

SHINAGAWA TECHNICAL REPORT

コーティング安定性に優れたセメント
ロータリーキルン用マグネシア・スピネル質
れんが

Magnesia-Spinel Brick with Good Coating
Property for Cement Rotary Kiln

伊賀棒 公 一
Koichi IGABO

宮 田 雄 斗
Yuto MIYATA



報文／REPORT

コーティング安定性に優れたセメントロータリーキルン用 マグネシア・スピネル質れんが

Magnesia-Spinel Brick with Good Coating Property for Cement Rotary Kiln

伊賀 棒 公 一^{*1}
Koichi IGABO

宮 田 雄 斗^{*2}
Yuto MIYATA

要 旨

セメントロータリーキルン焼成帯において、コーティングの安定はれんがの耐用に直結する重要な要素である。本報告では実際の使用後れんがの観察や、再現試験を通じてコーティング付着メカニズムの検討を行い、浸潤は主に細かい気孔のみを埋める形で進行するという特徴を確認した。また、再現試験からマグネシア原料の違いが液相の浸潤に与える影響は主に粗粒部で見られることも確認され、その知見を活かした新材質ELK-8X-1を開発した。

Abstract

The formation of a stable coating layer on bricks relined at the burning zone in cement rotary kilns is one of the important factors for enhancing the durability of refractories. By investigating samples of magnesia-spinel brick obtained from a cement rotary kiln as well as carrying out simulative experiments on liquid slag penetration into brick, it was clarified that stability of the coating layer is influenced by the anchor effect realized by penetration of cement clinker liquid phase into brick with a tendency for the cement clinker liquid phase to penetrate mainly into the micropores of magnesia-spinel brick. Based on the simulative experiment result in which liquid phase penetration into magnesia coarse grain was influenced by the type of magnesia raw material, a new magnesia-spinel brick, ELK-8X-1, was developed by implementing an improved coating property.

1. 緒言

セメントはビルやダム、橋梁、トンネル等の建設に必要な基礎素材であり、我々の生活には無くてはならないものになっている。そのセメントを生産するための重要な設備であるセメントロータリーキルンは、廃棄物や副産物を代替原料および代替燃料として活用しており、環境負荷低減という点でも重要な役割を担っている¹⁾。キルントラブルによる停炉はセメントの生産だけでなく、廃棄物の低減にも影響するため、安定操業がより一層求められている。

1. Introduction

Cement, a base material used for construction of buildings, dams, bridges or tunnels, is indispensable for our life at present. Large amounts of waste products and by-products generated in a variety of industries are utilized as alternative raw materials or fuel in the cement rotary kiln, which is an important facility for cement production. In this regard, it can also be said that the cement rotary kiln plays an important role in the reduction of environmental

^{*1} 技術研究所 第1研究部 第1研究室 主任研究員 Senior Resercher, Shaped Refractories R&D Sec., Research Dept. No.1, Research Center

^{*2} 技術研究所 第1研究部 第1研究室 Shaped Refractories R&D Sec., Research Dept. No.1, Research Center

セメントロータリーキルンにおいて、焼成帯と呼ばれるゾーンでは最高温度がおよそ1450℃に達し、れんがへの熱負荷が最も高い部位である²⁾。焼成帯では溶損のリスクが高くなるがコーティングと呼ばれる付着物層をれんが稼働面に形成することで稼働面を保護し溶損を防いでいる。また、付着物層による断熱効果によって炉壁内部の温度勾配が緩やかになり、シェルや支点部等の設備を保護することにも繋がるため、コーティングは操業の安定において重要な役割を果たしている。

今回、コーティング付着のメカニズムについて検討を行い、それに基づいて開発した新材質ELK-8X-1について紹介する。

2. コーティング付着メカニズムについて

2.1 実炉使用後れんがの調査

コーティングはその重要性の高さから付着性の改善やメカニズムの検討がこれまでもなされてきた³⁻⁵⁾。それらの報告から付着初期のれんが-クリンカー間の反応メカニズムについては多く知見が得られている一方で、それ以外の面については十分な検討がなされていない。そこで、筆者らのグループでは改めて焼成帯から回収された使用後れんががコーティング付着界面について調査を実施した⁶⁾。

