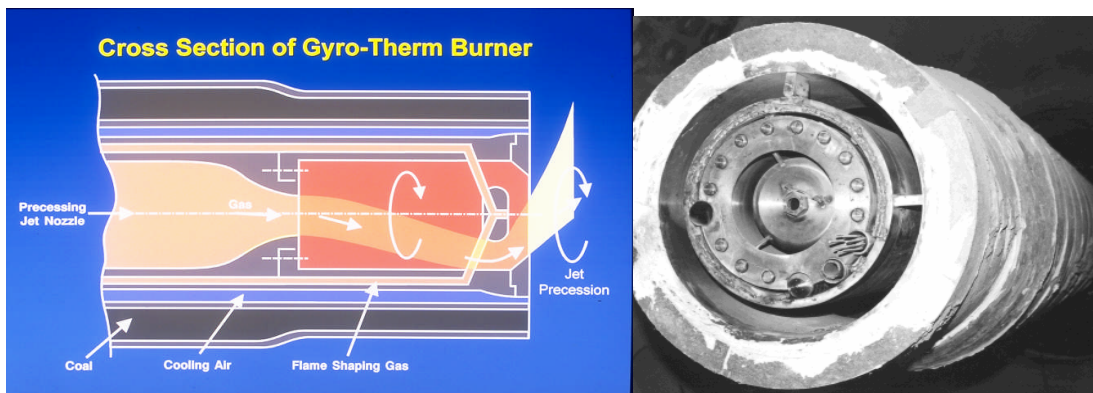


Figure 5: FCT *Gyro-Therm* gas burner nozzle

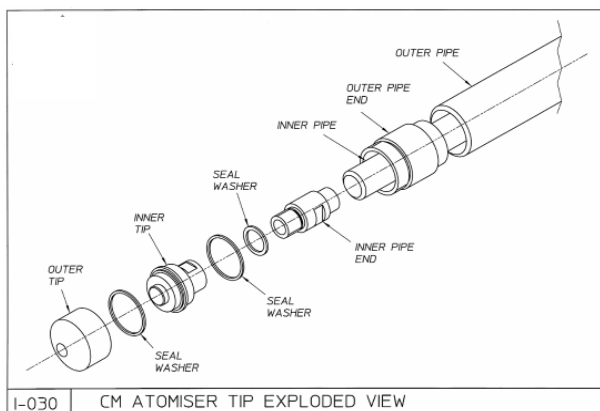
Liquid fuels, such as oil, burn by vaporizing and then reacting with oxygen. As smaller droplets vaporise easier, oil is sprayed (or atomized) as a fine mist when it is introduced into the kiln for firing.

Oil can be atomized using high pressure or steam. In high pressure atomisation the pressure energy of the oil breaks down the oil into fine droplets. The oil pressure is typically 400-600 psig. However, as oil flow is reduced, oil pressure and hence atomization efficiency is reduced. High pressure atomized oil burners typically have low turndown ratios of around 3:1.

When oil is steam (or air) atomized, the energy for atomization is provided by the steam. This makes the spray fineness independent of the oil pumping pressure. Therefore, a steam atomized oil burner has much greater turndown (e.g.10:1). Furthermore, the pressures needed to break down the oil are much lower, around 125 psig for the oil and 100 psig for the steam. Steam or air atomization provides mechanical and electrical savings at the expense of the cost of steam or air.

Care should be taken when firing waste oils to ensure that solids do not block the nozzle. Fineness of atomization is critical to ensure efficient combustion. Where filtration of the solids is not practical special nozzles are available for oils with high solids contents.

Figure 6 shows a typical steam atomized oil atomizer.



I-030 CM ATOMISER TIP EXPLODED VIEW

Figure 6: FCT Steam Atomized Oil Sprayer

Solid fuels also undergo a similar process to oil during combustion. The volatiles first vaporise, mix with oxygen and then burn. A carbon particle is left, into which oxygen diffuses and reacts. As this is a surface reaction, surface area is maximized when the fuel particle is smallest. Typically the residence time in a flame is about 1 second, and a 200 μm particle takes about 1 second to burn. As such, the maximum desired particle size for a solid fuel is about 200 μm .

