Green Refractories – Concepts, Approaches and Practices

Zhou Ningsheng, Liu Jiehua

Challenged by globally advocating environmental preservation and low carbon economy, it is imperative to develop "green refractories", as an important strategy in favor of present and future sustainable development of refractories industry, also contributive for refractory consuming industries to meet the challenge of green manufacturing. Concepts and countermeasures for implementing "green refractories" strategy are suggested, concentrating on making efforts in the development and enlarged adoption of monolithic refractories, resource conservation refractories, energy saving refractories and environment- and eco-friendly refractories. Particular technical approaches and suggestions are given to promote achieving such targets. To this connection, recent practices and developing trends at home and abroad have also been introduced.

1 Introduction

Facing the challenge of globally advocating low carbon economy, it is believed that developing "Green Refractories" is an important strategy for sustainable development of refractories industry, also meaningful to meet the challenge of green production for refractory consuming sectors, considering refractories are of fundamental materials for those high temperature related industries. What does "Green Refractories" mean? The Association of China's Refractories Industry has so summarized the concepts of Green Refractories as "Optimization in products variety and quality, conservation in energy and resource, eco-friendliness during production and harmlessness in application". In this paper, concepts and technical approaches for implementing "green refractories" strategy are discussed. To this connection, recent practices and developing trends are also highlighted.

2 Making efforts to develop monolithic refractories

In comparison with burned shaped refractories, monolithic refractories have been tremendously developed in the past 3 or 4 decades all over the world, thanks to such advantages as relatively less complicated production process, shorter production cycle, lower comprehensive energy consumption from preparation to installation, capable of conducting high efficient mechanical installation, reduced material consumption by partial repair and relining on residual lining, suitable for lining and mending complex configurations and convenient in adjusting composition and properties in accordance with installation and application requirements. The ratio of monolithic refractories over the total refractories has become as an important index to access technological developmental level of the refractories industry. Since the 1980s, as total outputs of refractories in developed industrial countries turned to decline, while the output of monolithic refractories maintained or increased, the ratio of monolithic refractories to shaped refractories has maintained an overall increase. As a leading country in refractories technology, Japan was the first to achieve the output of monolithics exceed shaped refractories' in 1992. Since 2011 the ratio of monolithics over the total refractories in Japan has exceeded 70 %. Such a ratio in U.S. and some well known European countries has reached or exceeded 50 % in recent years. Presently this ratio in China is about 40 %, according to the statistics by the ACRI for the previous three years, implying a relatively big space for further development of monolithics in China.

As products to be shipped, most monolithics do not need to be fired. Even for pre-cast shapes, usually a heat treatment at mild temperatures, instead of high temperatures, is necessary. From energy consuming point of view, monolithics are in accordance with the concepts of green refractories. Recently the Ministry of Industry and Information Technology of the PR of China has issued the Standard Conditions of the Refractories Industry (2014), in which comprehensive energy consumption per unit product is requested, see Tab. 1. As seen, monolithics consume a very low level of energy, compared to fired bricks. To help be aware of the meaningfulness of developing monolithics, a calculation of the fuel consump-

Zhou Ningsheng
High Temperature Materials Institute
Henan University of Science and Technology
Luoyang, Henan 471003
China

Liu Jiehua
Luoyang Refsource Industry and Trading Co., Ltd.
Luoyang, Henan 471000
China

Corresponding author: *Z. Ningsheng*
E-mail: E-mail: nszhou@163.com

Keywords: green refractory, monolithic refractories, resource conservation, energy saving, environment- and eco-friendly development trend

Tab. 1 The norm of energy consumption per unit refractory product

Product	Type/Technology	Energy Consumption per Unit Product [kg c.e./t]
Fireclay bricks (including low creep; irregular type ≤40 %)	–	172(1)
High alumina bricks (including low creep; irregular type ≤20 %)	–	318(2)
Silica bricks (irregular type ≤20 %)	–	338(3)
Magnesia based	Normal MgO bricks	184
	Medium grade MgO bricks	232
	High purity MgO bricks	256
	$MgO–Cr_2O_3$ bricks	205
	Direct bonded $MgO–Cr_2O_3$ bricks	268
	MgO–CaO bricks	179
	MA spinel bricks	245
C-containing products	MgO–C and $MgO–Al_2O_3–C$	31
Monolithics		10

(1) Comprehensive energy consumption increases by 15 kg c.e./t, when the ratio of irregular type (including low porosity dense bricks) increases by 10 %;
(2) Comprehensive energy consumption increases by 15 kg c.e./t, when the ratio of irregular type (including low porosity dense bricks) increases by 10 %;
(3) Comprehensive energy consumption increases by 20 kg c.e./t, when the ratio of irregular type increases by 10%; (4) Standard coal coefficient is 0,1229 kg c.e./kWh

Tab. 2 Assessment of energy and emission reductions by raising the monolithics ratio