コーティングが付着したクロムフリーれんが稼働面近傍の微構造写真 (Fig.1) より、稼働面近傍に緻密層が形成され、より背面側になると健全な層が確認された。Fig.2にはFig.1浸潤部の赤囲み部SEM画像を示す。輝度が高く白く見える部位にクリンカー由来の液相がれんが成分と反応しつつ細かい気孔を埋めるように浸潤している一方で、比較的大きな気孔には液相の浸潤が見られなかった。

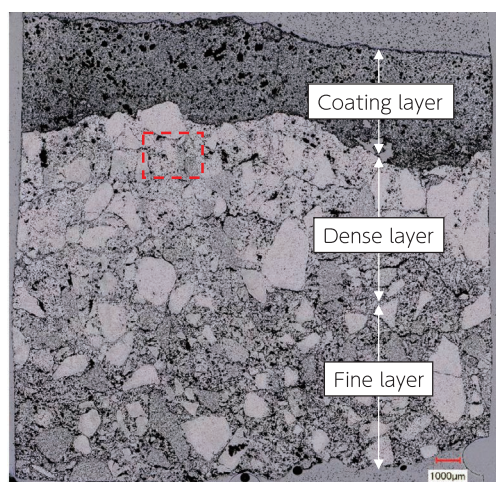


Fig. 1 Microstructure of chrome-free magnesia-spinel brick retrieved from burning zone⁶⁾.

pollution¹⁾. Since temporary cessation of rotary kiln operation caused by virous troubles influences not only cement production but also reduces reduction of waste treatment, stable operation of the rotary kiln is highly desirable.

Since the maximum temperature at the burning zone in cement rotary kilns is roughly 1450 °C, the thermal load to relined refractories is severe²⁾, and refractories relined at the burning zone tend to be corroded under severe circumstances. Build-up of an adherent material layer, so called as the coating layer, which is formed on relined bricks, protects the working surface of the bricks and prevents corrosive damage. In addition, since temperature distribution in relined bricks is eased by the thermal insulation effect of the coating layer, mechanical equipment of cement rotary kiln, such as the steel shell or kiln supporting rollers, are guarded from high temperature. In short, the coating layer plays an important role in stable cement rotary kiln operation and a good coating property is thought to be one of the essential characteristics of refractory brick used in the cement rotary kiln.

ELK-8X-1, a new magnesia-spinel brick for the cement rotary kiln, was developed by implementing knowledge attained by examining the coating layer formation mechanism.

2. Mechanism of Coating Layer Formation

2.1 Investigation of bricks used in cement rotary kiln

Improvement of the coating property of cement rotary kiln bricks by examination of the coating layer formation mechanism have been conducted³⁻⁵⁾ because it is so important to kiln stability during the operation. Much information on the reaction between relined bricks and cement clinker in the early stage of coating layer formation was attained by this investigation. However, other aspects in

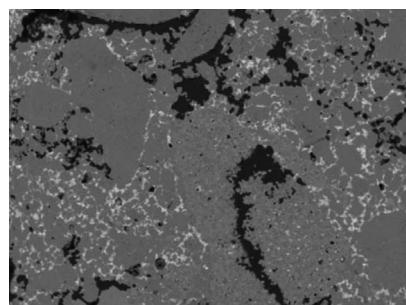


Fig. 2 SEM image of densified layer⁶⁾.

