Long Term High Temperature Stability of Microporous Calcium Hexaluminate Based Insulating Materials

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Abstract

High temperature insulating castables based on SLA-92, a newly developed high purity, microporous light weight insulating aggregate (aggregate density of 0.75 g/cm³) made from calcium hexaluminate (CaO·6Al₂O₃ or CA₆) were subjected to temperatures of 1400 and 1500 °C for extended duration of up to two weeks to test their long time high temperature stability. The specimen were examined with respect to their physical and thermomechanical properties and their morphological appearance. In addition the stability of phosphate bonded SLA-92 based materials were evaluated, as well as their stability under alkali contact and in contact with alumina silicate bricks.

The SLA-92 based insulation castables, with either cement or phosphate bonding, had fired densities of 0.9-1 g/cm³ and a porosity of 65-70 %. After 14 days holding time at 1500 °C the phosphate bonded castables showed low shrinkage of only 0.3%, whereas the cement castable had a shrinkage of 1.9 %. The castable pore size remained constant with an average of 1-3 µm after 7-14 days exposure at 1500 °C. This microporous structure resulted in constant low thermal conductivity over a broad temperature range from 300-1400 °C, i.e. as low as 0.33 W/m·K at 1400 °C. SEM pictures showed no visual detectable change in the SLA-92 aggregate morphology. The phosphate bonding of SLA-92 mixes results in the formation of the high refractory phase NC₂P, which supports the high performance at temperatures above 1500 °C.

Compared to currently established high temperature insulating products, SLA-92 based materials show excellent long time stability due to their high refractoriness and purity and low thermal conductivity up to high temperatures due to their microporous structure.

1. Introduction

The use of lightweight refractory insulating materials has increased drastically over the past years in conjunction with the continuous search for energy saving measures, faster processing cycles, or extended lifetime of aggregates. Established lightweight materials used for insulation at temperatures above >1350 °C are insulating mullite- and alumina-based bricks, insulating castables based on bubble alumina or lightweight chamotte, or ceramic fibres which currently offer the highest thermal insulation efficiency [1, 2].

The European Union legislation of Dec. 1997 classified ceramic mineral fibres as a category 2 carcinogen. The legislation was to be transferred to national law by end of 1998. Besides the need to mark fibre goods adequately, to follow strict working guidelines and apply protection measures, this legislation encourages the substitution of fibres with safe material alternatives [3, 4].

The target of developing SLA-92 was to have a high refractoriness, high purity microporous raw material for use in refractories

with low thermal conductivity at elevated temperatures (>1400 °C). The raw materials characteristics and positive properties of castables and bricks made thereof have been broadly discussed in a prior publication [5]. SLA-92 based refractories have been tested in numerous applications and showed good performance, i.e. in petrochemical plants, kilns or re-heating furnaces in the steel industry.

This paper focuses on the long term high temperature stability of SLA-92 based materials, but also investigates contact reactions with other materials. The test results are compared with conventional high temperature insulating materials.

2. Experimental

2.1 Test castables

In addition to the refractory formulations described in a prior publication [5], this study examined the thermal stability of some new cement and phosphate bonded high temperature insulating castable formulations. The compositions of the tested castables are shown in **Tab. 1**. Alcoa raw materials were used in these formulations except where otherwise noted. The chemical analysis of the tested castables can be seen in **Tab. 2**.

Tab. 1. Composition of the test castables

| Castable | | | 16/1 | P9 | P 14 |
|---------------------------|-------------------------------|---|----------|--------|--------|
| SLA-92 | all sizes (0-1;1-3;3-6 mm) | % | 70 | 93 | 80 |
| ground Al-hydrate | M 20 B | % | The gall | | 5 |
| Cement | CA-25 R | % | 30 | 5 | 10 |
| Na-Phosphate | Budit 8H* | % | 1 | 2 | 5 |
| Additives | the Francisco | % | m+14 | +1 | +0.5 |
| 0.5% cellulose** solution | | % | +60±10 | +60±10 | +60±10 |

