Refractories Usage in the Developing Cement and Mineral Processing Industries in 2016

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In any review of the development and use of refractories in a major process industry it may be useful to consider how and perhaps why the current technology has developed as it has done. Cement is an ancient and very basic commodity, which is today manufactured by modern processes and equipment sometimes by very new companies albeit some of these current organisations having been originally founded under entirely other names by different owners. In the last few years, the global cement industry has undergone very significant fundamental changes.

Introduction

Two years ago the installed capacity for cement production increased around the world and the actual output also appears to have grown very slightly in total while within individual companies and even within countries fortunes have varied widely (Tab. 1).

The United States Geological Survey suggests that cement capacity worldwide, increased in 2014 by 0,245 % to 4180 Mt. No reliable comprehensive statistics are available as yet for 2015. There has been however what is described as considerable consolidation with a series of mergers, acquisitions and disposals never seen before in the industry's long history. The effect has been to change the world rankings of cement production by country and by company, and this evolutionary process is still continuing at present. China is by far the world's largest cement producer with a capacity of 2500 Mt, with India in second place at 250 t and the USA third with just over 83 Mt. The three largest cement producers in the world are Lafarge Holcim, CNBM and Anhui Conch, but it is not possible in this report to list them in actual order because of all the changes still taking place. It would appear certain that Heidelberg, Cemex and CRH Groups have also risen up higher through the rankings in the last twelve months and it will be interesting to see the latest statistics when these are available in the near future.

Tab. 1 World cement production 2013 and 2014

	2013	2014
USA (includes Puerto Rico)	77 400	83 300
Brazil	70 000	72 000
China	2 420 000	2 500 000
Egypt	50 000	50,000
Germany	31 300	31 000
India	280 000	280 000
Indonesia	56 000	60 000
Iran	72 000	75 000
Italy	22 000	22 000
Japan	57 400	58 000
Korea, Republic of	47 300	47 700
Mexico	34 600	35 000
Pakistan	31 000	32 000
Russia	66 400	69 000
Saudi Arabia	57 000	63 000
Thailand	42 000	42 000
Turkey	71 300	75 000
Vietnam	58 000	60 000
Other countries (rounded)	536 000	525 000
World total (rounded)	4 080 000	4 180 000

(Courtesy of United States Geological Survey Report Mineral Commodities 2015)

In any study such as this, the origins of cement are in fact partly determined by what exactly is defined as cement. For this report, the term cement is used generically to cover a range of materials especially those where in the past it was a basic component in construction. Lafarge defined cement some years ago as "a hydraulic binder and the basic ingredient of concretes and mortars which over time has become a very technological group of products" (Tab. 2).

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Tab. 2 Typical ordinary Portland cement (Courtesy of Civil Engineering Dictionary)

Constituents	Analysis	[%]	Mineralogical Composition
Lime			
Silica			
Alumina			
Iron			
	CaO	60–67	
	SiO_2	17–25	
	Al_2O_3	3–8	
	Fe_2O_3	0,5–6,0	
	MgO	0,5–4,0	
	Alkalis	0,3–1,2	
	SO_3	2,0–3,5	
			Tricalcium silicate $3CaO \cdot SiO_2$
			Dicalcium silicate $2CaO \cdot SiO_2$
			Tetracalcium aluminoferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
			Tricalcium aluminate $(CaO)_3 \cdot Al_2O_3$

One source claims that a material similar to cement was formed in nature geologically some millennia ago, but it is certain that no one was around at the time to utilise it and so while interesting this is not of specific relevance in a modern context. Various other examples are quoted of the Assyrians, Babylonians, Chinese, Egyptians, Greeks and others making and using versions of cement and indeed concrete derived from it to build ancient structures such as parts of the city of Babylon, sections of the Pyramids and as a component in the Great Wall of China. There seems to be a general consensus however that it was not until the Romans took a serious interest in construction that a product more resembling a modern form of what we would recognise today as cement started to be developed and used more widely.