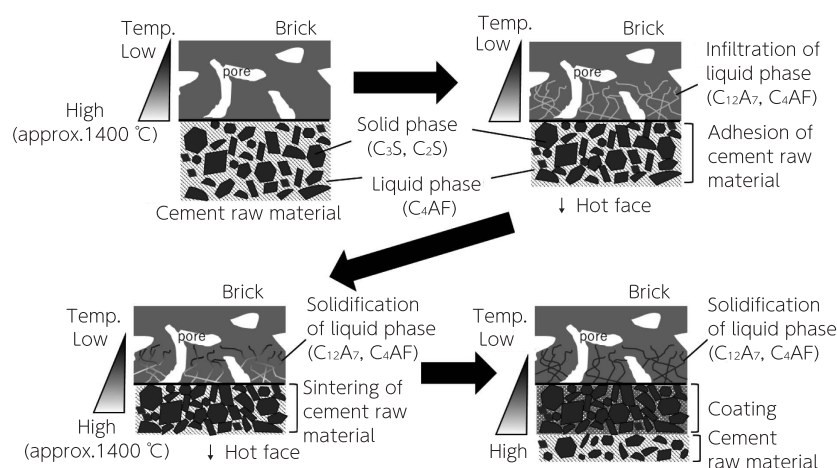


Fig. 3 Schematic diagram of coating layer formation on working surface of brick.

Table 1 Chemical composition of synthetic slag used in dipping test

	MgO	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃
mass%	2	17	4	51	26

観察結果を基に推定されたコーティング付着のメカニズムをFig.3に示す。

- (1) れんが表面に半熔融状態のクリンカーが接触する。
- (2) クリンカーの液相成分がれんが内に細かい気孔を通じて浸潤する。同時に、液相成分が減少したクリンカーがれんが表面に付着する。
- (3) れんが内部には温度勾配が存在し、浸潤した液相成分は内部に浸潤するにしたがって徐々に固化する。れんが表面に付着したクリンカーは更に液相が奪われ、焼結し塊状になる。
- (4) 塊状クリンカーがれんが表面を覆うと、断熱効果でれんが内部の温度が低下し、浸潤した液相成分の固化が促進される。固化した浸潤成分は気孔や粒界に根を張るように存在する、いわゆるアンカー効果^{3,4)}によってコーティングが安定する。

以上のように液相の浸潤がコーティングの安定に重要な役割を果たしていると推定しているが、浸潤は主に細かい気孔のみを埋める形で進行するという特徴が見られた。

2. 2 クリンカー液相成分へのれんが浸漬実験

実炉使用後れんがで見られた液相浸潤について詳細に検討するため、ラボ試験にて液相浸潤の再現を試みた⁷⁾。縦型電気炉内の白金るつばで、セメントクリンカー中の液相（フェライト相；C₄AF）に模した組成（Table 1）の液相に使用後れんがと同材質の未使用品を浸漬させた（試験条

coating layer formation have not been examined at full length. The authors investigate bricks obtained from the burning zone in a cement rotary kiln once again⁶⁾, the time, focusing on the brick surface on which the coating layer is formed.

A densified layer can be observed directly under the working surface along with unchanged original brick structure in the deeper region in Fig. 1, which is an image of the microstructure at the working surface area of a chrome-free magnesia-spinel brick obtained from the burning zone in cement rotary kiln is shown. Fig. 2 shows an SEM image of part of the densified layer circumscribed with red dotted line in Fig. 1. The many tiny white colored regions with high brightness are micropores into which liquid phase derived from cement clinker has penetrated while reacting with the original brick components. Penetration of cement clinker liquid phase into the relatively large size pores cannot be observed here. The mechanism of coating layer formation has been surmised as is illustrated in Fig. 3, based on observation results on the obtained brick.

