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Corrosion Mechanism of Refractory Bricks Lining the Cement Kiln

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ABSTRACT:

Present work investigates causes of damage of two types of refractories, the magnesite 80% MgO and high alumina > 70% Al_2O_3 lining kiln of ordinary Portland cement at the burning and lower transition zones respectively. To estimate degree of penetration of cement clinker during kiln operation, chemical analysis was conducted for bricks after use for a limited period of time ,and also for clinker before and after burning to eliminate detrimental corrosive materials (like alkalis, sulfur, chlorine).

Measurements of corrosion with time were reported and an experimental test was conducted to study the alkali attack on high alumina and its effect on the thermo-mechanical –chemical corrosion.

The results showed that alkali attack on alumina brick is the main factor of its damage. The damage of magnesite brick refers to peeling of clinker coating during the cooling of the kiln as well as the immigration of chromites from hot to cold face decreasing the toughness of the brick.

Key words / Corrosion , Magnesite ,Alumina .

الخلاصة

يدرس البحث أسباب تآكل نوعين من الطابوق الحراري المبطن لأفران الاسمنت هما الطابوق المغنيسي والطابوق العالي الالومينا والمستخدم في منطقتي الاحتراق والمنطقة الانتقالية السفلى على التوالي.

تم اجراء التحليل الكيميائي لكلنكر الاسمنت وكذلك لنوعي الطابوق قبل وبعد التعرض لحرارة الفرن لغرض تحديد مدى تغلغل الكلنكر داخل الطابوق ،كما تم مراقبة التآكل مع الزمن للنوعين.وقد اعتمد فحص مختبري خاص لدراسة هجوم القلويات على الطابوق العالي الالومينا وتاثير ذلك على التاكل الحراري-الميكانيكي-الكيميائي.

وقد بينت النتائج ان السبب الرئيسي لتآكل الطابوق عالي الالومينا هو هجوم القلويات الموجودة في الكلنكر.أما تآكل الطابوق المغنيسي فيعود الى تقشر طبقة الكلنكر المغلفة له اثناء تبريد الفرن بالاضافة الى انخفاض متانة الطابوق بسبب هجرة مركبات الكروم من السطح الحار الى البارد.

Many types of these refractories are used for lining cement kilns as shown in **Fig 1** . There are two advantages for using these refractory ; to maintain the kiln temperature, due to their low thermal conductivity and to protect the kiln shell from corrosion by abrasive wear of clinker.

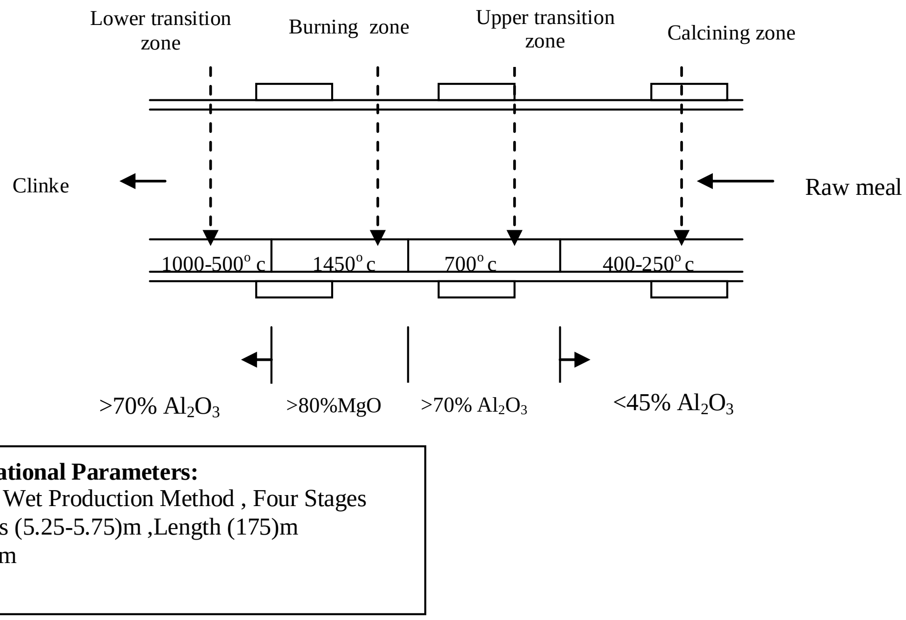


Fig 1: Cement Kiln Zones ,Types of Refoctories used and Operational Parameters (Kufa cement factory).

