MINIMIZE REFRACTORY CHALLENGES IN SUSTAINABLE WAY WHEN USING ALTERNATIVE FUELS IN CEMENT PRODUCTION PROCESS

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Summary

Due to scarcity of fossil fuels worldwide and to cut down the fuel cost, most of the high temperature processing industries are switching to alternative fuels like pet coke, waste from agriculture, households, pharmaceutical etc. These economical substitutes of fossils fuels emit less CO_2 when burnt, but have a higher percentage of volatile matter, especially alkalis, sulfur, chlorides, and ash forming matter which leads to increased coating formation, corrosion, and erosion of refractory in most of the cement plants. Tests with ash/slag from waste and biomass incineration and post-mortem analyses on refractory castables help to understand the corrosion mechanism and to choose the right refractory material. At many cement plants worldwide, a Precast Refractory Solution by HASLE Refractories A/S has proven to enhance the lifetime of the refractory lining for the critical areas of the cement plant in a more sustainable way.

Introduction

Cement manufacturing is a high energy intensive process and fuel consumed accounts for almost 30-40% cost of production of cement. To meet this energy requirement, the industry has mostly depended on fossil fuels like coal, petroleum, and natural gases since the beginning of cement production. But due to scarcity of these natural resources and high emission of CO_2 when burning fossil fuels (approximate 5% of global CO_2-emission comes from the cement industry), the industry has in the last 2-3 decades started using different alternative fuels (AF) like pet coke, agriculture waste, municipal solid waste, pharmaceutical waste, rejected tyres etc. (Picture 1).

Many of these alternative fuels have a higher calorific value (Table 1) compared to fossil fuel which make it economical to use and, at the same time, when burnt, many alternative fuels produce less CO_2 and green house gases.

