Industrial application experiences with microporous calcium hexaluminate insulating material SLA-92

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Abstract

The microporous Calcium Hexaluminate insulating material SLA-92 has been introduced as an alternative to refractory ceramic fiber and other insulating refractory materials. Key properties can be listed as: high chemical purity, long term high temperature stability up to 1500 °C, low thermal conductivity up to 1500 °C, and high thermal shock resistance. The properties of the new material and various applications in the steel and ceramic industries have been reported in previous papers. The current paper summarises the industrial application experiences with the new innovative refractories based on SLA-92.

Introduction

SLA-92 was introduced to the refractories industry in 1998 by van Garsel, et al. [1] as a new insulating raw material for high temperature applications, followed by investigations [2] for long term temperature stability of this new lightweight aggregate up to 1500 °C.

It has unique properties regarding chemical purity and mineral composition and is a microporous, silica-free Calcium Hexaluminate (CA_6 – mineral name: Hibonite) and was developed as an innovative alternative to commonly used refractory ceramic fibers.

SLA-92 chemical and physical data and mineral composition are listed in **Table 1**, microstructure, open and relative porosity are depicted in **Figure 1**.

Tab.1. SLA-92 product data

Chemical Composition [wt.-%]	Typical	Min.	Max.
Al_2O_3	91	90	
CaO	8.5		9.2
Na_2O	0.40		0.5
SiO_2	0.07		0.2
Fe_2O_3	0.04		0.1
Physical Properties			
Loose Bulk Density [kg/l]	0.5–0.6		
Bulk Specific Gravity [g/cm^3]	0.80		0.95
Mineral Phase Composition	CA_6 ($CaO \cdot 6\,Al_2O_3$) Major CA_2 Minor α-Al_2O_3 Minor		
Available Sizes	3–6 mm 1–3 mm 0–1 mm		

