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PRESENT STATE OF BASIC REFRACTORY LINING

OF THE SINTERING ZONE

by

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Present state of basic refractory lining of the sintering zone

1. Introduction

In the present state of the science, refractory bricks of basic grade are used for lining the sintering zone (burning zone) as well as the adjacent transition zone 1 and outlet zone (discharge zone) in modem rotary kiln plants. Magnesite bricks with 80 - 90 % MgO content, magnesite-chrome bricks with 60 - 70 % MgO content and chemically bonded dolomite bricks are used for the purpose.

Whereas up to only a few years ago, satisfactory working life used to be obtained w;th highalumina bricks containing between 60 and 80 $A1₂O₃$ in linings of low-capacity rotary kilns (approx. 300 - 500 tonnes per day), those brick grades have, with development of heateconornizing large rotary kilns, been entirely superseded.

The most important requirement that the sintering zone bricks have to satisfy is that they possess high chemical resistance against attack by the basic and partly liquid (fused) klinker. This requirement can best be met by materials based on MgO or or. MgO and CaO.

The technological evolution that has taken place in cement kiln construction has thus, in recent years, led to an increase in the size of the basic-lined sections in relation to overall kiln length.

Fig. 1 shows the proportion of basic brick lining of big cement kilns for various kiln systems. Whereas in the wet-process kiln only about 23.5 % of the overall length is, on an average, lined with basic brick, in the Lepo: kiln the cor:esponding average figure is 40.5 %, while it is 47.5 % in the preheater kiln plant. In individual cases as much as 60 % of the kiln length is basic-lined.

The proportion of basic lining in precalcining systems will, as experience so far has shown, only slightly change compared to the conventional preheater kiln.

There 1s no doubt that the durability of the sintering zone lining in large modern kiln plants decisively affects the operational availability of the kiln. More particularly in recent years the relevant relationships have been the subject of a number of pub!ications issuing from the kiln construction engineers and from the manufacturers of refractories.

The developments that have occurred in basic refractory products show that even in the sintering zone, which used to be regarded as the zone with relatively uniform conditions of service, now often different grades of basic brick are installed side by side.

A comparison of lining life figures shows that the durability of magnesite and dolomite bricks in that part of the sintering zone where the lining carries a coating is, on the whole, much the same for these two types of refractory. The ceramically bonded dolomite brick, however, is less expensive and therefore offers to some extent a more favourable price/durability ratio.

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In so far as there are reasons for using dolomite bricks at all in the main part of the sintering zone, where stable coating conditions exist, it nevertheless remains true that ir. the adjacent zones $-$ i.e., the transition zone 1 and the discharge zone $-$ the only suitable types of brick are still the magnesite brick or the magnesite-chrome brick. The reason is that, in the absence of coating or with poor coating formation, these brick types are superior to the dolomite brick in respect of service life. On the other hand, the severer conditions to which these bricks are new exposed in the transition zone 1 and discharge zone as a result of increased thermal ratings, have in some cases led to the use of magnesite-chrome bricks of a type, originally developed for use in steelmaking furnaces and known as high-fired or direct-bonded bricks.

2. Factors affecting basic bricks in the sintering zone

In order to characterize the wear behaviour of basic refractory bricks in the sintering zone it will be necessary first to consider the conditions of service to which the lining is exposed in that zone and in the adjacent zones. Although the brick life is affected by a multitude of factors, there are three factors that predominate. These are:

- (1) mechanical stresses
- (2) thermal attack and stresses
- (3) chemical attack

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In most cases these various actions occur in conjunction with one another.

These are cases where the destruction of the lining is caused only by mechanical stress, that leads to spalling which is due to deformations of the kiln shell. Fig. 2 shows the type of flat spalling which may be due to shell deformations, but could alternatively be attributable to varying conditions of coating in the kiln.

Destruction of the lining due to combined mechanical and thermal actions may occur, for example, when the kiln is exposed to a heavy shower of rain or to extreme temperature variations, as a result of this thermal shock the kiln shell changes at least temporary dia· meter and length.