Refractories are chosen in cement kiln according to the conditions they will face and their type (acidic or basic). Due to the basic environment condition the cement kiln have ,the basic refractory (like magnesite) and neutral refractory (like Alumina) can be used , acidic refractory like zirconia and fire clay can not be used because they will easily eroded.

Corrosion of refractory used in cement kiln is a common phenomenon, involving not only chemical wear but also physical / mechanical wear (such as erosion /abrasion) processes that may act simultaneously .

Studies of wear mechanisms for the refractory brick lining the cement kiln especially the lower transitions and burning zones defined several types of wear ;(Bartha 1999) Infiltration of alkali sulfate and chlorides, Penetration by the clinker liquid phase, and Physical stresses.

Sulfur and chlorine can combine with refractory especially the magnesite to form magnesite sulfate and chlorides, weakening the refractory. Alkali attack on high alumina refractory can be significant contributor to refractory wear. Magnesite are more resistance to reaction with alkali than high alumina brick due to its basic properties (Bartha 2005).W.E. Lee and S. Zhang (Lee 2004) developed a theoretical model for penetration and dissolution mechanism by liquid silicate slag for two types of refractories. They conducted an experimental test to estimate the reaction rate between the slag and the refractories .They found that corrosion rate is depending on the type of refractory material and temperature . S. Serena and others (Serena 2004) studied the corrosion behavior of MgO/ $CaZrO_3$ refractory by clinker of Portland cement. The attack mechanism of 80% MgO – 20% $CaZrO_3$ (wt%) was established .They discussed the results of research in term of the phase diagram. J.L.Rodringuez and others (Rodriguez 2007) investigated the mechanism of corrosion of magnesia – calcium silicate by cement clinker . They found that the diffusion of the liquid clinker phase into the refractory substrate is the main cause of corrosion, and also the dissolution of $CaZrO_3$ produces the enrichment with zirconium of the liquid phase increasing its viscosity and hindering the liquid phase diffusion. Raymond P. and others (Raymond 2005) studied the corrosion rate of magnesite, alumina and the spinal magnesium Aluminates $MgAl_2O_4$ by slag. They found that operational changes such as increasing in temperature and service time play important role in refractory life.

The present work investigate causes of damage of two types of refractories, the magnesite 80% MgO and high alumina > 70% Al_2O_3 lining kiln of ordinary Portland cement at the burning and lower transition zones.

2-EXPERIMENTAL WORK

2-1-RAW MATERIALS

Table 1 shows the chemical composition and physical properties of magnesite 80% and high Alumina >70% which are used in the burning zone and lower transition zone of the cement kiln respectively.

Table- 1 : Composition and Properties of magnesite and high alumina refractories (Brazilian company for refractory bricks –Magnesita-)

Approximate Chemical Composition (wt%)					
Magnesite (Coelex-80-R)					
MgO	Al_2O_3	CaO	Fe_2O_3	SiO_2	Cr_2O_3
80.00	<7.0	<0.6	<4.3	<3.5	5.00
High Alumina (Alumex 70-E)					
Al_2O_3	Fe_2O_3	SiO_2	TiO_2	K_2O	
72	2.5	22	2.2	0.9	

Physical Properties	**Magnesite (Coelex-80-R)**	**High Alumina (Alumex 70-E)**
Density (g/cm^3)	3.12	2.47
Thermal Conductivity (W/m.K) at 600ºc	4.67	3.84
Thermal expansion coefficient($dL/L.K^{-1}$) x 10^6	13.2	8.4
Apparent Porosity %	13.2%	16.7%

Cold crushing strength (MPa)	72	67
Thermal shock resistance from 1200 °C to room temperature (cycles)	45 min	38 min

2-2-Experimental Methods

A-Chemical Analysis:

To eliminate the detrimental corrosive material (like alkalis, sulfur, chlorine) the clinker contain, a chemical analysis on clinker before and after burning was achieved as shown in **Table 2** .