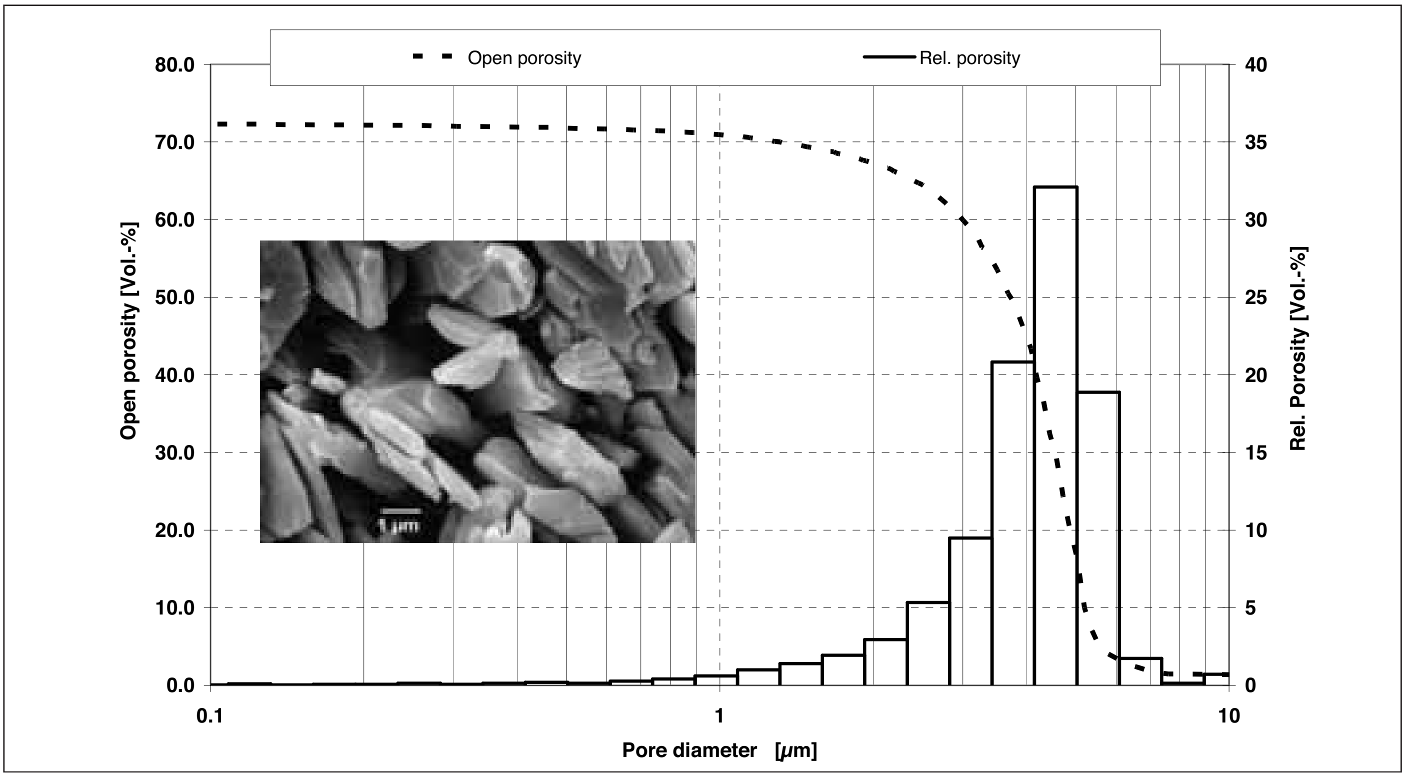

Fig.1. SLA-92 microstructure of calcium hexaluminate platelets (scanning electron microscope) and micropore size distribution (Hg-intrusion method)

Measurements on experimental castables show excellent resistance to thermal shock. The low density in combination with the microporosity, which hampers heat transfer by radiation on temperatures exceeding 1000 °C, results in a low thermal conductivity of 0.4 W/mK at 1300 °C, details are reported in [1].

This makes SLA-92 an innovative alternative to refractory ceramic fibers and it is an unmatched insulating aggregate for preferred use in state-of-the-art monolithic concepts, offering interesting application opportunities in the wide field of demanding high temperature insulation.

Since the introduction, numerous papers and publications report about the use of SLA-92 as a key raw material for high temperature insulation materials in a variety of applications. On closer examination of the papers, topics are mainly focused on:
- Fiber replacement
- Innovative raw material for improved performance

Besides advantages resulting from chemical purity, physical properties, microporosity, long term high temperature stability and resistance to demanding thermal shock, obviously one main driver for use of SLA-92 is to have a feasible substitution of refractory ceramic fibers, which are classified as category 2 carcinogens by EU legislation. A German public sponsored research and development project [3] reports about substitution of fiber containing concepts by SLA-92 based insulating materials in high temperature processes in the steel making, ceramic and other industries.

This paper summarises the industrial application experiences with the new innovative refractories based on SLA-92.

Applications in the Steel Industry

Often the steel industry as main consumer of refractories is also the driver for refractory innovations. A focus since several years is on the replacement of refractory ceramic fiber (RCF's), so far mainly for pre-heaters applied in steel making processes and the variety of reheating furnaces at hot rolling mills.

Ladle pre-heater cover lining

Duhamel and Verelle [4] report about a new design of lids for ladle preheating in Dunkirk Steelworks. The objective was the elimination of drawbacks due to handling, installation and removal of refractory ceramic fibers, along with significantly increased service live and availability of the ladle lids. Emphasize is also on health aspects and additional cost involved by wrecking RCF linings and disposal of fiber wastes in compliance with the environmental legislation. A castable based on SLA-92 has been a key component of the solution to achieve the objective. Even at initial higher material cost of about 54% compared to the RCF lining, the reduced manpower requirement and increased service life by at least 100% results in substantial total saving for the SLA-92 based castable solution. The work of Duhamel and Verelle was rewarded with the "Young Engineer of the Year Award" of the Institute of Refractories Engineers (IRE) in the year 2000.