The most frequent mechanical/thermal reason of lining destruction is, however, to be ob-5erved when the basic refractory is heated up for the first time. If there is not sufficient compensation for thermal expansion, the expansive force acting in the brickwork may cause large sections of material to fracture or spall off on the hot face. This is more particularly liable to occur at temperatures below the creep temperature of the material, i.e., in the temperature range where it has not yet sufficiently developed its thermoelastic properties.

Fig. 3 shows dished spalling due to restraint of expansion in the axial direction.

Because of the rotational motion of the kiln in continuous service the lining subjected to compressive, tensile and shearing forces whose degree has hitherto proved very difficult to estimate with any accuracy.

Besides causing spalling, these forces are liable to cause loosening (Fig. 4) and spiral displacement of the brickwork (Fig. 5) if the latter is not securely fixed. The relative brick movements with respect to the kiln shell are detectable by typical abrasion marks. In most cases there is also some crushing of the brick at its base (Fig. 6).

The chemical/thermal action to which the lining is subjected in due in part to the feed (material), more particularly the action of clinker granules, pieces of detached coating, clinker melt (liquid phase). and alkali melt and vapour.

Another important chemical and thermal controlling factor is the flame. It acts more specifically through the fuel components, the condition of the kiln atmosphere and the temperature developed.

Chemical/thermal destruction of the basis lining differs from the mechanical/thermal wear because it proceeds at a slower rate. The rate is determined more particularly by the temperatures at which a more or less aggressive chemical reaction occurs between the brick components and the cement clinker. Chemical wear is accompanied by migratory movements of material which in general start from the interior of the kiln and advance in the direction of the temperature gradient, through the open pore space, into the brick. During the course of chemical changes and diffusion processes the texture and mineral structure of the brick undergo changes which occur in a zonal sequence from the hot to the cold face. As a result, the refractory properties as well as the physical properties of the brick are altered.

Mechanical/thermal wear is primarily determined by brick properties such as the coefficient of thermal expansion, thermal conductivity and strain modulus.These are material-dependent properties which in turn are largely determined by the main components of the brick, such as MgO or CaO. They can be modified within limits by special measures applied in the manufacture of the brick, such as controlled granulometric composition, firing temperature and variation of the brick matrix.

The wear behaviour of basic bricks for sintering zone linings will now be discussed from the point of view of thermal/chernical and thermal/mechanical wear. The wear mechanisms will be considered in the following order: magnesite bricks with silicate bond, magnesite bricks with direct bond, and fired dolomite bricks.

2.1 **Magnesite bricks with calcium silicate bond**

It is typical for silica bonded magnesite bricks that the MgO crystals which are responsible for the refractoriness of the brick are embedded in a matrix of silicate phases and, in some instances, ferritic phases. Characteristic of this type of brick is its creep behaviour at temperature above 1200 °C. Brickwork construction with mortar and steel plates presents no problems as regards excessive expansion. Any shortcomings in the arrangement of expans on joints are largely compensated by the so-called creep properties, so that in general there is no

spalling due to mechanical/thermal causes. On the other hand, the silicate matrix, which favourably affects the creep properties of the brick, is easily transformed into a pyroplastic condition when exposed to overheating and suffering increasing chemical reaction with the cement clinker, as a result of which the brick surface is liable to suffer rapid erosion-like wear. In such cases the lining is said to be "burnt out". A brick overheated in this way, with adhering clinker which, as its structure indicates, must have been almost liquid, is shown in Fig. 7.

Fig. 8 is a micrograph showing periclase and infiltrated clinker phases at the hot face of such a brick.