Increased Percentage and to be Achieved Monolithics' Ratio	5 (to Reach 45 %)	10 (to Reach 50 %)	15 (to Reach 55 %)
Saved coal equivalent [10^3 t/a]	150	300	450
Emitted CO_2 reduction [10^3 t/a]	373,95	747,90	1121,85
Emitted SO_2 reduction [t/a]	11250	22500	33750
Emitted NO_x reduction [t/a]	5625	11250	16875

tion and emission reduction is made by Tab. 2, based on the following assumptions. As shown in Tab. 1, the average consumption of coal equivalent (c.e.) per tonnage of fired refractory product is above 170 kg up to 338 kg, a saving of c.e. by producing per ton of monolithic is accordingly at least 150 kg. The emission of CO_2, SO_2 and oxynitride is theoretically 2,493; 0,075 and 0,0375 kg respectively from burning 1 kg of standard coal. The total refractories consumption in China is around 20 Mt, and the monolithics ratio is supposed to grow, by a 5 % step from 40 % up for calculation purpose, the reductions of c.e. consumption and emissions are tremendous, as shown in Tab. 2, worth of the authors great efforts.

To promote the popularization and application of monolithics, the following aspects, i.e., pre-cast shape, user friendliness, high performance and high efficiency in installation and application, are worth of attention and endeavor.

2.1 Pre-cast shapes

Pre-cast shapes of castables have been increasingly adopted in recent years due to the following advantages:

(1) Pre-cast shapes can, in many cases, be used as alternatives of bricks or castables to simplify the installation. In-plant mixing, casting or ramming and related facilities can thus be saved.

(2) As casing, curing, drying and first heat-up have been carried out in production under controlled conditions, time can be saved for consumers to increase thermal equipment circulation or turnover ratio.

(3) The installation is independent of environmental and climate conditions, not like the case in hot summer and cold winter, which is not suitable for in-plant casing castables.

(4) Complicated configurations or shapes and big (>10 t) or small (<1 kg) sizes of castables can be fabricated by casting, which may otherwise hardly be made by pressing, such as BF trough skimmer and EAF roof, baffle bricks for regenerative furnace with through-hole diameter of 4~5 mm and thickness of 2~3 mm.

(5) As the installed pre-cast shapes can be put into use without long time drying-out under stringent heating-up schedule, it is more user friendly.

(6) Top size in castables can be much bigger than in bricks.

This virtual trend of "shaped monolithics" brings good ways for refractory manufactures to insert added values in the products. Recent years have seen an increasing adoption of pre-cast shapes of castables for many applications, e.g., for BF tuyere, ceramic burner, troughs of middle- and small-size BFs, working lining, purging plug, well block and impacting pad of steel ladles, tundish weirs and impacting blocks, roofs and burners of reheating furnaces, even pre-cast sliding plates, etc. There store also the possibility and necessity of adopting pre-cast shapes in torpedo car, iron ladle, hot-metal mixer, etc.

2.2 User friendliness

Installation related performance is an important thing of monolithics, differing from shaped refractory products. Taking castable for instance, the setting and hardening behaviors are affected by multiple factors, in terms of binder type, impurities from raw materials, micropowder feature, ambient temperature, etc. The sensitivity of castables to them may bring about inconveniences during application. Therefore, both R & D and producing workers involved in monolithics must give their attention to as much as stable installation behavior of monolithics.

It is known that the setting behavior of CA cement bonded castables is likely to be affected by ambient temperature, particularly at low temperature, the initial setting will be too long or even never occur. To tackle with this problem, Almatis developed a new type cement, called temperature independent cement. A comparative investigation of

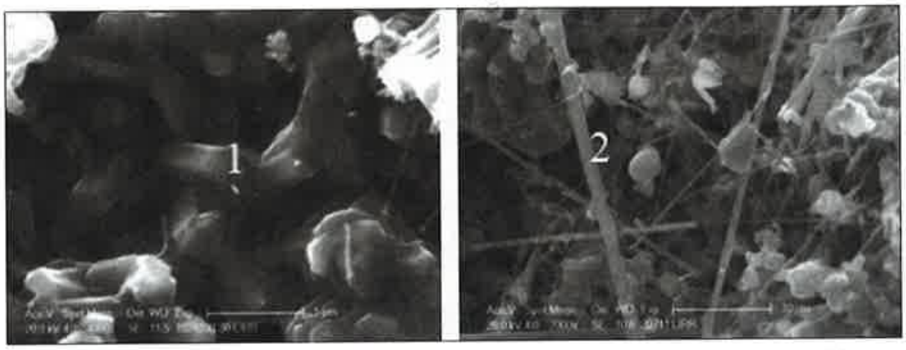

Fig. 1 In-situ generated hexagonal and fibrous SiAlON crystals in SiC-based castable nitrided at 1420 °C (Si powder addition: 7 %)

