QATAR NATIONAL CEMENT COMPANY

Cement Rotary Kiln

Questions & Answers

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2013

"In the name of Allah, the Beneficent, the Merciful"

"Read in the name of thy Lord Who creates-①Creates man from a clot ② Read and thy Lord is most Generous ③ Who taught by the pen ④ Taught man what he knew not ⑤"

CEMENT ROTARY KILN

Questions & Answers

Question-1: **What is the maximum continuous shell temperature a kiln stands without permanent damage to the shell?**

Answer-1: The maximum recommended kiln shell temperature varies by plant, by country and by kiln manufacturer, despite the fact that most kiln shells are made of low alloy carbon steel. Age of the kiln shell, distance between the tires, and structure of the shell are some important points should be considered before deciding what the maximum allowable temperature for a kiln is. Let us explain these points briefly:

1. Age and condition of the kiln shell: Old kilns shells have been exposed to creep for a long time and are more prone to develop fatigue cracks than newer shells.

2. Distance between tires: The longer the shell span, the less it will resist high temperatures without sagging. Therefore, longer spans have more tendencies to develop permanent deformation than shorter spans.

3. Kiln shell structure: Kiln shells are made with structural rolled steel plate, such as A.S.T.M. A36. The tensile strength of this type of steel at room temperature is 50,000 to 80,000 psi. As stated before shell strength is measured at a room temperature. Figure-1 is showing how shell strength drops considerably as its temperature is raised. It is interesting to notice that there is a gain in strength between room temperature and 200 °C, followed by a sharp loss in strength as the temperature goes up. At 430 °C the ultimate strength of the steel drops from 75,000 psi to 50,000 psi (a hefty 33%) loss. Some investigators report a 50% strength loss for the same temperature range.
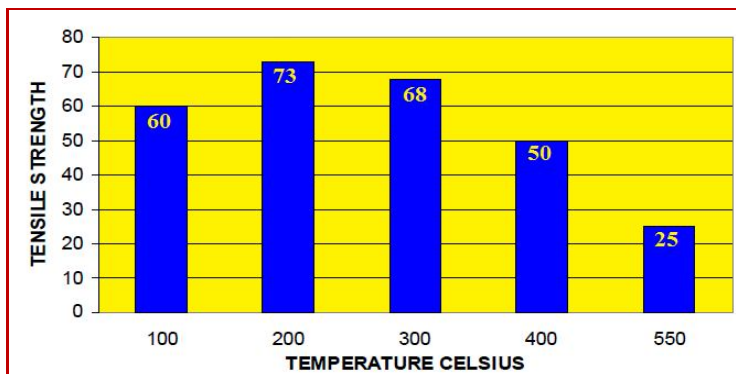

Figure-1: Kiln shell strength as temperature raise

Question-2: **What is the difference between kiln shell hot spot & red spot?**

Answer-2: Hot spot is isolated area on the kiln shell with abnormally high temperature. It is quickly detected by a shell scanner or with a portable infra-red pyrometer. It can't be seen during the day, and can hardly be seen at night (figure-2). Therefore, based on the visible radiation spectrum for hot surfaces, their maximum temperature must be below 550°C.

Red spot (figure-3) differ from hot spot in that it is visible at night. While a hot spot is just a warning, a red spot always demands some kind of action from the kiln operator.

Figure-2: Hot spot with a temperature of 570°C

Figure-3: Red spot with 830°C temperature

Question-3: **What is the maximum red spot temperature on the shell force kiln to stop?**

Answer-3: The short answer is 550ºC if the spot is permanent and persistent. This is a short answer, but when we talk about red spot, damaging of shell, long kiln stoppage, and losing millions of Riyals or Dollars; this answer cannot be

acceptable. A number of factors are absolutely necessary to be considered in any red spot before taking the decision of kiln stoppage:

1. Proximity of the red spot to the tires or gear: Red spots near tires and bull gears require immediate action. These spots almost invariably force the kiln down. Shutdown procedure must start immediately to avoid damaging the kiln shell.

2. Extension of the red spot: The longer the circumferential extension of the red spot, the greater the risk of shell permanent deformation or collapse. If there is any persistent red spot covering more than 10% of the kiln circumference (figure-4); Kiln should stop immediately.

3. Kiln alignment conditions: Misaligned kilns induce localized stresses along the kiln length. If the red spot coincides with an area of stress concentration, the shell sometimes elongates or twists beyond recovery.

4. Whether the red spot is exposed or under roof: If the kiln shell is directly exposed to the elements and a heavy rainstorm hits the red spot, the shell may develop cracks under sudden quenching. Sometimes the brick results severely crushed in the red spot area.

5. The presence of shell cracks in the vicinity of the spot: The presence of cracks in the vicinity of the hot spot calls for an immediate kiln shutdown to avoid shell splitting.

Figure-4: Circumference red spot

Question-4: What is "Oxygen Enrichment Technology"?

Answer-4: It is an oxygen injection system connects to kiln burner or precalciner burner to enhance the combustion of the fuel. In general, the use of oxygen enriched combustion air in the clinker burning process allows an increase of the energy efficiency, production capacity or substitution of fossil fuels by low calorific value or (secondary) fuels and that way the specific CO_2 emissions can be reduced.

By the use of additional oxygen the nitrogen fraction of the combustion gas is decreased, which has to be heated up in the case of combustion with ambient air. Therefore the adiabatic flame temperature rises and the flame becomes shorter and brighter. The measure is limited by increasing damages of the kiln refractory and higher NO_X emissions due to increasing thermal NO_X formation in the sintering zone. In practice the application of the oxygen enrichment is still at an early stage, meaning that the technology contains potential for further optimization with respect to NOx emission reduction. Due to reduced secondary air flow the heat recuperation in the clinker cooler might be affected for example with a higher secondary air temperature as well.

The oxygen enrichment technology is established in some cement plants in order to improve production capacity. An increase of 25% to 50% (short term experiments) kiln capacity by oxygen enrichment to 30-35 vol.% in the combustion air has been reported. Oxygen enrichment has not been applied to reduce CO_2 emissions so far. But the use of enriched combustion air may result in fuel savings and thereby avoids CO_2 production. The decision for a dedicated oxygen supply system (on-site/off-site) depends on the specific need of the cement plant. Oxygen production itself leads to comparatively high additional power consumption.

Surely; there are a number of plants using oxygen enrichment technique but still not commercially due to its high cost. If market demand exists with good prices for cement then oxygen enrichment can be a good option. Table-1 shows a number of kilns in the USA using oxygen enrichment of either the main burner or the precalciner.

Company	Type	Base Production (tpd)	New Production (tpd)	% Increase
A	Precalciner	1,300	1,490	15
B	Precalciner	4,000	4,360	9
C	Wet	550	660	20
D	Wet	850	920	8
E	Precalciner	3,800	5,000	32
F	Precalciner	2,000	2,140	7

Table-1: Typical production gains using Oxygen Enrichment Technology

Question-5: What is the basic principle in classifying precalciners?

Answer-5: The vast diversity of precalciner systems makes their classification difficult. In particular, the design differences include: swirling or non-swirling flow, extended riser duct systems or separate combustion chamber, the system of supplying combustion air (separate duct or through the kiln), number of stages, and number of strings. But since combustion in precalciners is the most

important process, it is appropriate to review the three basic types of precalciners (figure-5) from this standpoint. These types are:

1- Total flow precalciner: In total flow precalciners, combustion takes place in a mixture of kiln exit gases and tertiary air. Combustion therefore starts in gases with about 10% to 14% oxygen and ends in about 1% to 3% oxygen. Raw meal from the preheater is fed into the bottom of the precalciner and is conveyed through the precalciner to the lowest stage cyclone by the precalciner gases. During this time, fuel combustion and heat transfer to the raw material are occurring.

2- Tertiary air flow precalciner: In tertiary air flow precalciners, combustion takes place in air flow. In other words, it starts in gases with 21% oxygen and ends in about 1 to 3% oxygen. Raw meal from the preheater is fed into the precalciner at the level of a burner end and is conveyed to the bottom stage cyclone.

3- Hybrid precalciner: Hybrid precalciners are essentially a combination of the total flow and tertiary air flow precalciners. In hybrid precalciners, combustion starts in tertiary air with 21% oxygen, as in tertiary air flow precalciners, but is completed in a mixture of kiln off-gas and tertiary air, similar to total flow precalciners.
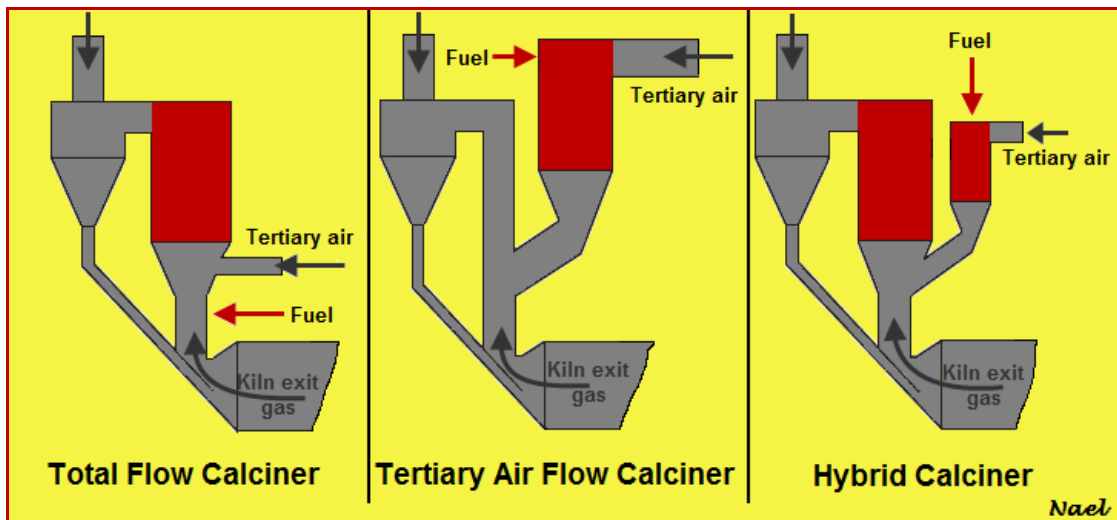

Figure-5: Types of precalciners

Question-6: Generally calciners (in cement books) classify to three types: In-Line calciner, Off-Line calciner & Separate-Line calciner. The definitions of these three types are as the following:

1. In-Line calciner is installed in the kiln exhaust gas flow which means that the combustion takes place in an air/kiln gas mix. This precalciner can be considered an enlarged kiln riser duct.

2. Off-Line calciner is installed off the kiln exhaust gas flow. The combustion takes place in pure (tertiary) air which is also responsible for lifting up the meal.
3. Separate-Line calciner is off-Line calciner with a separate preheater string.

My question is why does FLSmidth classify their calciners to only two types; In-Line and Separate-Line calciner with no Off-Line calciner?

Answer-6: These are not strictly calciner definitions or classifications; they are terms used by different equipment suppliers to determine their product (calciner) design. If we make a comparison between the two classifications as shown in figure-6 and figure-7; the following results can be recognized.

1. FLS In-Line Calciner (ILC) is similar to In-Line Calciner in your definition, the calciner is placed in the riser duct from kiln inlet to bottom stage cyclone and combustion takes place in a mixture of kiln exhaust gas and tertiary air.