^{*} Budit 8H - Budenheim, Germany; ** Blanose 7M - Aqualon, Germany

Tab. 2. Chemical analysis

| | | 16/1 | P9 | P 14 | P 14 |
|---------------------------------------------|----|------|------|------|------|
| firing temp. | °C | 1500 | 1500 | 1500 | 1500 |
| holding time | h | 5 | 5 | 5 | 336 |
| Al ₂ O ₃ (calculated) | % | 88.4 | 88,7 | 86.2 | 86.7 |
| CaO | % | 10.4 | 8.1 | 8.3 | 8.2 |
| Na ₂ O | % | 0.54 | 1.40 | 2.02 | 1.64 |
| P ₂ O ₅ | % | 0.01 | 1.26 | 2.77 | 2.71 |
| Fe ₂ O ₃ | % | 0.05 | 0.04 | 0.04 | 0.05 |
| SiO ₂ | 96 | 0.11 | 0.11 | 0.14 | 0.10 |
| MgO | % | 0.51 | 0.45 | 0.54 | 0.65 |

2.2. Preparation and testing

Preparation and treatment of the test pieces and testing follows the European standard ENV 1402 "Unshaped refractory products", Part 5 and Part 6.

The dry ingredients were mixed for about 1 minute. After addition of about 60 % of a 0.5 % cellulose solution (Blanose 7M, Aqualon/Henkel) the mixing was continued for another 4 minutes. The castable was cast under vibration into the mould. Vibration time was 30-60 sec with an amplitude of 0.2-0.5 mm depending on the specimen size. The following test pieces were prepared:

- 230x64x54 mm for testing the conventional properties (ENV 1402-6)
- 230x114x64 mm for testing thermal conductivity (hot-wire parallel method, EN 993-15) and for long firing tests up to 14 days

The vibrated test pieces were cured at room temperature in the mould for 24 h and after demoulding they were cured for another 24 h in air at ambient temperature with a relative humidity of ≥90 %. The pieces were dried for 24 h at 110 °C and fired up to 1500 °C with a soaking time of 5 h. For the long time temperature treatment, the samples were kept at 1400 or 1500 °C for another 24 h, 7 days or 14 days.

For alkali resistance tests, crucible cups of 80x80x65 mm were prepared, filled with 15 g salt, covered and held in a furnace at $1250\,^{\circ}\mathrm{C}$ or $1350\,^{\circ}\mathrm{C}$ for 5 h. The cooled specimen were cut and examined visually for cracks and by XRD for phase changes.

2.3 Conventional properties of the tested castables

The physical properties are compiled in **Tab. 3**. The grain size distribution of SLA-92, especially of the fine fractions, has a certain variation which results in variations in the required mixing water additions (Tab. 1) to get a vibratable castable consistency, and therewith in the castables properties with respect to bulk density and strength.

Tab. 3. Physical properties

| | | Pre- Treatment (°C) | 16/1 | P9 | P 14 |
|-------------------------------|-------------------|---------------------------------------------------------------------|-----------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------|
| Bulk density | g/cm ³ | 110 250 450 1000 1500 1500/336h | 1.10 n.a. n.a. 1.02 1.03 1.15 | 0.97 0.97 0.98 0.99 0.97 1.00 | 0.95 1.07 1.06 0.93 0.92 1.02 |
| Cold modulus of rupture CMOR | N/mm ² | 110 250 450 1000 1500 1500/336h | 0.8 1.5 0.6 0.5 0.7/1.9 | 0.5 0.4 0.6 0.7 0.3/0.8 0.3 | 0.7 0.6 0.5 0.6 0.5/0.7 |
| Cold crushing strength CCS | N/mm ² | 110 250 450 1000 1500 1500/336h | 5.0 4.3 4.7 4.1 7.6 6.0 | 1.1 1.6 1.9 1.9 3.4 5.3 | 6.7 4.7 4.3 1.0 1.9 4.6 |
| Permanent linear change | % | 110 250 450 1000 1400 1400/336h 1500 1500/336h | 0 0 0 0 -0.06 -0.21 -0.68 -1.9 | 0 0 0 0 +0.27 +0.76 +0.26 -0.27 | 0 -0.09 +0.04 0 +0.09 +0.16 +0.17 -0.25 |