For efficient combustion solid fuels are normally ground to a fineness of 10-15% residue on a 75 μm (200 mesh) sieve. A coal nozzle is essentially an open annulus, as shown in Figure 4. The key design parameters are the free area and the injection velocity. While there are basic guidelines for sizing a solid fuel annulus, FCT uses mathematical modeling to predict solid fuel particle burnout. Figure 7 gives a typical output.

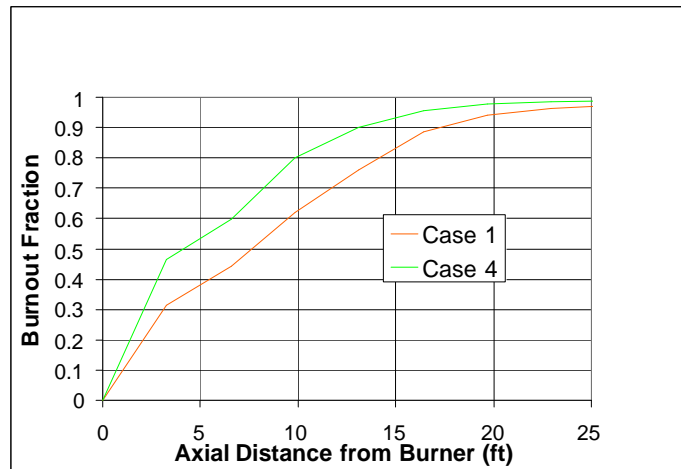


Figure 7: Coal particle burnout depends on particle size

Proper introduction of fuel, as described above, is a pre-requisite for efficient burner design. However, the flame shape is also strongly dependant on air flows. These include primary air (introduced through the burner) and hot secondary air, the air the flows around the outside of the burner.

The momentum (mass and velocity) of the air streams creates turbulence and promotes mixing of fuel and oxygen. For each kiln there is an optimum momentum between the two.

Most of the primary air is axial, but it can also be swirled. Swirled primary air creates mixing close to the burner nozzle and promotes flame stability. It also makes the flame wider. Therefore, the ratio of axial and swirl air can be used to control flame shape. Increasing axial air makes the flame narrower, while increasing swirl air makes the flame wider.

Secondary air enters the kiln via the cooler. This accounts for 85-90% of the air in a preheater/precalciner kiln. This air is not controlled by the burner, but has a strong influence on flame shape.

In order to determine the correct burner primary air flows for a kiln, FCT uses physical modelling techniques, see Figure 8. These allow visualization of the air flow patterns in a kiln and the corresponding flame shape. The physical modelling results provide critical burner information such as primary air, optimum excess oxygen, burner insertion distance and burner angle.

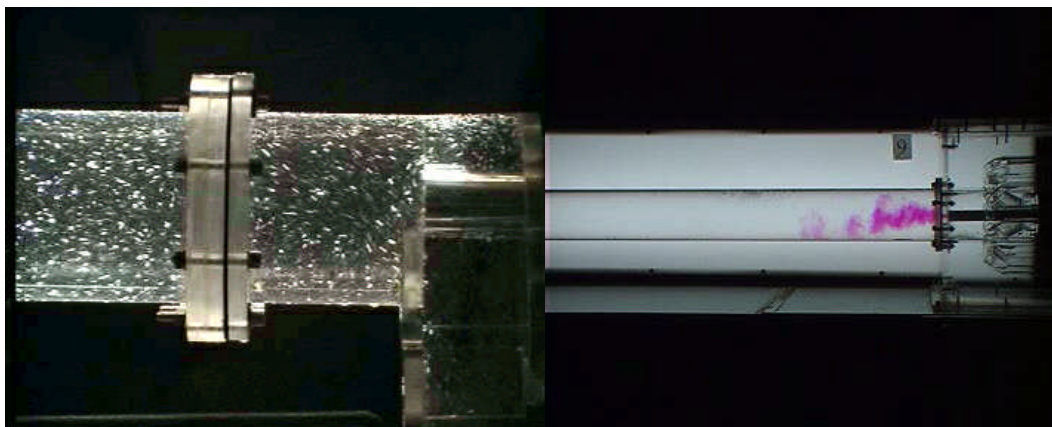


Figure 8: Physical modelling techniques. The left image shows a water bead model illustrating air flow patterns. Right is an acid/alkali simulation of flame shape.