2. FLS Separate-Line Downdraft (SLC-D) Calciner is similar to Off-Line Calciner in your definition.

3. FLS Separate-Line calciner (SLC) is similar to Separate-Line Calciner in your definition.
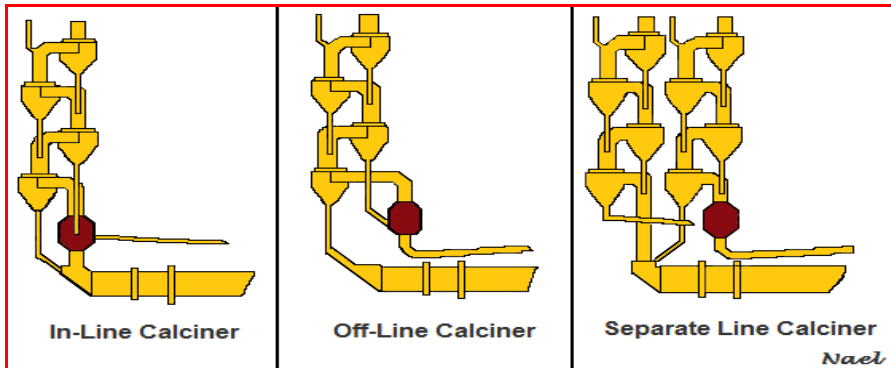

In-Line Calciner   Off-Line Calciner   Separate Line Calciner
                                                            Nael

Figure-6: Calciners general classification

FLS In-Line Calciner   FLS Separate-Line Calciner   FLS Separate-Line Calciner
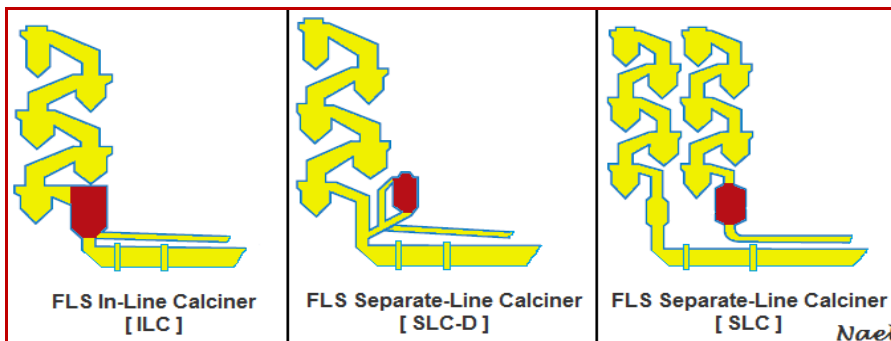[ILC]   [SLC-D]   [SLC]   *Nael*

Figure-7: Calciners FLSmidth classification

Question-7: What are the factors affecting the number of cyclone stages in preheater kiln system?

Answer-7: The number of cyclone stages in a preheater system largely determines the system heat efficiency. It also depends on the intended use of the

heat of the exit gas leaving the system. In modern practice, most of the kiln gases from a preheater or precalciner system are used for drying in both the raw mill and the coal mill. As a rule, the throughput and moisture content of the raw materials and fuels, which have to be dried by the remaining exhaust gas heat, decide whether 2, 3, 4, 5 or 6 cyclone stages are used. There are criteria for selecting the number of preheater stages other than drying the materials. Typical determining factors include construction cost, electricity and fuel price, gas conditioning system, heat exchange efficiency, radiation losses, and pressure drop (figure-8) which is one of the most important factors affecting the number of cyclone stages.
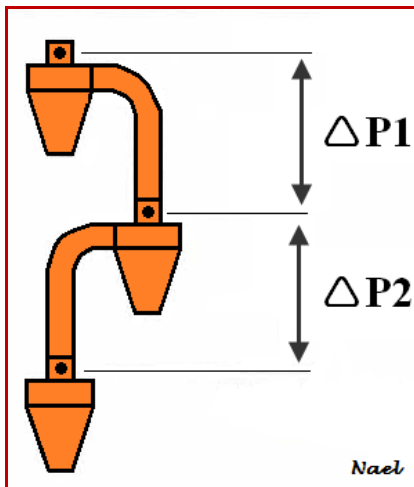

Figure-8: Pressure drop across one stage of cyclone

Initially number of stages used to be 4 only. Pressure drop across a 4 stage preheater used to be 500 to 550 mmwg. Any increase in number of stages resulted in additional pressure drop which unfavorably offset gain in fuel efficiency. Therefore cement industry continued for quite some time with 4 stage preheaters till cyclones of low pressure design were developed. Attention was paid by designers of preheaters to the geometry of cyclones and their internals to reduce pressure drop. As a result designs have become similar and pressure drops comparable As a result, fuel consumption has steadily gone down and specific gas volume expressed in Nm^3/kg clinker has also come down. Presently pressure drops in 6 stages preheater are comparable to or even less than that in a 4 stage preheater of old designs (Table-2).

No. of Stages	Pressure Drop Across Preheater (mmwg)	Temperature of Gas at Exit (°C)
4	280 - 300	350
5	320 - 370	300
6	400 - 450	270

Table-2: Pressure drop with 4, 5, and 6 stages preheater

With reduced pressure drop, temperature and reduced gas volume specific power for preheater fan expressed in kwh/ton of clinker has also come down. Table-3 & figure-9 shows typical values for specific fuel consumption, specific gas volume and specific power for preheater fan. It would be seen that development of low pressure drop cyclones has resulted in bringing close specific power consumption of preheaters of 4 to 6 stages. Thus with this development, it has been possible to increase number of stages from 4 to 6 without paying penalty in terms of power consumption.

Stages	Sp. Fuel Consumption (kcal/kg)	Sp. Gas Consumption (Nm^3/kg)	Sp.Power Preheater Fan (Kwh/ton)
4	800	1.65	5.75
5	750	1.55	6.05
6	700	1.45	6.3

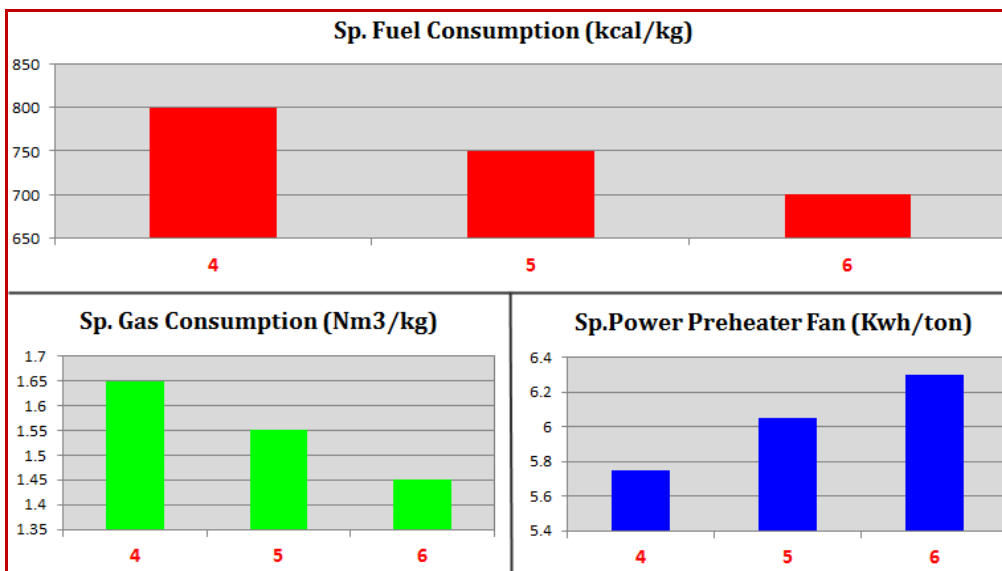Table-3: Energy consumption with 4, 5, and 6 stages preheater

Figure-9: Energy consumption with 4, 5, and 6 stages preheater

Question-8: **What is the significance of liquid phase in clinker formation?**

Answer-8: The liquid has a critical role in clinker nodulization and clinker mineral development and properties. Solid-solid reaction is very slow process while solid-liquid reaction kinetics is much faster, so without liquid phase (figure-10) the diffusion of Ca ions towards C2S would be extremely slow, and the conversion of C2S and free lime to C3S would be almost impossible in the kiln. The amount of liquid phase in the burning zone varies between 23% and 29%. Higher values can be damaging to most refractory bricks in the absence of a stable coating. As the brick is infiltrated and saturated with liquid, its elastic

modulus (relation between stress and strain) increases and so does its tendency to spall off. This simple fact explains why hotter than normal temperatures are so beneficial to clinkering and yet so harmful to the refractory lining as low viscosity liquid infiltrates the refractory lining faster, leading to its premature failure.

Figure-10: Liquid phase

Question-9: **Every year cement industry loses millions of dollars in unexpected kiln shutdowns caused by rings build-up inside the kiln. What are the reasons behind formation such type of build-up?**

Answer-9: Kiln Build up (figure-11) or ring formation mechanism can be divided depend on formation chemistry or formation location as the following:

a). Rings with regard to formation chemistry:

1. Sulphur Rings: Sulphur-induced rings are formed when the molal sulfur to alkali ratio in the system is more than 1.2. In such cases, there is a considerable amount of free SO_3 circulating in the kiln. At a certain concentration level in the kiln gas, sulfation of the free lime occurs with anhydrite formation ($CaSO_4$). If the kiln is burning under slightly reducing conditions, more volatile and lower melting sulfur salts may form, therefore increasing the severity of the problem. The salts, in molten state, coat the traveling clinker dust, forcing it to stick to the kiln wall in the form of rings. Sometimes the chemical analysis of such rings does not indicate high sulfur concentrations, proving that even a small amount of free sulfur is sufficient to cause rings.

2. Spurrite Rings: Carbonate or spurrite rings are formed through CO_2 desorption into the freshly formed free lime, or even through belite re-carbonation. These rings are hard, layered, and exhibit the same chemistry as regular clinker. Spurrite is a form of carbonated belite. When the carbonate in the spurrite is replaced with sulfur the new mineral is called sulfated spurrite. Spurrite rings form whenever the partial pressure of CO_2 above the bed of material is high enough to invert the calcining reaction.

3. Alkali Rings: The third type of ring occurs whenever the sulfur-to-alkali molal ratio is less than 0.83, usually in kilns with heavy chlorine loads. In such cases, low-melting potassium salts provide the binder for clinker dust travelling up the kiln. Through a "freeze-and-thaw" mechanism, these rings can assume massive proportions. Alkali rings are far less common than other types because sulfur and carbonates usually are in excess relative to potassium.

Figure-11: Kiln build-up

b). Rings with regard to formation location:

 1. Intermediate Rings: Intermediate rings are dense, hard and seldom fall off during kiln operation. They are elongated, being some 10-15 meters long and extending from 7 to 11 kiln diameters from the outlet. This ring is clinker-like in colour indicating it being composed of well burnt material. They have a layered structure, according the curvature of the kiln shell. Their chemical composition is very similar to that of clinker. No increase in concentration of SO_3 or alkalis takes place, and often the ring shows lower volatile element values than for clinker. The alite of the inner layers may decompose into belite and secondary free CaO, resulting from cooling down of the inner layers to a temperature lower than the stability temperature of the alite (1260°C).
The mechanism of bonding is the freezing of the alumino-ferrite melt. The smallest clinker particles of 150-450 mm are carried back by the gas stream, fall down and are deposited on the kiln refractory lining, in a zone where temperatures of below 1250°C exist. The clinker dust particles freeze in place, and because the kiln charge is still fine, it does not possess sufficient abrasive action to remove the growing ring.

2. Sinter Rings: These rings occur in the burning zone inlet, some 4-5 diameters from the kiln outlet. They are greyish-black in colour, hard and formed by small clinker nodules and clinker dust. Because of the presence of large pores and voids, no layered structure is formed. Their chemical composition is that of the clinker with no concentration of volatile elements. The alite of the inner layers may decompose into belite and secondary free CaO.

The bonding is created by the freezing of the clinker liquid phase. This phenomenon occurs especially in the burning zone inlet, where the liquid phase is just starting to form, at approximately 1250°C. Due to the rotation of the kiln, the material freezes with each kiln rotation and deposit of clinker particles having less than 1 mm diameter may reach a large thickness.

3. Coal Ash Rings: In kilns fired with a high ash content coal, rings can form at 7-8.5 diameters from the kiln outlet. They are dense, with a layered structure and sometimes glassy in appearance and built up from particles some 150-250 mm in size. They are rather less dense and have larger pores and voids than intermediate rings. Their chemical and mineralogical composition is very similar to that of clinker. As the ring grows up and the temperature of the inner layers falls down the alite may decompose into belite and secondary free lime.

The bonding mechanism is the freezing of molten coal ash particles and perhaps to a slight extent, the freezing of the clinker liquid phase. The molten coal ash droplets adhere to the kiln refractory lining in a zone where the temperature is high enough so that they are still partially sticky. When this layer passes under the kiln charge, one ach kiln rotation, a portion of the still very fine kiln charge adheres to it.

Question-10: What is the formation mechanism of "Snowman", "Rhino horn", and "Boulder" in kiln system?

