Hydration resistance and mechanism of regenerated MgO–CaO bricks

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Regenerated MgO–CaO refractory brick samples were prepared from spent MgO–CaO bricks and fused magnesia. Hydration resistance was investigated by hot water experiment, and its hydration reaction mechanism and hydration kinetic model were explored. The results showed a superior hydration resistance of regenerated samples. $\text{Ca}(\text{OH})_2$ was the only new generated phase after the hot water experiment, and it is indicated that the hydration of free CaO was the key point. Impurity elements Si, Fe, Al in the spent MgO–CaO bricks had enhanced the hydration resistance through decreasing free CaO content and improving the density of regenerated samples. Meanwhile, it is found that hydration reaction mainly occurred on the surface of regenerated samples, which was controlled by diffusion of H_2O , and the diffusion rate constant K was $0.70 \times 10^{-6} \text{ s}^{-1}$.

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1. Introduction

Magnesite chrome bricks are kinds of refractories which are widely used in steel making industry^{1,2)} and cement rotary kiln,³⁾ especially in China at present,⁴⁾ however, as a serious hazardous of hexavalent chromium, magnesite chrome bricks are restricted to be used in more and more countries,⁵⁾ so that the substitutes are urgently to be applied. MgO–CaO refractory bricks are considered as favourite replacements of magnesite chrome bricks, as their similar usability, such as kiln coating adherence.⁶⁾ However, there is a serious problem of MgO–CaO refractory bricks, namely, one of the main phase lime (free CaO, short for f-CaO) is prone to reacting with water to generate calcium hydroxide [$\text{Ca}(\text{OH})_2$], meanwhile, combined with a volume expansion of about 97 vol.%.⁷⁾ Therefore, MgO–CaO refractory bricks are limited to be used in the cement rotary kilns for their poor hydration resistance.⁸⁾ It is reported that hydration resistance had been improved by adding metal oxide such as iron oxide (Fe_2O_3) or aluminium oxide (Al_2O_3) powder to enhance the density.^{9,10)}

MgO–CaO refractory bricks annual consumption in China was about 250,000 ton in 2007,¹¹⁾ moreover, the spent bricks have not been reused adequately. These spent bricks not only occupy a lot of land which is already a kind of precious resource to China, but also cause severe resource waste. It is because that there are too many impurity elements such as silicon (Si), iron (Fe), and aluminium (Al), which could cause a significant decrease in refractoriness, so that it is difficult to reuse completely the spent MgO–CaO refractory bricks in refining furnace.¹²⁾ The utilization of spent MgO–CaO bricks was normally in two ways, one was used as MgO–CaO clinker in MgO–CaO refractory bricks, but the highest utilization was only 25 wt %, ¹¹⁾ another was to be made into MgO–CaO dry vibration material for tundish working linings,¹³⁾ which requested that the impurities content in the spent MgO–CaO bricks was lower enough.

Regenerated MgO–CaO bricks using spent MgO–CaO bricks and fused magnesia as raw materials, paraffin as a binder were prepared successfully in the preliminary work,¹⁴⁾ and the utilization of spent MgO–CaO bricks was 67 wt %. Since there were some in-situ impurity elements such as Fe, Al and Si et al. in the spent MgO–CaO bricks, the hydration resistance of regenerated bricks is supposed to be improved. Besides, the operating temperature in cement rotary kiln is about 1450°C which is lower about 200°C than that of refining furnace. Therefore, regenerated bricks are more suitable for cement rotary kiln than MgO–CaO bricks to replace magnesite chrome bricks. It not only makes full use of spent MgO–CaO bricks, but also protects environment as the decreasing of chrome pollution.

In this work the regenerated MgO–CaO brick samples were prepared under air sintering atmosphere. Hydration resistance, phases, microstructure of regenerated samples were investigated, and the hydration mechanism was described as results.

2. Experimental procedures

2.1 materials

Regenerated MgO–CaO brick samples were prepared as the flowchart which is shown in **Fig. 1**. The size of green bodies was 60 mm × 8 mm × 8 mm, and sintered under air condition at 1600°C for 2 h. Three groups regenerated samples were obtained, namely, containing 80, 70, 60 wt % of MgO respectively, and samples M80, M70, M60 were used for short accordingly. The composition and bulk density of regenerated samples are shown in **Table 1**.