Mechanical Considerations

The kiln atmosphere is harsh. Flame temperatures exceed 2,000°C, and the gases are extremely dusty. Furthermore, the dust can settle and build up on the burner body and nozzle, thus restricting the flow of fuel and air. These have a deleterious affect on flame shape and control.

A simple design is considered the best. The burner body should be of robust construction with mechanisms for alignment of the various pipes. Internal surfaces should be smooth and areas that are subject to wear, such as the coal/coke entry, should be lined with a suitable wear resistant material.

The burner nozzle is the most critical area of the burner as this affects the combustion performance. Special high temperature alloys are used at the face plate, with machined ports for air and gas to avoid distortion. Solid fuel channels are open ended and open ended pipes are also used for alternative fuels. Figure 4 shows a modern multi fuel burner with alternative fuel firing capabilities.

The design of the burner also allows for expansion and contraction during kiln warm up and shutdown. Furthermore, any welds are kept a distance from the surfaces exposed to heat.

4. Alternative Fuels

There are numerous types of alternative fuel. Some common ones of interest to the cement industry are:

- Petroleum Coke,
- Waste Tyres,
- Liquid Waste,
- Sawdust,
- Wood,
- Municipal Waste,
- Sewage Sludge, and
- Carbon anodes.

Appendix 1 provides further data on these fuels.

Alternative fuels are used because they are economically cheaper to use than the base fuel. There is also an environmental benefit in that high value fossil fuels are conserved, thus saving the corresponding CO₂ emissions. Maximum benefit is achieved when the alternative fuel is used as is, or with minimal preparation. This means that an alternative fuel may consist of large and irregular shaped particles, have variable calorific value, be of variable chemical content, and contain chemicals that may have a deleterious effect on kiln operation.

Irregular shaped and sized particles: Solid wastes are much larger than the maximum particle size for optimum firing, i.e. 200µm. Liquid wastes have solid particles in them, which makes atomization difficult. Alternative fuels are prone to fall onto the clinker and affect flame temperature and, hence, clinker formation.

Variable Calorific Value: This means that the energy supplied to the kiln will be variable. As such, flame temperature and, hence, heat transfer to the clinker will vary and affect clinker formation.

Variable Chemical Content: This will affect the clinker composition as well as crystalline structure. A change in the raw mix may be required.

Undesirable Chemicals: Many alternative fuels are high in various undesirable chemicals. Some chemicals contain alkalis, chlorine and sulfur, which can upset kiln cycles and lead to deposits. Sometimes a by-pass system is required to purge these.

Solid wastes are introduced into the kiln via an open pipe. Liquid wastes are sprayed using a large nozzle, as small holes needed for fine sprays can get blocked. The principles for primary air design and flame shape can still be applied as described above. However, it is inevitable that some of the alternative waste will burn on the clinker bed, and the flame temperature may vary. These have a significant impact on heat transfer, clinker chemistry and clinker mineralogy, generally in a negative manner.

To effectively burn an alternative waste, a well designed burner is imperative. The burner must exhibit excellent fuel and air mixing characteristics and allow for adjustment of the conventional fuel to cover for any variations in the characteristics of the alternative fuels. In addition, continuous knowledge of the clinker quality is needed. In the event that clinker quality deteriorates, the burner can be adjusted to compensate. The timeliness of this intelligence allows clinker quality to be maintained continuously and the amount of alternative fuel used to be maximized.