Table 2 : Chemical composition of Portland cement clinker.

Chemical analysis (wt%)	Raw clinker	Clinker after burning
Weight loss (loss of ignition)	35.08	0.28
SiO_2	13.3	21.00
Al_2O_3	3.41	5.28
Fe_2O_3	2.35	3.27
CaO	44.2	67.36
MgO	0.43	0.64
SO_3	0.31	0.59
Na_2O	0.09	0.12
K_2O	0.52	0.97
Mn_2O_3	0.09	0.12
P_2O_5	0.17	0.24

The Table show that clinker is contain the detrimental corrosive material (Na_2O , K_2O , SO_3).

To estimate the penetration of clinker into the refractory during the cement kiln operation , chemical analysis was achieved for magnesite brick in the burning zone at meter 35 of the kiln, and for alumina in the lower transition zone at meter 15 of the kiln.

B- Alkali Resistance Test:

To study the alkali resistance for high alumina, an experimental laboratory test (ASTM C-201) is done by taking a refractory cube of 50 mm length contain a half sphere of 25mm diameter as shown in **Fig 2** . The half sphere is filled with clinker which contain the alkali's (Na_2O , K_2O) and then heated to an elevated temperature of (1000 -1100 °C) with a heating rate of 5 °C/ min for reaction duration up to 6 hour.

Fig 2: 50 mm length cube specimen with 25 mm diameter half sphere for alkali attack test (high alumina refractory)

3-RESULTS AND DISSCUSSION

The results of chemical analysis for five samples of each magnesite bricks in the burning zone at meter 35 and alumina bricks in the lower transition zone at meter 15 after use in the cement kiln for 3 months are shown in **Tables 3** and **4** respectively .

Table 3. Magnesite brick after use in the burning zone.

Hot face distance	**0 to50mm**	**50 to 100mm**	**100 to 125mm**	**Bricks before use**
Bulk Density (g/cm^3)	3.28	3.21	3.14	3.03
Chemical analysis (%)				
Weight loss (wt%)	1.64	4.49	2.47	___
MgO	72.59	76.40	76.83	80.00
Al_2O_3	6.16	5.36	5.97	7.00
SiO_2	2.92	2.87	2.78	3.50
CaO	1.38	0.45	0.62	0.60
Cr_2O_3	4.39	3.85	4.61	5.00
Fe_2O_3	3.78	3.45	3.82	4.30
MnO	0.56	0.61	0.60	
Na_2O	2.72	1.25	0.96	
K_2O	0.12	0.15	0.18	
SO_3	5.34	5.56	3.59	

Table 4. High alumina brick after use in the lower transition zone.

Hot face distance	**0 to15mm**	**15 to 25mm**	**25 to 100mm**	**100 to 125mm**	**Bricks before use**
Bulk Density (g/cm^3)	2.92	2.83	2.65	2.51	2.57
Chemical analysis (%)					
Weight loss (wt%)	(0.73)	(0.44)	(0.27)	(0.09)	—
Al_2O_3	18.98	66.52	66.35	71.80	72.0
SiO_2	18.68	21.17	22.84	22.45	22.0
Fe_2O_3	4.32	1.78	1.99	2.09	2.5
K_2O	1.14	4.20	4.54	1.02	0.9
TiO_2	0.61	2.09	2.15	2.31	2.2
MgO	0.02	0.10	0.13	0.12	
CaO	50.88	3.89	1.71	0.03	
Na_2O	0.39	0.17	0.24	0.14	
SO_3	4.58	0.09	0.04	0.04	

Tables 3 and **4** show the penetration of clinker (which include alkalis) into the brick. The clinker diffused through the refractory substrate by grain boundaries and pores, this penetration causes parallel cracks near the hot face (as shown in **Fig 3**) and also cause densification of hot face as reported in **Tables 3** and **4** where density increased from 3.03 g/cm^3 to 3.28 g/cm^3 at the hot face for magnesite brick and from 2.57g/cm^3 to 2.92 g/cm^3 at the hot face for alumina. Brick pores are completely filled with clinker components, which consequently rendered the bricks more susceptible to peel off by thermo- mechanical abrasion as shown in **Fig 4** .