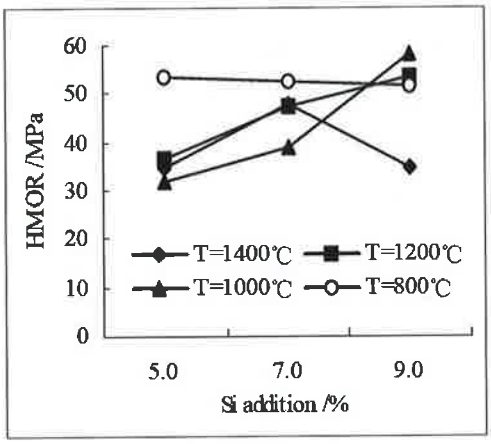

Fig. 2 HMOR of SiC-based castable specimens nitrided at 1420 °C

new cement vs conventional one on setting and strength development behaviors of the castables with different binding system and different microsilica at various ambient temperatures [1]. Repeated tests show that no matter in the LC or ULC system, using new cement leads to a better repeatability of testing results and less dependent of storage time of the dry mixes. Conventional cement is very sensitive to microsilica's quality, from quick setting to unsetting, while the new cement has less sensitivity to the quality of microsilica, initial setting time varies from 500 – 1500 min, showing a good adaptability. When andalusite is used to replace tabular alumina as aggregate, setting behavior of the microsilica containing LC castable shows that such less temperature sensitive cement has good adaptability to the change of aggregate. Under low temperature condition, adopting such new cement will facilitate strength development.

From the above, it is known that compared to normal CA cement, the new cement has not only less sensitivity to temperature, but also less sensitivity to impurity in the binding system. This brings users about convenience in ensuring installation stability, a kind of "user friendliness" in this way. For castables, Saint Gobain put forwarded at UNITECR'09 the concept of "multifunctional" and "multiple applications"[2], a good implementation of "user friendly" concept. Compared with shaped refractories, variety of monolithics is much more, bringing about difficulties in research, production and application. To implement "user friendly" concept, developing those with simplified formulations but more extensive adaptability will certainly be well received.

2.3 High performance

Development of high tech and value added monolithics will certainly help increase the share of monolithics in total refractories.

Oxide-nonoxide composite refractory products have become one of the hot topics of R&D, with many positive progresses. For example, Si_3N_4 and/or SiAlON bonded alumina based bricks have been used as ceramic cup in large BFs; Si_3N_4 bonded SiC based bricks have been widely adopted by aluminium and ceramics sectors; SiAlON composited Al_2O_3–C sliding plate, ZrB_2 incorporated ZrO_2–C submerging entrance nozzle, Al/Si–Al_2O_3–(ZrO_2–)C functional refractories, etc. have been applied in steelmaking sector, all with satisfactory results. Making in situ formed nonoxide composited products with complicated shape or big volume by pre-cast castable is a new approach to realizing high performance and functional refractories.

Wang Huifang, et al. [3] carried out a research on the approach to enhancing cold and hot strengths of SiC based ULC castables incorporated with silicon by in-situ formed SiAlON bonding phase through nitridation. After nitridation at 1420 °C, microstucture of the SiC based castable gets changed, with massive in situ formed SiAlON in the matrix, as shown in Fig. 1, leading to much increased cold and hot strengths, HMOR at 1200 °C reached more than 50 MPa, as shown in Fig. 2.

2.4 High efficiency in installation and application

The easiness of installation, curing, dryingout, detecting, maintenance and dismantling of monolithic refractories determines their acceptance. Experiences have demonstrated that the performance of on site installed monolithics depends largely on the qualities of installation and dryingout. Lack of advanced techniques for safe and efficient installation, dryingout and maintenance is obstructing the wide application of monolithics. It is very necessary to develop techniques for high efficient or even automatic installation, rapid curing, quick dryingout or dryingout-free, robotic detecting, maintenance, and fast dismantling. In these regards, China is behind many developed countries, in which techniques for shotcreting, robotic spraying, microwave drying, on-line hot patching, automatic thickness detecting and monitoring are already quite common.

D. Peters [4] with Resco/US introduced three approaches to improving efficiency of castables installation and speed up users' circulation in order to reduce total operation cost:

(1) Dust inhibitor: Dust produced from mixing can not only exacerbate the working environment and harm workers' health, but also cause installation delay and loss of some important ingredients that deteriorates the castables properties. Currently the problem can be overcome by addition of dust inhibitor.

(2) Easy mixing: Reducing mixing time is an approach for rapid installation and for sufficient working time of castables. Short time mixing can be realized by use of appropriate additives that are able to reduce wetting time of the mixes.

(3) Curing and drying out schedule: It is desirable to shorten curing time as much as possible or even eliminate curing procedure at all. The improvement should also alleviate the requirement for on site drying out equipment, reduce holding time at various temperatures during whole drying out process, and realize rapid drying out or even

non-drying out. As an example, the interruption period of a ceiling feed aluminum smelter was shortened to less than 1 day by means of a systematically optimized castable design.