5. On-Line Quality Control

It is well known that the performance of a cement plant, as well as the final cement product quality, is governed largely by the mineralogy of materials, and not just by the elemental composition. Burnability of raw feed, grindability of raw materials and clinker, strength development, and cement setting times are examples of important cement plant parameters controlled by mineralogy and not chemical composition. Even before mineral analysis was prevalent, cement chemists measured chemical compositions, using XRF for example, and then attempted to calculate minerals using the Bogue equations.

It is the clinker minerals C_3A , C_4AF , C_2S and C_3S (that are approximated by the Bogue formula) that need to be monitored to ensure quality.

X-ray Diffraction

Perhaps the most common technique for measuring mineral content is X-ray diffraction. The technique involves firing an X-ray beam onto a sample and then measuring its diffraction pattern.

When X-rays are fired onto a crystalline material they diffract off each layer of the crystalline lattice. At certain angles the diffracted X-rays will be in phase and the signal will be very strong, see Figure 9. At other angles they are out of phase and the X-rays cancel each other. The angle at which the diffracted rays are in phase is related to the distance between the lattice plane, and this is characteristic for a particular mineral. For example, the mineral tri-calcium silicate (C_3S) has a characteristic angle.

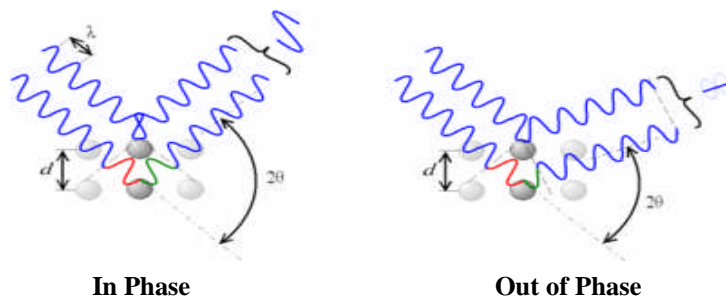


Figure 9: X-ray diffraction from a crystalline material.

When a composite material such as cement or clinker is analysed by X-ray diffraction, a range of diffracted peaks will occur. The angle of each peak can be used to identify the mineral while the intensity of the peak will indicate the relative amount present. Figure 10 shows a pattern for a typical cement type.

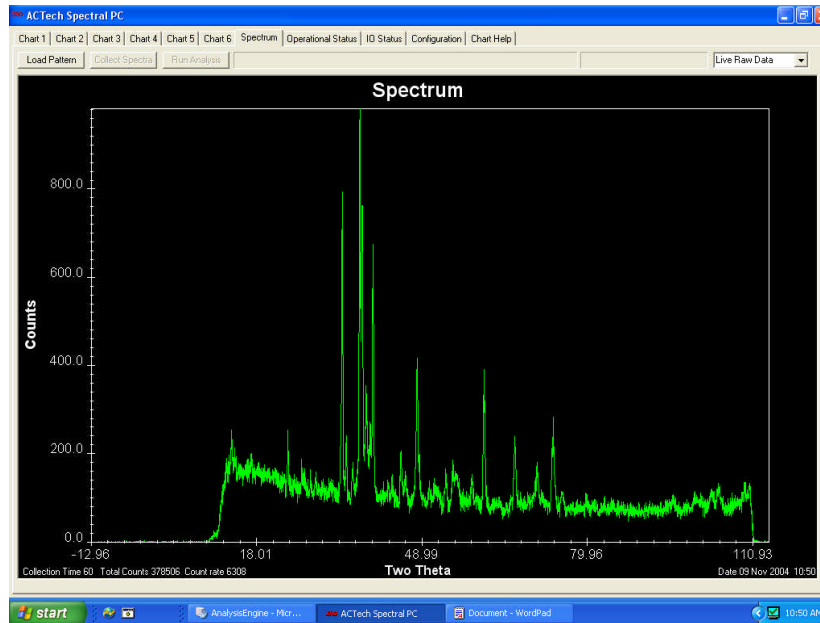


Figure 10: X-ray diffraction pattern of cement. Each compound contributes one or more peaks to the pattern.

There are, of course, many complicating factors. In order to arrive at the profile in the figure above and convert it into mineral composition, industrial machines use powerful software and the Reitveld analytical method.