Answer-10: The first two deposits are formed from small clinker nodules and clinker dust particles. Their chemical and mineralogical composition is identical to clinker, but in some cases enrichment up to 3.5% K_2O and 3.0% SO_3 has been noticed.

a). Snowman: Is a formation of large build-up on cooler first grate (static grate) or kiln discharge wall where the clinker falls from the kiln. Snowman (figure-12) may eventually grow to reach the mouth of the kiln, thereby blocking the discharge of clinker from the kiln. Snowman causes poor clinker distribution thereby poor heat exchange between clinker and secondary air. Snowman formation mechanism may divide to two:

1). Freezes of the clinker liquid phase as the clinker passes through the first cooling zone in the rotary kiln or on falling down the chute into the grate cooler. The clinker dust particles carried back by the secondary air stream from the clinker bed grate into the interior of the rotary kiln also play an important role on formation snowmen. The clinker dust particles, having a superficial liquid phase layer, strike against the chute wall and the refractory lining at

discharge side of the rotary kiln, lose their kinetic energy and the superficial liquid phase freezes immediately.

2). Occasionally large lumps of coating discharge from the kiln, these lumps of kiln coating act as "seeds" for the formation of snowmen. Snowmen form when fines fall from the kiln above, onto the top surfaces of these lumps on top of the clinker bed within the cooler. As layer after layer of the fines fuse onto the lump, snowmen "grow" upwardly into stalagmite-like structures. Figure-13 is showing snowman demolishing by "Pulling method".

Figure-12: Snowman in Grate cooler
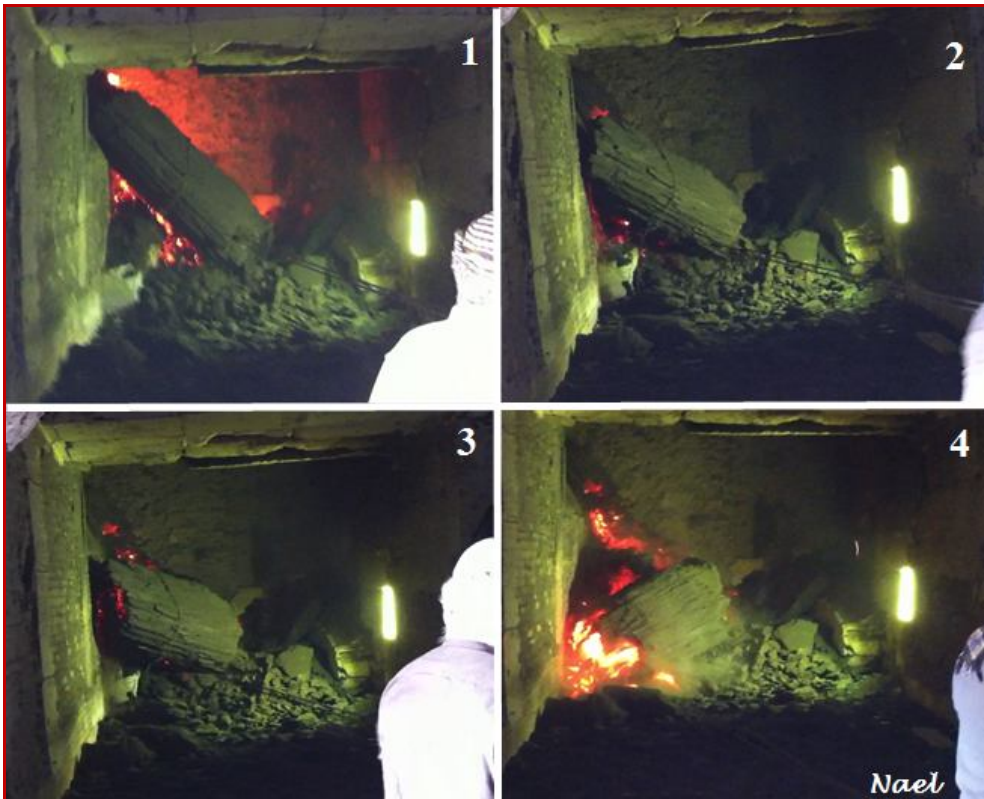
Figure-13: Snowman Demolishing

b). Rhino horn: is a build-up on the top of kiln burner pipe as shown in the figure-14.

Rhino horn formation mechanism: Clinker dust carried back to the kiln with the secondary combustion air loses velocity around the burner and that causes clinker dust to settle and build up on the top of the burner.
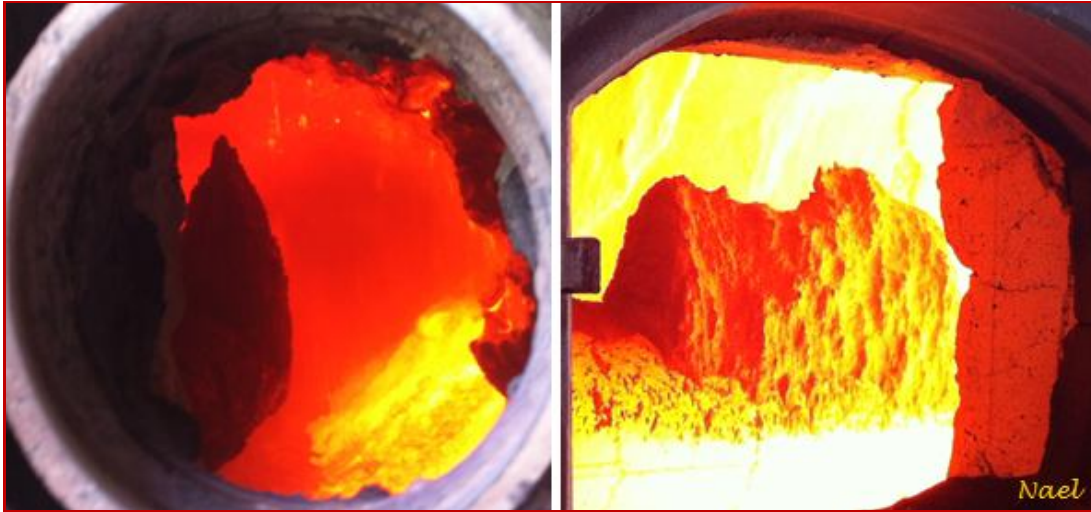
Figure-14: Rhino horn/ build-up on kiln burner

c). Boulder: Generally, clinker ball/ boulder formation is related to low clinker SM with high AM or related to very thick coating. Figure-15 is showing a boulder with 1.80 m in diameter.

Boulder formation mechanism: Large clinker balls initiate and grow behind a thick coating or ring. Build up often fall and slide into the kiln as large slabs and coming to rest behind a ring (if it is large enough). The slab can roll around behind the ring forming a ball which can then grow larger due to accretion.

Figure-15: Boulder

Question-11: What is reason of "Red River" phenomenon in grate cooler?

Answer-11: Red river is a phenomenon in grate cooler (figure-16); it is often a red hot narrow stream of fine clinker with a higher temperature than the neighbored clinker and appears far down in the cooler. The fact that especially large diameter type kilns tend to discharge fine clinker on the kiln's load side and coarse clinker on the opposite side can make it difficult to get good clinker distribution. In addition to the segregation, a clinker bed with unilateral or bilateral slope on static grate tends to slide fine clinker down as shown in figure-17.

Figure-16: Red river
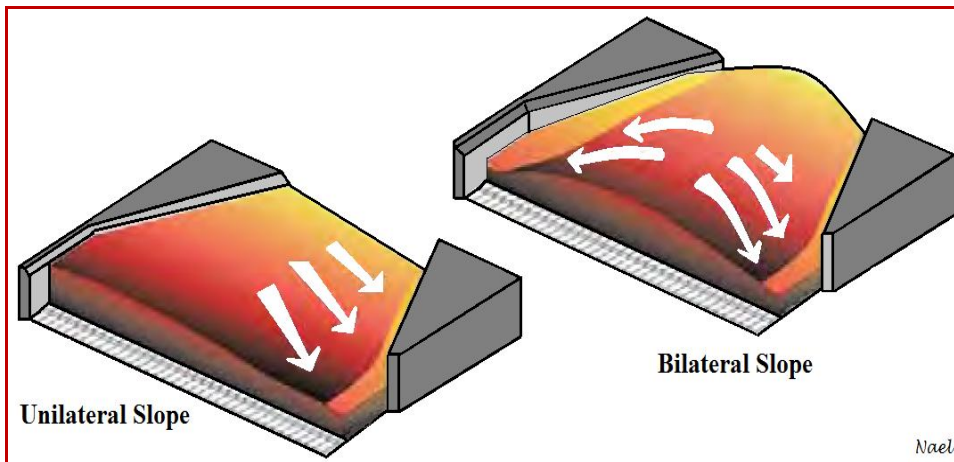
Figure-17: Unilateral & Bilateral Phenomena in grate cooler

Due to non-uniform clinker bed and high air resistance of fine clinker; red rivers often are inevitable (figure-18).
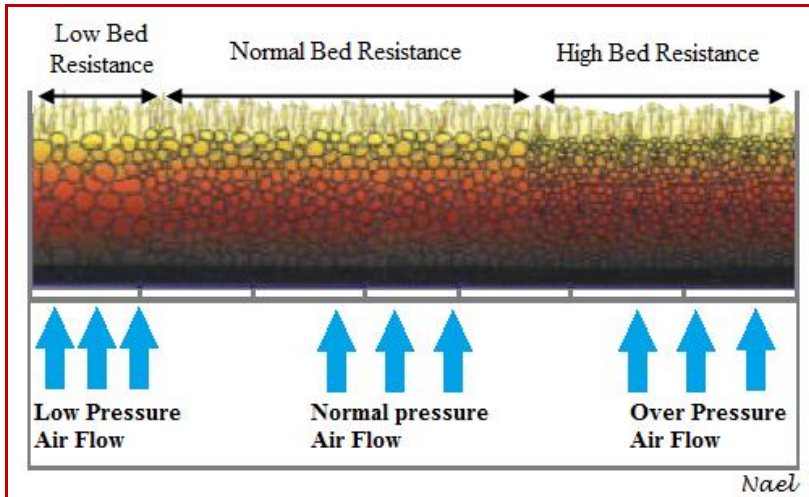
Figure-18: Non uniform clinker bed

A fine clinker has a higher resistance to the airflow than the coarse clinker, so the cooling air takes the path of least resistance, which intensifies the "Red River" formation. Figure-19 shows the pressure losses of various clinker sizes as a function of free air velocity. It can be seen that the particle size has a great influence on air distribution, which can be described by pressure losses.
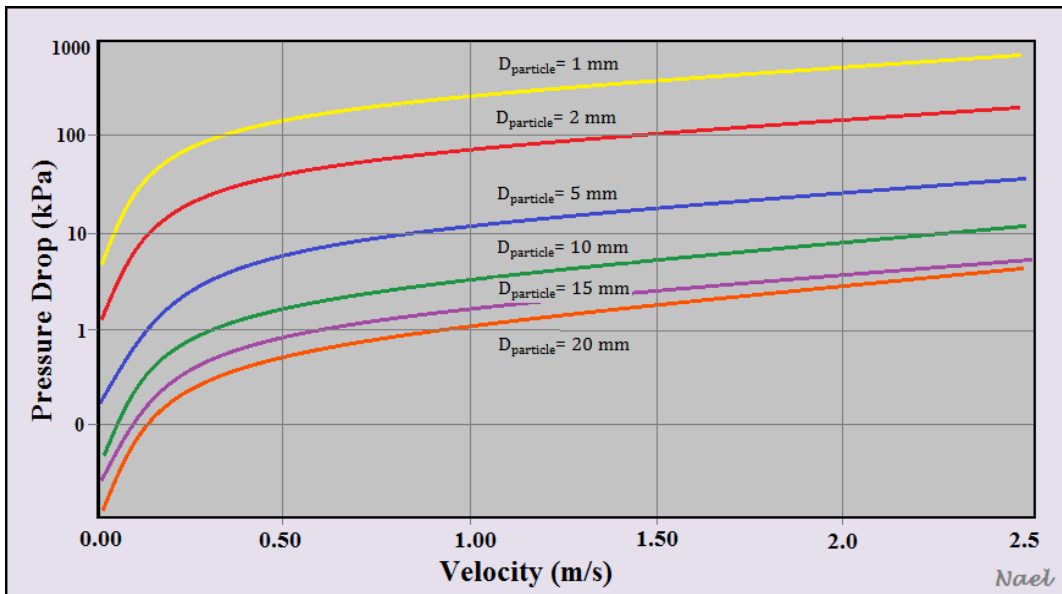

Figure-19: Press losses of various clinker sizes as a function of free air velocity

Proper clinker bed distribution on cooler grates by optimization cooler parameters may help us to avoid this phenomenon. Here are the main points need to be considered with grate cooler:

1). Increasing the clinker bed thickness by slowing grate s peed improves the overall clinker distribution and heat transfer, also has a positive effect upon grate wear rates. Slowing down the movement of the fine clinker bed diverts more fine clinker to the coarse cooler side, thus increases the overall clinker bed

resistance which pushes more air through the fine clinker bed. (good results have been experienced with clinker beds up to 1 meter deep).