Picture 1: Different type of alternate fuels

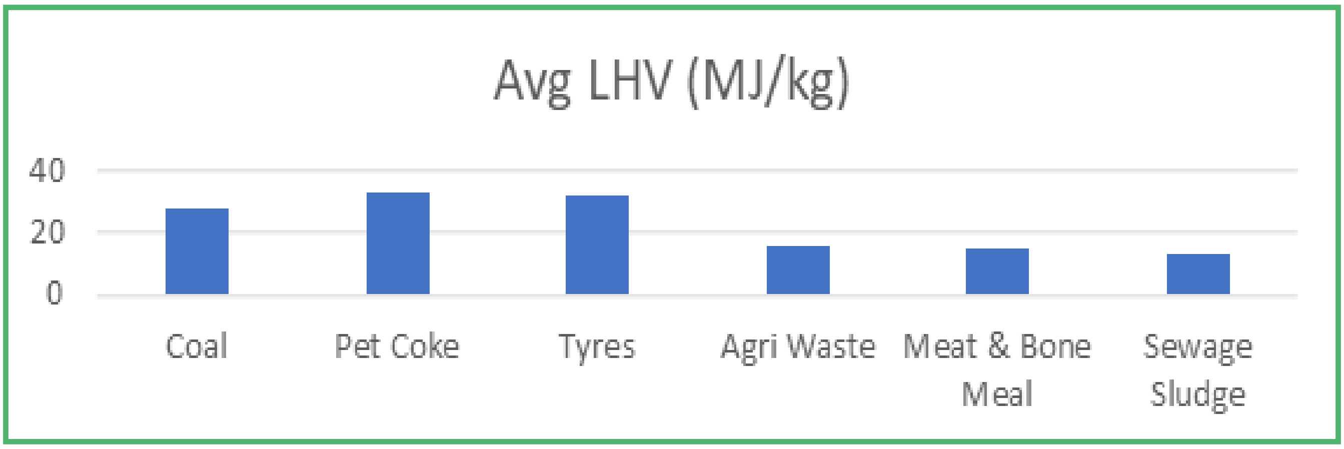


Table 1: Lower Heat Value (LHV) of different type of alternative fuels

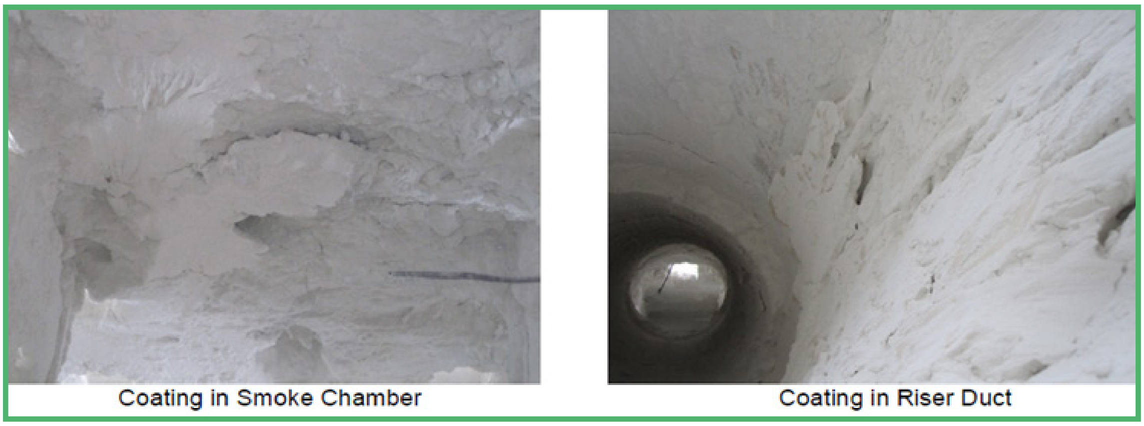
Hence, by substituting fossil fuel with alternative fuel, the cement industry can reduce its carbon footprint, make the society cleaner by consuming waste, preserve natural resources and at the same time minimize its cement production cost.

On the other hand, there are some process challenges like poor heat distribution, unstable pre-calciner operations, higher SO_2, NOx and CO emission, dusty kilns and a significant fraction of alternative fuels produce incombustible material that forms fly ashes during firing and a high extent of volatile matter such as alkalis (sodium and potassium), sulfur and chlorides which may occur in different proportions depending on the combination of fuels.

As an example, municipal solid waste normally forms ash with a high content of alkalis and chlorine. Combined with sulfur-containing pet-coke this gives a high risk of coating on the refractory lining (Picture 2). inside the cement kiln system. With this the mix of sulfur, sodium, potassium and chlorine, the circulation of volatile salts increase and cause build-up and clogging, especially in the lower preheater cyclones, feed pipes, riser duct and kiln inlet (Picture 4).Besides build-up, alkali vapours and oxides released from firing organic waste may infiltrate the refractory lining and cause spalling as they react with the refractory minerals and form crystalline changes that may burst the lining (Picture 3). Alkali problems are most common when firing municipal solid waste or agricultural waste.

Picture 2: Coating formed in Meal Pipes

Picture 3: Refractory Crack due to Alkali Spalling



Picture 4: Coating formed in smoke chamber and riser area

Chemistry Involved

Most of the refractories (except kiln basic bricks) used in cement plants are alumina-silica refractories. Alkalis (Na_2O, K_2O), sulphates (Na_2SO_4, K_2SO_4), chlorides (NaCl, KCl) and carbonates (Na_2CO_3, K_2CO_3) present in systems, infiltrate in refractory lining and react with alumina and free silica of refractory and form low melting compounds with refractory. This chemical corrosion starts at temperatures as low as 700°C and becomes more hazardous at elevated temperatures. The phases formed due to KCl and K_2SO_4 were kalsilite, kaliophilte (both $K_2O\cdot Al_2O_3\cdot 2SiO_2$ and leucite ($K_2O\cdot Al2O3\cdot 4SiO_2$) and exposure to Na_2CO_3 led to the formation of nepheline ($Na_2O\cdot Al_2O_3\cdot 2SiO_2$). The formation of these phases causes high volume expansions of between 20% to 25% in the refractory lining and leads to refractory crack and sometime bursting.

Alkalis from Feed (CaO, K_2O, Na_2O) + Sulphates & Chlorides from AF (SO_3, Cl) => Alkali Sulphates (Na_2SO_4, K_2SO_4) + Alkali Chlorides ($NaCl$, KCl)

$$3Al_2O_3.2SiO_2 + Na_2SO_4/K_2SO_4/\ NaCl/KCl \Rightarrow K_2O{\cdot}Al_2O_3{\cdot}2SiO_2/\ K_2O{\cdot}Al_2O_3{\cdot}4SiO2/\ Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$$

The introduction of this excessive concentration of alkali salts, sulphates, chlorides in the kiln system, hampers the overall performance of refractories and causes a lot of coating formation on refractory surface and premature failure of refractories (Picture 5), which in turn leads to unplanned breakdowns/ shutdowns of cement plants.

Picture 5: Refractory failure due to heavy chemical attack

To minimize these challenges when using alternative fuels, the refractory used should be of such quality that it does not allow these chemicals to react and infiltrate the inside matrix of the refractory. This is possible by using high grade raw materials to manufacture refractory and by maintaining a very low open porosity, which will not allow salts to react with and infiltrate the refractory.