Marcus Vitruvius Pollio was a Roman author, architect, civil engineer and military engineer during the 1st century BC, who in between his many construction projects wrote a ten volume work entitled De Architectura in which he had a great deal to say about bricks, cement and concrete as well as it seems many other subjects. He comments in some detail about raw materials and for example how to burn limestone before using it as an ingredient material for cement and concrete. He recommends the use of burnt lime and various aggregates with volcanic ash from Mount Vesuvius to form a hydraulic setting concrete which he says can also be used to construct piers under the sea. It is thought that the name cement in its Latin form was first commonly used around this time as was the term Pozzalana which referred to the hydraulic setting properties of a mix containing two parts volcanic ash mixed with one part burnt lime and water. While some major projects of the time were constructed from this type of material it is ironic that the skills of making and using cement and concrete seem to have then declined at least in Europe and were only revived sometime around the 18th century although technology it seems then greatly accelerated from the early 19th century until the present time.

The development of cement products in Asia and America seems to have evolved somewhat differently to those in Europe. The Great Wall of China which was built, repaired and subsequently extended throughout the 16th century was one of the largest construction projects in history. Using the British definition rather than the American definition of a billion, which is the estimated number of blocks in the wall, it may have required up to 6,25 Mt/a of hydraulically bonded cement mortar each year over its 100 year construction period. This may not seem much compared to the output of today's mega kilns but was certainly an achievement from small local plant sites at the time. Although the manufacture of blocks is documented as coming from a number of small vertical shaft kilns the manufacture of the cement component is not so clear. Chinese researchers are currently working on the composition of the cement used which when it was analysed was said to contain some traces of starch. This is believed to come from about 3 % of finely ground sticky cooked rice which was added to the cement just before use. Anyone who has seen the wall can attest that the cement in the joints is very white compared to the blocks themselves. This mortar is in generally good shape after more than 500 years and two major invasions from the Mongols and Manchu. Somewhat surprisingly perhaps the current Vietnamese Ministry of Agriculture and Rural Development has recently demanded that rice growers do not use cement as a fertiliser for their fields. The farmers seemed convinced that a small addition of cement was beneficial to their yield but the government insist that the cement added no nutritional value and that the addition of cement will eventually make the soil unsuitable for future rice and other crop cultivation.

The Moorish invasion of Spain introduced a form of cement mixed with very fine aggregate for construction in Spain. In the 16th century, Spanish explorers were then credited with introducing Tapia based on lime, sand and ground oyster shells with water and now better known as Tabby, to the south eastern United States seaboard where it was very widely used .

The main developments which have been documented since the 17th century were however generally credited to British, French and other European engineers. John Smeaton, an English engineer, constructed what was in effect the third Eddystone lighthouse tower which was built on the Eddystone rocks near Plymouth in Great Britain between 1755–1759 at a cost of about GBP 40 000. The cement used in the construction consisted of a mixture of lime and clay which was required to set hydraulically in the brief period between each successive high tide. It was so successful that it stood for about 125 years before it had to be demolished because the sea was eroding the rocks on which it stood rather than the structure of the lighthouse itself. Others experimenting with cement at this time included Vicat and Lesage in France, and Parker and Frost in England, but the materials that they worked on and the results they achieved were naturally quite varied and different. Fifty years or more later, other developers who may not have been fully aware of Smeaton's work, included Dobbs in Great Britain, and Cheliev in Russia, all of whom made significant advances in cement technology. The first modern version of cement was patented in England in 1824 by Joseph Aspdin, a bricklayer in Leeds. The product was named Portland cement because Aspdin believed the colour was identical to the limestone deposits at Portland in Dorset. The patent gave few details of the product, but in 1844 Isaac Charles Johnson clearly defined a much improved product which he manufactured in a vertical shaft kiln in a plant at Swanscombe in Kent. This was one of the first of 45 such plants with about a thousand kilns producing over 25 000 t of cement per week and launched a huge building boom in Great Britain. Parallel developments were also starting to take place in Europe in Belgium and Germany as well as in Canada and the USA.