The mechanism is described in four steps as follows:

- (1) Semi-melted cement clinker contacts brick surface.
- (2) Liquid phase contained in cement clinker penetrates in brick through micropores, and the cement clinker of which the liquid phase has been absorbed into the brick adheres to the brick surface.
- (3) Because of the temperature distribution in the relined brick, the penetrated liquid phase gradually solidifies in accordance with the

件の詳細はtable 2に記載)。

Fig.4に浸漬後サンプルの切断面写真を示す。れんが内部に液相が浸潤しており、液面よりも高い位置でも浸潤が確認された。Fig.5に液面近傍のSEM画像を示す。輝度が高く白く見えている部位に液相が浸潤しており、細かい気孔への浸潤が確認される一方で、比較的大きな気孔への浸潤は見られなかった。この結果は実炉の観察と同様であり、同じメカニズムで液相の浸潤が起きていると推定される。また、液面よりも高い位置で浸潤が見られており、毛細管力が液相浸潤の駆動力となっていることが示唆された。

Table 2 Dipping test conditions

Ambient temperature during dipping process / °C	1400
Dipping time / s	30
Dipping depth / mm	10
Preheating temperature before dipping / °C	1230
Preheating time before dipping / s	1200

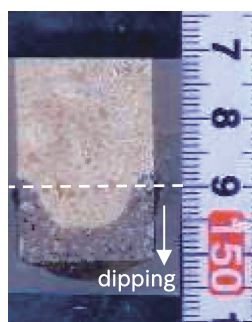


Fig. 4 Cross section of dipping test sample⁷⁾.

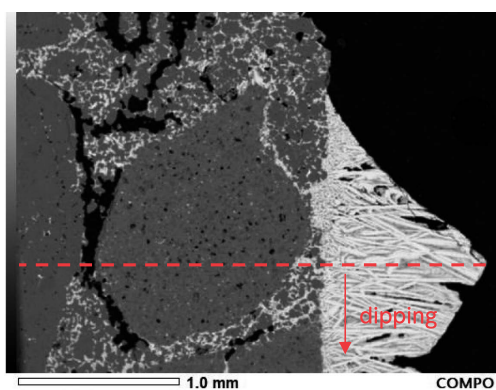


Fig. 5 SEM image of dipping test sample near melted slag surface⁷⁾.

penetration depth into the brick. In association with further depletion of liquid phase, cement clinker adhering to the brick surface becomes bulky by sintering.

- (4) When the brick surface is covered with sintered bulky cement clinker, namely, the newly formed coating layer, the temperature in the brick is lowered by the thermal insulation effect of the coating layer, which promotes completion of liquid phase solidification. Since the solidified liquid phase is entrenched in the micropores or grain boundaries as if spreading roots, the coating layer is stabilized by the anchor effect^{3,4)}.

In above surmised coating layer formation mechanism, it is inferred that penetration of the liquid phase in the cement clinker into the relined brick plays an important role. The liquid phase has the unique tendency of penetrating so as to fill micropores preferentially.

2. 2 Brick dipping test in cement clinker liquid phase

In order to examine the penetration behavior of cement clinker liquid phase into bricks which were observed in investigation work on bricks retrieved from the burning zone in a cement rotary kiln, reproduction of liquid phase penetration into brick was carried out with a laboratory experiment⁷⁾. That is, a sample specimen of new magnesia-spinel brick which was similar to a retrieved brick was dipped into melted synthetic slag in a platinum crucible in a vertical type electric furnace. As shown in Table 1, the chemical composition of the synthetic slag imitated that of cement clinker liquid phase, namely, ferrite phase (C_4AF). 10 mm of a brick sample tip, which was preheated to 1230 °C was dipped into melted synthetic slag, of which the temperature was kept at 1400 °C, for 30 seconds. The experimental conditions are summarized in Table 2.