2). Optimization of cooler air flow as too high amounts of air promote fluidization of the clinker. As the finer clinker particles are likely to be entrained in the locally intensified air flow, high amounts of dust cycles between kiln and cooler are likely. Dust particles might also be picked up from highly fluidized areas and concentrate in others, thereby intensifying any red rivers. It is recommended that maximum airflow not exceed approximately 140 normal cubic meters per minute per square meter of cooler grate area.

3). A successful way to improve clinker distribution is to narrow the cooler grate area on the fine clinker side. By doing so, the clinker bed becomes narrower and often eliminates a severe segregation of fine and coarse clinker. It is recommended that the cooler inlet grate width not exceed 2.5 m for kiln capacities up to 2,500 metric tons per day of clinker.

4). Corner areas often have a low clinker load which results in heavy air channeling and bypassing the clinker load. Blanked off air holes ensure that cooling air is diverted into the clinker load.

5). Optimization of secondary air temperature as too high secondary temperature tends to form "snowman" which cause poor clinker distribution at cooler inlet where improvement should start from.

Question-12: How does magnesia bricks hydration occur? How does it affect negatively on bricks service life?

Answer-12: Generally; magnesia bricks (magnesia-, magnesia-chromite-, and magnesia-spinel-bricks) must be stored in ventilated and dry rooms with protection against weather conditions (snow, rain, splashing water, etc.) as they are sensitive to hydration and can be damaged if stored improperly. In 2002 the commissioning of an ilmenite smelter on the North Coast of South Africa was extended by three months due to the failure and subsequent replacement of the magnesia-based refractory lining. The lining failed due to the hydration of magnesia caused by an unexpected source of water. The incident resulted in significant financial losses and a prolonged insurance claim which was settled in 2009.

Hydration of magnesia (MgO or periclase) in refractory material occurs when the material comes into contact with humid air, water, or steam. This exposure can occur during storage, construction, or operation. The optimal conditions for this hydration occur when water is present at 40°C to 120°C. This process is characterized by the transformation of magnesia into magnesia hydroxide according to this reaction: $MgO + H_2O \rightarrow Mg(OH)_2$

The rate of the reaction depends on temperature, the magnesia content of the brick, and pressure (if water is present in the vapor phase). The hydration rate with liquid water is slow, but as soon as the water penetrates as steam the

hydration becomes faster. Hydration of magnesia to magnesium hydroxide or brucite (consist of powder) results in an increase in volume of the bricks due to density change up to 115% (figure-20).
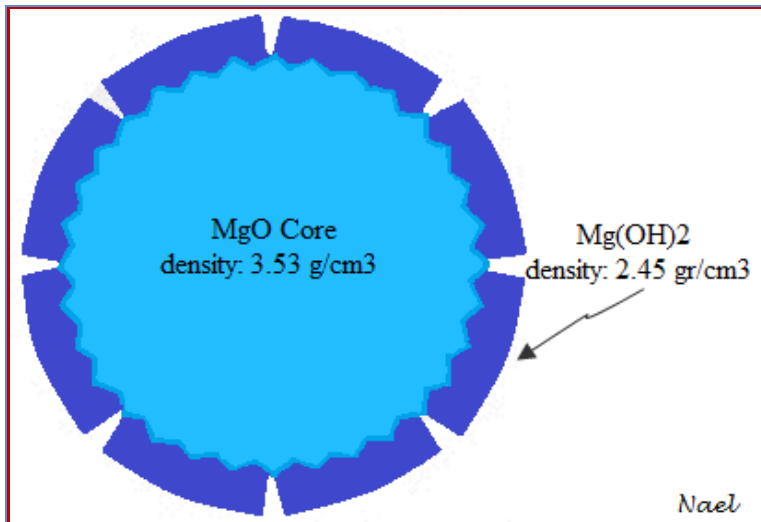

Figure-20: Volumetric expansion due to differences in densities

Figure-21 shows how extensive hydration leads to crack formation in the bricks and can subsequently lead to disintegration of the whole brick.
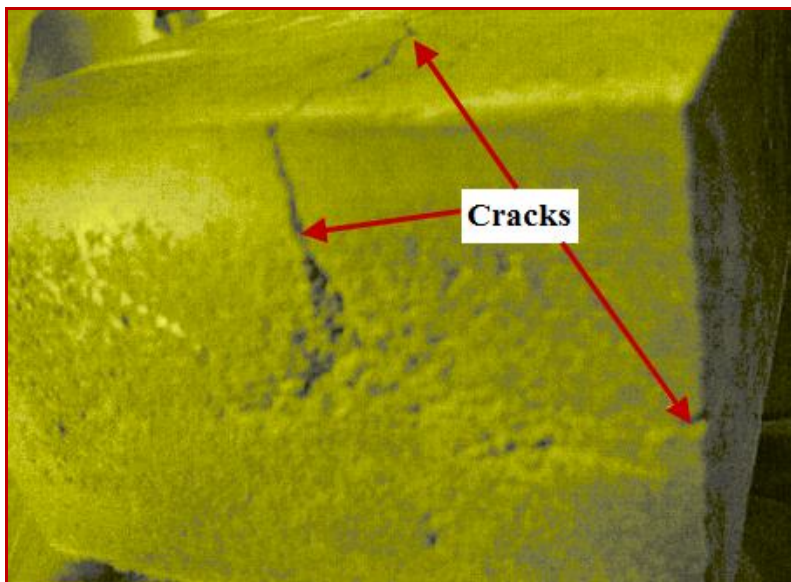

Figure-21: Hydrated magnesite bricks after one month of service

In industry, this mechanism is referred to as 'dusting' (figure-22). On the other hand, the volume expansion leads to brickwork movement which can affect directly on refractory lining inside the kiln. Hydrated bricks should not be used during construction and kiln shouldn't be operated if such bricks are present in the structure.
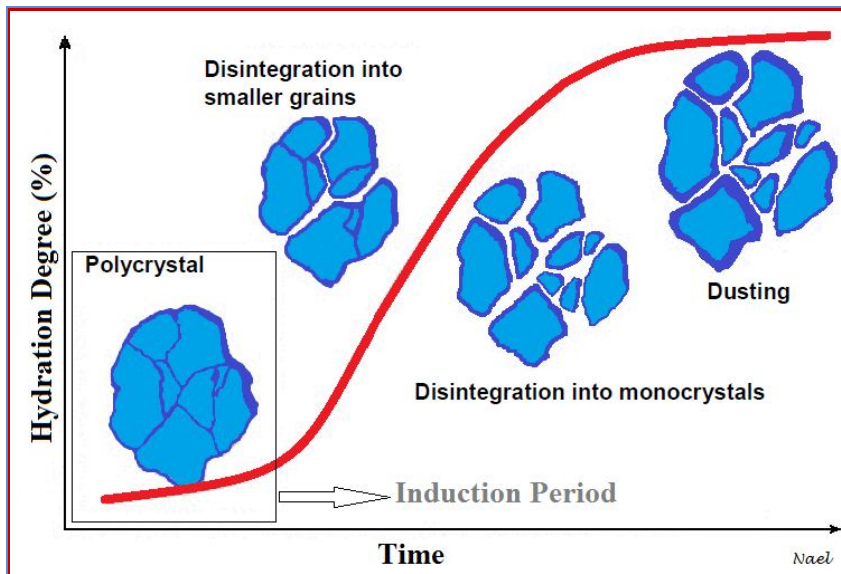
Figure-22: Hydration mechanism of polycrystalline magnesia

Magnesia hydroxide decomposes thermally at approximately 330°C, and the last traces of water are expelled at higher temperatures to yield MgO as shown in the reaction: $Mg(OH)_2 \rightarrow MgO + H_2O$

Although the reaction is reversible, the damage to the bricks in the form of cracks has already taken place. Reversing this reaction will therefore result in more porous bricks, which will lead to an increased and deeper molten material penetration.

The most important steps need to be considered to avoid or reduce the possibility of magnesia bricks hydration are:

1). Magnesia bricks must be transported in a container to protect the material against moisture.

2). Magnesia bricks should be stored inside storage rooms where it is dry, free of frost, ventilated, and with a temperature between 10°C and 30°C (see figure-23). Note that magnesia bricks storage underneath a tarpaulin cover outside is not sufficient.

3). Bricks may not be stored for more than four weeks prior to installation and preheating.

4). Lining should be protected against moisture during installation and preheating.
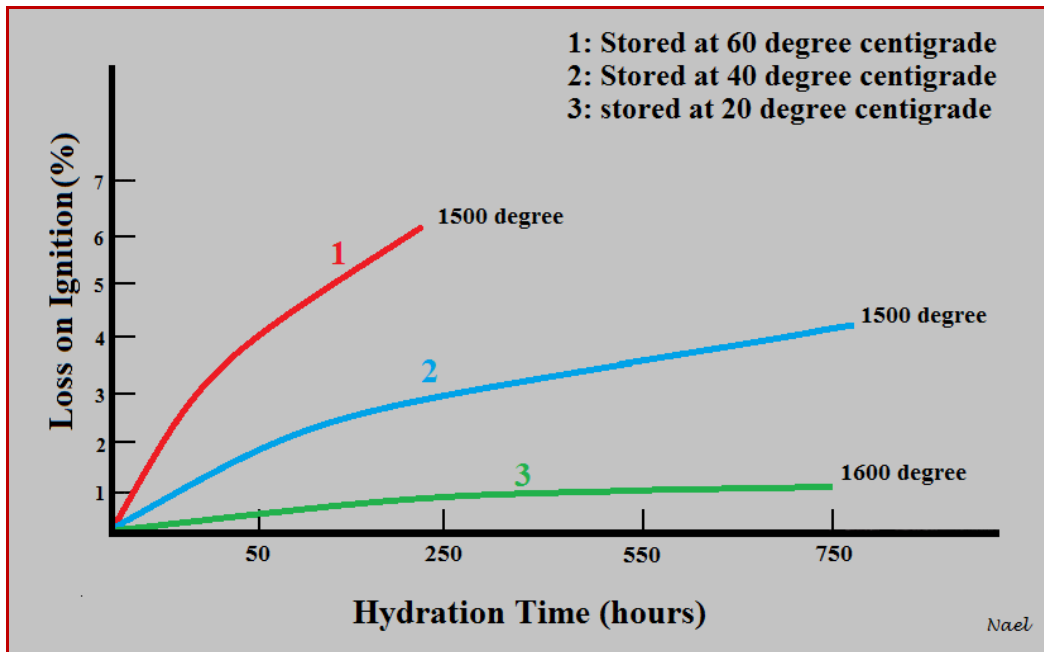
Figure-23: Magnesia bricks storage with different temperature

Figure-23 is showing the relation between magnesia bricks storage temperature and the degree of hydration in term of "loss on ignition". As the temperature of storage room reduce, the hydration degree of magnesia bricks reduce.

Question-13: How can hydration of magnesia bricks be test throughout its life cycle?

Answer-13: The easiest ways to test the hydration of magnesia bricks are summarized below as the following:

1. The extent of hydration in magnesia bricks can be tested by light tapping with a metallic hammer. A metallic sound is an indication that the brick has not been hydrated and is usable, whereas a dull sound indicates that the brick has been hydrated and is unusable.

2. A white coating on the external face of a brick which is associated with brittleness, loose structure and cracking, is a sign of hydration. The white outside layer may not adversely affect the serviceability of the bricks, but if the white $Mg(OH)_2$ continues to the inside of the brick, the degree of hydration is advanced. Testing for deeper brick hydration is a destructive process, since the brick must be broken to perform a visual inspection.

3. The best and exact degree of hydration can be determined by loss in ignition test. This is done by drying brick pieces at 110°C for four hours and measuring the weight. The dried brick is then placed in a furnace and heated for 12 hours at 1050°C, after which the weight is measured again. The difference in weight between the dry specimen and the furnace-heated specimen is an indication of the degree of hydration . Ignition loss of a not hydrated (new) magnesia-chrome brick is approximately 0.2%.