A further breakthrough occurred in 1877, when Crampton patented one of the first rotary kilns, and in 1885 when Ransome introduced improvements although these early kilns were very small being about 1 m in diameter and about 5 m long. A kiln which was designed to Ransome's specification was introduced into Keystone Portland Cement/US in 1889. Firing of the kiln was modified to work with oil from Ohio rather than gas or coal which had both been widely used prior to that. This greatly improved performance with regards to cement production, but probably resulted in the start of serious refractory wear in rotary kiln linings, and created the concept of using a coating to protect the refractories and prolong their life.

Wet-process kilns then developed rapidly and were often over 2 m in diameter, and 150 m long fed with slurry consisting of the solid ingredients held in a suspension with water. The first entry section of these kilns was unlined, with no refractories, but contained heavy duty chains to break up the feed cake as it dried out. The intermediate areas of the kiln, where heating took place, were lined first with firebricks and then with high alumina bricks as the temperature progressively increased. In the burning zone, high alumina bricks were used, but eventually superseded by basic magnesite chrome bricks as the burning temperature was elevated. In the cooling zone, high alumina bricks were again used for economy, and the clinker was discharged either over the kiln lip or sometimes into part-lined refractory planetary coolers.

Today, almost all modern kilns are short dry-process kilns with preheaters, and sometimes also precalciners. These units ensure a higher throughput of feed which enters the kiln at high temperature. This allows the kilns to be up to 6,5 m in diameter and around 90 m long. Such dry process rotary kilns theoretically may produce up to around 12 000 t/d, but it may possibly be the case that this process has now reached its limits. The feed in a modern preheater or precalciner process enters the kiln at temperatures of around 1100 °C before being further heated in excess of 1350 °C within a very short dwell time which may only amount to perhaps 10 min or 15 min in total (Fig. 1).

The parameters of the kiln configuration are based on complex calculations involving many factors which are not covered in detail in this report, but as stated most modern kilns can and do produce high tonnages of product every day that they are in operation. In fact, there is a view that some parts of the rotary kiln production process would benefit from being scaled back. One example of this is that instead of having one large diam-

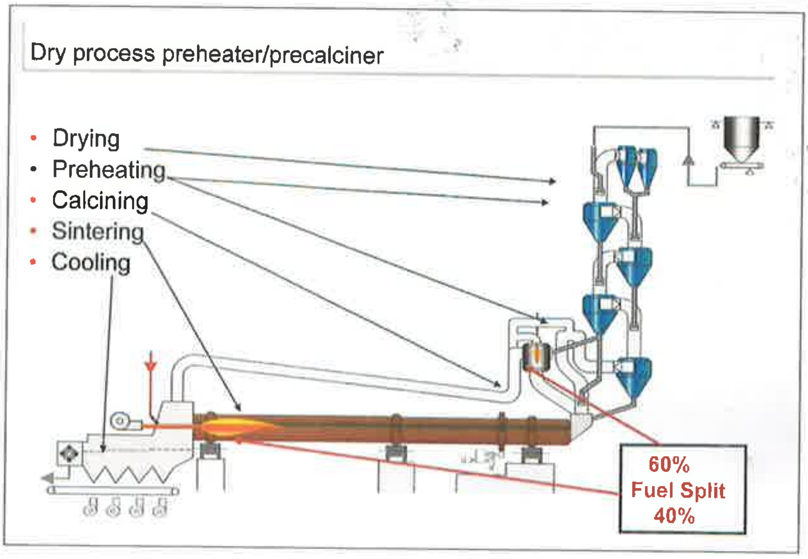

Fig. 1 Modern dry-process kiln (Courtesy of Holcim 2010)

eter tertiary air duct at least part of it could be bifurcated as this would be beneficial in the performance and lives of refractory in the ducts and in the associated dampers. There are economies of scale when a modern plant is working, but adverse economic consequences when it is not operating as it is not very flexible in terms of cutting back on production levels if market demand is reduced.