Fig. 2. Ladle pre-heater refractory lining after 12 month usage without any repair [5]. Lining life achieved is 39 months

Fundamental properties of a new steel ladle pre-heater technology at CORUS Steelworks IJmuiden are described by de Wit, et al. [5]. The introduction of a new near netshape casting machine required substantial metallurgical process changes and an adjustment of the steel ladle refractory lining. It became necessary to optionally reheat empty steel ladles during the ladle cycles. The focus was on ceramic fiber-free refractory linings of the ladle pre-heater covers. An SLA-92 based castable was selected to cope with the requirements of such linings. In this case a refractoriness of at least 1400 °C is required, which is up to 200 °C above service temperature, in order to tolerate temperature hot-spots and contribute to long term stability. Additionally a low specific weight and a low thermal conductivity is important to achieve a low weight of the lining to keep the preheater steel construction and the hydraulic power within reasonable limits.

Most important is the resistance to thermal shock to withstand numerous cycles between 1200 °C and ambient temperature with rapid, almost immediate heating up and cooling down. **Figure 2** shows the SLA-92 based ladle preheater refractory lining after 12 months use without any repair. In the meantime the linings showed a tremendous service life of up to 3 years without intermediate repairs.

Submerged Entry Nozzle Insulation

The non-fibrous insulation of submerged entry nozzles (SEN) for continuous casting has been investigated by Gotthelf et al. [6]. Positive results have been achieved by coating the nozzles with a SLA-92 based slurry as an alternative to fibrous material wrapping. **Figure 3** shows that the spray coating procedure also enables to apply the insulation material in the port-holes of the sub entry nozzle in order to further reduce thermal stress and reduce prone to failures. The trials showed that SLA-92 based spray coating yields a better thermal insulation in comparison to fibrous material which required doubled thickness (6 mm versus 3 mm) to achieve comparable insulating results.

Steel Reheating Furnaces

Wuthnow et al. [7] report about the special insulating demands in steel reheating furnaces at Hoesch Hohenlimburg and Thyssen Krupp Stahl AG Bochum. The variety of steel grades produced in that mills require numerous and fast changes of the kiln temperature during use. These steelworks run walking beam furnaces or pusher type furnaces for reheating the steel slabs in temperature ranges from 1080 °C to 1350 °C. SLA-92 based material was tested in 3 main application areas: Pre-cast shapes for stator and cross beam insulation in walking beam furnace versus refractory ceramic fibers, lightweight gunning mix for bricked furnace roof repairs and pre-cast shapes for furnace roof replacing high alumina insulating bricks. The furnace roofs are lined with lightweight refractories to accelerate the adjustment of kiln temperature between different steel grades to be reheated prior rolling.

The thermal shock resistance of the refractory lining needs special attention due to frequent process temperature changes and es-

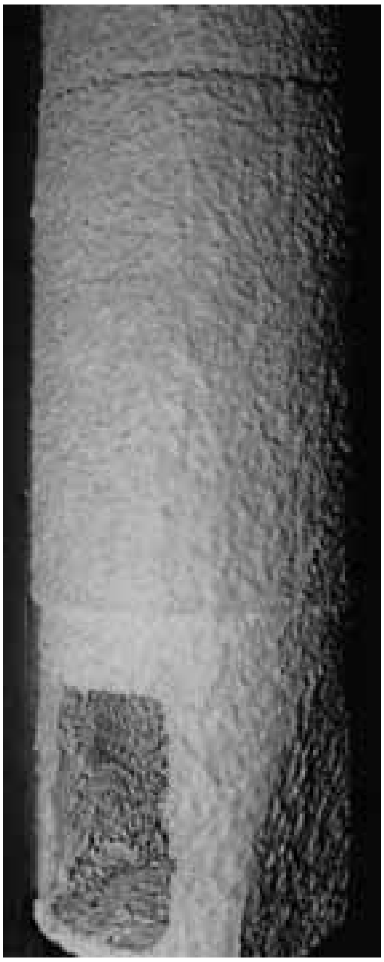

Fig. 3. Submerged nozzle with sprayed on microporous insulation on the surface and in the port holes [6]