Laboratory Tests

To check this chemical inertness and infiltration of salts in the refractory, HASLE does a refractory cup test in their own laboratory. A cup of castable is made and subsequently coating collected from a cement plant site or different combinations of salts like (Na_2SO_4, K_2SO_4, $NaCl$, KCl, Na_2CO_3, K_2CO_3) are kept inside the cup and heated to 11000 C. This temperature is held for 5 hours. After cooling the sample, the cup is cut into two parts and chemical reaction and infiltration can be seen on the surface of the refractory (Picture 6).

Picture 6: Cup test to check infiltration of chemicals in the refractory

In another test where the refractory is not able to resist these salts, a chemical reaction takes place and the chemical goes deep inside the castable which leads to alkali spalling and heavy erosion of the refractory (Picture 7).

Picture 7: Cup test to show Alkali Spalling and Infiltration of Chemicals in Refractory

Experimental Setup and Laboratory Analysis

Effect of Volatile Compounds from ash on Low Cement Castables

To study the effect of volatile matter from waste incineration on different low cement castables, ash/slag was collected and homogenized to grain size < 200µm. A container sized 200x200x200 mm was casted from an alkali resistant alumina-silica low cement castable and pre-fired at 1300°C. In this container 3 x 3 castable samples size 40x40x160 mm were embedded with ash placed in layers to ensure that each castable specimen was exposed to ash from all sides. The container was covered by a lid and placed in an electrical furnace at 950°C for 48 hours.

Table 2: Chemical analysis of ash and experimental set up, where castable specimens were embedded in ash and heated to 950°C to study the effect of gaseous phases.

Oxide	Percentage
SiO_2	10.55
Al_2O_3	3.01
Fe_2O_3	3.54
TiO_2	0.19
CaO	48.95
MgO	9.39
K_2O	10.80
Na_2O	0.91
MnO	4.31
P_2O_5	4.38
SO_3	2.74

After exposure to the ash the castable samples were analysed with respect to physical performance and microstructure.

Effect of liquid phases from slag on low cement castables

Coating occurs as the alkali-sulfur-chloride compounds lower the melting temperature of the refractory material and particulate matter sticks to the surface. The coating can be more or less liquid depending on temperature and does not only build-up on the surface but may also corrode the lining.

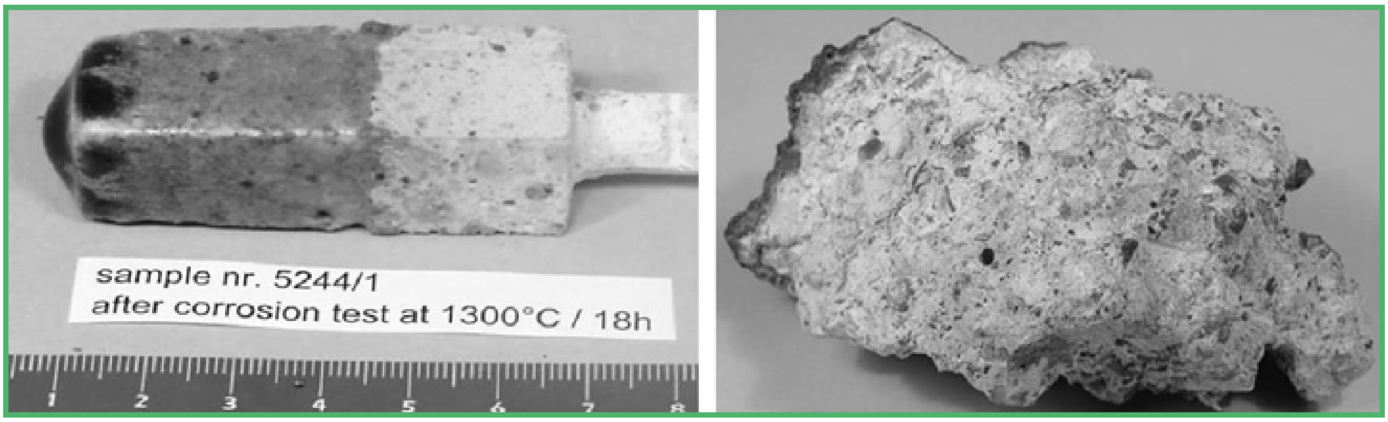


Figure 8: Dynamic finger dip test (left) of melted slag from waste incineration against HASLE LCC and post-mortem sample of the castable (right) after one year of operation.