Part of the recent process improvement is also derived from homogeneity of the feed along with the use of increasing quantities of preheat, and a varied assortment of alternative fuels which are added at various stages in the process. These advances however beneficial or necessary for consistently high levels of production inevitably put additional strain not only on the mechanical equipment, but also on the refractories which are used to line key areas of the plant. In addition to very high mechanical stresses and higher temperatures there are also likely to be sulphur compounds and alkali salts in gaseous, liquid or solid form building up within the system as its operating life progresses due to the widely ranging chemical composition of the fuels and feed. It is certainly true, that rotary cement kilns are still the largest moving high-temperature process plant in the world. A fully loaded large kiln can weigh up to 1000 t, so that the refractory lining as well as the kiln itself needs to be of the highest quality for safety, consistency and optimum cost effectiveness.

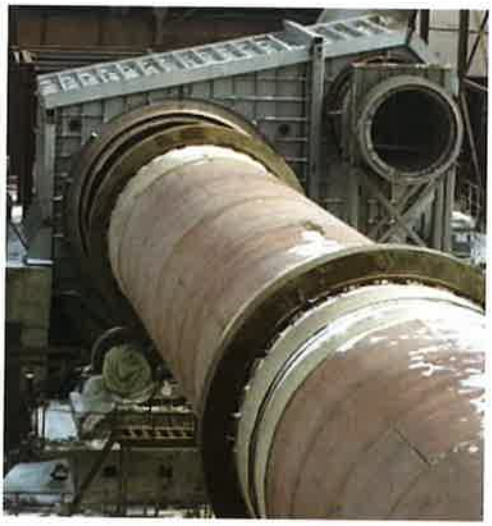

Fig. 2 Kiln firing hood with TAD damper housing (Courtesy of Steppe Cement)

It has been said, that the refractories are an unseen part of the process, but the effects of refractory wear and sometimes even premature failure in critical areas of the process are far from unseen and can result in extremely costly stoppages in terms of lost production costing several 10 000 of Euros per day and of potential consequential damage to linings or equipment elsewhere in the system.

Refractories usage

Refractories in general should always be designed and installed to provide wherever possible a balanced predictable economic life. There are many reasons for a kiln to come off stream, but in the case of refractories, reparation normally includes cooling down the entire system which can be extremely problematical as well as expensive. It is therefore critically important to try and achieve campaigns of at least 12, or 24 months rather than 15 or 27 months, or any other period that does not easily coincide with scheduled maintenance repairs. Because of the wide range of cement plant sizes and types, it is not possible to have a standard refractories recommendation which all plants can adhere to. It is desirable however to follow general guidelines which will improve refractory life in each zone of each kiln and its ancillaries and give optimum performance as well as minimum cost with fewer lining outages and increased reliability. This needs a careful detailed study of each individual kiln or ancillary unit.

In line with a global trend in refractories usage across most industries, the total proportion of bricks in most cement plants has reduced except in the kiln itself while the total proportion of monolithics has increased. There are several reasons for this, such as the availability and cost of bricks as well as the declining availability of really skilled bricklayers. Monolithics in general are more readily available on short delivery and allow more flexibility in design and installation. They also require skilled installers, but the skills are quite different to those of bricklayers. Monolithics installers require an understanding of the way chemical additives alter the rheology and properties of refractory monolithic materials, along with the ability to operate quite complex machinery as these are prerequisites for the installation of successful linings. Because monolithic refractory linings in the field have the potential for inherent variations in quality and require careful curing, drying and heating, after installation there has been a significant move to the use of precast blocks in some applications where refractories are subjected to particularly severe physical operating conditions or corrosive attack.

