Effect of Hydration in Magnesia Based Refractories for Lime Kiln Industry

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Abstract

India is at the threshold of rapid growth in steel sector and all efforts are being made for achieving 300 MTPA of production by the year 2025. Since, lime is an integral part of steel making process, increase in steel production requires enhancement of production capacity of lime by installing additional/ new lime kilns.

While executing the recent expansion programme of various steel plants, it is observed that in most of the lime plants, brick lining collapsed during commissioning or prior to commissioning due to hydration of magnesite bricks. Hydration of magnesia (magnesium oxide or periclase, MgO) in refractory material generally occurs when the magnesia comes into contact with humid air, water, or steam. Presence of brucite phase in the sample indicates hydration and also there is a volume expansion up to 115%, due to density change. Extensive hydration leads to crack formation and subsequently disintegration of the whole brick, resulting in total damage of refractory lining inside the kiln.

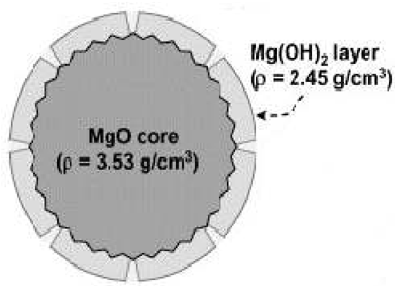
There are quantitative and qualitative methods to assess the degree of hydration of magnesia based refractories. This paper focuses on the study of hydration behavior for magnesia based refractory bricks in correlation with its internal properties along with external properties like manufacturing, storage, transportation and application criteria for such type of refractories are also illustrated here in view of practical aspect.

01. Introduction and fundamentals:

Magnesia based Refractories are widely used due to their high refractoriness, corrosion resistance and basic characteristic. Magnesia refractories are installed in refractory linings for various furnaces and kilns due to their superior properties. Magnesia bricks when compared to other type of refractories, there exists a great concern regarding their vulnerability during exposure with water vapour. Hydration of Magnesia (magnesium oxide or periclase Magnesia) in refractory material occurs when the material comes into contact with humid air, water or steam. This exposure can occur during storage, installation and drying. Magnesia in presence of water produces hydroxides. The hydration of magnesia to magnesium hydroxide [brucite, $Mg(OH)_2$] results in an increase in volume due to change in density.

The extensive hydration leads to crack formation in the brick and can subsequently lead to disintegration of the whole brick. The disintegration occurs as the magnesium hydroxide (brucite) consists of powder which additionally has a bigger volume compared to the original magnesia. Generally, magnesia used in lime kiln refractory is either of dead burnt or fused type, which is produced from natural magnesite ($MgCO_3$) or extracted from sea water.

The physical and chemical properties of magnesia based refractories are more complicated than those of pure magnesia due to different level of impurities. Accordingly hydration reaction is also affected. Hydration reaction may take considerable time also.



02. Theoretical study & experimental results:

The hydration of MgO refractories in lime kiln application was extensively studied. This study presents the experimental results on commercially available magnesia bricks used in lime kiln while tested for hydration resistance at various temperatures, during storage and even during service.

The speed of hydration depends on the contents of magnesia in the brick, its structure and to a great extent on the temperature. By nature MgO tend to react with humidity, even from air and most effective between 40^0C & 120^0C in the following way.

$MgO + H_2O = Mg(OH)_2$

Under water, the hydration is not fast but as soon as the water penetrates into it by evaporated form hydration becomes faster. Magnesia bricks are therefore particularly endangered in humid hot climate and during heating up in the kiln in case wet bricks have been installed.