2.2 Test methods

Hydration of regenerated MgO–CaO bricks under normal air at room temperature is very weak,¹⁴⁾ hence, it is necessary to speed up the hydration to explore the whole hydration mechanism. Hydration resistance was detected by hot water experiment,¹⁵⁾ during which regenerated samples were boiled in burning water for 1 h, after that dried at 110°C for 24 h. Mass gain rate η was

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Fig. 1. Synthesis flowchart of regenerated MgO–CaO brick samples.

Table 1. The composition and bulk density of regenerated MgO–CaO brick samples

Sample	Mass fraction/%					Bulk density (/g·cm ⁻³)
	MgO	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	
M80	80.00	15.16	1.12	2.67	0.65	2.82
M70	70.00	24.13	1.57	2.87	0.96	2.95
M60	60.00	33.10	2.01	3.07	1.27	3.07

calculated by using Eq. (1), which was a characterization of hydration resistance of the regenerated samples.

$$d\eta = \frac{dW}{W} \times 100\% \quad (1)$$

Where, $d\eta$ - Differential increment of mass gain rate;

dW - Mass differential increment of regenerated sample;

W - Mass of sample before experiment, g.

A special experiment was carried out to compare the hydration degree of MgO and CaO which were the main components and hydration targets in the regenerated samples. M80, M70, and M60 regenerated samples powders (1 g, ≤ 0.1 mm) were dropped into excess boiling water for 1 h, and the volume of water was kept to 500 mL during the experiment. The hydration production $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ generated, although the solubility of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are lower, the excessive water was ensured soluble of Ca^{2+} and Mg^{2+} , so that the concentration of Ca^{2+} and Mg^{2+} could be detected and used to judge the hydration of CaO and MgO.

The phases of regenerated samples were analyzed by the MXP21VAHF X-ray powder diffraction (XRD). Ca^{2+} and Mg^{2+} concentration in the water after hot water experiment was measured by the Optima 7000 DV inductively coupled plasma (ICP). The microstructure of regenerated samples before and after hot water experiment were detected by MLA250-FEI Quanta scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS).

3. Results and discussion

3.1 The mass gain rate after hot water experiment

Table 2 shows that the mass gain rate of samples M80, M70, M60 was 0.74 wt %, 0.84 wt %, 0.90 wt % respectively. Literature¹⁶⁾ reported the mass gain rate of MgO–CaO bricks

Table 2. Comparison of mass gain rate between regenerated MgO–CaO brick samples and literature report¹⁶⁾

Sample	Total CaO content/wt %	Mass gain rate/wt %
M80	15.16	0.74
M70	24.13	0.84
M60	33.10	0.90
Literature report	15.00	3.77
	25.00	3.12
	35.00	6.72

Fig. 2. XRD patterns of regenerated MgO–CaO brick samples before (a) and after hot water experiment (b).

which contained similar content of CaO is also shown in Table 2. It can be seen that the mass gain rate of regenerated samples were all smaller than that of corresponded reporting, which is indicated the better hydration resistance of regenerated samples.

3.2 Phases characterization of regenerated MgO–CaO brick samples before and after hot water experiment

XRD patterns of regenerated samples before and after hot water experiment are shown in Fig. 2. It shows that the main phases of regenerated samples were both MgO, f-CaO, Ca_3SiO_5 (C_3S for short) and slight $\text{Ca}_2\text{FeAlO}_5$ (C_4AF for short) before and after the experiment, while $\text{Ca}(\text{OH})_2$ also appeared in regenerated samples after hot water experiment, which proved the hydration of f-CaO. It is worth pointing out that the character diffraction peaks of C_4AF and $\text{Ca}(\text{OH})_2$ were not observed in sample M80, as its fewer impurities content and better hydration resistance than that of the samples M70 and M60, which was in accordance with the results shown in Table 2.