Sometimes with bricks or even precast blocks, but much more so with monolithic refractories installed in the field, the initial heating when the plant is started or restarted and which is largely uncontrolled can be sufficient to cause further refractory damage. For this reason, refractories which are designed to be commissioned under conditions where heat may be applied fast and

Fig. 3 Precast kiln outlet nosering system (Courtesy of Hanson UK)

Fig. 4 Cooler sight port precast block (Courtesy of N. G. Johnson Northern)

unevenly may be worth paying extra for. The new generation of sol-gel bonded castables may be a solution in some of these cases. These products have similar aggregates, but differences in the bonding systems. The aim has been to replace calcium-aluminate cement binders. This is to attempt to overcome problems associated with shelf life, curing, green strength and explosive spalling from relatively rapid and often uneven heating. It is also claimed, that no-cement castables have improved hot strength, abrasion resistance and resistance to alkalis and other contaminants such as sulphur. There are still issues however with the installation regarding mixing and use of these multi-component materials especially in temperature extremes.

Preheaters and precalciners

In preheaters and in precalciners, the aim is to install refractory linings which are as thin as possible while providing high wear resistance, retaining mechanical stability and providing minimum or at least acceptable heat losses through the lining itself. To achieve these objectives, it is possible to install well-designed and safely-anchored refractory monolithic linings, partly in precast format where maximum mechanical properties are required, and partly as shotcrete or gunned linings where this is more convenient or more cost effective. Precast items can include the vortex finders in lower cyclones, blasters in ducts, or the kiln feed areas such as the feed chute and kiln tray. In relatively narrow ductings, the linings are best installed initially cast into the steel work off site but fortunately these items when well-designed and installed last for many years. Some of the newer preheater systems incorporate external combustion units to handle secondary fuels, such as shredded or whole automobile tyres, and these are best looked at individually to evolve the most cost effective refractory solution as refractory operating conditions are severe and extremely variable in different units.

Rotary kilns

While older kilns may still have numerous zones each with its own refractory requirements, the latest kilns have fewer zones and fewer different higher quality refractories in them operating under much more severe thermomechanical conditions. Depending on the degree of pre-treatment of the feed, modern kilns have zones with high alumina or magnesia bricks in the inlet section and magnesia-alumina spinel bricks in the burning and outlet zones. Only the inlet rings and outlet rings at either end might be installed in monolithic or in special precast shapes, to take account of the different conditions in the extremities of the kiln. Even in the older and smaller kilns, the use of fired dolomite has almost disappeared and the use of magnesite and magnesite chrome has greatly decreased. Instead, there is an increasing tendency to use synthetic magnesia and magnesia-spinel high fired bricks. The use of kiln blocks has also diminished in favour of either the VDZ or ISO standard bricks systems where basic bricks are mainly made in VDZ sizes and high alumina bricks in ISO sizes. Several major manufacturers provide detailed information on both of these ranges along with how brick sizes can be combined to turn different kiln diameters, and how these bricks can be quickly and safely installed to best current practice using pneumatic bricking rigs.

Firing hoods

Firing hoods and the areas leading from them, such as the entry to the tertiary air duct, may still be in high alumina bricks, but more often today are cast in-situ, shotcreted, or gunned in high-alumina monolithic materials. The use of monolithic refractories allows for thinner and potentially cheaper linings which, since they usually incorporate insulation backup, can still be more thermally efficient than a much thicker lining. Some installations have recently been made using no-cement castables relying on a sol-gel system rather than calcium aluminates as binder. These products are expensive and technically sophisticated, but may be affected by ambient temperatures, and need skilled as well as experienced installers to ensure the optimum cost performance in service (Fig. 2).

