



# Burning the mix

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**This paper, this year's prizewinning presentation at the IEEE/PCA Meeting in Florida, discusses clinker formation, its relation to kiln feed properties, and the importance of optimising burnability by careful mix control, good mix homogeneity, and tailoring the burning process to the raw mix. The burnability and kiln feed are discussed in relation to specific fuel consumption. Emphasis is placed on the effects of changes in raw material burnability and clinker formation on kiln operations, finish mill productivity, and the properties of the resulting cement.**

A comprehensive understanding of the chemical and physical aspects of raw material transformation into clinker is an important foundation to increasing production, reducing costs, and improving quality at the cement plant. Clinker formation relies on numerous kiln feed properties and pyroprocessing conditions. Understanding the influential properties of the feed (chemistry, fineness, uniformity, and mineralogy) can lead to improvements in its burnability and therefore in the efficiency of plant operations.

When the raw materials available make it hard to achieve burnability goals, the use of fluxes and/or mineralisers may be helpful. Fluxes and mineralisers indirectly affect burnability promoting earlier clinker phase formation; their effect on clinker formation and cement quality is briefly described here. Fluoride-containing compounds have proven to be the most effective mineralisers in cement clinkering reactions. However, an excessive amount of fluoride may delay cement setting time.

## Transforming raw materials

Plant management is constantly under pressure to maintain or increase production rates and reduce costs, without sacrificing quality. These three are challenging goals, especially achieving all three simultaneously. Understanding the process of clinker manufacture – how raw materials are transformed into clinker – is the key.

This transformation involves both chemical and physical processes. The microstructure of clinker is a function of kiln feed properties and the pyroprocessing conditions. Knowing what happens where, why, and how, can lead to optimising production, costs, and quality. In turn, the clinker microstructure and composition directly affect how the phases hydrate and contribute to cement performance in fresh and hardened concrete.

Given its relationship to both plant operation efficiency and cement performance, the importance of clinker formation cannot be overestimated.

## Clinker

Stated simply, the chemical aspect of clinker formation is the combination of silica with calcium to produce hydraulic compounds. However, the actual transformation of the raw materials into clinker involves a combination of chemical and physical processes as the material passes through the kiln system. The general process of clinker formation is described in Figure 1. The transformation concludes with the primary clinker phases:

- alite: impure tricalcium silicate, generally termed  $C_3S$
- belite: impure dicalcium silicate, normally termed  $C_2S$
- aluminate: tricalcium aluminate,  $C_3A$
- ferrite: nominally tetracalcium aluminoferrite,  $C_4AF$

## Improving pyroprocessing efficiency

The amount of energy needed to form clinker depends on various properties of the raw materials. Using a burnability equation such as that shown below can identify the specific factors that influence burnability at a particular plant, and

provide the information needed to make appropriate improvements. This approach can also be used to anticipate changes caused by the introduction of new raw materials. Replacing raw materials with others because they are less expensive, or to correct the chemical composition may change how difficult it is to burn the new kiln feed.

### Raw material properties and burnability

The raw materials used are designed and proportioned to provide the appropriate amounts of the various clinker phases. Specific properties of the materials are critical to plant efficiency and energy consumption, based on their burnability.

Burnability is the ease with which the raw materials are transformed into the desired clinker phases, and is commonly measured by the amount of free (unreacted) lime remaining in the clinker (low free lime indicates an easy-to-burn mix). Ordinarily, the burnability is a measure of the ease of formation of alite from belite and free lime, as formation of the other phases is normally much easier to achieve. The lower the temperature at which the targeted free lime can be obtained, the better is the burnability of the kiln feed.

The burnability of a raw mix is determined by its chemical composition, the mineralogy of its component materials, and

its fineness. There are a number of equations that relate the burnability of a feed to the composition and fineness of the minerals (Fundal 1979, Petersen and Johansen 1979, Christensen 1979, Ludwig 1973). One example is the burnability equation developed at FLSmidth (Theisen 1992), provided below. The importance of a burnability equation is not to provide an exact value of the free lime of clinker made from a given raw mixture; it is more important that it gives insight into the effect of raw material properties on the resulting

free lime (clinker burnability) on a relative basis.