Fig.4 shows a cross section of dipping test sample. The penetrating liquid phase is observable not only in the dipped area of the brick sample but also in the undipped area of the brick sample, which was above the melted slag surface. SEM image of a dipping test sample near the melted slag surface is shown in Fig. 5. The white colored regions with high brightness correspond to the areas into which liquid slag has penetrated. Penetration of liquid slag into micropores is clarified in SEM image, but liquid slag penetration into the black colored large pores is not observable in the image. Since the dipping

2. 3 マグネシア原料の違いが液相浸潤へ与える影響

浸漬実験にて実炉の液相浸潤を再現できたことから、マグネシア・スピネル質れんがの主原料であるマグネシア原料単体でれんがを作成し、原料の違いが液相浸潤へ与える影響を調査した。マグネシア原料はTable 3に示す特性の2種類を用意した。マグネシア原料Aは当社クロムフリーれんがに使用している代表的な高純度原料、マグネシア原料Bは出発原料や製造方法が原料Aと異なり、純度や粒物性が異なっている。れんがが化す際の各粒度の使用比率や製造条件はセメントキルン向けのクロムフリーれんがと同様とした。浸漬実験の条件は2.2で実施した条件と同じとし、試験後切断面写真とSEM画像で評価した。

Fig.6に切断面写真と浸潤部を拡大したSEM画像を示す。切断面の浸潤状況はどちらのサンプルもクロムフリーれんがの場合と大きな違いはなく、れんが内部に液相が浸潤しており、液面よりも高い位置での浸潤も確認された。SEM画像からマトリックス部では原料A、B共に細かい気孔への浸潤も確認された一方で、粗粒部の粒子については

test results are quite similar to observation results on the obtained brick, it is inferred that liquid slag penetrated with a similar mechanism described in the previous sub-section. The fact that liquid slag penetration is observed in the undipped area of the brick above the liquid slag surface indicates that slag penetration is driven by capillary force.

2. 3 Influence of type of magnesia raw material on liquid phase penetration

Penetration of cement clinker liquid phase into magnesia-spinel brick, which plays an important role in coating layer formation, was reproduced in the dipping test. The influence of type of magnesia raw material on liquid phase penetration was investigated by preparing test brick samples made of solely magnesia, the major raw material of magnesia-spinel brick. The major specifications of the two types of magnesia raw materials used for test brick samples are compared in Table 3. Magnesia raw material A is a typical high purity magnesia which is commonly blended in chrome-free magnesia-spinel

Table 3 Major specifications of two types of magnesia raw material

		Magnesia Raw Material A	Magnesia Raw Material B
Apparent porosity / %		0.9	4.3
Bulk density / -		3.43	3.29
Chemical composition / mass%	MgO	98.6	97.2

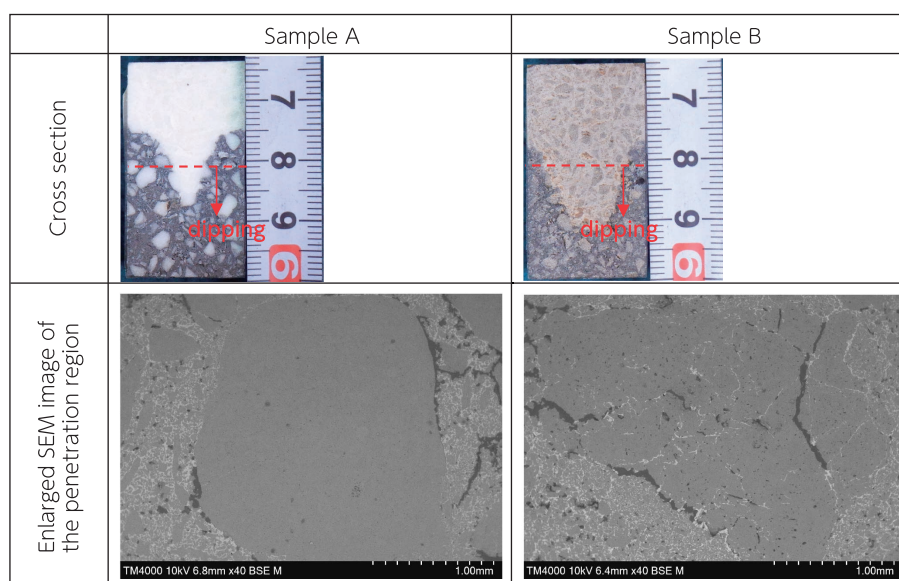


Fig. 6 Cross section near slag surface and SEM images of liquid slag infiltration area of test brick samples A and B.