Under normal conditions, changes in a refractory brick occur only after a fairly long period of use, manifesting themselves in the development of three different zones in the direction of the temperature gradient (Fig. 9). At the hot face the brick consists chiefly of recrystallized periclase containing iron oxide in solid solution. Chrome ore, whict. originally was present in all parts of the brick, has largely or entirely disappeared from this first zone. The attack upon the chromite is predominantly due to the action of potassium upon the kiln feed materiat, giving rise to the formation of potassium chromate, which can be observed as a yellow deposit between the lining and the kiln shell after the brick has cooled. The liquid phase of the clinker then forms low-melting phases with the rest of the brick matrix, and these migrate into the middle zone. On account of this migration of matter and incipient recrystallization, the hot face of the brick displays increased porosity, reduced density and a weaker bond than the original brick.

The middle zone increases its density, as it absorbs the liquid phases entering from the direction of the hot face. Because of these mineralogical changes, the brick properties at the boundary of the hot face zone and middle zone likewise undergo a change. Cracks extending to a depth of about $5 - 7$ cm occur at this boundary.

These cracks are liable to result in destructive damage to the brick, especially at kiln shutdowns. When the kiln cools, or if coating falls off, the recrystallized hot face layer will spall from the rest of the brick.

In a used brick the zone at the cold face is generally unchanged in structure and mineral content. Some increase in the content of alkalies, sulphates, chlorides and chromates is detectable, however. Fig. 10 shows a concentration diagram of a magnesite brick removed from a kiln.

2.2 Magnesite bricks with direct bond

Direct-bonded magnesite bricks are generally classified as bricks in which the fine-grained components material consists partly of chrome ore which, as a result of high-temperature firing, reacts with the periclase and develops a highly refractory bond. Contrarv to magnesite bricks produced with silicate-ferritic bond, the MgO crystals in high-fired bricks are interconnected via a complex chromite-spine! phase. Silicates already present are displaced into the interstices of the periclase-chromite structure and thus no longer constitute the actual "bonding substance" of the brick. Fig. 11 shows such a "solid-solid" bond between chrome ore and periclase.

One of the most important properties of direct-bonded magnesite brick is its high mechanical strength at high temperatures.

But what do these properties mean to the cement manufacturer? The properties of directbonded bricks arc characterized by high hot compressive strength, the elimination of silicate bond, the possession of a chemically resistant matrix and high bond strength in the mineral phases. Such refractory material can be expected to attain a long life in the kiln. This is not always so, however.

Examination of used direct-bonded bricks have so far shown that the changes already described with reference to the silicate-bonded magnesite brick also occur in principle in the direct-bonded brick, but are confined to a region only $1 - 2$ cm in depth at the hot face. Furthermore, because of the higher refractoriness of the matrix, overheating does not cause such rapid softening and disintegration of the brick surface.

Witn the advantages offered by the direct-bonded brick, there are, however, some problems associated with the use of such brick, which have not yet been satisfactorily solved. Because of the high compressive strength under hot load and its resistance to creep such brick require great allowances for expansion which can lead to unstable brickwork. Another problem arises from the *iact,* that, if the bricks are laid with steel plates, reactions of the latter with the brick may cause expansion of the joints. (With silicate-bonded bricks the steel plates oxidize and the iron is combined with the MgO to form magnesioferrite which soaks into the bricks and "cements" them together.)

Examination of wear phenomena affecting used magnesite bricks has so far revealed that wear occurs mainly as a result of spalling due to inadequate possibility for expansion (Fig. 12). The efforts of the manufacturers of refractories are therefore aimed more particularly at solving this problem by means of suitable bricklaying systems and variously formed sheetsteel or other inserts, e.g., perforated plates, mesh, etc. All the same, these have not yet provided a satisfactory solution.

2.3 Dolomite bricks

Fired dolomite bricks have, on account of their favourable price-to-life ratio, been used in the sintering zones of rotary cement kilns for a number of years. Their chemical resistance to the action of clinker is to be rated as good, as the liquid phase (the clinker melt) is stiffened by the CaO present in the dolomite brick, so that deep infiltration into the brick is prevented.

Examination of used dolomite bricks has revealed that, in complete contrast to what happer.s in magnesite bricks, destruction is due primarily to diffusion of $CO₂$ and $SO₂$ into the interior of the brick. These gases react with the free CaO present in the brick, forming calcium sulphate, calcium sulphide and calcium carbonate.