Pierre Meunier, et al. [5] from Calderys introduced an approach of quantitative investigating into drying out behavior of castables, i.e., on-line monitoring, by a internally set probe, temperature and strength evolution at different positions inside the testing castable during drying out process, as schematically shown in Fig. 3. Quantitative measuring indicates that from hot face towards inside, the location and time for a maximum temperature and a maximum pressure to occur are not synchronized. Such a simulation of practical drying out behavior is guidable and helpful to setting up reasonable drying out schedule.

Monocon is renowned for its expertise in hot monitoring and repairing steel converter, ladle and EAF linings. The ladle repairing "robotics" provided by this company is controlled by computer and is able to detect and repair slag line, side wall and bottom including the damaged area around purging plug. Its patent pending device, a bowl type spray patching system, can do both horizontal patching (ladle side wall and slag line) and perpendicular patching (ladle bottom). This system uses computer to control the whole procedure starting from damage detection and patching design to hot patching. Such a high level automation is of great beneficial to elongate ladle service life, speed up ladle circulation, reduce refractories consumption and alleviate labor intensity.

3 Making efforts to develop resource effective refractories

Refractories industry is of a highly resource consuming sector. In recent years, some important natural raw materials, bauxite, graphite, etc. in particular become tight in supply and soaring in price. A lot of heat energy is consumed for producing raw materials by high temperature calcination or fusion, while prices of fuels in terms of coal, natural gas or electric power, are growing. Survival stress is imposed on refractories producers due to growing price of both natural and synthesized raw materials. Resource effective refractories are worth our efforts, for which some recent approached and practices are highlighted below.

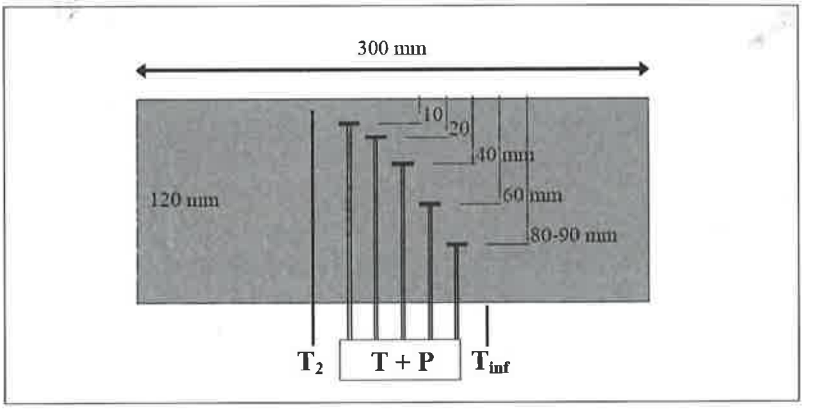

Fig. 3 Position of the probes in the castable

3.1 Rational allocation of raw material, product property and application requirement

Properties and quality of refractory products are directly influenced by raw materials. Requirements on raw materials and products depend on their working conditions. In the past, since most common raw materials in China were much cheaper than those from abroad, they have been, in many cases, lavishly applied, little is attached on a good match of properties and specific application condition, having led to an underutilization. Nowadays, a surplus of Al_2O_3 content in the Al_2O_3–SiO_2 refractories is commonly seen in China, for example, Al_2O_3 content in abrasion resistant castables for CFB in power industry is usually over 70 %, some even over 85 %. It seems that the higher the alumina content, the better the abrasion resistance and higher durability. In some overseas companies, Al_2O_3 content in castables for large CFBs is designed not as high as we may have imagined, some even less than 60 %. This indicates a difference in design concept and selection of raw materials. A too high Al_2O_3 content tend to result in troubles in terms of thermal shock resistance, spalling resistance, volumetric stability, thermal conductivity, etc.

The above mentioned is, to some extent, equal to some resource waste. To make best use of refractory raw materials and products deserves to be a goal to pursue. Due to different working conditions, industrial furnaces and thermal devices have different damage causes and ways, and their service lives are usually determined by the life of the weakest part. Comprehensive lining by using different quality or grade of materials will help realize balanced damage and reduce refractory consumption. Although this concept has been accepted in designs of various linings, consideration on material allocation remains to be rough and material selection tends to have an excessive safety factor, leading to a waste in both function and material consumption.

With regard to a complex use of raw materials, restrained by the price, only for some costly high-grade products, this has been adopted. The concept of complex use of raw materials should be applied to produce all possible products, to reduce cost for raw material or even improve product efficiency. Two-dimensional complex structure of furnace lining can be fulfilled by using different raw materials to reach different properties, which will help reduce the lining cost and bring about comprehensive benefits, such as lightening furnace lining, energy saving, etc.