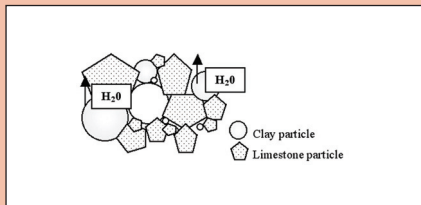
The first part of the equation (first bracket) represents contribution from the chemical properties of the raw mix. The LSF (lime saturation factor) represents the CaO of the mix, while the SR (silica ratio or modulus) is related to the amount of liquid phase at the burning zone temperature. Decreasing the SR is equivalent to increasing the amount of liquid phase; since the liquid is the transport medium for the reactants, more liquid can transport more reac-

tants during a given time and therefore, the burnability is improved. Note the relative magnitude of the coefficients for LSF and SR; the role of the liquid for the clinker reactions is important, not only for the chemical reactions but also for the formation of clinker nodules (the physical aspect of clinker formation).

The second part of the burnability equation (second bracket) represents the contribution to the burnability from the mineralogy and fineness of the raw mix. The percentages of coarse particles represented by  $C_{125}$ ,  $Q_{45}$ , and  $R_{45}$  are determined by the overall fineness of the raw mix on the one hand, and the mineralogical properties of the raw materials on the other. Differences in the mineralogy of the mix components leads to differences in grindability, which in turn will result in variations in the chemical composition of the different size fractions of the raw mix. For example, since quartz is hard to grind, the  $SiO_2$  content of the coarser fraction of the mix will normally be higher than that of the finer fraction. Note that the quartz fineness is more significant than fineness of other materials, as indicated by its larger coefficient in the equation.

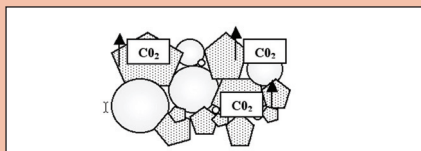
The equation provides a 'virtual burnability test' to analyse the factors affecting burnability and free lime of the clinker. There is a relation between the free lime determined by the 'virtual burnability test' and the free lime of the clinker. Although not identical, it can be assumed that the virtual burnability free lime will correspond to a certain constant clinker free lime for a given constant kiln operation. Further, for a given kiln and set of raw materials, if the virtual burnability free lime of the kiln feed changes and the kiln process parameters remain the same, the clinker free lime will change in a way so the ratio between the virtual free lime value and the clinker free lime remains the same as before the change. For instance if the virtual free lime is 3.2 per cent and the average clinker free lime is 1.4 per cent for a given steady state of kiln operation, the ratio is 2.3. This defines a burning index and is a measure for how the kiln in that state of operation on average burns the kiln feed. Reasons for variations in burnability could be insufficient raw mix control and/or homogenisation of the kiln feed. The resulting clinker will vary in free lime content, and the normal reaction from kiln operators is to burn harder and eventually operate the kiln on the 'hot side' to avoid

Figure 1: a simplified view of the clinkering reactions in a Portland cement kiln (Hills 2000)



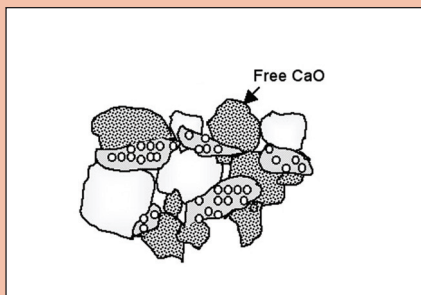
To 700°C

- Water is lost from clay minerals
- Dehydrated clay recrystallises
- Some reactive silica may displace  $CO_2$  from  $CaCO_3$



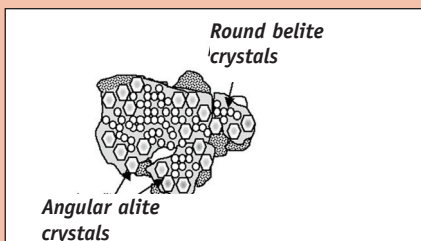
700-900°C

As calcination continues, free lime increases. Calcination maintains feed temperature at around 850°C. Lower-limed aluminate and ferrite form.