- Bricks with (0.2% to 0.6%) ignition loss; don't damage during heating-up and can be used.
- Bricks with (0.6% to 1.0%) ignition loss; indicate that there is danger of destruction during heating-up .
- Bricks with more than 1.0 % ignition loss; indicate that the serviceability of bricks is restricted .

Example: (Loss on Ignition Test)

Two samples of magnesia bricks (figure-24) were heated in the furnace up to 110°C & then to 1050°C. Weight of the samples after heating and ignition loss measurement were noted and recorded:

Sample-1: MAGKOR-B-RA [fired chromite ore free magnesia spinel]
- Magnesia content: 92-93%
- Initial Weight: 388.7 grams
- Weight after heating at 110°C for 4 hours: 387.3 grams
- Weight after heating at 1050°C for 12 hours: 368.6 grams

Loss on Ignition = (387.3 - 368.6) / 387.3 = 0.483 %

Sample-2: PERILEX 83 [magnesia chromite]
- Magnesia content: 81 - 85%
- Initial Weight: 405.8 grams
- Weight after heating at 110 °C for 4 hours: 404.2 grams
- Weight after heating at 1050 °C for 12 hours: 403.3 grams
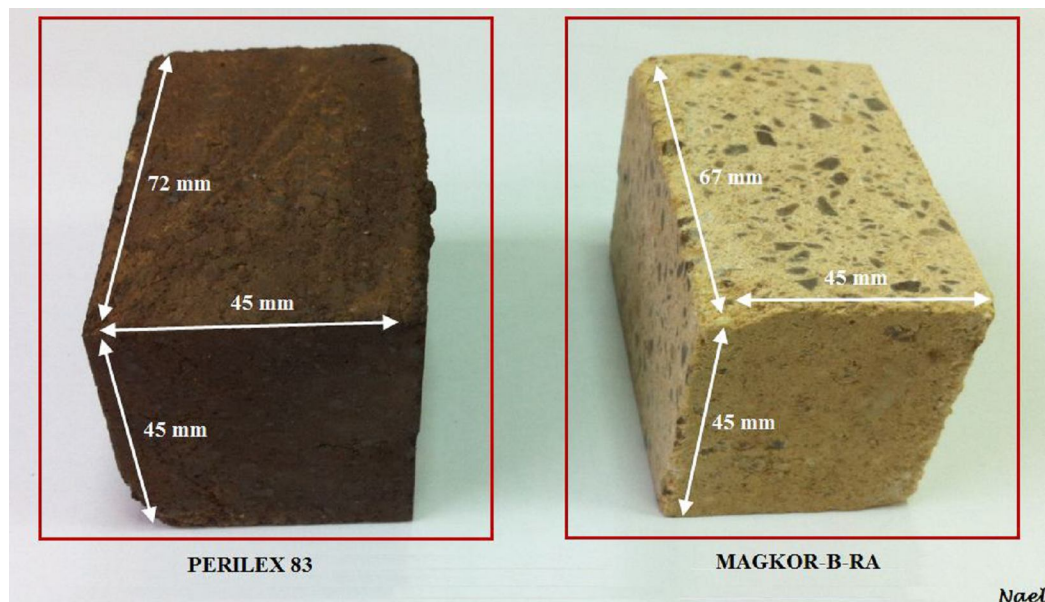
Loss in Ignition = (404.2 – 403.3) / 404.2 = 0.022 %

Figure-24: Magnesia brick samples after heating to 1050°C

Question-14: **What is the basis need to be followed in refractories Classification?**

Answer-14: Refractories can be classified on the basis of chemical composition form, physical form, dense or insulating form, or methods of manufacture form.

a). Classification Based on Refractories Chemical Composition: Refractories are typically classified on the basis of their chemical behavior. Accordingly the refractory materials are of three classes

1. Acid Refractories: are those which are attacked by alkalis (basic slags). These are used in areas where slag and atmosphere are acidic. Silica refractories (greater than 92% SiO_2) and siliceous refractories (78% to 92% SiO_2) are examples of acid refractories.

2. Basic Refractories: are those which are attacked by acid slags but stable to alkaline slags, dusts and fumes at elevated temperatures. Magnesia (MgO) is a very common example. Other examples include dolomite and chrome-magnesia. 3 . Neutral Refractories: are chemically stable to both acids and bases and are used in areas where slag and atmosphere are either acidic or basic. The common examples of these materials are Carbon graphite (most inert), chromites (Cr_2O_3), and alumina.

b). Classification Based on Refractory Physical Form: These are the shaped and unshaped refractories. The former is commonly known as refractory bricks and the latter as "monolithic" refractories (figure-25).

1. Shaped Refractories: are those which have fixed shaped when delivered to the user. These are what we call bricks. Brick shapes divided into two groups; standard Shape and special Shape.

2. Unshaped Refractories: are without definite form and are only given shape upon application. It forms joint less lining and are better known as monolithic refractories. These are categorized as Plastic refractories, ramming mixes, castables, gunning mixes, fettling mixes and mortars.

- Castable Refractories: These are the materials that contain cement binder usually aluminate cement, which imparts hydraulic setting properties when mixed with water.
- Coating Refractories: This type of product is used to protect refractory linings usually against chemical attack.
- Mortars: Are generally neither classified under refractory brick nor monolithic refractories. These are finely ground refractory materials, which become plastic when mixed with water.
- Gunning Mixes: Are granular refractory materials sprayed on application area, used for patching and maintenance works for kilns and furnace.
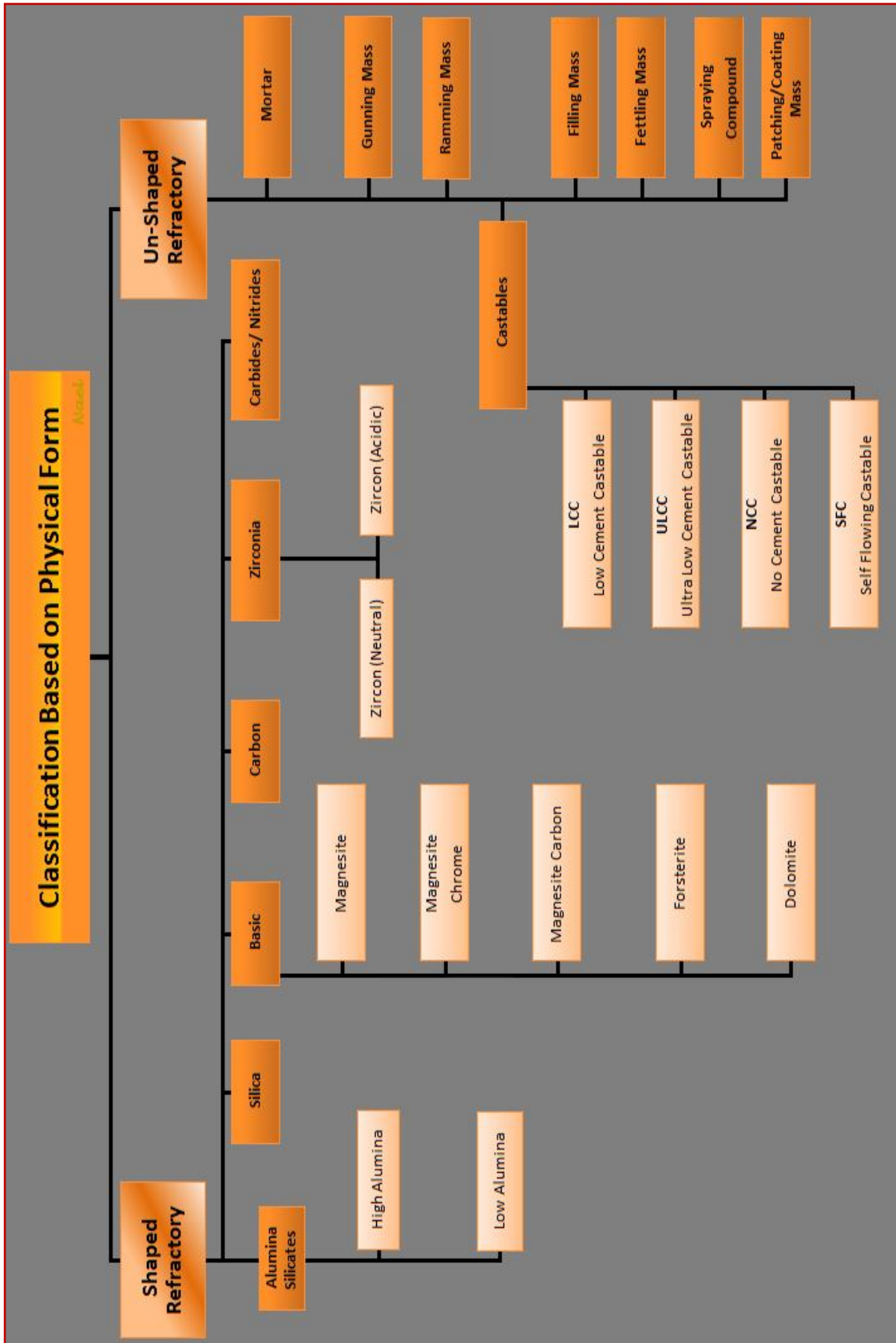
Figure-25: Physical Form Refractory Classification

c). Classification Based on Insulating or Dense Form:

1. Insulating Refractories: have lower densities and provide insulating properties, while offering resistance to corrosion and chemical reactions with the operating environment. Generally; refractory thermal conductivity depends on the chemical and mineral composition of the material and increases with decreasing porosity. Figure-26 shows the thermal conductivities of some common refractories.
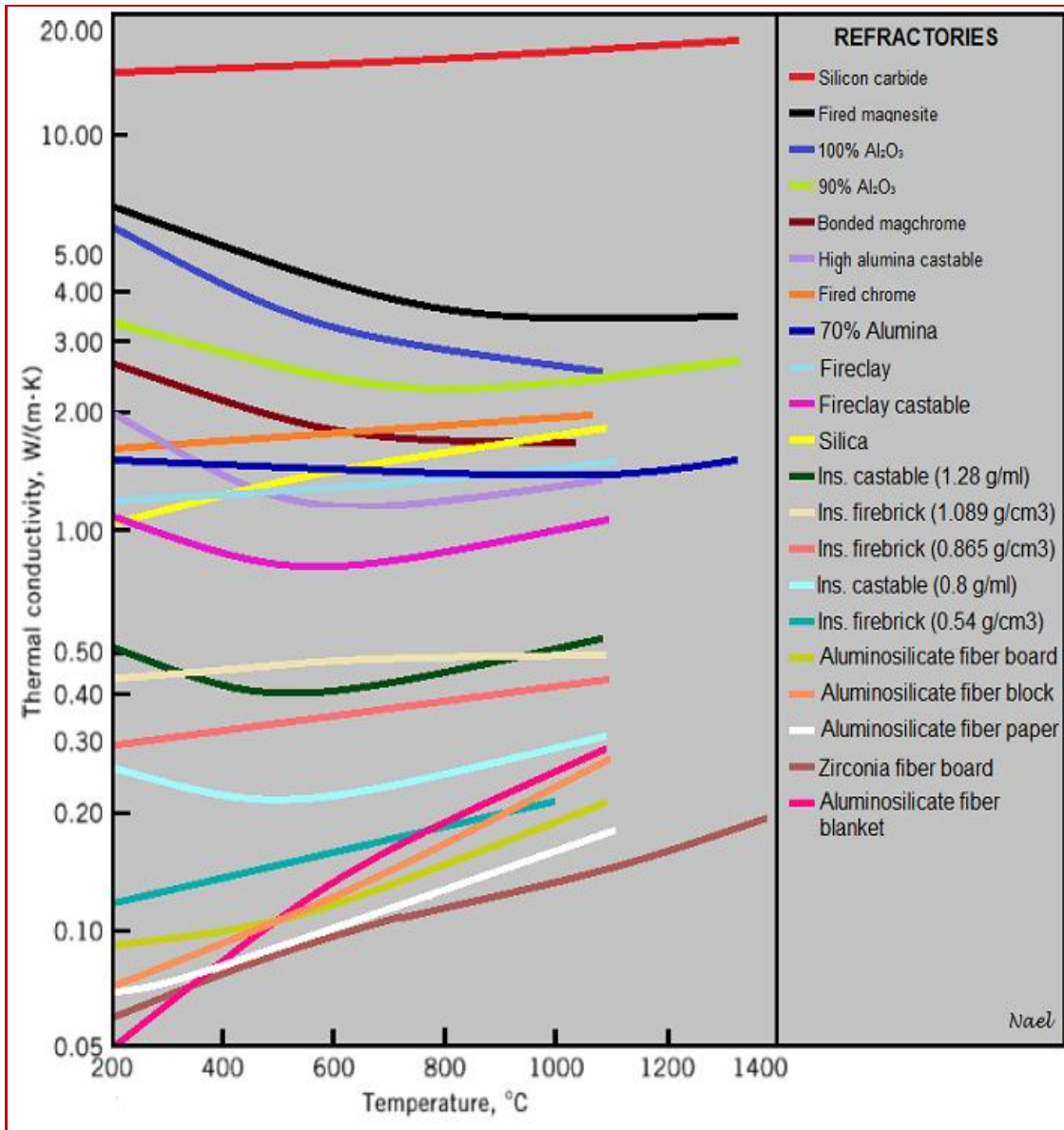