3.2 Direct use of mineral based natural raw material

When subjecting to elevated temperatures, physical and chemical changes occur to natural minerals, accompanying decomposition and volumetric change. From this concern, most of raw minerals, when used as raw materials in refractory products, especially as aggregates, have to be calcined at enough high temperature. For monolithic refractories, however, a heterogeneous system consisting of multi-composition and multiphase is the feature differing from shaped fired products, i.e., before putting in service, the matrix portion is far from an equilibrium state, and the matrix components, when subjecting to high temperature and time during service, will react each

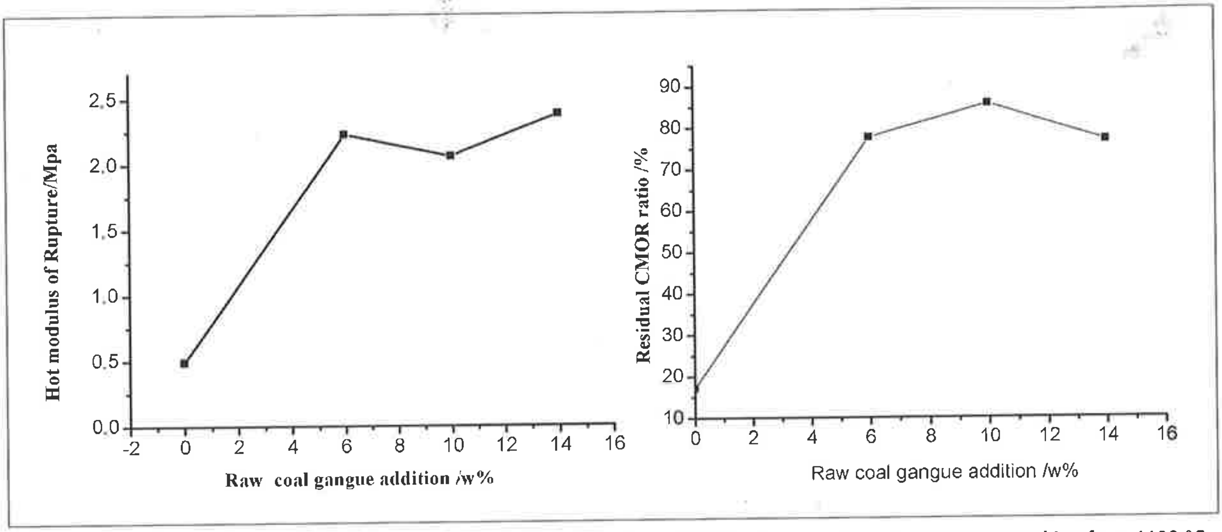

Fig. 4 Effect of raw coal gangue addition on HMOR at 1400 °C and residual CMOR ratio after 1 cycle of water quenching from 1100 °C of Al_2O_3–SiO_2 LC castable

other and tend to reach an equilibrium, following phase equilibrium relationship. If properly designed and controlled, favorable reaction products and microstructure in the matrix can be obtained in favor of properties.

Hou Wanguo [6] investigated the effect of raw bauxite and raw coal gangue on properties of Al_2O_3–SiO_2 castables and concluded that up to 10 % addition of raw bauxite has little negative effect on properties of the castables and at appropriate addition of raw coal gangue, HMOR and thermal shock resistance can even been improved, as shown in Fig. 4.

It can be seen that, depending on domestically rich refractory mineral resources, such as bauxite, flint clay, coal gangue, andalusite, etc., natural raw materials can be directly added into Al_2O_3–SiO_2 castables without calcination or with light calcination for dehydration, which can not only save the energy for calcination, but also play a positive role in improvement of some properties. However, with regard to changes or reactions during heating-up to occur in the raw materials, lots of research work still need to be carried out to make it under good control and even improve some properties of the castables, such as explosion resistance, hot strength, thermal shock resistance, etc.

3.3 Recycling of used refractories

China is not only the largest country for refractories production, but also for refractories consumption. In recent years, China's annual refractory consumption is around 20 Mt. Suppose 65 ~70 % to be worn out for calculation, annually there are 6–7 Mt of wasted refractories. From this viewpoint, used refractories are of very important secondary resource for refractories industry, and if they can be reasonably reused, not only can large amount of raw materials be saved, but also solid waste discharge be reduced, in favor of environment protection and improvement.

Refractory materials are deteriorated during their service due to the attack by various contacted media, and some foreign matters or inclusions may also be introduced during service, lining dismantling and transportation, leading to certain instability in constitution of the wasted refractories, which may leave troubles for a safe reuse of used refractories. Separation and removal of harmful matters are thus very necessary, awaiting combined efforts of multi techniques. Good example to this connection is color separation technique developed in Japan, to which high pressure airflow separator system is incorporated. It has been used in removing included slag (dark color) in wasted refractories with a light color [7].