Fig. 5. Pre-cast shape for walking beam reheat furnace stator insulation

pecially during annual or bi-annual maintenance periods with complete cooling down from 1300 °C to ambient temperature. SLA-92 based pre-cast shapes for furnace roofs (see **Figure 4**) were used in comparison to commonly used standard lightweight bricks ASTM class 30, which usually show extensive spalling after 18 months of use. The pre-cast shapes (bulk density at 1.12 g/cm^3) outperform the high alumina insulating bricks (bulk density at 1.08 g/cm^3) with regard to thermal shock resistance and insulating behaviour and the SLA-92 based material is successfully tested over a period of more than 3 years.

A parallel development for stator and cross beam insulation is reported by Kikuchi et al. [8]. The focus was on the replacement of the commonly used fiber insulation in this application. The test results clearly demonstrate the excellent performance of the SLA-92 based insulating castable compared to fiber insulations regarding resistance to slag and spalling. Lining options for stators are pre-cast shapes (see **Figure 5**) or on site installations. During the introduction period pre-cast shapes have been used. In the meantime the pre-cast shapes are replaced by more cost efficient on-site lining with the additional advantage of an installation without joints. Occasionally superficial cracks have been observed during use. This has been overcome by replacing calcium aluminate cement with hydratable alumina binder in the insulating castable. Kikuchi et al. report a service life of the lining with SLA-92 of more than 2 years, and it is expected to exceed the service life of the conventional ceramic fiber insulation. The use of SLA-92 in insulating on-site installed castable for stators and cross beams in walking beam furnace is now an established application at a Japanese steel plant.

Fig. 4. Microporous pre-cast shapes for kiln roof, 400 × 350 × 160 mm with high alumina anchor brick and two 50 mm calcium-silicate plates on top [7]

Applications in the Petrochemical Industry

Petrochemical applications with direct contact of the refractory lining to the process atmosphere are hydrogen reformers and gasifiers operating with reducing gases containing hydrogen and carbon monoxide gases. Process conditions are pressures around 25 bar and temperatures in the range of 950–1100 °C. Additionally, fluid catalytic cracking units (“cat crackers”), ethylene furnaces, pressurized fluid bed boilers, and transfer lines can be included as demanding refractory applications [9].

Important requirements of petrochemical applications are the stability of the refractory oxides against reduction, resistance against CO attack, and abrasion resistance due to high the high velocities of catalyst bearing gas streams in the vessels. Oxides with lower stability like SiO_2 can be reduced by the process gases to gaseous SiO, which afterwards condenses in heat exchangers (“fouling”) and reduces the efficiency of this unit. Due to the SiO_2 decomposition the strength of the refractory lining decreases and the porosity increases. The hydrogen attack is discussed in more detail by Tassot et al. [9].

SLA-92 provides an interesting alternative to bubble alumina for high purity insulating materials, which are stable even under severe reducing conditions. Bubble alumina materials have a thermal conductivity of about 1 W/mK, which is increasing remarkably towards higher temperature. SLA-92 materials have a stable low thermal conductivity of about 0.4 W/mK over the entire temperature range.