The hydration of magnesia at room temperature with water vapor proceeds in four steps:

I. Formation of a layer of chemically and physically absorbed water.
II. Diffusion of Mg^{2+} and OH^- ions in the layer of physically absorbed water.
III. Nucleation of brucite.
IV. Crystal growth of $Mg(OH)_2$

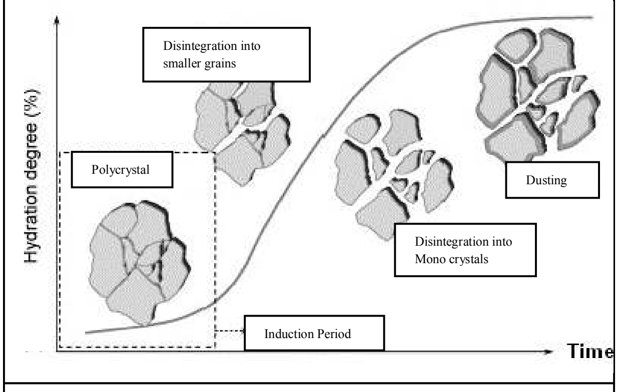
The hydration reaction of magnesium oxide with liquid water or water vapor is a heterogeneous reaction and very dependent on the characteristics and physical properties of magnesia, such as reactivity and surface area. These properties are strongly influenced by the preparation of magnesia, such as the chemical form from which MgO is prepared (i.e. $Mg(OH)_2$, $MgCO_3$, etc.), the calcinations temperature along with the holding time and the preparation atmosphere (vacuum, air, etc.). Both the temperature and the vapor pressures affect the hydration rates for vapor phase hydration.

Since hydration starts from the surface, the specific surface area of magnesia is particularly important for the hydration process. Fine magnesia particles (i.e. with large specific surface area) have high hydration rates. The surface properties of magnesia, such as specific surface area and reactivity are determined by the temperature of the calcinations process and starting materials. The surface area reaches a maximum and then decrease with increasing the calcinations temperature. For example, the surface area of magnesia produced by dehydrating $Mg(OH)_2$ changes from about 320 m^2/g at 350 ^oC to 70m^2/g at 700 ^oC. However, the surface area of magnesia obtained by decomposition of magnesite ($MgCO_3$) increase with the temperature up to 900 ^oC .

The open porosity of magnesia particles is another important property that influences hydration. Solid MgO reacts slowly with water vapor. For porous magnesia, the reaction proceeds between MgO and water condensed in the micro-pores and absorbed on the surfaces of magnesia particles from water vapor. A sintered magnesia clinker has a higher hydration rate than a fused clinker, because typically the sintered magnesia is higher in porosity (8-11%) than the fused magnesia (porosity 3-5%). Also, the fused magnesia has larger crystals, which give a lower surface area; consequently the resistance to hydration is higher than for sintered magnesia. In other words, well-fused magnesia of high density, low porosity, and large crystal size has high hydration resistance.

If fused magnesia single crystals and highly pure polycrystalline magnesia clinker were heated under water vapor at various temperatures from 135 ^oC to 200 ^oC (Temp 135 $^oC \rightarrow 150\ ^oC \rightarrow 165\ ^oC \rightarrow 180\ ^oC \rightarrow 200\ ^oC$) using a specially designed autoclave, the following results were obtained.

1) The transformation of MgO into Mg $(OH)_2$ has an accompanying volume expansion of about 1.5 times.
2) Micro cracks due to volume expansion of hydration, cracks are thought to form during cooling under the influence of temperature and pressure changes.
3) In the hydration rate curves, accelerated hydration in the initial period corresponds with the stage of reaction when the hydration products collide with each other at grain boundaries. With the formation of cracks along the grain boundaries results in destruction of the grain boundaries. In the final stage (2 – 4 hrs) with grain boundary destruction, the hydration reaction is naturally enhanced due to the increased surface area of grains and a dusting reaction takes place, which continues until the ultimate size of single crystals finally reached. No dusting occurs with hydration of single crystals.