Figure-26: Thermal Conductivity of Refractories

In most cases, glass (silica), mineral wool, high alumina, mulite, or zirconia are the base materials and can be used to temperatures as high as 1593°C. This class of materials has a lower density that varies from 0.064 to 0.19 g/cm^3 offers

higher thermal resistance compared to firebricks. In all cases, thermal conductivity of the insulation increases significantly as temperature increases. Insulating materials can be classified with respect to application temperature as showing below:

- Heat resistant insulating materials for application temperatures up to 1090°C as calcium silicate materials and alumino-silicate fibers.
- Refractory insulating materials for application temperatures up to 1370°C as lightweight chamotte, kaolin bricks, mixed fibers and aluminum oxide fibers.
- High refractory insulating materials for application temperatures up to 1700°C as lightweight mullite and alumina bricks, lightweight hollow sphere corundum castables and bricks, and special high refractory fibers.
- Ultra-high refractory insulating materials for application temperatures up to 1980°C as zirconia lightweight bricks and fibers.

2. Dense Refractories: Refractories with a density higher than 1.9 g/cm^3. They offer excellent resistance in challenging operating environments, such as slags with different chemical compositions, fumes, dust, and gases. Dense refractories classified to several groups as below:

- Fire-clay brick Refractories: Fire-clay bricks comprise about 75% of the production of refractories on a volume basis and are essentially hydrated aluminum silicates. They subdivided into four major classifications (figure-27) depending primarily upon fusion temperature.

Fireclay Brick	SiO_2 (%)	Al_2O_3 (%)	Others (%)	Melting Temp. (°C)
Super Duty	49-53	40-44	5-7	1746-1760
High Duty	50-80	35-40	5-9	1691-1746
Medium Duty	60-70	26-36	5-9	1635-1691
Low Duty	60-70	23-33	6-10	1521-1593

Figure-27: Classification of fireclay bricks

- High Alumina Refractories: Alumina is one of the most chemically stable oxides known, which offers excellent hardness, strength and spalling resistance. The refractoriness of high alumina refractories increases with increase of alumina percentage.
- Silica Refractories: Silica brick is a refractory material containing at least 93% SiO_2. From a volume standpoint silica brick are second only to fire clay brick. The outstanding property of silica brick is its excellent mechanical strength at temperatures approaching their actual fusion point.

- Magnesite: Magnesite refractories are chemically basic materials, containing at least 85% magnesium oxide. These are made from naturally occurring magnesite ($MgCO_3$) and Silica (SiO_2). The physical properties of this class of brick are generally poor, and their great value is primarily in their resistance to basic slags.
- Dolomite: The natural double carbonate dolomite ($CaCO_3$– $MgCO_3$) can be converted to refractory dolomite (CaO- MgO) by high temperature firing. Dolomite refractories is found to be the most compatible material with the cement kiln clinker as it provides excellent coating stability, has very good resistance to thermal shock & alkali attack in varying kiln operating conditions.
- Chromite Refractories: A distinction must be made between chrome-magnesite refractories and magnesite-chrome refractories.
  Chrome-magnesite refractories: Usually contains 15-35% Cr_2O_3 & 42-50% MgO. These materials can withstand corrosive slags and gasses and have high refractoriness.
  Magnesite-chromite refractories: Magnesite-chromite refractories contain at least 60% MgO and 8-18% Cr_2O_3. Magnesite-chromite usually has a better spalling resistance than chrome-magnesite.
- Zirconia Refractories: Zirconium dioxide (ZrO_2) is a polymorphic material. There are certain difficulties in its usage and fabrication as a refractory material.
- Monolithic Refractories: This name generally given to all unshaped refractory products. Castable and gunning materials are common monolithic refractories.

The figure below (figure-28) is showing refractories classification based on insulation which has a density less than 1.12 g/cm^3 or dense which has a density more than 1.9 b/cm^3.
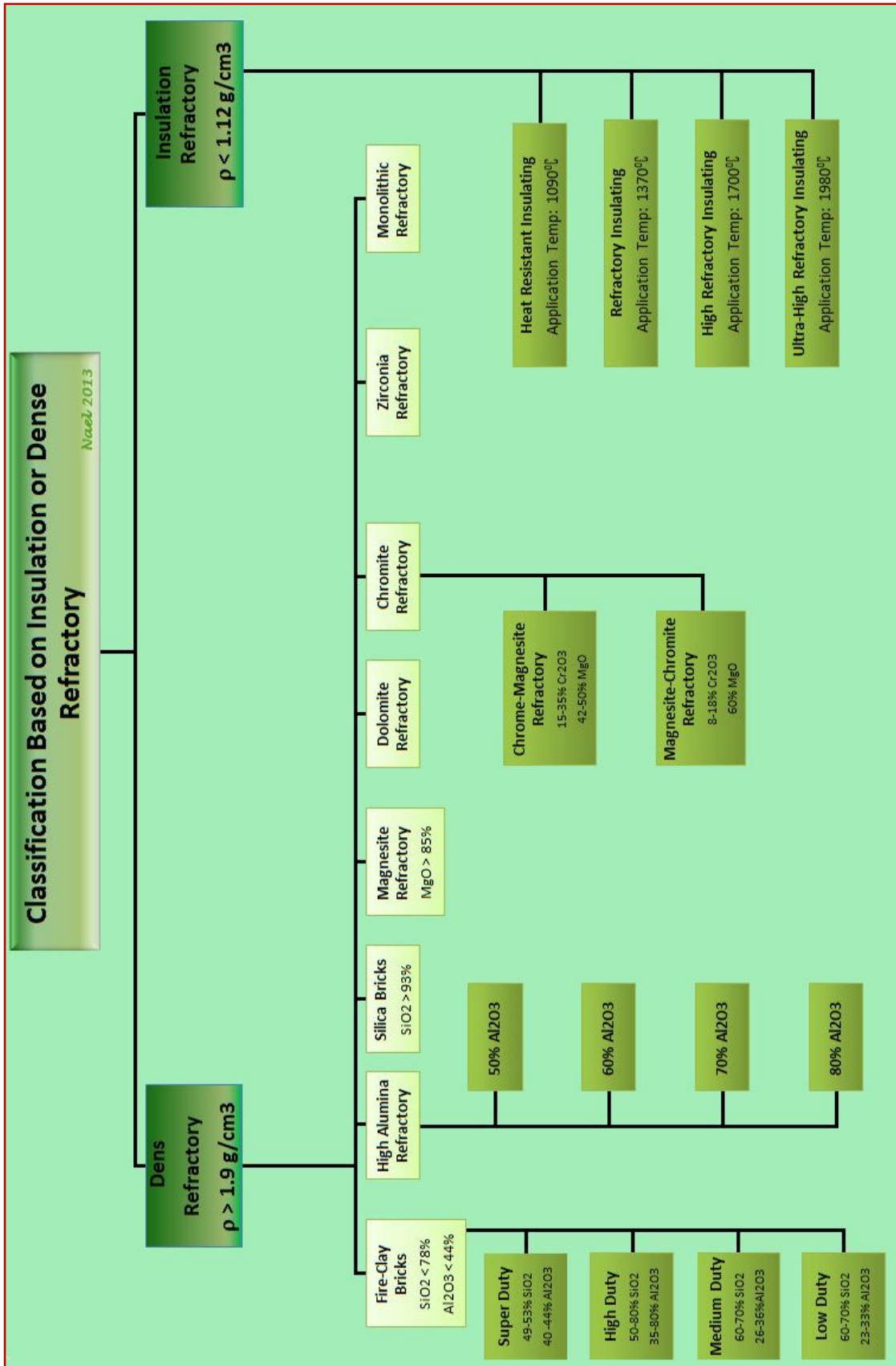
Figure-28: Insulation or dense refractory classification

Dense refractories, like most other solids, expand upon heating, but much less than most metals. The degree of refractories expansion depends mainly on the chemical composition. A diagram of the thermal expansion of the most common refractories is shown in figure-29.
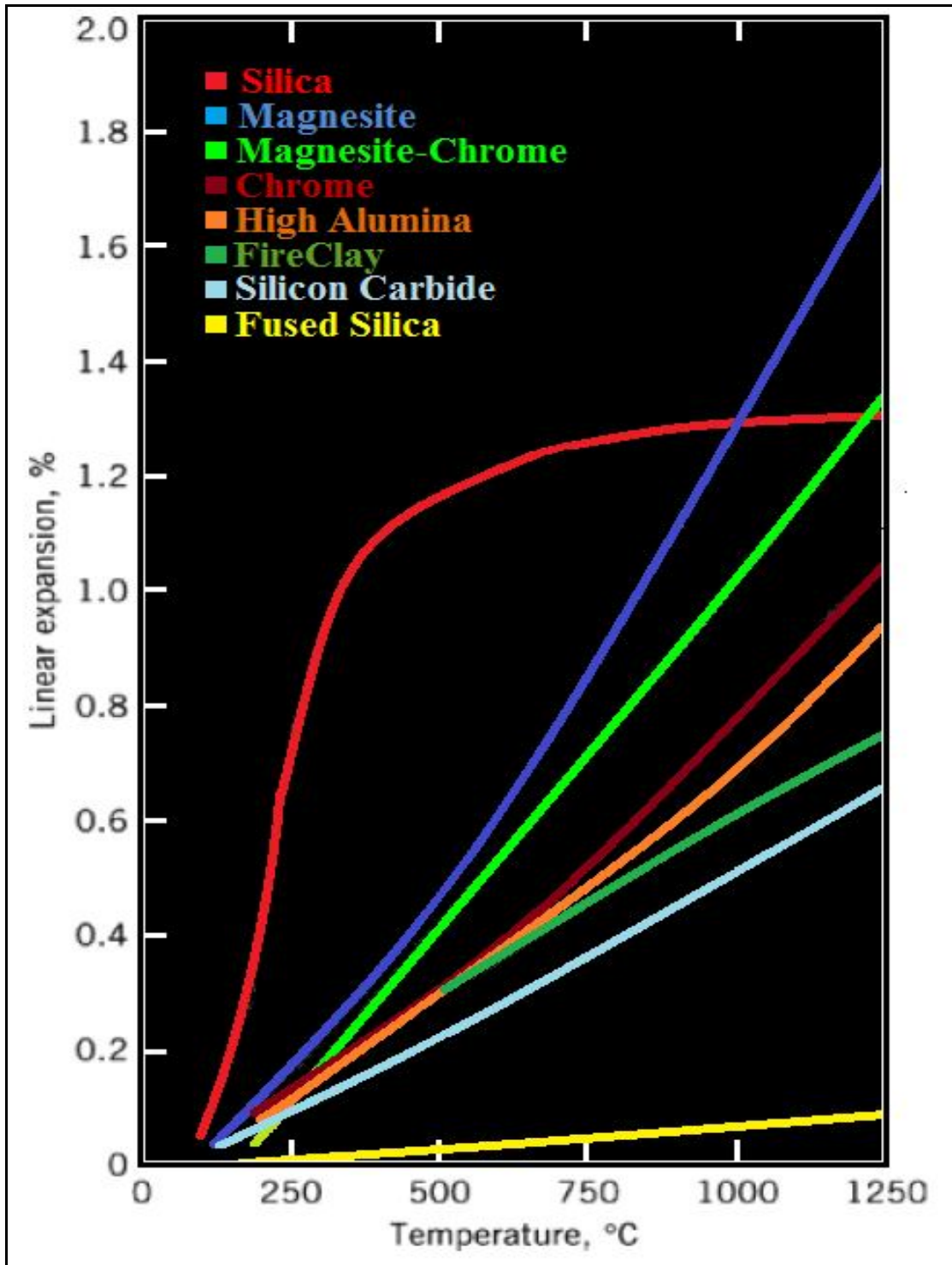

Figure-29: Thermal expansion values of common dens refractories

d). Classification Based on Method of Manufacture: The refractories can be manufactured in either of these methods: Dry Press Process, Fused Cast, Hand Molded, Formed (Normal, Fired or chemical bonded), and Unformed (Monolithic – Plastics, Ramming mass, Gunning, Cast able, Spraying).

e). ASTM Classification: ASTM also publishes a list of classifications covering a wide variety of refractory types (figure-30). According to ASTM; refractories are classified to:

1. Fireclay & High Alumina Brick: High alumina bricks are classified according to alumina content, starting at 50% and continuing up to 99% Al_2O_3.