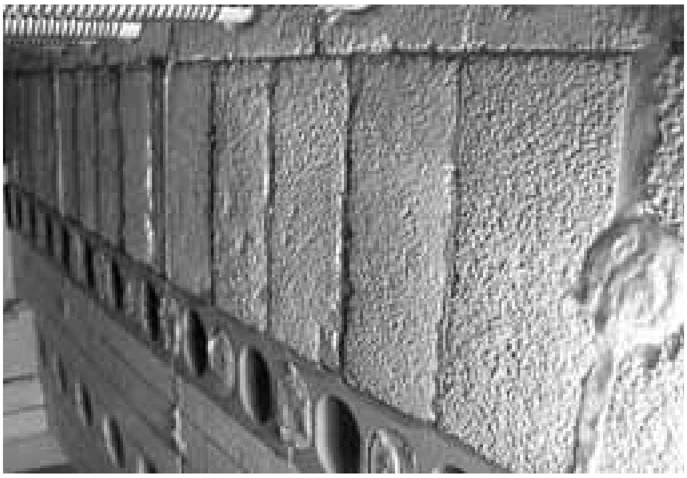

Fig. 7. Wall area of a roller kiln with special pre-cast insulating bricks [13]

In a recent investigation by DIFK/Bonn, a SLA-92 based castable was classified for CO resistance to class A after 540 °C pre-firing and class B after 1095 °C pre-firing according to the norm ASTM C 228.

SLA-92 based material are successfully used for petrochemical applications, but not reported in the literature so far.

Applications in the Glass Industry

Windle and Bentley [10] discuss trends in the glass industry for oxy-fuel fired melters, primarily driven by regulation of both NOx and particulate emissions, which show significant reduction utilising this technology. Besides associated benefits including decrease in fuel, increased melting rate and improved overall productivity, drawbacks are increased alkali concentrations from 1.5 to 6.0 times when compared with conventional melting. This would result in a severe wear of traditional silica crowns. Improvements for alkali resistance are achieved by the use of magnesium aluminate spinel for the hot face in crown applications. Regarding the back-up insulation for this spinel lining concept, calcium hexaluminate based insulating bricks were used since they show an improved resistance to alkali attack compared to the previously used calcium-silicate based insulation material. Due to increased temperatures at the outside face of the spinel crown, the high refractoriness of calcium hexaluminate has advantages over commonly used calcium-silicate based insulation material which would run very close to its classification limits [10].

Applications in the Ceramic Industry

Modern ceramic fast firing uses very short cycles, e.g. 60 minutes for ceramic tiles from cold to cold with a maximum temperature of 1140 °C, or porcelain 300 minutes from cold to cold with a maximum temperature of 1400 °C. Often the kilns are turned off during weekends, which is an additional challenge with regard to the thermal shock resistance of the refractory linings.

In 1999, Stainer and Kremer [11] predicted an interesting potential in ceramic processing using the new microporous calcium hexaluminate SLA-92. The key selection criteria is the excellent thermal shock resistance which is hardly found on other insulating materials at temperatures up to 1450 °C.

Periodic kilns used in the ceramic industry benefit from a lowest possible bulk density of the refractory lining because it reduces energy loss through the heat capacity. Pörzgen et al. [12] describe an innovative kiln car lining for decoration firing of ceramic products. The lining is based on an insulation castable with SLA-92 for precast shape manufacturing. The key advantage for this concept is the combination of low thermal conductivity and high thermal shock resistance. This reduces significantly the thermal spalling of the lining compared to conventional insulating bricks but also provides advantages versus refractory ceramic fibers, which de-vitrify during use and become brittle. The increased spalling resistance leads to a reduction in the amount of small particles formed which would otherwise be blown by the burners of the kiln and deposit on the decoration, downgrading the quality of the fired goods and reducing yield.

A new system of kiln car lining concept for decoration firing with SLA-92 pre-cast shapes and refractory plate on top is shown in **Figure 6**. Firing condition in the kiln is 90 minutes cold to cold with a maximum firing temperature of 1260 °C and each kiln car performs 40 cycles per week. The new lining design has been successfully tested over a period for 6 months, namely for about 1000 firing cycles. Excellent thermal properties could be achieved and no damage by thermal shock was observed. Later investigations showed that SLA-92 based material exceeds the lining life of conventional systems, which is between 12–24 months.