Figs. 13 and 14 show the profile of a used dolomite brick before and after being cut open after 10 months' service in a Lepol kiln. The pattern of wear presented by the brick is representative of the chemicomineralogical changes of dolomite brick during use. Althcugh the brick has retained almost all of its original thickness, its chemical and mineralogical character has undergone considerable changes. Fig. 15 presents a concentration profile showing the new minerals formed in the brick from the hot to the cold face; the positions of the cracks that have developed are also indicated.

A triple zonal subdivision of the lining is discernible, resulting in mechanical separation and extensive spalling of the brick zones. The zone at the hot face is characterized mainly by the absorption of ferritic phase from the clinker and by crystal growth of the CaO and MgO present in this zone. In the denisified middle zone of the brick the alkali sulphates from the kiln atmosphere have crystallized after attaining their solidification temperatures. At the same time, the SO_2 from the kiln gases has reacted with CaO to form calcium sulphide. Recar- α bonation of CaO to CaCO₃ has occurred at the cold face. The MgO content of the dolomite brick has not participated in the reactions with SO_2 and CO_2 .

As a result of the conversion of CaO into the specifically lighter compounds CaS and CaCO₃ which is accompanied by an increase in volume in the brick matrix, together with the infiltration of alkali sulphates, the original particle structure has been weakened and the thermomechanical strength of the middle zone reduced. Cracking has occurred approximately at the zone boundaries.

From what is known about the wear of dolomite brick it is possible to explain the phenomenon observed in practice, namely, that the good or indeed very good behaviour of this material is limited to the sintering zone where a stable coating is formed on the lining.

This coating protects the dolomite brickwork from attack by the kiln gases. An increased content of free $SO₂$, introduced through' sulphur-rich fuel or as a result of "sulphatization" cf the raw meal, will in any case shorten the service life of a dolomite lining.

3. Conclusions

It emerges from what has been said above that, under presend-day conditions, only bricks which corsits mainly of magnesite or dolomite have sufficiently good chemical resistance to the action of cement clinker and liquid alkali phases at sintering zone temperatures. Dolomite bricks, however, possess good durability only in the zone where a stable coating is picked up by the lining and only if no gypsum for "sulphatization" is added to the raw meal.

Magnesite and magnesite-chrome bricks with good creep properties (i.e., calcium silicatebonded bricks) behave better against mechanical stresses, caused by restrained thermal expansion or to kiln shell deformations, than so-called direct-bonded and therefore "rigid" magnesite bricks. These latter bricks merely offers some slight advantage over calcium silicated-bonded bricks against overheating and/or infiltration by liquid phase from the clinker. Present-day bricklaying techniques cannot as yet fully cope with the considerable thermal expansion of these bricks. It should be considered in each individual case, depending on the special operating conditions, which type of basic brick should be installed in the transition zone 1, the sintering zone or the outlet zone.

Fig. $1:$ Proportion of basic-lined kiln zone in relation to total kiln length for various kiln systems

Fig. 2: Flat spalling due to deformation of the kiln shell or to variations in coating

Fig. 3: Dished spalling due to restrained axial expansion

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Fig. 4: Loosening of brickwork

Fig. 5: Spiralwise displacement of brickwork

Fig. 6: Abrasion marks due to heavy twisting of the brickwork

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Fig. 7: Magnesite brick with overheated clinker coating

Fig. 8: Micrograph of an overheated magnesite brick with infiltration of clinker minerals (magn. 400 x)

Fig. 9: Profile of a used magnesite brick

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Fig. 10: Concentration diagram of a used magnesite brick

Fig. 11: Micrograph of a solid-solid bond between chrome ore and periclase (magn. 400 x)

Fig. 12: Dished spalling due to restraint of expansion

Fig. 13: Profile of a used dolomite brick

Fig. 14: Profile of a used dolomite brick

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