Table 3. Concentration of Ca^{2+} and Mg^{2+} of the water after hot water experiment/($\text{mg}\cdot\text{L}^{-1}$)

Ions	M80	M70	M60
Ca^{2+}	84.09	148.80	224.70
Mg^{2+}	—	—	—

The hydration of MgO in regenerated samples was not observed in Fig. 2, which shows that there was a large difference of hydratability between MgO and f-CaO in regenerated samples. Reactions between H_2O (l) and MgO (s), f-CaO (s) are shown in Eqs. (2) and (3), respectively. It is indicated that the maximum Gibbs free energy of Eqs. (2) and (3)¹⁷⁾ are separately -24.74 and -55.61 kJ/mol at 100°C (boiling water temperature). This illustrates that both two reactions can occur from 25 to 100°C from point of view of thermodynamics. It is reported that the hydration mass gain rate was proportional to the specific surface areas of MgO and f-CaO.¹⁸⁾ In the regenerated MgO–CaO samples, the grain size of MgO was about $30\text{--}60\text{ }\mu\text{m}$, while it was about $20\text{--}40\text{ }\mu\text{m}$ for f-CaO grains. It is indicated that there was not obvious gap of the specific surface area between MgO and f-CaO grains. Therefore, their hydratability was attributed to their nature.

$$\Delta_r G^0 = -38.54 + 0.0377T \text{ kJ/mol}$$

$$\Delta_r G^0 = -66.05 + 0.0287T \text{ kJ/mol}$$

The concentration of Ca^{2+} and Mg^{2+} in the water after hot water experiment of regenerated sample powders is shown in Table 3. It shows that the hydration of MgO could not be detected, and it is proved that the MgO in regenerated samples was not hydrated in hot water experiment. Therefore, hydration of regenerated samples was almost exclusively caused by the hydration reaction of f-CaO.

3.3 Microstructure of regenerated MgO–CaO brick samples before and after hot water experiment

The microstructure of regenerated samples before and after hot water experiment is shown in Figs. 3 and 4, among which Fig. 3 was surface images and Fig. 4 was fracture ones. From Figs. 3(a) and 4(a) before hot water experiment, it is indicated that regenerated samples were very dense and crystal grains grew completely. The increasing of density of regenerated samples could be seen from Table 1 and Fig. 4(a), along with the increasing of the spent MgO–CaO bricks content. Because impurity elements Fe, Al in the spent MgO–CaO bricks reacted with f-CaO to form liquid phases at sintering temperature, and improved the sintering, so that the density was enhanced.¹⁴⁾

The hydration happened on the regenerated samples surface, which is shown in Fig. 3 M80-(b), M70-(b) and M60-(b), was obviously serious than that of inside of regenerated samples [Fig. 4 M80-(b), M70-(b) and M60-(b)], accordingly. The microstructure of regenerated samples surface [Fig. 3 M80-(b), M70-(b) and M60-(b)] shows that fewer hydration happened in sample M80 compared with that of samples M70 and M60. However, hydration of the internal in regenerated samples was hardly observed, except trace amounts of hydration such as morphology A and B in Fig. 4 M80-(b), it is because that the bulk density of sample M80 was the lowest one among samples M80, M70 and M60 as shown in Table 1, which is indicated that it was more

Fig. 3. Surface SEM images of regenerated MgO–CaO brick samples before (a) and after hot water experiment (b).

Fig. 4. Fracture SEM images of regenerated MgO–CaO brick samples before (a) and after hot water experiment (b).

porous in sample M80. Therefore, water could be easier to access to the inside of sample through open pore and react with f-CaO in sample M80, and the hydrated product of Ca(OH)_2 is shown as the morphology A and B in Fig. 4(b). Samples M70 and M60 were much denser than sample M80, hence, their inside hydration

Table 4. The content of f-CaO, C₄AF and C₂F in regenerated MgO–CaO brick samples

Sample	Mass fraction/%		
	f-CaO	C ₄ AF	C ₂ F
M80	6.19	3.10	0.17
M70	13.94	4.58	0.10
M60	21.70	6.06	0.03

was hardly observed. However, by comparison the morphology in Figs. 3 and 4, it is indicated that hydration occurred mainly at the surface of regenerated samples, and there was almost no change inside on the contrary. Hence, the hydration mass gain rate of sample M80 was lower than that of samples M70 and M60, though, inside hydration of sample M80 was more obvious.