900-1150°C

Reactive silica combines with CaO to begin stages of  $C_2S$  formation.



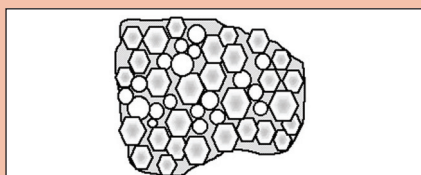
1150-1200°C

- When calcination is complete, temperature increases rapidly.
- Small belite crystals form from combination of silicates and CaO.

1200-1350°C

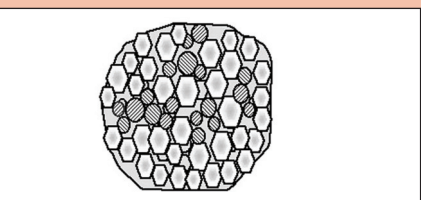
Above 1250°C, liquid phase is formed.

- Belite and free CaO form alite in the liquid.



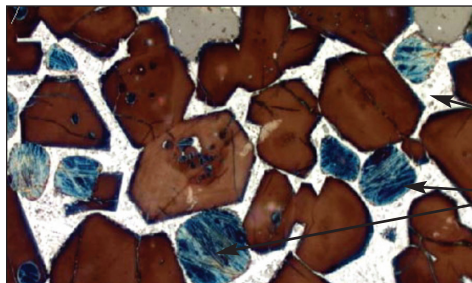
1350-1450°C

- Belite crystals decrease in number, increase in size.
- Alite crystals increase in size and number.



Cooling

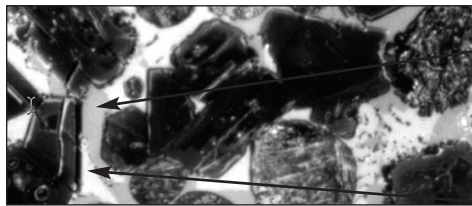
- Upon cooling, the  $C_3A$  and  $C_4AF$  crystallise from the liquid phase.
- Lamellar structure appears in belite crystals.



**Figure 2: clinker silicate phases as observed under a microscope (polished section with nital etch)**

**Alite (C<sub>3</sub>S) normally hexagonal crystals observed in cross-section, 25-50mm in length.**

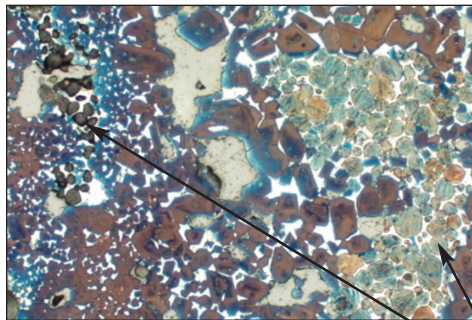
**Belite (C<sub>2</sub>S) normally 25-40mm rounded crystals with multidirectional lamellae.**



**Figure 3: phases in clinker interstitial (polished section with nital etch)**

**Tricalcium aluminate (C<sub>3</sub>A): observed in etched and polished clinker as blue to gray angular crystals in the interstitial. High alumina ratio will produce greater amount of aluminate than ferrite.**

**Ferrite (C<sub>4</sub>AF) appears more reflective than C<sub>3</sub>A in an etched polished surface**



**Figure 4: clinker photomicrograph demonstrates reaction between belite and free CaO to form alite (polished section with nital etch)**

**Either properties of the raw materials, mix homogeneity, or the pyroprocessing conditions did not allow the complete transformation to alite to take place.**

**Belite crystals**

**Free CaO crystals**

large variations in the clinker free lime. One penalty that results is increased specific fuel consumption.

An example of the relation between the burnability index and the specific fuel consumption is the result of analysis of data from a 2000tpd kiln with planetary coolers, as shown in Figure 5. Based on averages of kiln feed chemical composition and fineness, the virtual burnability free lime was determined and together with the average clinker free lime for the same period, the burning index ratio calculated.