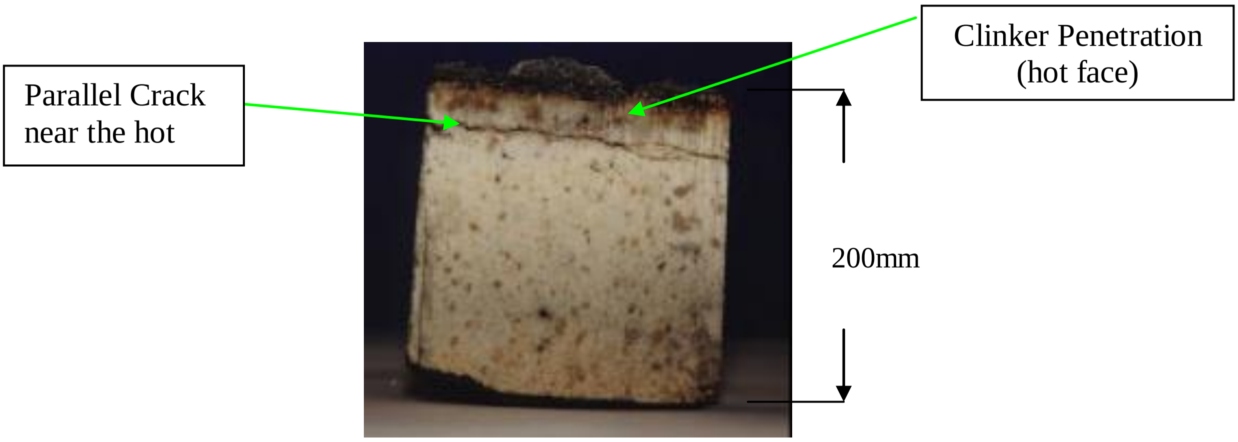


Fig 3: Penetration of clinker into the hot face of brick causes a densification and long parallel crack (high alumina brick after use for 5 weeks).

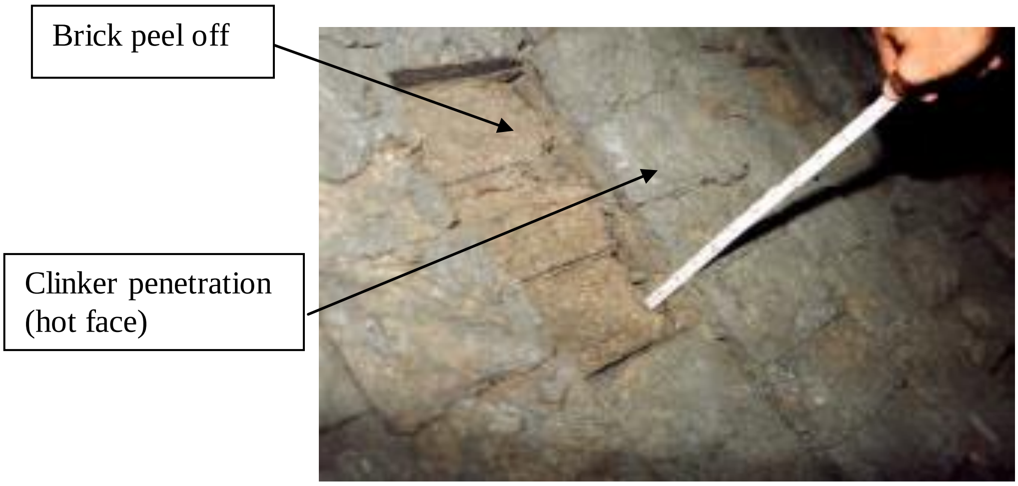


Fig 4: Brick peel-off by clinker penetration and thermo-mechanical abrasion mechanism. (High alumina brick in the lower transition zone).

The experimental test of alkali resistance for high alumina specimens results visible cracks as shown in Fig 5 , the alkali resistance is measured by evaluating the degree of cracking in the samples.

Fig 5: The alkali attack test result in visible cracks caused by volume increasing (High alumina brick).