Hydration Mechanism of poly crystalline magnesia

03. Effect of Impurities in the Hydration Process of Magnesia

CaO: Up to 5 wt% of CaO can be soluble in MgO. The CaO content in the MgO solid solution decreases as temperature is reduced. The hydration activity of calcium oxide is greater than that of magnesium oxide by approximately 8 times.

SiO_2: Silica can form compounds with MgO. Magnesia forms forsterite (Mg_2SiO_4) at elevated temperatures, which remains along the grain boundaries of periclase crystals and works as a coating to restrict contact with water, improving the hydration resistance of periclase.

CaO/SiO_2 Ratio: Calcium oxide and silica can form a secondary phase around magnesia grains. With an increase in the CaO/SiO_2 ratio, the secondary phases may be monticellite ($CaMgSiO_4$), mervinite ($Ca_3MgSi_2O_8$), dicalcium silicate (Ca_2SiO_4), or a CaO-rich silicate glass. Phase with a higher content of CaO like dicalcium silicate (Ca_2SiO_4) are more sensitive to hydration than periclase, resulting in an increase of the hydration rate of magnesia. Therefore, magnesia refractories with a high CaO/SiO_2 are more sensitive to hydration. A low CaO/SiO_2 ratio (<0.5) results in a high hydration resistance, due to the existence of a silicate glass or forsterite (Mg_2SiO_4) along the magnesia grain boundaries.

Al_2O_3: Alumina may form a solid solution in MgO and magnesia-spinel ($MgAl_2O_4$) with MgO at high temperature. When alumina is present in the magnesia during burning, spinel forms and is then precipitated along magnesia grain boundaries during cooling. The spinel has the effect of a coating on periclase grains and subsequently enhances the hydration resistance of magnesia. This coating effect is most evident when the content of Al_2O_3 is between 2 and 4 wt%. When the content of Al_2O_3 exceeds 4 wt%, the magnesia resistance to hydration is lower, due to the increase in the porosity of the magnesia clinker, caused by the volume expansion of the spinel.

B_2O_3: Small amounts of B_2O_3 usually improve the hydration resistance of magnesia in the presence of CaO and SiO_2 by forming a glass phase along the magnesia grain boundaries. The B_2O_3 apparently increases the solubility of dicalcium silicate (C_2S) in the glass phase, even at concentration of B_2O_3 as low as 0.1% because it reduces the hot strength and corrosion resistance of MgO refractories, therefore, the amount of B_2O_3 in Magnesia based refractories must be restricted.

04. External Appearance of Hydrated Bricks

The hydration of magnesia containing bricks shows an external white coating with brittleness, loose structure and cracking. Only outside whitish coating in bricks cannot be considered as hydrated bricks. If the white magnesium hydroxide continues to the inside of the brick which can be checked by breaking it through, the degree of hydration may be considered in advanced-stage.

Fig-1: Hydrated brick

05. Site Test To Measure Degree of Hydration

Test Specimen (Sample Brick of 2 kg)

↓

Samples dried at 110^0C for 4 hours → Weigh (W1)

↓

Heated in Furnace at 1050^0C for 12 hours → Weigh (W2)

The weight difference between the dry specimen and the heat-treated specimen is an indication for the degree of hydration.

- Bricks with an ignition loss up to 0.6% are generally not damaged during heating-up, provided adequate heating-up procedure according to the instruction (24 hours for approx. 1200 ˚C) were followed.
- With 0.6 to 1% ignition loss there is an increased danger of destruction during heating-up.
- With more than 1% ignition loss the serviceability of bricks is restricted.

06. Lab test report of some hydrated bricks in lime kiln

The combustion zone of lime kiln is lined with basic bricks which are prone to hydration. Once installed and if the kilns are not commissioned early, the bricks get exposed to the humidity and the resultant hydration not only causes expansion of bricks but also reduces its inherent strength. The loss of strength is irreversible. Collapse of refractory lining was reported from several lime kiln projects in recent years.