An increasing burnability index means harder burning, resulting in higher specific fuel consumption. Figure 5 can be used to analyse the effect of kiln feed homogeneity on the specific fuel consumption. As an example, consider a kiln with average feed composition corresponding to LSF = 98 per cent and silica ratio, SR = 2.8 (corresponding to about 66 per cent C<sub>3</sub>S), with virtual burnability free lime of 3.2 per cent and an average clinker free lime 1.4 per cent. For a steady state kiln operation and a constant homogeneous kiln feed, the burning index is 3.2/1.4=2.3. In reality the kiln feed composition will vary between certain limits. In the first example, assume the variations in LSF and SR

are +/-0.6 per cent and +/-0.07 respectively. Using the equation for the virtual burnability test given above, these variations correspond to a variation of the virtual burnability test free lime between 3.8-2.6 per cent. For the steady state kiln operation referred to above, with burning index = 2.3, this will result in clinker free lime between 1.7-1.1 per cent. In the second example let the kiln feed composition vary +/-2 per cent in LSF and +/-0.23 in SR. This corresponds to variations in the virtual burnability free lime between 4.5 and 1.9 per cent, and for constant kiln operation a variation of the clinker free lime between 2-0.8 per cent. As a result of the less homogeneous kiln feed in the last example, the clinker free lime will vary within wider limits. If the operation is changed to harder burning in order to bring the maximum clinker free lime down

to the average value and narrow the variation in free lime, the burning index will change from the original 2.3 to 4.5/1.4=3.2. From Figure 5 such a change corresponds to an increase of about six per cent in specific fuel consumption.

Once again, an understanding of burnability and free lime content is important. There is a relation between the 'virtual burnability' free lime and the free lime of the clinker from the kiln. This burning index ratio can be used as a process parameter. If the kiln is operated in steady state, the ratio is constant. However, if the 'virtual burnability' deteriorates (ie decrease in mix fineness or change in chemistry), and the kiln is kept in the same steady state, then the clinker free lime will increase. The usual operator reaction to an increase in clinker free lime is to burn harder. However, if an examination of the kiln feed were performed to identify the cause for the increase in 'virtual burnability' free lime, the corresponding increase in clinker free lime would be anticipated. The kiln operators would therefore know what to expect, and would not necessarily constantly operate the kiln on the hot side. The examples given above also emphasize the importance of good raw mix control and kiln feed homogenisation vis-à-vis the specific fuel consumption.

Most often, the mineralogy and fineness change little compared to the chemical composition unless the raw material sources are changed. Therefore, using the chemical contribution portion of the burnability equation is helpful. This calculation will give an indication of feed burnability very quickly. An example of chemical analysis and calculation of its contribution to burnability is below. Note that the trend in burnability is more easily detected when looking at the calculated chemical contribution instead of the individual factors of LSF and SR alone.

### Fluxes and mineralisers

The use of fluxes and mineralisers can promote clinker phase formation, and therefore improve efficiency of the pyroprocessing system. By definition, a flux promotes a reaction by increasing the amount of liquid at a given temperature; for example, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are fluxes for the formation of alite. A mineraliser promotes the formation of a particular solid

$$CaO_{1400^{\circ}C} = [0.343(LSF-93) + 2.74(SR-2.3)] + [0.83Q_{45} + 0.10C_{125} + 0.39R_{45}]$$

Where:

CaO<sub>1400°C</sub> = is the free lime after burning for 30 minutes at 1400°C

LSF = %CaO/(2.8% SiO<sub>2</sub> + 1.18% Al<sub>2</sub>O<sub>3</sub> + 0.65% Fe<sub>2</sub>O<sub>3</sub>)

SR = % SiO<sub>2</sub>/(% Al<sub>2</sub>O<sub>3</sub> + % Fe<sub>2</sub>O<sub>3</sub>)

Q<sub>45</sub> = % quartz grains coarser than 45µm

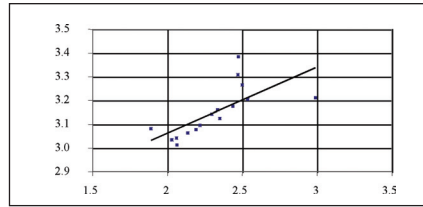
C<sub>125</sub> = % calcite grains coarser than 125µm

R<sub>45</sub> = % other acid-insoluble minerals, (eg feldspar) coarser than 45µm

phase through its incorporation in one or more of the solid phases (normally either alite or belite). A general view demonstrating the process of clinker formation using a flux or mineraliser, contrasted with using neither is outlined in Figure 6.