Corrosion by liquids can be studied in the laboratory by dynamic tests as the finger dip test (CEN/TS 15418) and gives a good indication of castable resistance against slags (Figure 8, left). The most accurate way to understand the corrosion mechanisms is to analyse samples of castables that have been in operation (Figure 8, right).

Results and Discussion

The influence of volatile elements in ash from waste incineration on exposed castables

Gaseous phases of alkalis in ash are highly mobile and react almost instantly with the refractory material. Following exposure to the alkali-rich ash for only 48 hours, the properties of the castable have significantly changed; the compression strength (CCS) and bending strength (MOR) are lowered and the open porosity has increased (Table 3).

Castable Properties	Change (%)
Density	nd
Cold crushing Strength	-8.3
Cold modulus of Rupture	-23.7
Open porosity	+7.6

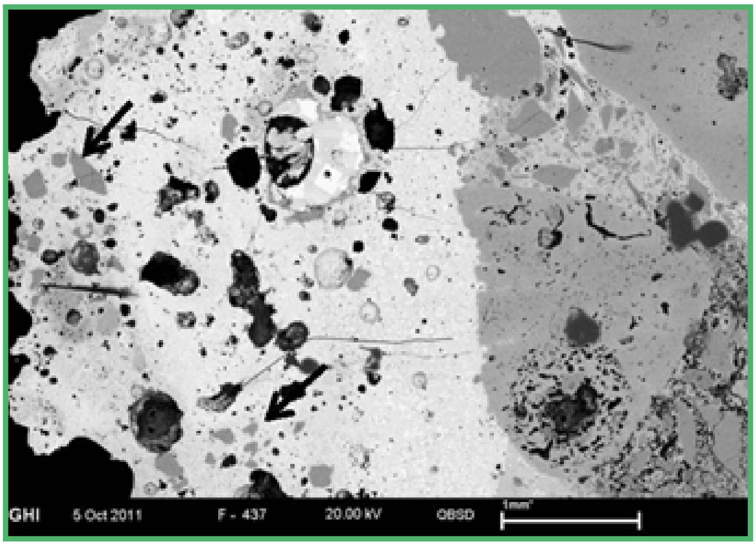
Castable microstructure	Chemical compostion(%)			
	Al_2O3	SiO_2	Fe_2O3	K_2O
Reaction zone ash vs castable	39.1	15.2	1.1	44.6
Glassy phase	26.9	60.6	0	12.5
Dense aggregate	77.9	19.8	0	2.3

Table 3 : Relative change of physical parameters of a low cement alumina-silica low cement castable after exposure to ash and the chemical composition of the reaction zone and surface layer (right)

Volatile potassium infiltrates and migrates into the refractory lining, whereas sulfur was not found inside the casted pieces in this case (Table 3). The reaction zone between the castable and the ash was heavily enriched by potassium and the zone appeared porous and fragile. Under the reaction zone patches of SiO_2 rich glassy phases were found with high potassium content which indicates that alkalis to some extent have been encapsulated. Potassium was also found in more dense alumina-rich grains near the surface.

Analysis of Post Mortem Sample

Analysis by scanning electron microscopy of the sample from waste incineration (Picture 9) shows that the slag has infiltrated the matrix and slowly eroded the refractory lining by washing out grains of aggregates that are subsequently embedded in the coating and adds to the build-up.



Picture 9: The coating (light part) on a post-mortem castable sample (dark part). The melted slag has infiltrated the castable and small fractions of the castable can be seen in the coating (arrows)

These relatively simple experimental set-ups and analysis clearly illustrate how the gaseous and liquid phases from thermal treatment of alternative fuels concurrently affects refractory materials, and may cause deleterious effects in a cement kiln. Alkalis react with the alumina-silicates of the refractory and may even infiltrate aggregates causing structural changes, whereas the liquid phases infiltrate the matrix and corrodes the lining by washing out grains and forming build up.