Implementing of the green refractories concepts in China is also represented by actively recycle and reuse of used refractories. Examples are many, including relining of monolithic steel ladle on residual lining by castables, relining of iron ladle by shotcreting, recycling and reuse of used Al_2O_3–SiC–C monolithics for BF troughs and MgO–C bricks for BOFs and ladles, repair of used sliding plates, and recycling of high purity refractory bricks including alumina based, Al_2O_3–Cr_2O_3, Al_2O_3–ZrO_2, Cr_2O_3-based, ZrO_2-based, SiC-based, etc.

"Zero emission" concept is summarized by Nippon Steel Co. as 3R [7], i.e. Reduce, Reuse and Recycle. Reduce means to reduce refractory consumption, for instance, to reduce workload on industrial furnace lining, to enhance lining durability, etc. Reuse refers to repeatedly use wasted refractories as auxiliary raw materials for furnace lining or as slag-forming constituent, etc. Recycle means to use processed wasted refractories as raw materials added in new refractories.

In addition, it is worth following that refractory suppliers are encouraged to recycle used refractories by their end users in Japan, some European countries, Taiwan, etc., and the costs are to be deducted accordingly from their following orders.

4 Making efforts to develop energy saving refractories

Refractories industry and its user industries are of the focal object of energy saving and emission reduction, as both sectors are greatly consuming energy. Energy saving refractories deserve to be a type of green refractories with vigorous perspective. More adoption of lightweight insulating refractories is an effective measure to realize energy conservation of industrial furnaces. It is very necessary to find effective solutions to such problems brought by using conventional insulating refractories as insufficient strength, limited service temperature, unsatisfactory

Tab. 3 Chemical composition of chrome ore, spinel and pleonastic spinel [%]

	Chrome Ore	Spinel	Pleonastic Spinel
SiO_2	0,5–2	<0,5	<2,0
Al_2O_3	10–25	67	51
Fe_2O_3	14–28	<0,5	23
Cr_2O_3	30–48	–	–
MgO	12–20	32	24
CaO	<0,8	<0,5	<0,5

One should utilize waste heat as much as possible. Research indicates that exhaust gas from a kiln, for raw material calcinations or product firing, could carry away sensible heat as much as 35~40 % of the total heat consumed in the process, if no heat recycling measures are taken [12]. It is obvious that waste heat recycling is a very important task, otherwise large amount of heat will be lost and become detrimental to the environment.

5.2 Hazard-free raw materials

Raw materials are of an important basis for production and development of refractories. The prerequisite for development of green refractories is the capability of producing durable, environmental friendly and high quality raw materials that can satisfy needs of the industries involved in high temperature processing and thermal insulation. ZrO_2-containing refractory products have widespread applications because of their superior properties. However, attention should be paid to the radioactivity of zirconia as a raw material. Carbon bonded refractories use binders such as pitch, resin, etc., which contaminate environment and harmful to human health during service. Some inorganic binders such as sulfates, chlorides, etc. will release toxic gases when heated. It is noteworthy for both refractory manufacturers and users to consider the development and adoption of harmless raw material and additives in substitution of the aforementioned ones.

5.3 In- and after-service hazard-free refractories

The so called in- and after-service hazard free refractories has three aspects, i.e. harmless to human body, harmless to the environment and harmless to the quality of hot melts in contact with the refractories. These aspects are addressed by the following examples.

5.3.1 Chrome-free refractories

Cr_2O_3 containing refractories are widely used as working linings in steelmaking, cement, glass, and non-ferrous industries, owing to their good thermal shock resistance and superior corrosion resistance to molten slag. However, the chrome in the products may become Cr^{6+} species when used with the presence of alkali and in oxidative atmosphere at high temperature. The Cr^{6+} species are water-soluble and contaminate the environment and expose to humans and animals, making them vulnerable to cancer. Because of this concern, globally the use of chrome containing refractories has been reduced dramatically since long. Use of magnesia-chrome bricks in cement and lime kilns in America and Europe has been strictly restricted. Chrome free refractories are thus of great importance for China's development of environment and eco-friendly refractories.

At present, the development of Cr_2O_3 free refractories is on going in various application areas, with different focuses. For secondary refining of steel, replacement of $MgO–Cr_2O_3$ bricks are mainly by $MgO–Al_2O_3–TiO_2$ [13] and $MgO–ZrO_2$ [14] products. Successful attempts have been carried out to use $Al_2O_3–MgO$ castable as alternative of $MgO–Cr_2O_3$ brick for RH snorkel in steel plants of Baosteel Group and Ma'anshan I. & S. Co. in recent years. Development of chrome free refractories for nonferrous metallurgy is dedicated to spinel based [15]. The availability of chrome free refractories for cement kilns can be dated back earlier, for which the material system is relatively rich. Currently cement kilns use dolomite, magnesia-spinel bricks, hercynite containing, $MgO–CaO–ZrO_2$, MgO-pleonastic spinel bricks, etc. as chrome free refractories. Among them, hercynite containing basic bricks were firstly developed and proposed by RHI, featured by superior toughness and good coatability, while the resistance to clinker corrosion needs to be further improved. For this purpose, Refratechnik Cement GmbH/DE incorporated magnesia to the hercynite containing brick and developed new bricks in the $MgO–Fe_2O_3–Al_2O_3$ system (pleonastic spinel), with improved clinker corrosion resistance and satisfactory service performance was demonstrated by in-plant application [16]. Comparison of chemical composition of chrome ore, pleonastic spinel and hercynite is shown in Tab. 3 [16].