Tertiary air ducts and dampers

The tertiary air ducts between the firing hood and the preheater on some new kilns can now have a similar diameter, or even larger than some of the older kilns. While these may be either bricks or monolithics lined, there is a strong argument for the ducts to be bifurcated to limit the size of tertiary air duct dampers. There are benefits in new plants for the dampers to be installed at the upper ends of the duct, as far from the firing hood as possible to reduce the stress on the refractory. Tertiary air duct dampers work at elevated temperate under high tensile stresses, and anything that can be done to ameliorate these conditions will prolong the life of the dampers and increase plant reliability. The solution for these units has been to move from metal plates to air-cooled metal boxes with refractory veneers, and now to all refractory precast monolithic dampers with suitable anchorage and support, sometimes still with internal air cooling and with dams as all of these

Fig. 5 Precast cooler wall blocks after two years in service (Courtesy of Wahl Refractories)

factors reduce tensile stresses. Alkalis from alternative fuels can however build up to very high levels within the system and may be carried around the system in gaseous state to condense and attack refractory dampers.

Burner pipes

Burners pipes in rotary kilns have always presented problems which do not seem to have been entirely overcome, since dust still tends to build up on top of them and heat is reflected from the lining preferentially onto part of the lower section. High temperature and entrained dust also cause severe wear over the first 2 m. One major company had a specification, to cast the burner lining while supported vertically even if it was up to 11 m long, weighed several tons and was hard to manipulate. This system called for a climbing shutter where the bottom 2 m would be cast in a material such as tabular alumina, low-cement castable and most of the remainder in a lower alumina bauxite based castable. To prevent the build-up of dust on the top of the burner while operating, air blasters are often cast integrally into the structure to keep it clean, but this often complicates the actual casting of the burners in a vertical position. Very often now, the shuttering has been modified to cast the burner pipe lining horizontally, or even to manufacture precast shapes which are fitted to the tip to provide better performance due to their being fired to give premium properties. These can have hidden fixings protected from the very fierce heat at the tip which can reach temperatures in excess of 1600 °C on the refractory surface.

Nose rings

Nose rings have seen a gradual evolution from the use of cut bricks set between a kiln retaining ring about 1 m from the end of the shell and the end casting, or castings on the exit end of the shell itself. This progressed in many cases to the use of low-cement castables often containing silicon carbide aggregate cast in-situ behind shuttering while rotating the kiln as necessary to complete the ring. This required installation and removal of shuttering was slow and labour intensive, and required careful drying and curing before commissioning. A development from this was the use of shotcreting, but this involves the use of complex and expensive equipment which may not be justified for the installation of only a few tons.

One optimum solution has been the development of precast blocks custom-designed to replace all of the expensive castings and end-refractory and bolt straight onto the kiln shell. Because most modern kilns have air cooling of the outlet ring, this allows a steep thermal gradient and low mean temperatures within the block. When manufactured from materials containing some silicon carbide aggregate and melt extract stainless steel fibres, such custom-designed blocks can give multiple campaigns in service. The design of these blocks along with internal reinforcement and fixings are also very critical to the success of these precast solutions which in some cases work for several campaigns (Fig. 3).

Coolers

Most plants have progressed from the partially refractory lined planetary type coolers to high-efficiency grate coolers and many of these are now lined with precast block inlet chutes, side walls and roofs, including any bullnoses which separate zones within the cooler itself. High wear areas at grate level benefit from premium precast blocks reinforced with a proportion of the aggregate in silicon carbide or very coarse aggregates (Fig. 4). Blaster nozzles in the feed-end wall and panels containing observation ports in the side walls can also be precast for longer life and lower refractory costs (Fig. 5).

A dialogue between user, supplier and installer is also almost always desirable, if not absolutely essential. Previously, many individual plants have used local contractors, and some plants still do so.

Where groups have recently now contracted with installers for the refractory maintenance of multiple kilns, there have occasionally been severe pressures on resources, such as skilled labour and sophisticated equipment, as the repairs often coincide in winter.

Since cost is what one pays and value what one gets, it may be that not only are refractories to some extent hidden from view, but also the valuable contribution from experienced and skilled installers with local knowledge and high commitment.