Fluxes and mineralisers have been studied in laboratory experiments and in practice (Flint, 1939, Johansen and Christensen, 1979, Surana and Joshi 1990, Erhard, 1994, Altun, 1999). A series of different compounds have been used; however, the ones with the most practical application are fluorides.

Fluoride-containing mineralisers have been used since the late 1800s (Bhatty, 1996). Fluoride-containing compounds such as  $\text{CaF}_2$ , NaF,  $\text{BaF}_2$ , and  $\text{MgF}_2$ , are all effective primarily as mineralisers, although  $\text{CaF}_2$  has enjoyed the greatest use. Alkali- and alkaline-earth fluorosilicate salts like  $\text{Na}_2\text{SiF}_6$  and  $\text{MgSiF}_6$  can also achieve similar mineralising effects (Lea, 1971). The effect of 5-10 per cent



**Figure 5: Burning Index Ratio (virtual burnability free lime/clinker free lime). Each point represents the average over a 4-week period. No corrections were made for kiln downtime during the 4-week periods, which might explain the outliers**

ings in combination with gypsum/fluorspar and others; all showed some effect either as fluxes or mineralisers but the studies did not result in practical use.

The benefits of added fluoride in achieving desired free lime levels at lower temperatures are illustrated by a study in which the same rather hard-burning raw mix was burned with and without the addition of 0.25 per cent fluoride. In this particular case, the fluoride was added as a fluoride salt. The mixes were burned at 1450°C (2640°F) for 60 minutes. The resulting free lime content of the control clinker was 5.05 per cent, while that of the clinker to which fluoride was added was 2.31 per cent. A further demonstration of the benefits to burnability of added fluoride was carried out using the so-called 'sandwich' technique. In this technique, two compacts are prepared. The first is calculated to be an alite/free lime mixture, while the second is calculated to be an alite/belite mixture after clinkering. The compacts had the compositions shown in the table below.

Pairs of compacts were made, with and without added fluoride. The individual compacts were burned at 1450°C for 30 minutes, cooled rapidly to room temperature, and the free lime levels determined. The low lime compacts had negligible free lime levels (<0.12 per cent), and the high

lime compacts had free lime levels around 13 per cent. The high lime and low lime compact cylinders were placed in intimate mutual contact, and the cylinders re-burned at 1500°C for one hour. Figure 7 demonstrates this 'sandwich' technique.

The resulting clinkers were cut, transverse to the joint, etched with Nital etchant, and examined under reflected light microscopy. The results, shown in Figures 8 and 9, illustrate the broadening of the region near the joint where no belite or free lime exists – ie, where alite formation has occurred between the high and low lime compacts. The much broader width in the fluoride-doped clinker (about twice as wide) shows how much faster alite forms in the presence of 0.25 per cent fluoride.

With regard to fluxes and mineralisers in general, Bhatty (1996) reports a survey regarding their use in the cement industry. The fluxes and mineralisers referred to were fluoride-based (primarily fluorspar), and other non-fluoride-based materials. The latter were industrial by-products or waste-derived materials primarily used as corrective materials in the mix. They contained iron oxide and alumina and resulted in decreasing of the silica ratio of the raw mix. This silica ratio reduction is equivalent to an increase of the clinker melt content, and hence to an improvement of the burnability. The study indicates that cement plants outside North America use fluxes and mineralisers with better results than do the North American plants. In most cases improvements in burnability, kiln operation, energy savings, and cement quality were noted. With the fluoride mineraliser, setting time was reported to increase in some cases. Christensen (1980) suggested a mechanism for the effect of mineralisers that implies increased setting time, which is in line with observations with using fluoride compounds.