Generally, refractories are rigid and tend to crack; the crack here is due to change in volume and external stresses. High alumina brick react with the penetrated alkalies (mention in **Table 4**) like soda (Na_2O) to form sodium alumina silicate and potash (K_2O) to form potassium alumina silicate (Hall 2002). This alkalies reaction are detrimental because they are expansive in nature, so the alkali Alumina silicate have much greater volume than the original refractory and the affected brick will crack (as shown in **Fig 5**) to relieve the stress caused by the increasing in volume.

In the case of magnesite a protective coating of clinker is formed on brick during the kiln operation .Coating is formed due to the high thermal conductivity of magnesite brick and its location in the burning zone. However, Carlos (Carlos 2001) reported a similar behavior when clinker mass adhered on the magnesite brick as clinker severe from changes from a liquid to a solid state.

When the kiln operates under equilibrium conditions , the coating will maintain itself, any change in operation temperature lead the coating to come off, when the kiln temperature is cooled the penetrated portion of magnesite become denser (as reported in **Table 3**) and peel off easily causing the corrosion phenomena as illustrated by a sketch in **Fig 6** .

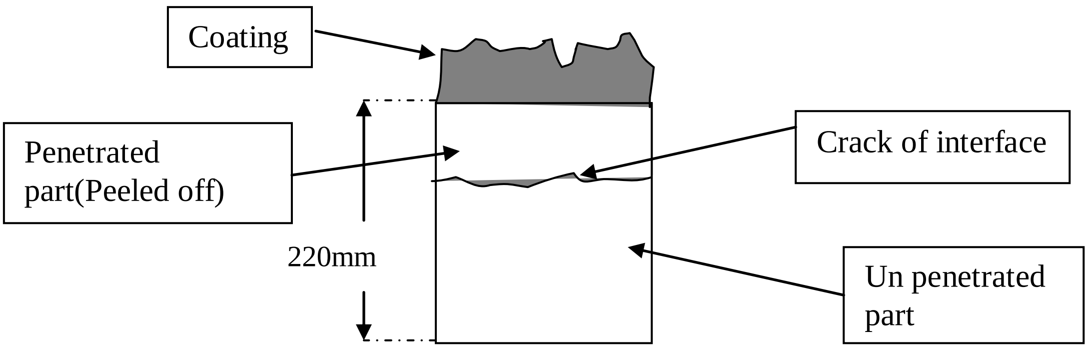


Fig 6: A sketch showed coating, penetrated part and crack of interface (MgO brick).

The difference between corrosion mechanism by clinker penetration for magnesite and alumina bricks are shown in **Fig 7**.