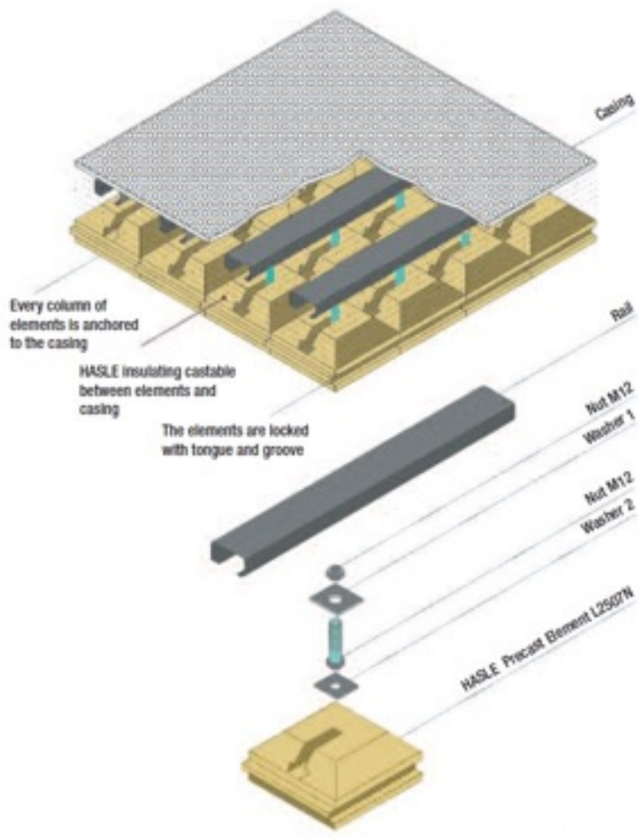
An optimal refractory lining in the critical areas at a cement plant must be strong and dense and with a low open porosity to minimize the infiltration of both gaseous and liquid phases. Very low open porosity of refractory materials can be achieved by optimization of the particle size distribution. HASLE Precast is characterised by very low values of open porosity; 10-11% at 1000-1500°C as these precast elements are made under very strict supervision for water addition, mixing, casting and most important preheating in very controlled atmosphere to ensure a low apparent porosity and high strength of the precast elements.

Preheating reduces the number of micro cracks that inevitably are formed by thermal shock during fast heat-up which increases the risk of chemical attack from both gaseous and liquid phases of alkalis, sulfur and chloride.

HASLE Precast Modular Lining

As an optimal alternative to preheating on site, the best castable performance can be achieved by using precast and preheated elements that are made ready-to-use. At HASLE Refractories A/S we manufacture lining systems under controlled condition in our production facility. Castable mixing, casting and preheating are optimized to give the elements a very low porosity and dense surface, which in combination with raw material properties ensures protection from corrosion.

Some of the cement plants in India had serious problems with coatings in the kiln inlet area, feed pipe caused by alkali and sulfates from the use of alternative fuels; in this case rubber combined with pet-coke and coal. Heavy build-up and clogging in the preheater cyclone feed pipes and riser ducts lead to reduced production capacity and unstable calciner operation. HASLE precast Modular Lining was selected to solve the problems.



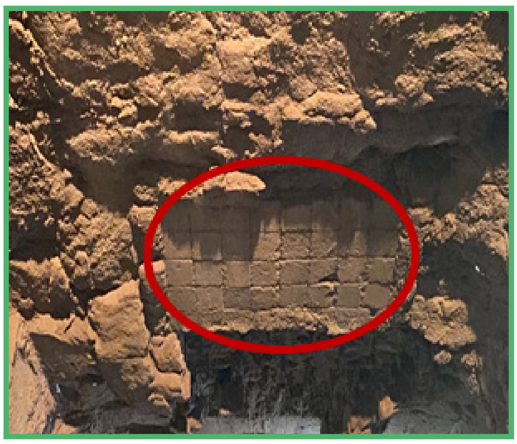
Picture 10: HASLE precast modular lining

HASLE's well known Modular Lining system is based on 248 x 248 mm precast elements. Each element is secured by a bolt and washer which slide into a steel rail. This system can be installed on all kinds of roofs, vertical and sloping walls. On vertical walls a foundation block is used to support the system. The benefits of this flexible system have been proved in many cement plants worldwide, for their smoke chambers and riser ducts, preheater cyclones, feed pipes, inlet arch, grate cooler walls and bull nose etc.

The Modular Lining system not only helps reduce coating on refractory and increase the lifetime of lining but also lining thickness can be reduced up to 185 mm with same thermal profile. This way plants can reduce their refractory consumption for unit square meter area. This way, the Modular Lining also supports the cement plant in achieving its sustainable development goals.