One must be aware of side-effects of using some materials as fluxes or mineralisers. In North America, the most commonly reported problem when using fluoride-based fluxes/mineralisers is the blockage of preheaters caused by fines and volatiles. To prevent these blockages, it is recommended to tightly control kiln temperature and the thermal profile to prevent overheating of the load and generation of additional volatiles and fines. In other words, the burning zone tem-

LSF	SR	Chemical contribution [0.343(LSF-93) + 2.74(SR-2.3)]
95.2	2.2	0.48
95.6	2.3	0.89
94.9	2.8	2.02
95.9	3.1	3.19
95.8	3.2	3.43

Alite	Alite	Alite	Alite	Alite
Belite	Free lime	Belite	Alite	Free lime
<0.12% free lime	13% free lime			

**Figure 7: diagrams demonstrate the clinker 'sandwich' before (left) and after (right) re-burning**

fluorspar on the clinkering of two cement compositions was reported (Klemm, 1976) and as expected, these massive additions resulted in both a reduction in clinkering temperature and a consequent retardation of cement setting. However, there was little effect on the 28-day strength of hydrated cements.

Although fluoride-containing compounds have been proven to be the most effective mineraliser in cement clinkering reactions, a number of other possible fluxes and mineralisers have been studied. These have included gypsum and sulphate mineral tailings, fluoro-gypsum, phosphorus-containing calcareous tail-

Reagent	High lime compact, %	Low lime compact, %
Calcium carbonate	78.9	74.3
Quartz ( $\text{SiO}_2$ )	10.73	15.33
Alumina ( $\text{Al}_2\text{O}_3$ )	3.86	3.86
Ferric oxide ( $\text{Fe}_2\text{O}_3$ )	1.93	1.93
Magnesium hydroxide	3.05	3.05
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	0.51	0.51
Potassium carbonate ( $\text{K}_2\text{CO}_3$ )	1.02	1.02

perature reduction that has now become possible because of the use of mineralisers must be implemented.

Fluoride can also be a retarder in cement hydration if present at too high a level. In the example provided below, a particular plant produced two Type I cements with differing fluoride levels; the fluoride ratio varied by a factor of four based on the raw materials. The high-fluoride cement had an initial setting time of 2.4 times longer than the low-fluoride cement. The conduction calorimeter, which measures the hydration profile of cement pastes at constant temperature, gave a very graphic picture of the difference in hydration of the two cements, as shown in Figure 10.

The graphs demonstrate the delay in the  $C_3S$  peak for the cement with high fluoride content. The maximum hydration rate is delayed from about nine hours to about 17 hours. It appears from these results that the amount of fluoride present in the high-fluoride cement was too high for acceptable cement setting behaviour. The behaviour of cements with optimum fluoride addition may be considered somewhat analogous to that of cements hydrated at low temperatures, or to cements hydrated in the presence of retarding admixtures. Although the early hydration is delayed, the ultimate hydration may indeed lead to better late strengths (Moir, 1982). It is not unusual for cements experiencing slight retardation in setting time to develop 28-day strengths higher than those of their faster-setting counterparts.

### Operations and performance

Changes in burnability and/or clinker formation can have important practical impact on what happens in the kiln, the mill, and the product. If the mix is hard to burn, the operator will be obliged to

Figure 8: clinker 'sandwich' after re-burning

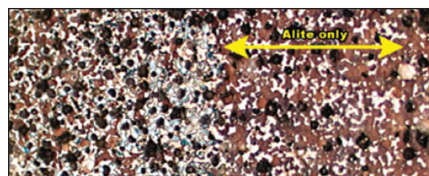


Figure 6: simplified clinkering reactions in a Portland cement kiln with no additions, with mineraliser, and with flux