Overhoff et al. [13] report recently about successful tests with SLA-92 based insulating material in kiln cars for the porcelain industry and special wall bricks for a roller furnace. Particularly for high-alkali, reducing kiln atmospheres and temperatures between 1300 and 1500 °C, the material was identified as a highly interesting alternative to lightweight corundum bricks, which have a much higher density and higher thermal conductivity. The excellent ther-

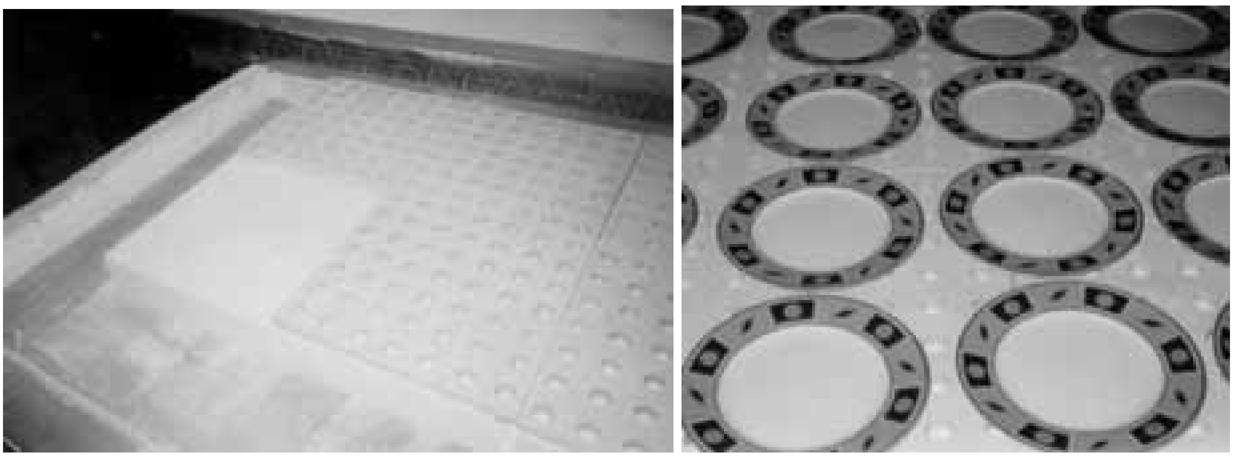

Fig. 6. (Left) Kiln car lining with microporous pre-casts shapes (white) and refractory plate on top. The bottom layer is made of moler bricks [12] (Right) Kiln car with decoration firing kiln feed [12]

mal shock resistance enabled the production of very complex and large-sized components. **Figure 7** shows an application in a special roller kiln using pre-cast shapes as large sized bricks with 250 × 250 × 125 mm dimension. Even after 16 months in use, the wall is still in excellent condition.

Conclusion

The comprehensive application experiences with the microporous calcium hexaluminate SLA-92 clearly demonstrate that this insulating aggregate provides both a technical and an economical alternative to conventional refractory ceramic fibers and other insulating materials. As a refractory aggregate it allows the formulation of monolithic concepts for pre-cast shape manufacturing and on-site installations as well as gunning mixes for repairs.

Unmatched properties like high chemical purity, high refractoriness up to 1500 °C, low thermal conductivity at about 0.4 W/mK and high thermal shock resistance are the basis for the outstanding performance observed in various applications over the past years. They led to versatile use in various industries including steel making, glass, ceramics and other refractories and made SLA-92 the material of choice for demanding high temperature insulation. Even under severe conditions, as for example exposure to harsh thermal shock conditions or alkali attack, service life has by far exceeded initial expectations. Obviously the most established and growing application is the insulation lining in steel reheat furnaces for hot rolling mills.

It is expected that to-date applications will further broaden and that SLA-92 will be the basis for other new innovative high temperature insulation concepts for a growing market in all regions world wide. (F 19)

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