3.4 Effects of impurity elements on the hydration resistance of regenerated MgO–CaO brick samples

As CaO/SiO₂ (molar ratio) > 3, Al₂O₃/Fe₂O₃ (molar ratio) < 1 (Table 1), the chemical reactions between f-CaO and impurity elements such as Si, Fe and Al in regenerated samples are shown as Eqs. (4)–(6). It shows that impurities could react with CaO and generate C₃S, C₂F and C₄AF. The content of f-CaO in regenerated samples could be calculated by Eq. (7),¹⁹⁾ and the result is shown in Table 4. It shows that it is the impurities that reduced the content of f-CaO to enhance the hydration resistance of regenerated samples.

$$w(\text{f-CaO}) = w(\text{CaO}) - 1.1w(\text{Al}_2\text{O}_3) - 0.7w(\text{Fe}_2\text{O}_3) - 2.8w(\text{SiO}_2) \quad (7)$$

Where, $w(\text{f-CaO})$ - Content of f-CaO, wt%;

$w(\text{CaO})$ - Content of total CaO, wt%;

$w(\text{Al}_2\text{O}_3)$ - Content of Al₂O₃, wt%;

$w(\text{Fe}_2\text{O}_3)$ - Content of Fe₂O₃, wt%;

$w(\text{SiO}_2)$ - Content of SiO₂, wt%.

Besides, the melting point of C₃S, C₄AF and C₂F was 2070, 1415 and 1449°C²⁰⁾ respectively. Therefore, the phases of C₄AF and C₂F were in form of liquid phase at sintering temperature (1600°C). The content of C₄AF and C₂F could be calculated by Eqs. (8) and (9),¹⁹⁾ and the result is also shown in Table 4. It shows that the more impurities content, the more liquid phase content in regenerated samples at sintering temperature, it is benefited to sintering, hence, the density of regenerated samples increased with the increasing of impurities content (Table 1). Subsequently, H₂O was blocked to diffuse inside of regenerated samples and their hydration resistance enhanced.

$$w(\text{C}_4\text{AF}) = 4.77w(\text{Al}_2\text{O}_3) \quad (8)$$

$$w(\text{C}_2\text{F}) = 1.7[w(\text{Fe}_2\text{O}_3) - 1.57w(\text{Al}_2\text{O}_3)] \quad (9)$$

3.5 Hydration mechanism of regenerated MgO–CaO brick samples

In order to investigate the hydration mechanism of regenerated MgO–CaO bricks, sample M60 was selected to carry out following hot water experiment. Ten M60 samples were put

Fig. 5. Mass gain rate vs. time of regenerated samples content 60 wt% MgO.

Fig. 6. Sketches of diffusion controlled model, (a) before hot water experiment, (b) after hot water experiment.

into boiling water simultaneously, while taken out ones every three minutes interval, and then the relationship of mass gain rate and reaction time was obtained as shown in Fig. 5. It shows that mass gain rate rapidly increased in the first three minutes, and then the increasing was relatively moderate. Because the surface of regenerated samples contacted directly with water, f-CaO on the surface immediately reacted with H₂O and led to the increasing of mass gain rate rapidly, and serious hydration happened on the surface of the samples. This stage was controlled by chemical reaction. However, during the rest reaction time, water entranced into the inner of regenerated samples, and this stage was supposedly controlled by diffusion.

Diffusion controlled model of regenerated sample is shown in Fig. 6. As the length of sample L was much longer than the width a_0 , and the mass gain rate was very small, the hydration reaction on top and bottom surfaces and corners in Fig. 6 were ignored. Diffusion controlled kinetic equation could be calculated by correcting the formulas in literature.⁷⁾

As shown in Fig. 6, the width of sample section after hydration reaction at time t was a , the thickness of product layer was $(a_0 - a)/2$, the thickness of reaction layer was $d(a/2)$. When

$t = 0$, $a = a_0$, Eq. (10) could be obtained based on the parabolic law supposing diffusion is the controlled condition.

$$(a_0 - a)^2 = 2K_n t \quad (10)$$

Where, a_0 - Width of sample section before hydration reaction, cm;

a - Width of sample section after hydration reaction, cm;

K_n - Constant, cm^2/s ;

t - Hydration reaction time, s.