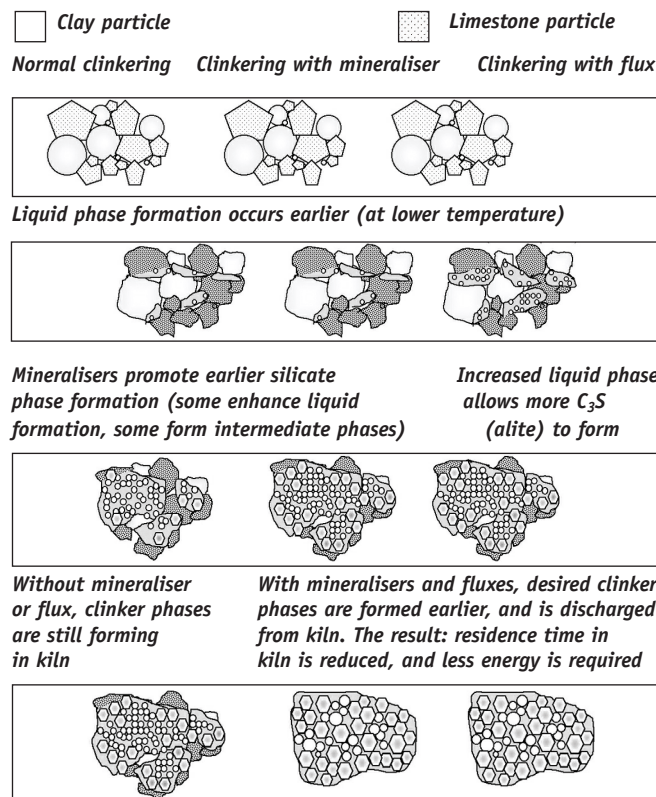
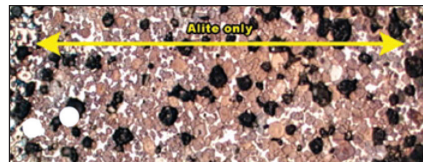
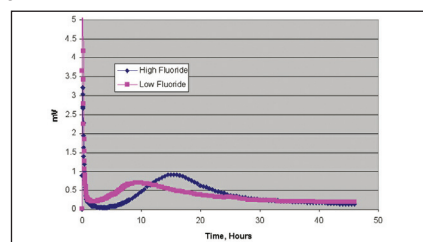


Figure 9: clinker 'sandwich' with fluoride after re-burning



increase the burning zone temperature to achieve the desired free lime level. Hard burning will tend to cause low clinker porosity, large crystals of alite, and often contributes to generation of dust and/or large clinker balls, instead of good, nodular clinker. It also slows down the resulting cooling process, both because the maximum temperature is higher, and because the low porosity clinker is more difficult to cool. This can often result in generation of cement with reduced strength potential and increased water demand. Clinker temperatures exiting the cooler may increase,

Figure 10: calorimeter results of high and low fluoride cements



further increasing fuel consumption and presenting handling problems. The high temperature conditions may lead to reductions in clinker alkali and sulphate level, colour variations, and increases in water demand attributable to increased levels of aluminate. The reduced clinker alkali and sulphate will affect setting time, decrease early strength and increase later-age strength; and fresh concrete might develop admixture incompatibility and changes in its rheological behaviour.

### Conclusion

Specific properties of cement raw materials are critical to plant efficiency and energy consumption, based on burnability. This involves the chemical properties of the raw mix, along with the mineralogy and fineness of the materials. Determining a 'virtual burnability' using these parameters identifies the critical areas where changes could be made to improve burnability and lower fuel consumption.

When the quarry and the raw materials available make it hard to achieve burnability goals, the judicious use of fluxes and/or mineralisers may be a prudent measure. Fluxes and mineralisers promote clinker phase formation to occur earlier, thereby improving the efficiency of the pyroprocessing system. Fluoride-containing compounds appear the most effective mineraliser in clinkering reactions. An experimental study demonstrated quicker alite formation in the presence of 0.25 per cent fluoride.

Changes in raw materials and/or clinker formation can influence what happens through the kiln, the mill, all the way through to the cement performance.

This paper demonstrates the importance of optimising burnability and clinker formation by careful mix control, good mix homogeneity, and tailoring the burning process to the raw mix. Real energy savings, potential production increases in kiln and mill, and product enhancement are the rewards for following these principles.

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