Continuous On-Stream Mineral Analysis

Until recently most X-ray diffraction analysers were laboratory based. A sample was collected, prepared and analysed. From the pattern, the composition of a small sample was determined. The fastest lab analysers take many minutes to analyse the data and provide the results.

FCT provides a field X-ray diffraction analyser, the Continuous On Stream Mineral Analyser or COSMA, which analyses minerals continuously. This instrument has a curved X-ray detector that picks up the complete X-ray pattern continuously (see Figure 11). It is this unique feature that differentiates COSMA from other instruments, and allows the monitoring of minerals. A typical process flow diagram of COSMA on clinker is given in Figure 12 and a typical output from the machine is provided in Figure 13.

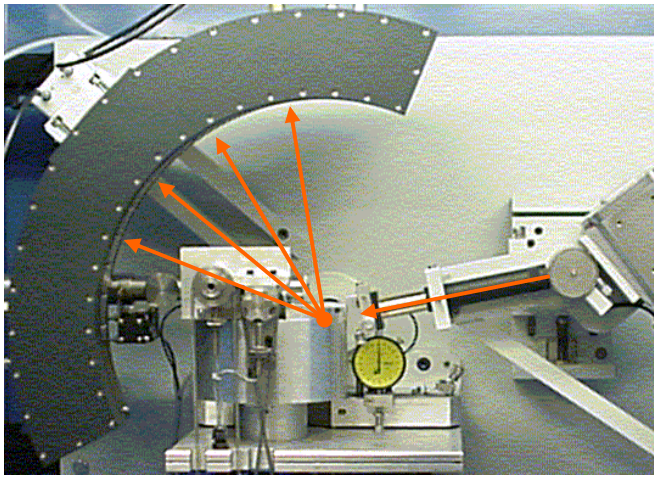


Figure 11: X-rays are diffracted continuously from a moving stream to COSMA's patented curved detector.

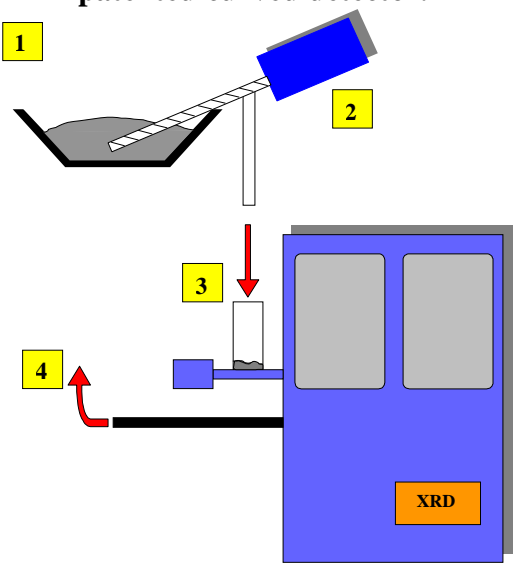


Figure 12: Typical process flowsheet of a COSMA installation showing sample acquisition.

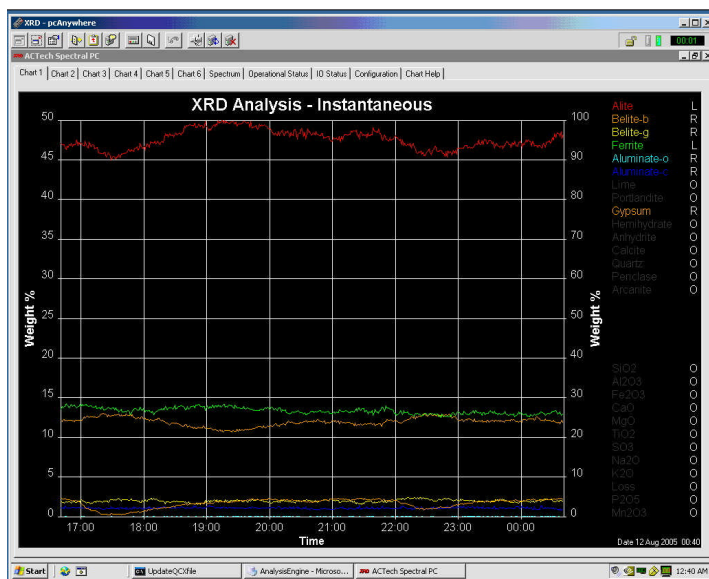


Figure 13: Typical display of clinker minerals from COSMA

The benefits of using continuous monitoring compared to conventional laboratory based XRD techniques include:

- extremely rapid turn-around times for analyses,
- improved accuracy, and
- lower limits of detection for the phases.

Approximately 600 g of sample per minute is analysed by COSMA. An analysis is provided each minute, based on data averaged over the preceding 10 minutes to reduce variations. Software is adjustable to suit the particular application.

As X-rays used in XRD instruments do not penetrate the surface of the powder more than a few microns, laboratory instruments only analyse a very small amount of the material sample. Continuous XRD, on the other hand, analyses significantly more material because a fresh stream of material is continuously passing under the X-rays. COSMA analyses several thousand times more material than a laboratory unit in a given time period.

Such frequent analysis allows trending of results and provides the ability to control processes 'on-line'. Figure 14 shows how the machine monitors free lime, alite and belite content. These are key components that determine kiln operation. In this example there was a free lime excursion that was caused by a cool kiln, as alite reduced and belite increased. If, however, free lime had increased without a corresponding decrease in alite, then the excursion would have been due to a raw mix proportioning variation.

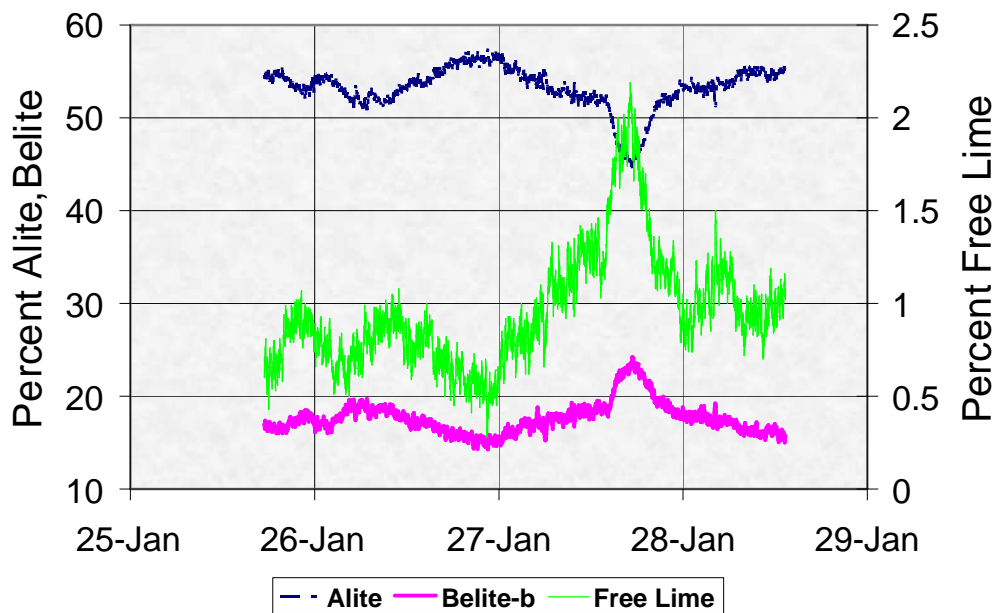


Figure 14: Free lime, generated by a cold kiln, is monitored by COSMA

6. Conclusions

The mineralogical processes that lead to clinker formation are highly time and temperature dependant. The final reactions that determine clinker and cement properties occur in the hottest parts of the rotary kiln. As such, the fuel burner must be designed to ensure that the correct temperature profile is attained. This is possible by applying fundamental knowledge of fuel combustion and flame simulation techniques. By doing this a burner can be optimized for clinker formation.