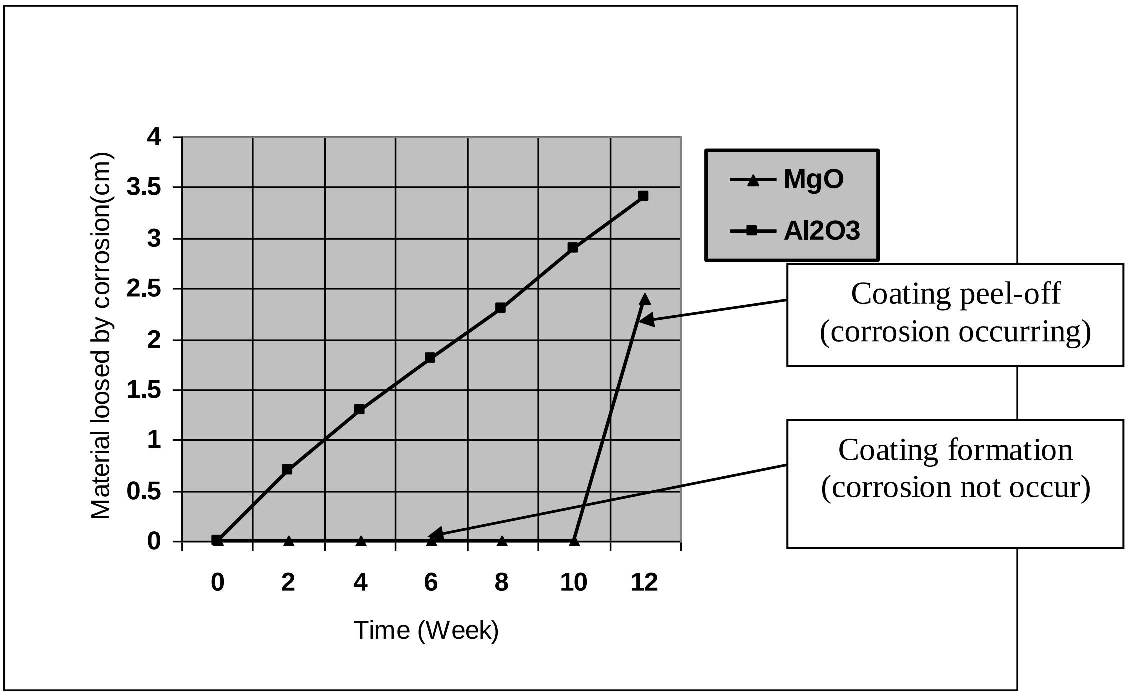
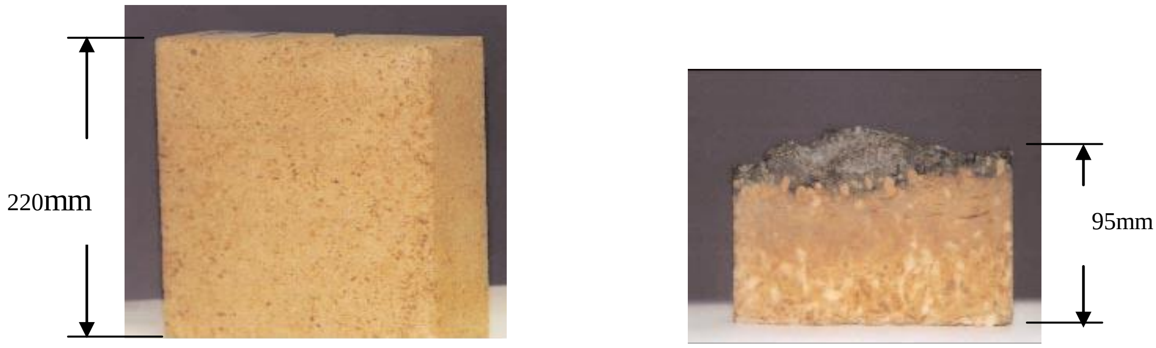


Fig 7: Material loosed from the hot face for Magnesite and Alumina bricks (practical results).

Chemical analysis (**Table 3**) for magnesite brick shows a decrease in chromite(Cr_2O_3) ratio at the hot face, which may refers to immigration of Cr_2O_3 from hot face to cold face by diffusion mechanism. This immigration weakening the

refractory resistance due to the fact that chromite is responsible of the brick toughness (Geraldo 2002) .**Table 3** also shows an infiltration of sulfur(SO_3) into magnesite brick, forming magnesite sulfate which is leads to a weakness in brick substrate.

The corrosion of magnesite brick used in burning zone (after approximately 8 months) is shown in Fig 8 .The figure shows the damage occurred on brick as a result of thermo mechanical- chemical corrosion which caused by clinker penetration .
Magnesite brick usually replaced after about 8-months while aluminite brick replaced after about (4-6) months.



-a- -b-

Fig8: Magnesite brick.
a-before use.
b-after use in cement kiln for approximately 8 months.

4-Conclusion and Recommendations:

Conclusion:

From the results of this work the following conclusions can be reported:

- The alkali attack on alumina brick is the main factor of its damage.
- The damage of magnesite brick refers to peeling off clinker coating after the cooling of the kiln.
- Immigration of chromites in magnesite brick from hot to cold face decreases the toughness of the brick.

Recommendations

- Using a new product of refractory brick called spinal ($MgO-Al_2O_3$) which improve durability of bricks.

- Brick Installation: Brick should be firmly installed against the kiln shell. Brick that tilt or hacks against the shell should be corrected with refractory mortar.

- Using the MgO- $CaZrO_3$ brick .The dissolution of the $CaZrO_3$ phase increase the viscosity and hindering the liquid clinker penetration.

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