2. Basic Brick: Chrome brick, chrome–magnesite brick, magnesite–chrome brick, and magnesite brick. There are six classes of chrome–magnesite and magnesite–chrome brick starting with 30% MgO and increasing in 10% increments to 80% MgO.

3. Insulating Brick: Insulating firebricks are classified by groups as shown in figure-30 corresponds to the service temperature divided by 100. For example, group 16 corresponds to a test temperature of 1600∘F (871∘C).

4. Mullite Refractories: This brick must have Al_2O_3 content between 56 and 79% and contain less than 5% impurities.

5. Silica Brick: Silica bricks are classified in two types. Types A and B silica bricks are classified according to chemical composition and strength. Type A brick must have a flux factor ≤ 0.5. The flux factor is equal to the percent alumina plus twice the percent of alkalis. Type B is all other silica brick covered by the standard chemical and strength specifications.

6. Zircon Refractories: Zircon refractories are classified in two types. Types A and B have the same chemical requirements of not less than 60% ZrO_2 and not less than 30% SiO_2.

7. Castable Refractories: Hydraulic-setting refractory castables are classified into five classifications:

a). Conventional or Regular Castable (CC): Conventional castable class contains hydraulic setting cement and has total calcium oxide content greater than 2.5%. This class is subdivided into a normal strength and high strength class.

b). Low Cement Castable (LCC): Low cement castable is classified on the basis of calcium oxide with a value of 1-2.5 %.

c). Ultra-Low Cement Castable (ULCC): Ultra low cement castable is classified on the basis of calcium oxide with a value of 0.2-1.0 %.

d). No-Cement Castable (NCC): No-cement castable is classified on the basis of calcium oxide with maximum value of 0.2 %.

e). Insulating Castable Refractories: The lime content is not a result of a hydraulic setting cement constituent but comes from aggregate impurities.
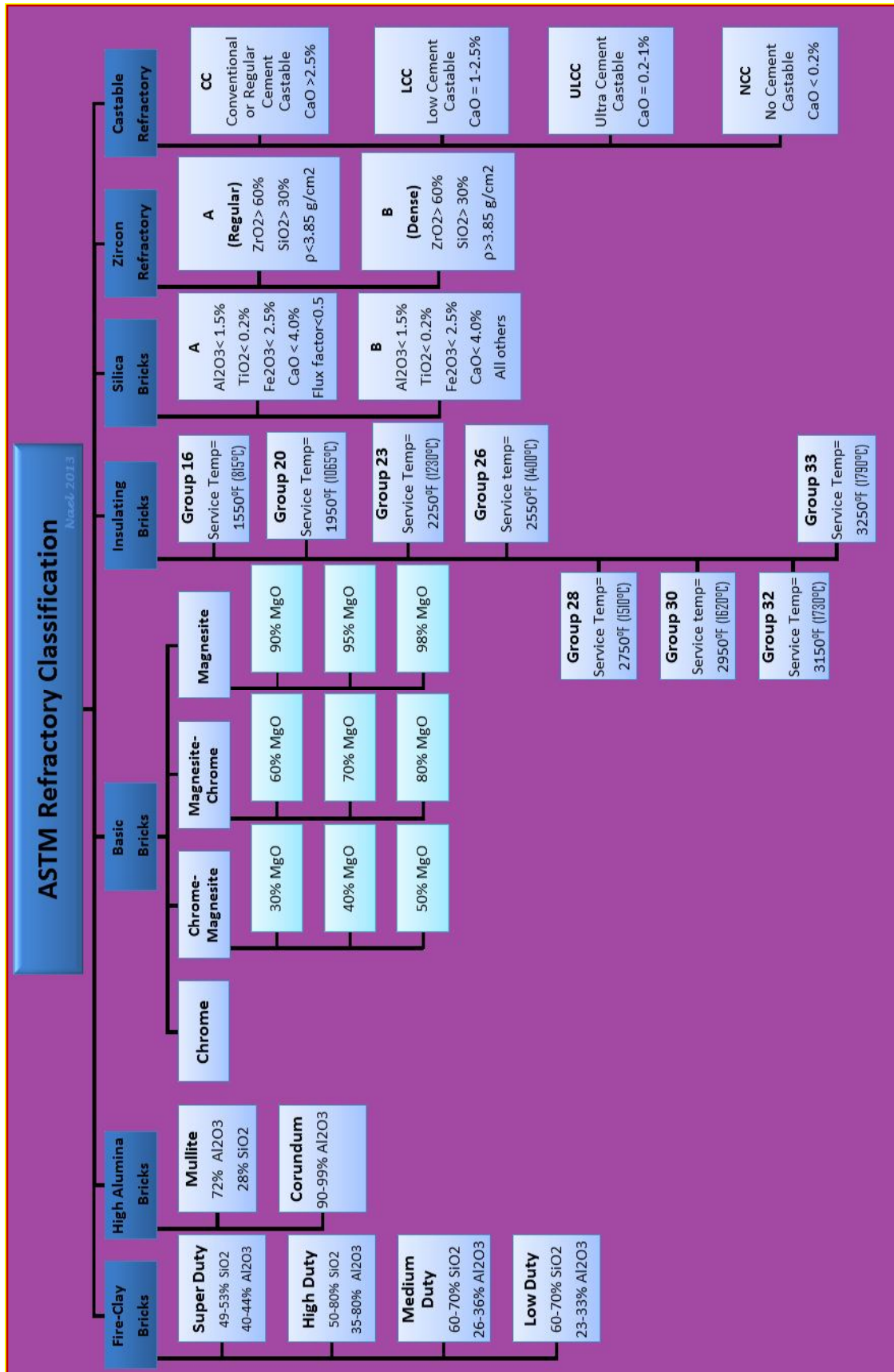
Figure-30: ASTM refractory classification

Question-15: What is the mechanism of kiln shell corrosion behind the refractory lining?

Answer-15: Corrosion of the rotary kiln shell behind the refractory lining has become an increasingly serious problem for cement industry as it acts silently and reduces the shell thickness to below critical structural and mechanical limits of stability of kiln shell. Understanding the factors influencing the kiln shell corrosion and its formation mechanism is the best way to inhibit it. Corrosion of kiln shell behind the refractory is influenced by a number of factors such as composition of the metallic shell and its environment, temperature of the shell, cleanliness or roughness of the shell surface, its contact with other materials and severe process conditions. Carbon dioxide and sulphur dioxide are active scaling agents of iron and steel. The main reason of shell corrosion can be attributed to alternate oxidation at high temperature and acidic reaction at low temperatures when the kiln is stopped for repairs. The corrosion phenomenon takes place mainly due to presence of oxides, chlorides and sulphide at high temperature. There are three different kinds of kiln shell corrosion are observed in cement kiln systems:

1- Corrosion during kiln operation resulting in *scaling* of the kiln shell by oxidation of the metallic iron at elevated temperature (so-called high temperature corrosion) as shown in figure-31/A.

2 - *Rusting* during longer kiln shut downs caused by condensation or absorption of humid (moist air, water) as shown in figure-31/B.

3 - *Wear* of oxidized kiln shell during longer kiln shut downs caused by small blackflies eating iron compounds (called Ferrum Pedis syndrome) as shown in figure-31/C.
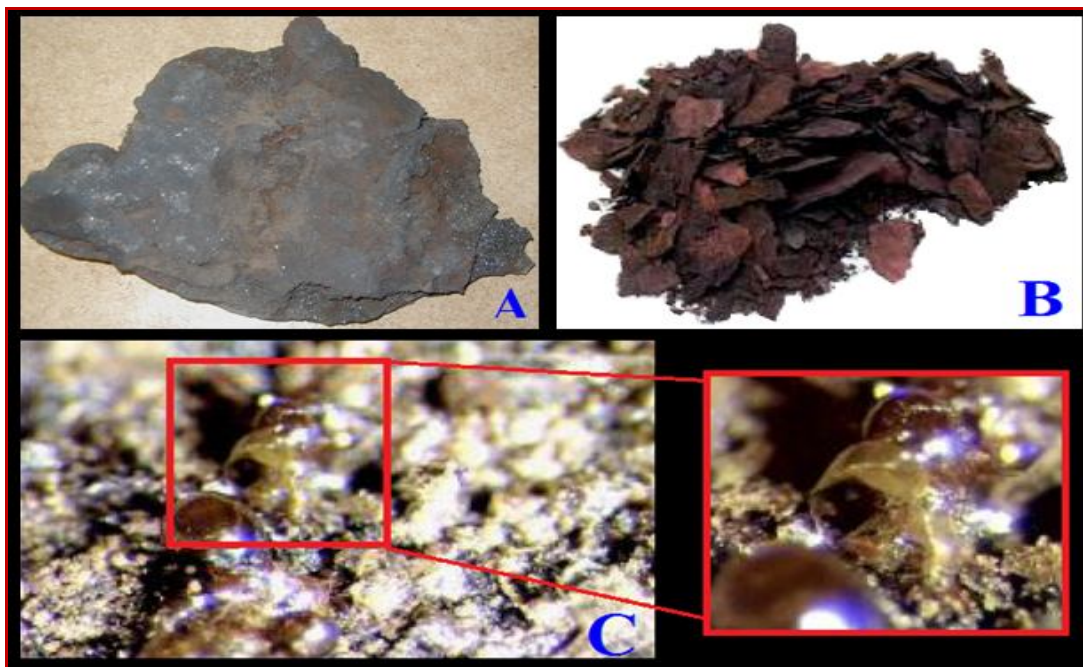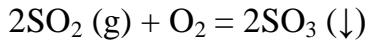

Figure-31: The different kinds of kiln shell corrosion forms behind refractory

The reactions inside the kiln are different from reactions on the kiln shell surface since both the temperature and atmosphere are different. One of the most important reactions in the lining is the oxygen consumption where SO_2 consumes oxygen and condenses as SO_3:

$2SO_2 (g) + O_2 = 2SO_3 (\downarrow)$

The SO_3 formed condenses as calcium or magnesium salts. The result can be that an oxidizing environment inside the kiln turns into a reducing environment at the kiln shell.