The burning zone lining of China's cement kilns still consumes large quantity of $MgO–Cr_2O_3$ bricks each year. It is worrisome that the used bricks contain as high as 0,1–0,5 % (1000–5000 ppm) of Cr^{6+}, hard to handle. They need huge amount of water to dilute (for clean water, Cr^{6+} level must be under 0,05 mg/L). Currently, the used bricks are either to be piled somewhere or to be ground to fine powders and then added into cement. In order to avoid this hazard, the Policy and Regulation Department of the Ministry of Environmental Protection of China has included $MgO–Cr_2O_3$ bricks for cement kilns as restricted products, whereas the chrome free ones, such as $MgO–Fe_2O_3$, $MgO–Al_2O_3$, $MgO–Fe_2O_3–Al_2O_3$, MgO–CaO and MgO-pleonastic spinel bricks, are taken as environment friendly products, strongly recommended to be adopted in cement kilns.

5.3.2 Hazard-free refractory fibers

Conventional aluminosilicate refractory fibers have the problem of non-degrading when inhaled into human body. Because they are harmful to health, their use has got restricted in developed countries. EU has already included such fibers as the second class of potential cancer inducers. It is necessary to develop novel thermal insulating materials as substitutes for such conventional fibers. Current research and development are focused on bio-soluble refractory fibers and, on the other hand, novel lightweight castables.

Bio-soluable refractory fibers are ceramic fibers that can dissolve in pleural fluid and can be used persistently at elevated temperatures. Their major properties are equivalent to conventional aluminosilicate fibers, while the solubility constant is significantly higher than that of the conventional ones. They are not threats to human health and thus be-long to green refractory products. In recent years, profound progress on biosoluable refractory fibers has been made in developed countries. The related R & D is also carried out in China, what can be referred to X. Wang's work [17].

As known, Almatis developed a novel lightweight castable (SLA-92) that uses calcium hexaluminate as lightweight aggregates [18]. It is harmless to human health and its thermal insulation performance is even better than ceramic fiber products at high temperature. The product has already used in ladle lid as well as reheating furnaces, etc.

5.3.3 Improvement in binding system of dry mixes for tundish

Currently there two installation methods for tundish lining, wet spray or dry vibration. The latter is easier to carry out and the so installed lining can be baked quickly. During the service, it undergoes an inward sintering and densification, which retards cracks propagating through the lining. The density of the unfired layer remains rather low, imparting the lining with low thermal conductivity and reduced heat loss. In addition, the residual lining after service is easy to be dismantled. These advantages lead to an increase adoption of such dry mixes.

In order to obtain strength and slag resistance after baking, dry mixes need to use organic binder, usually pitch and/or phenolic resin powders. The use of such organic binders brings in some troubles, i.e. (1) baking induced smoking that contaminates the environment; (2) release of unpleasant and irritable orders harmful to health of the workers; and (3) contamination of molten steel with carbon and hydrogen from the binder. In order to overcome such problems, new binding systems for environment friendly tundish dry mixes have been developed. For example, dry mixes with new type of raw materials and binders was reported at UNITECR'09 [19]. It is believed that the new binders are not only friendly to environment and harmless to worker's health, but favorable to steel quality as well.

6 Systematic engineering for "green refractories"

"Green refractories" is an embodiment of sustainability strategy in refractories sector. As a strategy, it needs a sense of overall arrangement. Our understanding of and action on green refractories should under the guidance of systematic engineering and make comprehensive arrangements. Refractory manufacturers should have scientific and systematic considerations, from raw materials preparation to products production, installation, use, maintenance, and after-use disposal. Efforts should be made to avoid focusing R & D only on one aspect or emphasizing one but overlooking another.