Fig-2: Brick collapsed from kiln

Sl. No	Plant	Erection of Refractories done at site	Refractories found hydrated/ collapsed
1.	IISCO Steel Plant	Supplied: Nov, 12 Erected: April, 13	Collapsed: June, 14 (Before heating up)
2.	Neelachal Ispat Nigam Limited (NINL)	Supplied: Feb., 12	Hydrated: July, 13 (At site)
3.	Rourkela Steel Plant	Supplied: Jan, 13 Erected: April, 13	Collapsed: Oct., 2014 (During heating up)

Case Study-1

In one reference project, the lime kiln was kept idle without taking precautions for more than a year. Subsequently the bricks were got hydrated and collapsed. The debris collected at the bottom of the kiln which indicated that most of the collapsed bricks were the basic bricks. Two brick samples were collected from the affected area of lime kiln. One unused brick was also collected from the store for comparative study.

The damaged bricks as well as the unused brick were subjected to detail physico-chemical analysis and mineralogical studies using XRD.

Sample Details

Our Laboratory Identification No.	
Sample-1	Brick hydrated and collapsed from lime kiln
Sample-2	-do-
Sample-3	Bricks collected from the store in loose stock

We have prepared one set of specimen for evaluation of physical properties and composite sample for other tests of samples 1 & 2.

- Appearance of Un-used brick (sample-3)

Fig. 3

- Appearance of used brick (sample-1)

Fig. 4

Fig. 5

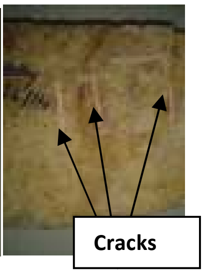


Fig. 6

Appearance of used brick (sample-2)

Fig. 7

Fig. 8

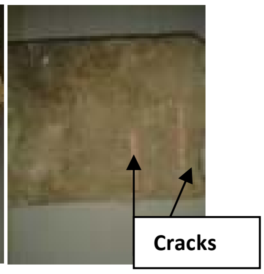


Fig. 9

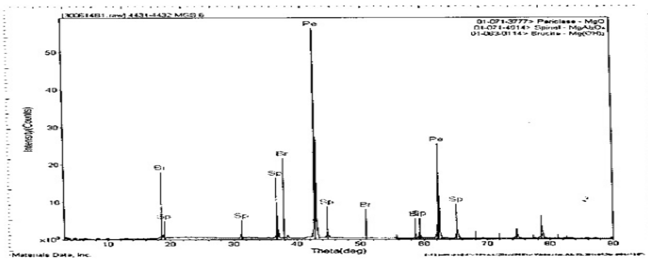
Physical Properties

The physical properties of the bricks were determined as per the standard test method and the results are given below:

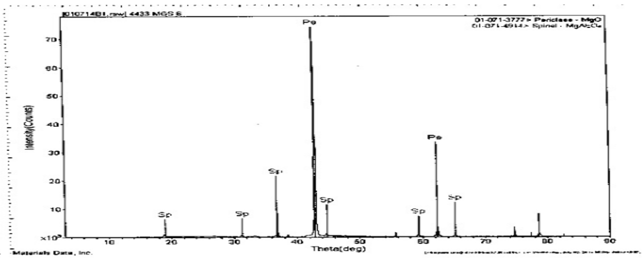
Parameters	Sample-I & 2	Sample - 3	Spec.
AP (%)	14.0	18.0	17-19
BD (g/ cc)	3.03	2.92	2.80 – 2.95
CCS (Kg/ cm2)	360	466	450 (min)

Phase Analysis: Phase analysis of the powder sample was done by XRD. One composite sample was prepared by combining used brick (samples 1 & 2); and another sample was prepared from unused brick (sample 3). These samples were ground in Tungsten Carbide grinding bowl and XRD analysis were done. The major phases in both the samples are Periclase and Magnesio-Alumina spinel. XRD pattern of used samples (Sample 1 & 2) shows the presence of Brucite (Magnesium Hydroxide).