差異が認められた。原料Aでは粒子中への液相の浸潤はほとんど見られないが、原料Bでは粗粒の粒子内の気孔を埋めるように液相が浸潤していた。このようにマグネシア原料の違いが液相の浸潤に与える影響は、マトリックスを構成する微粉では明確に確認されないが、粗粒部では明確に見られた。

3. コーティング安定性に優れたELK-8X-1

れんがへのフリッカー液相成分の浸潤について調査を実施して、得られた知見を基にコーティングの安定性向上を狙った新規クロムフリーれんがELK-8X-1を開発した。標準品質表をTable 4に示し、製品の切断面写真をFig.7に示す。

コーティングにおいてれんが内部への液相浸潤はアンカー効果^{3,4)}を発揮する上で極めて重要となるが、従来からクロムフリーれんがに使用されている原料Aは粗粒部への液相の浸潤が起こらず、マトリックス部ではアンカー効果が得られるものの粗粒部でのアンカー効果が十分に発揮されないと推定された。ELK-8X-1では、粒子中へも液相の浸潤が確認された原料Bを粗粒として採用することで、マトリックスから粗粒部までまんべんなくアンカー効果が発現してコーティング安定性の向上が期待される。

Table 4 Major specifications of ELK-8X-1

		ELK-8X-1
Apparent porosity / %		14.8
Bulk density / -		3.02
Cold crushing strength / MPa		42
Chemical composition / mass%	MgO	90.1
	Al ₂ O ₃	7.5



Fig. 7 Cross section of ELK-8X-1.

brick. Magnesia raw material B, of which the starting material and fabrication process differ from those of magnesia raw material A, exhibits slightly inferior purity and physical properties. The magnesia brick test samples were named sample A and sample B. Particle size distribution of the blended material, as well as fabrication conditions, were adjusted so as to duplicate those of chrome-free magnesia-spinel brick commonly used for cement rotary kiln. Dipping test of these two test brick samples was conducted with similar experiment conditions to those summarized in Table 2. After the dipping test, the magnesia brick test samples were halved for visual and SEM observation of the cross sections.

Fig.6 compares the cross sections near the synthetic slag surface and SEM images of the liquid slag penetration area of test brick samples A and B. No significant differences are observed between the cross section photographs of samples A and B. That is, a similar manner of liquid slag penetration can be observed in dipping test of in both magnesia-spinel brick samples A and B. There was liquid slag penetration at the undipped area of both test brick samples above melted slag surface. Liquid slag penetration into micropores can be observed in SEM image of both samples A and B. However, a clear difference between samples A and B can be observed in the manner of liquid slag penetration into the coarse grains. That is, no liquid slag penetration into the coarse grains can be observed in sample A. While, liquid slag penetrates and fills pores in the coarse grains in sample B. In summary, despite no difference in liquid slag penetration into micropores existing in the brick matrix between samples A and B, slag penetration into the coarse grains in sample B was more marked than that in sample B.

3. New Magnesia-Spinel Brick with Good Coating Property, ELK-8X-1

Based on knowledge attained by a series of investigations on the penetration of cement clinker liquid phase into brick, a new chrome-free magnesia-spinel brick, ELK-8X-1, in which conventionally blended magnesia raw material A was replaced with magnesia raw material B, was developed. The aim of the investigation was to improve the coating property. The major specifications of ELK-8X-1 are shown in Table 4, and an exterior cross section of ELK-8X-1 is shown in Fig. 7.