$d\eta$ could be calculated according to Eq. (1), and dW and W can be calculated from Eqs. (11) and (12),

$$dW = w\rho \times k \times dV \quad (11)$$

Where, w - Mass fraction of f-CaO in regenerates sample, wt.%;

ρ - Density of f-CaO, $\text{g}\cdot\text{cm}^{-3}$

$k = 18/56$ - Net addition mass of regenerated sample per unit mass of f-CaO.

$dV = 4aLd(-a/2)$ - Volume differential increment of reaction layer.

$$W = \rho' \times V \quad (12)$$

Where, ρ' - Bulk density of regenerated sample, $\text{g}\cdot\text{cm}^{-3}$.

V - Volume of regenerated samples, cm^3 .

Substituted Eq. (11), Eq. (12) into Eq. (1), When $a=a_0$, $\eta = 0$, Eq. (13) was obtained.

$$a^2 = a_0^2 \left(1 - \frac{28}{9} \times \frac{\rho' \eta}{\rho w} \right) \quad (13)$$

Combined Eqs. (10) and (13), here, $\rho' = 3.07 \text{ g}\cdot\text{cm}^{-3}$ (Table 1), $\rho = 3.32 \text{ g}\cdot\text{cm}^{-3}$, $w = 21.70 \text{ wt}\%$ (Table 4), substituting into Eq. (13), diffusion controlled kinetic equation could be calculated as shown in Eq. (14),

$$f(\eta) = [1 - (1 - 13.26\eta)^{1/2}]^2 = Kt \quad (14)$$

Where, $K = 2K_n/a_0^2$ - Constant of diffusion rate, s^{-1} .

It can be seen that the relationship of $f(\eta)$ and reaction time t was a linear relation. The value of $f(\eta)$ could be obtained by substituting the mass gain rate η into Eq. (14), and fitted it with reaction time t , the result is shown in Fig. 7. It is indicated that the hydration reaction after three minutes was accorded with diffusion controlled kinetic equation as the R -squared (R^2) was 0.9801, and the constant of diffusion rate K was also obtained, it

Fig. 7. $f(\eta)$ vs. time of regenerated samples contenting 60 wt% MgO.

was $0.70 \times 10^{-6} \text{ s}^{-1}$. Compared with the literature report whose constant of diffusion rate K was $1.00 \times 10^{-6} \text{ s}^{-1}$ in the hydration resistance experiment of MgO–CaO clinkers (CaO/MgO was 40/60, mass fraction),⁷⁾ the two results of K were similar. It shows that the diffusion model was suitable to the regenerated samples. Therefore, it could be concluded that the hydration reaction was firstly controlled by chemical reaction in a very short beginning time, afterward it was rapidly transformed into diffusion controlling in the rest of reaction time, and the diffusion rate was very slow.

4. Conclusions

Regenerated MgO–CaO brick samples M80, M70, M60 were prepared respectively by using spent MgO–CaO bricks and fused magnesia as raw materials. Hydration resistance and mechanism were investigated by hot water experiment. The results are summarized as follows:

- (1) Mass gain rate of regenerated samples M80, M70, M60 was 0.74, 0.84, and 0.90 wt % separately, which showed the excellent hydration resistance.
- (2) Impurity elements Si, Fe and Al had decreased the content of f-CaO which was the key point to the hydration reaction of regenerated samples, and moreover they enhanced the density of regenerated samples.
- (3) Hydration resistance mainly occurred at the surface of regenerated samples, and the hydration reaction was controlled by chemical reaction in the very short beginning time, and followed by diffusion controlling in the rest of reaction time. Diffusion rate constant K was $0.70 \times 10^{-6} \text{ s}^{-1}$, which is indicated the superior hydration resistance of regenerated samples.

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