Kiln Smoke Chamber and Riser

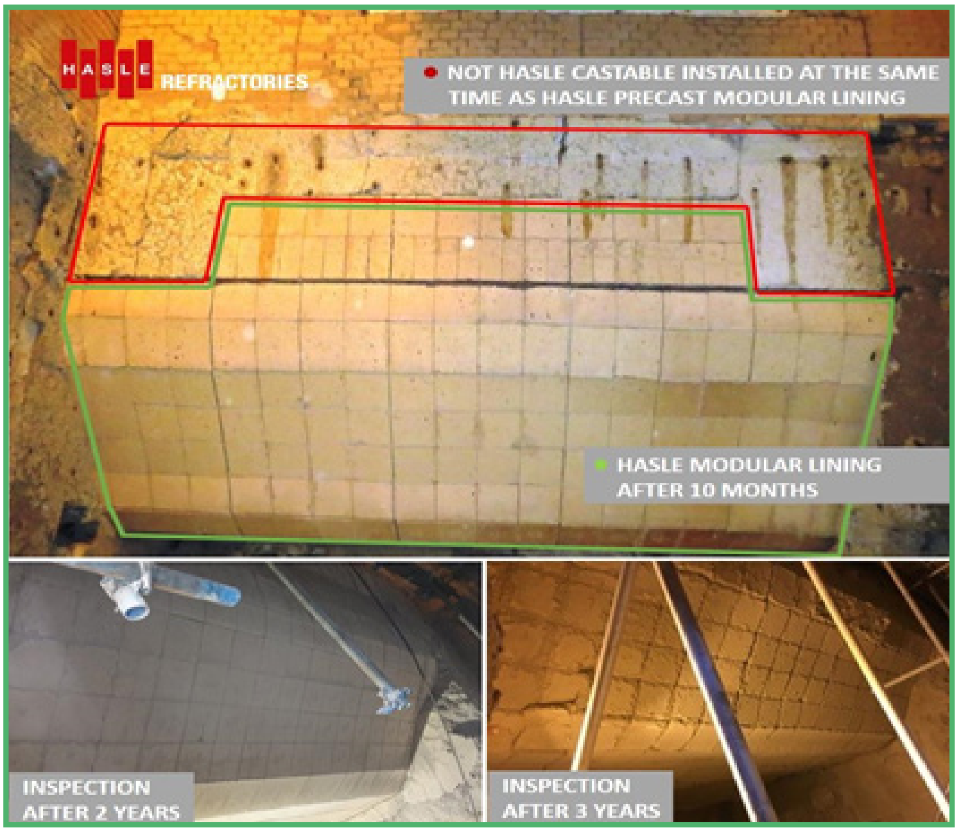
Kiln smoke chamber and riser are prone to heavy coating deposition and chemical attack which frequently cause refractory failure. Consequently, low cement castable needs to be replaced every year.



Picture11: Modular Lining in Kiln Smoke Chamber Riser Area after installation (left) and after three years of operation (bottom right).

Precast solution for cooler bull nose

Cooler bull nose is subjected to high abrasion by clinker dust, chemical attack and high temperatures which challenges the refractory lining. With the HASLE Modular Lining solution a lifetime of three years was achieved against one year by using low cement castable.



Picture12: Cooler bull nose precast after one year, two years and three years of operation

Kiln Burner Pipe

Kiln burners (Picture 13) are the most critical area from a refractory point of view as it is prone to high chemical attack, high temperature and high abrasion from clinker dust. By using a HASLE Low Cement Castable performance of refractory can be improved a lot.

Picture13: Kiln Burner after 12 months of operation using HASLE D59A castable

Cylindrical Precast lining for Feed Pipes

The increased use of alternative fuels challenge the feed pipes (Picture 14) in the preheater tower. Many cement plants face increased build up formation leading to reduced production capacity followed by stoppages for cleaning and repairs. Replacing the high altitude pipes too often requires many resources and safety precautions. HASLE offers a precast solution especially made for pipe linings which performs more than 8 years with good anti coating property.

Figure14: HASLE Cylindrical Precast solution for Feed Pipes and condition after two Years (Extreme right)

Conclusion

The combination of selected material properties, unique particle size distribution, production and design gives the unique performance of HASLE precast and castable solutions in various cement plant applications. The reduced build-up formation on the precast linings ensures not only longer lifetime but also a more trouble-free campaign with less stoppage and cleaning.

HASLE unique refractory lining solution supports cement plants to use more and more alternative fuels with longer refractory life and trouble-free operation with less stoppages in thermal efficient way. Also, longer life of refractory means lesser consumption of refractory and other resources like manpower, metallic anchors, transportation etc. which overall reduces the CO_2

footprint of cement plants. This way, HASLE supports cement plants to make their production process to be more sustainable and economical.

Acknowledgements

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