Burning alternative fuels causes complications because they are highly inconsistent in both form and composition. Some particles of alternative fuel do not lend themselves to efficient combustion due to their size. These may burn on the clinker bed and the operator must compensate for this by having excellent control and flame shaping ability. When and how the changes are made can only really be determined by clinker quality.

Continuous knowledge of the clinker phases provides immediate information to the kiln operator to act upon. In the event that heat transfer is reduced (e.g. low free lime and alite content) the operator can increase the rate of fuel.

COSMA continuously measures the quality of clinker. The machine takes a solid stream and analyses it using standard X-ray diffraction techniques, but in a continuous manner. This provides a direct measurement of mineralogical content.

Due to the nature of alternative fuels, it is likely that by increasing its rate a point will be reached when heat transfer and clinker quality is diminished, even with the best designed burner. A continuous knowledge of clinker quality will immediately indicate when this



point is reached. COSMA provides this intelligence. Using data from COSMA the kiln operator can adjust burner parameters, kiln parameters and raw mix as necessary.

A combination of COSMA and optimized burner, therefore, creates a powerful tool to optimize alternative fuel firing, while maintaining clinker quality.

Appendix: Some Data on Alternative Fuels

	Coal #1	Coal Fines	Pet Coke	Liquid Hazardous Waste	Wood	Saw Dust Hog Fuel	Municipal Waste	Tires
Moisture	6.6%	18.5%	0.6%	16.0%	8.0%	6.3%	19.7%	0.1%
Carbon	69.73%	50.53%	83.87%	62.83%	52.55%	51.80%	40.20%	74.92%
Hydrogen	4.75%	3.15%	7.09%	13.19%	6.08%	6.30%	6.30%	7.05%
Nitrogen	1.55%	0.53%	0.24%	0.82%	0.00%	0.10%	0.30%	0.50%
Oxygen	7.50%	6.40%	2.17%	2.90%	33.25%	35.00%	15.40%	0.90%
Sulfur	0.58%	1.17%	1.23%	0.25%	0.00%	0.00%	0.10%	1.30%
Ash	9.28%	19.71%	4.78%	4.00%	0.12%	0.50%	18.00%	15.25%
Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

	HHV		LHV		Available Heat At 700°C (1292°F)	
	Kcal/kg	Btu/lb	Kcal/kg	Btu/lb	Kcal/kg	Btu/lb
Waste Tires	7889	14200	7525	13545	6017	10830
Petroleum Coke	7222	13000	6854	12337	4965	8937
Coal	6920	12456	6638	11948	5359	9647
Liquid Hazardous Waste Derived Fuel	6167	11100	5396	9712	3250	5851
Coal Fines	5133	9240	4866	8758	3936	7085
Hog Fuel Sawdust	5072	9130	4712	8481	3693	6647
Wood	4944	8900	4586	8254	3520	6337
Municipal Waste	3611	6500	3174	5713	2022	3640

	BITUMINOUS COAL	PET COKE	MEAT AND BONE MEAL	SEWAGE SLUDGE	CAR TYRE RUBBER	COAL-PETCOKE MIX
C (%-wt, dry)	66,6	89,5	42,1	42,9	87,0	75,1
H (%-wt, dry)	3,99	3,08	5,83	9,00	7,82	4,20
N (%-wt, dry)	1,07	1,71	7,52	1,84	0,33	1,70
S (%-wt, dry)	1,22	4,00	0,38	0,12	0,80	3,00
O (%-wt, dry)	8,85	1,11	15,3	27,2	1,81	4,90
Ash(%-wt, dry)	18,4	0,50	28,3	17,9	2,20	11,1
Volatiles (%-wt)	28,3	10,0	64,5	85,0	66,6	20,0
C-fix (%-wt)	47,9	89,5	7,20	5,00	31,1	69,2
H ₂ O(%-wt)	2,35	1,50	8,09	5,20	0,73	1,30
LHV(MJ/kg)	25,3	33,7	16,2	15,8	35,6	29,71
HHV(MJ/kg)	26,2				37,3	28,97