Figure-32 is showing the mechanism of kiln shell corrosion which passes mainly through four phases:
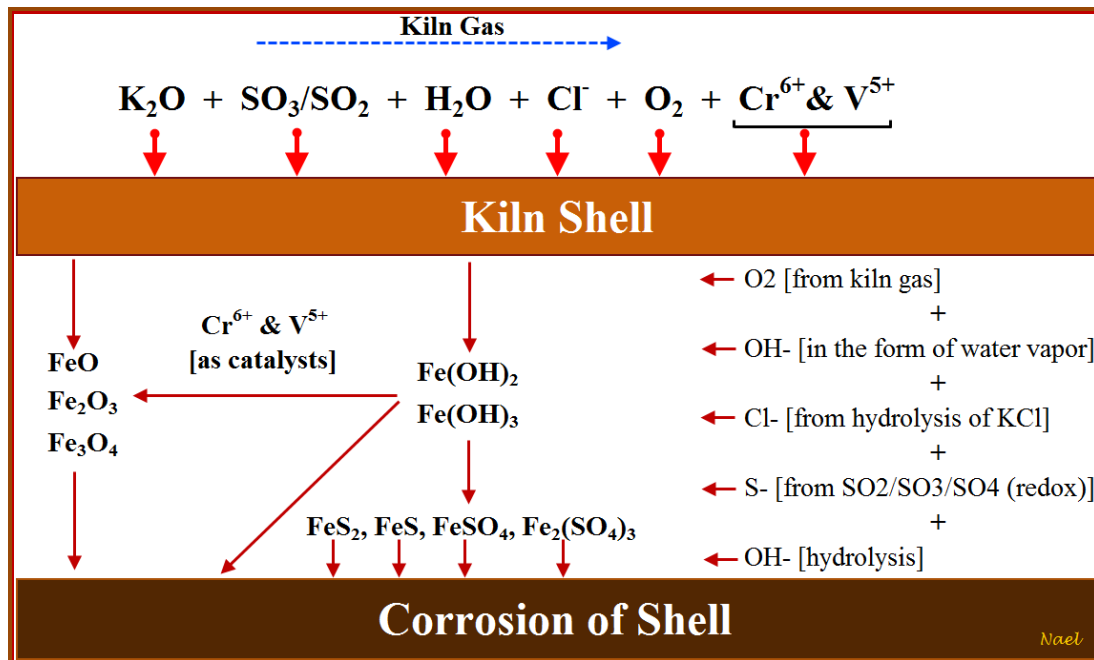

Figure-32: Schematic mechanism of kiln shell

1- Oxidation under high temperature:
In an oxidizing atmosphere, the iron from the steel shell will react with oxygen to form an oxide scale. Generally, this oxide scale is formed by more or less firm layers of different iron oxides. The compound with the highest oxygen content (Fe_2O_3) finds at the scale-brick interface and the compound with the highest iron content (FeO) at the metal-scale interface.

2- Sulphidization under high temperature:
When no oxygen is present, SO_2 takes over as the oxygen donor and a different reaction occurs. The reaction may be written as follows:

$4Fe + 2SO_2 (g) = Fe_3O_4 + FeS_2$
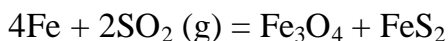
Accordingly, a sulphidization reaction can be identified by the occurrence of either pyrite (FeS_2) or pyrrhotite (FeS) in the corrosion products.

As sulphide layers are more porous than oxide layers, the corrosion rate of the shell will increase. However, experience from different plants shows that, as long as chlorides are not present, the corrosion rate stays at an acceptably low level.

3- Chloride attack under high temperature:

Sulphidization is enhanced by the presence of chlorides, mainly because they affect the morphology of the corrosion scale, hindering the formation of a strong, protective oxide layer.

The total reaction is a chain process taking place at different temperatures. A temperature gradient between the kiln atmosphere and the kiln shell is created by the porous deposit and the refractory lining. The first reaction of the chain process takes place in the kiln and can be described as high temperature hydrolysis of the thermally unstable alkali chlorides (KCl) to form the more stable sulphates as showing in figure-33 and the reaction below:

$$2KCl(g)+H_2O(g)+SO_2(g)+\tfrac{1}{2}\,O_2(g) = K_2SO_4+2HCl(g) \quad [T > 900^{o}C]$$
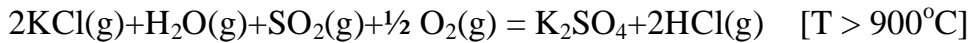
This reaction step is followed by re-oxidation of hydrogen chloride gas (by oxygen or SO_2) at lower temperatures to produce elemental chlorine (Cl_2) which attacks the kiln shell.

$$2HCl\ (g) + \tfrac{1}{2}\,O_2\ (g) = \mathbf{Cl_2\ (g)} + H_2O \quad [T < 400^{o}C]$$
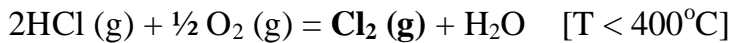
Once Cl_2 (g) is formed, it can reach the kiln shell through the refractory bricks or through the gaps/joints within and between rings and will react with either the oxide-sulphide layers or (most likely) directly with the kiln shell according to the following reactions resulting in the corrosion of the kiln shell:

$$FeS+Fe_3O_4+4Cl_2 = 4FeCl_2+SO_2+O_2 \quad [\text{Reaction with the oxide-sulphide layers}]$$

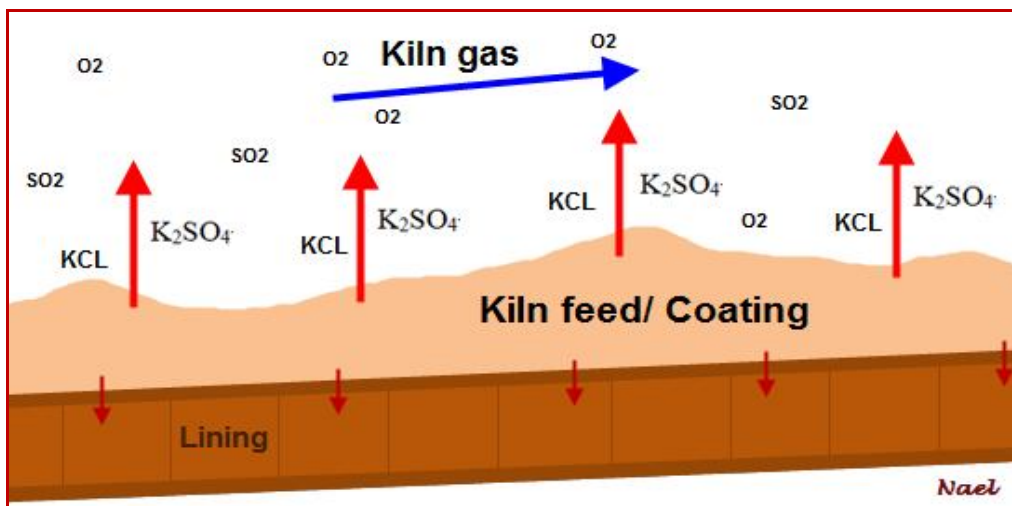$$Fe+Cl_2 = FeCl_2 \quad [\text{Reaction with the kiln shell}]$$
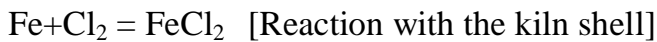

Figure-33: Hydrolysis of thermally unstable potassium chlorides

4- Hygroscopic material attack:

During kiln shutdowns, deposit of salts containing potassium chloride in particular on the shell becomes active because being hygroscopic (absorbs atmospheric moisture). The chloride can reach the kiln shell in the form of gases but alkalis can only penetrate refractory lining as a part of liquid potassium and Sodium salt melts. So if product of corrosion contain substantial amount of potassium and sodium, the form of corrosion is termed as hot corrosion indicating that liquid phase take part in reaction.

See the figure below (figure-34) which is showing the analysis of seven different samples of scales. Note the formation of Magnetite (Fe_3O_4), Hematite (Fe_2O_3), Pyrrhotite (FeS), and Pyrite (FeS_2) in each scale sample.

Sample	A	B	C	D	E	F	G
Chemical analysis (wt.%)							
Fe_2O_3	44	90	88	17	56	n.a.	81
SO_3	11	7	5	1	1		-
K_2O	24	-	2	43	16		6
Na_2O	4	-	-	-	2		1
Cl^-	6	1	4	36	11		6
F^-	7	-	-	-	-		-
PbO	-	-	1	-	-		-
Mineral Phases (XRD)							
Fe_3O_4		xxx	xxx	x	xx	xxx	xx
Fe_2O_3	xxx			x	xx		xxx
FeS		xx	xx	x	x	xx	
FeS_2		xx					
$Fe(OH)_2$				x			
$FeSO_4.H_2O$						x	
K_2SO_4	xx						
KCl	xx		x	xxx	xx	xx	xx
Na_2SO_4				x	x		
NaCl							x
NaF	x						
$Pb_2(SO_4)O$			x				

Figure-34: Composition of different scales

Question-16: What are the actions require stopping the kiln shell corrosion phenomenon?

Answer-16: It is really difficult to stop the shell corrosion phenomenon as it is difficult to control all the factors influencing the shell corrosion. Surly; there are a number of preventive actions which may help us to minimize the tendency and rate of shell corrosion. These actions could be summarized in 8 points:

1. It seems to be more successful to apply different type of gas-tight coatings or paints on the inner kiln shell to lessen the chloride attack. The inner kiln shell

should be coated with the available anti corrosive paint (figure-35) immediately after de-lining. This will also help in preventing the absorption of atmospheric moisture by hygroscopic compounds such as KCl.

Figure-35: Kiln shell painting

2. Silicon Carbide compounds are an effective solution for corrosion resistance. At operating temperature, decomposition and oxidation form specific glass phases blocking the porosity and forming new phases with the alkalis without disruptive growth.

Figure-36: Kiln shell after de-lining

3. As kiln shell temperature is of major importance to the speed of shell corrosion (figure-37), the shell temperature from outside should not exceed 300°C. Additional cooling fans should be provided for effective external cooling. In addition, the selection of bricks in this area should be reviewed with respect to their thermal conductivity and wear rate pattern. If there is no coating on bricks in that area, high wear rate leads to reduced residual lining thickness leading to higher shell temperature. Therefore, Refractory bricks with relatively lower thermal conductivity and high wear resistance should be preferred in the corrosion affected area.

Figure-37: Corroded high temp area of kiln shell after removal of brick lining

4. Application of spreader jack should be done in each ring at the time of closing the individual rings and due care should be taken so that bricks do not crush or develop internal cracks due to pressure applied by spreader jack. By using Spreader jack we can fix the brick ring with very less gaps in between refractories. So chances of alkali attack through gap in between brick will be very less. The ring should be closed using key bricks instead of cutting and fixing with the help of hammer.

5. Basic reason of corrosion is alkalis so to remove these alkalis we can use alkali by-pass system (figure-38).
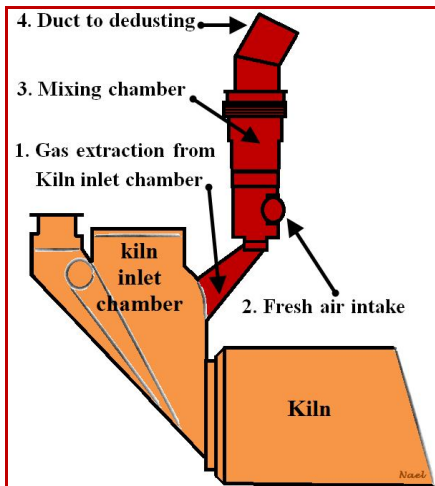

Figure-38: Bypass system

6. Although basic refractories are costlier than neutral refractories, high quality basic refractory is highly recommended as they provide more service time and more resistance to corrosion and alkali attack.
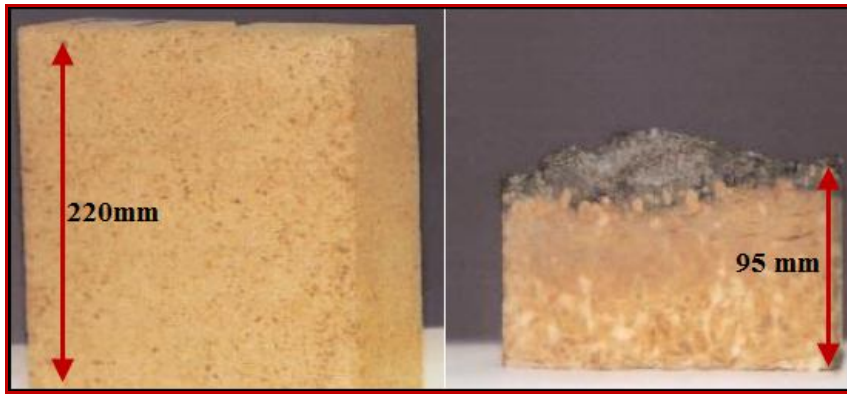
Figure-38: Excessive wear of brick in short time

7. As the intrusions of volatiles take place not only through the bricks but also through joints and gaps created during the campaign. It is recommended that a thorough study of lining quality, attention should be given to two characteristics, namely permeability and reversal thermal expansion of bricks. While permeability plays a role in allowing gases/liquids to reach up to kiln shell, the reversal thermal expansion gives an idea of extent of shrinkage a particular brick undergo when the kiln temperature is reduced from its normal operating temperature to any lower temperature.

8. The shell corrosion is attributed to a large extent to poor oxidizing conditions prevailing in the kiln. The best measure against chloride promoted sulphidization is to keep a steady and sufficient supply of fresh air to the surface of the kiln shell. The oxygen at kiln inlet should be maintained at 1.5 % minimum to ensure proper oxidizing conditions with CO not exceeding 0.1% at this point.

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