A system for refractories does not only involve refractories manufacturers, but also connects to their upstream firms such as mining and raw material enterprises, and their downstream firms such as makers of steel, cement, ceramics, glass, non-ferrous metals, etc., or even some further aspects. Refractory manufacturers should pursue active collaborations with their upstream and downstream partners as well as the related R & D institutions. By such active collaborations, they are more able to obtain widespread application of green refractories and fully exercise their advantages in energy saving, consumption reduction and economic benefits creation. It is worthwhile paying attention to the following:

- Enhance manufacturers' capability in comprehension, innovation and service. Manufacturers must think and act from their users' points of view, and change the traditional concept of taking selling as the only purpose. Only when they are able to use advanced technologies to produce high duty products and perform everything-good services to help their users in reducing the costs for safety, operation, repair and maintenance, as well as various consumables, to create values for customers, will they be able to win the market and hence obtain their own interests.
- A refractory manufacturer should know its own situation and its own feasibility for realization of green refractories, and enhance its management capacity. It needs to improve and refine its innovation policy and management, actively update processing and characterization facilities and optimize its technologies and products. Through these approaches, its competitiveness can be strengthened.
- Manufacturers engaged in unshaped refractories should emphasize inter industrial and inter technological collaborations. Such collaborations will help accelerate and facilitate improvements and optimizations in installation, dryingout, use, monitoring, maintenance and after-use disposal of unshaped refractories, so as to reduce processing time, labor, energy and facility consumption, and give a full play of the "green" advantages of unshaped refractories.

"Green strategy" has been taken as important policy for advancement of refractories and attracted attentions from refractories sector itself as well as other related partners. Researchers and engineers in refractories area have made profound achievements in R & D and application, based on "green refractories" concepts. Such accomplishments are lying good bases and offering experiences for further implementing the "green" concepts. However, we must be aware that there are still a lot of tough problems to be overcome. Refractory workers should take the whole into consideration, do the job bit by bit, face the reality and emphasize things important. Collaboration and coordination among manufacturer, researcher, developer and designer are greatly advocated and encouraged. Refractory enterprises should work together and also work together with research institutions and end users to make new breakthroughs in technology for green refractories. The effective collaboration and hard work are expected to achieve, before long, substantive breakthroughs in key and generic technologies for better development and application of green refractories.

To refractories industry, green refractories are of both a challenge and also an opportunity.

References

[1] Buhr, A.; Schmidtmeier, D.; Wams, G.: New Results for CA-470TI Temperature independent cement – robustness against low temperature and impurities [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 051

[2] Frasson, S.C.; et al.: New multifunctional castables for multiple applications [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 214

[3] Wang Huifang; et al.: Enhancing cold and hot strengths of SiC-based castables by In-Situ formation of Sialon through nitridation [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No.179

[4] Peters, D.: Improved monolithic refractory lining system [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 002

[5] Meunier, P.; Soudier, J.: The drying of refractory castables: from tests to models [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 044

[6] Hou Wanguo: Effects of in-situ reactions of raw bauxite and raw coal gangue on properties of castables in Al_2O_3–SiO_2 system [D for M. Sc.]. Luoyang: Henan University of Science and Technology, 2009

[7] Hanagiri, S.; et al.: Recent improvement of recycling technology for refractories [J]. Nippon Steel Technical Report **98** (2008) 93–99

[8] Shan Guoqiang: Investigation on factors affecting properties of micropored lightweight mullite aggregate [D for M. Sc.]. Luoyang: Henan University of Science and Technology, 2010

[9] Zhao Mingtao: The synthesis of lightweight forsterite and its application in lightweight MgO–SiO_2 castable [D for M. Sc.]. Luoyang: Henan University of Science and Technology, 2012

[10] Zhou Ningsheng; et al.: Concept and Practice of High-Performance Lightweight Castables. 2nd China International Refractory Production and Application Conference, 15–17 May 2013, Wuxi, China

[11] Primachenko, V.; Martynenko, V.; Kaznacheyeva, N.: The research into the properties of thermal insulating microporous anorthite castable after thermal treatment in carbon-containing medium [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 115

[12] Dai Bin; Li Xiaoming: Reutilization and reclaim of extra heat for gas furnace. J. Industrial Furnaces **27** (2005) [2] 39–40

[13] Ghosh, G.; et al.: Development of chrome free brick for RH degass [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 080

[14] Chen Rongrong; et al. : Research of slag corrosion resistance of chrome free refractories for RH-vessel lining [J]. Naihuo Cailiao (Refractories in Chinese) **39** (2005) [5] 357–360

[15] Petkov, V.; et al.: Chemical corrosion mechanisms of magnesia-chromite and chrome-free refractory bricks by copper metal and anode slag [J]. J. of the European Cer. Soc. **27** (2007) 2433–2444

[16] Klischat, H.; Wirsing, H.: Practical application of mineralogical variations for cement kiln refractories [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No.171

[17] Wang Xitang; Liu Hao; Zhang Baoguo; et al.: Dissolution behaviors of refractory fibers in simulated lung fluid [J]. Naihuo Cailiao (Refractories in Chinese) **43** (2009) [6] 401–404

[18] Wuthnow, D.; Potschke, J.: Experiences with microporous calcium hexaluminate insulating materials [EB/OL], www.almatis.com/CN/refractory/technical-papers.aspx

[19] Bross, R.; Fechner, R.; Goedecke, M.; et al.: Dry-vibrating mixes versus wet-gunning mixes: new material concepts and lining technologies with respect to clean steel production [C]. Proc. of UNITECR'2009, Salvador, Brazil, 2009, No. 243