Penetration of cement clinker liquid phase into

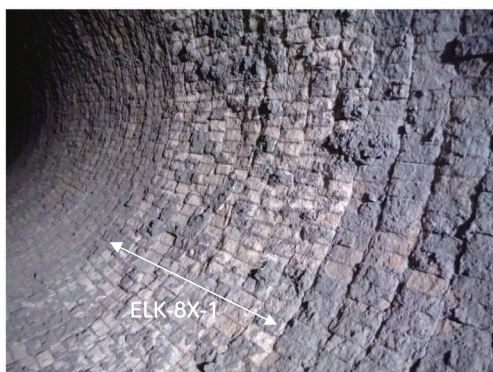


Fig. 8 Exterior appearance of ELK-8X-1 used at 1.0-1.5 of L/D in cement rotary kiln for half-year.

実炉でELK-8X-1が使用された後の状況をFig.8に示す。
L/D (L: 落ち口からの距離, D: セメントキルン径) が1.0
～1.5の焼成帯で、高い熱負荷を受ける環境下だったが、約
半年間問題なく使用された。

4. まとめ

セメントロータリーキルンにおけるコーティング付着メ
カニズムについて調査した結果、コーティングの安定には
クリンカーの液相成分の浸潤に伴うアンカー効果が影響す
るが、従来のマグネシア原料では粗粒部では不十分な可能
性があった。

新規に開発したクロムフリーれんがELK-8X-1は、粗粒
にも液相が浸潤するマグネシア原料を採用することで、れ
んが組織全体にアンカー効果を持たせ、コーティング安定
性向上を図っている。

brick plays an important role in coating layer
formation with its anchor effect^{3,4)}. It is inferred
that cement clinker liquid phase penetrates
only into the micropores in matrix but not into
magnesia A in conventional magnesia-spinel
brick, resulting in insufficient anchor effect for
coating layer formation. A reinforced anchor effect
which is combinedly materialized by liquid phase
penetration into micropores in the matrix and liquid
phase penetration into magnesia B coarse grains
is expected to improve coating formation in newly
developed magnesia-spinel brick, ELK-8X-1.

Fig. 8 shows the exterior appearance of ELK-8X-1
which was relined in the burning zone so as to cover
1.0-1.5 of L/D (L: distance from clinker outlet point,
D: diameter of cement rotary kiln) in the cement
rotary kiln and has experienced high thermal load
for half-year. After half-year operation, relined
ELK-8X-1 exhibited a healthy appearance with no
severe damage.

4. Conclusion

It was clarified by this investigation work on the
mechanism of coating layer formation on relined
bricks in the cement rotary kiln that stable coating
layer formation is influenced by the anchor effect
created by penetration of cement clinker liquid
phase into brick. In conventional magnesia-spinel
brick, however, such anchor effect is insufficient
because of no liquid phase penetration into
magnesia coarse grain occurs. A new chrome-free
magnesia-spinel brick, ELK-8X-1, was developed by
blending a different type of magnesia raw material
into which effect of the liquid phase penetration
is highly advantageous. The improved coating
property was realized through a reinforced anchor
effect which is a result of liquid phase penetration
into both micropores in the matrix and into magnesia
coarse grain.

References

- 1) Japan Cement Association HP, <https://www.jcassoc.or.jp>(2024.09.27)
- 2) Edited by TARJ: Refractory Handbook Ver. 12, pp461-464
- 3) Y.Yasuda, K.Itoh, M.Takemoto and J.Kadono: Shinagawa Technical Report, **34** 43-62 (1991).
- 4) K.Igabo, M.Koga, K.Inoue and M.Ogata: Shinagawa Technical Report, **57** 25-38 (2014).
- 5) S.Ishihara, K.Nishida and T.Yamamoto: Proceedings of 31th Conference on Refractories for Cement kiln, 1-10 (2015).
- 6) Y.Miyata, Y.Toda and E.Ishihara: Proceedings of 39th Conference on Refractories for Cement kiln, 1-10 (2023).
- 7) Y.Miyata, K.Igabo and E.Ishihara: Proceedings of 40th Conference on Refractories for Cement kiln, 37-45 (2024).