XRD Result:



Sample-1 & 2



Sample-3

Case study - 2

Another reference project in which hydration of refractories was found before installation, i.e. during storage at site. The refractories materials were exposed to the moisture for almost one year. Appearances of some of the refractories material were '***Whitish***' where some of the bricks were found in '***Normal conditions'***. Affected bricks as well as good bricks were collected from site by engineers and sent to the laboratory for testing. Results of collected samples are as follows:

Si. No.	Sample No.	Description of Item	AP (%)	BD (gm/cc0	CCS (Kg/cm2)	LOSS ON IGNITION (%)
1	W-1	Whitish (230*114*76mm)	1808	2.87	509	0.83
2	W-2		17.98	2.9	514	
3	W-3		18.44	2.89	524	
4	W-4		17.01	2.91	534	
5	W-5		17.38	2.87	454	

7	G-1	Normal material from store (230*114*76mm)	17.69	2.91	663	0.29
8	G-2		17.14	2.93	627	
9	G-3		17.79	2.92	652	
10	G-4		16.34	2.91	697	
11	G-5		16.83	2.91	653	

07. External measures to avoid hydration of bricks

Bituminous substances have been used as protective coatings for several years. Their effectiveness is based on largely upon their resistance to moisture and chemical attack. The current major volume of bituminous materials, by products of the coal and petroleum Industries, have been developed and used as protective coatings for long period. This has been due to their ready availability, low cost per unit volume and for their performance characteristics. The product should be applied to avoid hydration after complete erection and when there will be delay in commissioning of kiln. The product used for coating should be in line with the following specification:

PRODUCT INFORMATION: Bituminous substances		**SURFACE PREPARATION**
Color	Black	The surface to be painted should be dry and free form oil and grease, dust and loose matters
Flash Pint	Above 30ºC	
Volatile Matter (% by mass, max.)	55	**APPLICATION DETAILS**
Water content (% by mass, max.)	0.5	Method or application : Brushing/Spraying
Mass in kg./10 lt . of material	8.8 +/- 0.01	
Flexibility and Adhesion (After 96 hr. of air- drying)	Passes as per IS101-1964	

Precautions:
- Adequate ventilation to be provided while application & drying in confined areas.
- Application should be avoided when temperature falls below 10 ºC or rises above 50 ºC and when relative humidity rises above 90% during rain, fog or mist.
- For proper curing of film ambient temperatures should be >20 ºC.

Shelf life:
- One year as the sealed containers are kept on standard storage condition.

08. Conclusion:-

From the result of the study, it can be concluded that:

1. Microstructure of magnesia i.e. porosity, grain size etc influences hydration resistance.

a) Open porosity of magnesia particles influence the tendency of hydration

b) Fused magnesia of high density, low porosity and large crystal size shall be used due to its high hydration resistance property.

2. Selection of raw material can also enhance hydration resistance of magnesite refractories.

a) Impurities of raw material (i.e. CaO, SiO_2, Al_2O_3 etc) play significant role in hydration of magnesite refractories.

- Magnesite refractories with high CaO/SiO_2 ratio are more sensitive to hydration.
- Al_2O_3 content shall not be more than 4 wt (%).

3. The longer the exposure to the humid hot climate, higher the hydration rate with different consequences of physico- chemical properties.
4. Proper care should be taken for transportation & storage of such type of refractories.
5. External coating should be given after installation of magnesia bricks during unavoidable circumstances like fuel unavailability etc. when these is a possibility in delay commission of kiln
6. Kiln should not be kept idle for long time after erection of magnesia bricks.

Execution of kiln is not something that occurs on a regular basis. Lessons learnt due to failure of refractories because of hydration, allow us for constructive thinking on best practices to follow. We should keep in mind that significant time and cost involves for relining of refractories due to hydration effect.

09. References :-

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10. Acknowledgment :

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