The total porosity of the test castables range between 65-70 vol.-%; no closed porosity are evident. All test mixes were volume stable after firing at temperatures up to 1400 °C. At 1500 °C the cement bonded castable 16/1 shows a shrinkage of about 0.7 %, while the phosphate bonded mixes P9 and P14 exhibit a low expansion of about 0.2 %. At 1600 °C the test pieces of all tested castables bend but shrinkage remained relatively low with about 1.5-2.5 %. Firing at 1700 °C showed the expected high shrinkage of about 10 %, but no sign of melting or fusion of the specimen.

2.4 Thermal expansion behaviour

Linear change of dimension of unshaped refractory materials especially on the first heating up has a significant relevance for constructing a refractory lining. Small test pieces of 10 mm square and 50 mm length cut out of the only dried material were used to determine thermal expansion on repeated heating up to 1450°C and cooling down in a dilatometer.

Results are shown in **Fig. 1**. With both the cement and the phosphate bonded test castables an accelerated expansion is observed on first heating up beginning at about 1100 °C and ending at about 1350 °C, followed by shrinkage. The effect is more pronounced with the phosphate bonded material P9. After the first or second heating up a reversible thermal expansion of about 0.8 % at 1000 °C is reached.

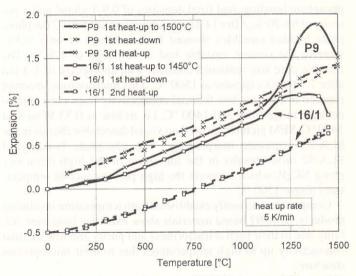


Fig. 1. Thermal expansion up to 1500 °C for mix 16/1 and P9

X-ray examinations of the cement bonded mix 16/1 fired at $1200~^{\circ}\text{C}$ showed – compared to the unfired material – the formation of CA_2 and additional CA_6 . In the phosphate bonded material no change in mineralogical composition on firing up to $1450~^{\circ}\text{C}$ could be noticed, phosphate phases were not detected. The reason of the accelerated expansion could not yet be fully clarified.

2.5 Long time firing

Standard brick size test pieces (240x114x64 mm) were heated in an electrical furnace at 1400 °C and 1500 °C up to 14 days (336 h) to evaluate the influence of long term service on the properties of the new materials.

Microstructure of the specimen

Fig. 2 shows a scanning electron microscope image of the cement bonded mix 16/1 after 168 h (7 days) at 1500 °C. The crys-



Fig. 2. Scanning electron microscope image of mix 16/1 (broken surface) after 168 h (7 days) at 1500 °C

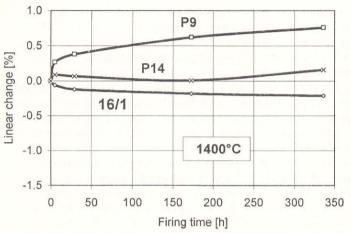


Fig. 3a. Permanent linear change of dimensions at 1400 °C

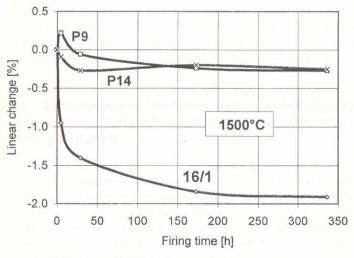


Fig. 3b. Permanent linear change of dimensions at 1500 °C

tals have a comparable structure to previous examination on the SLA-92 raw material [5].

Change in chemical analysis of phosphate bonded materials

The chemical analysis of mix P14 was analysed again after 336 h (14 days) at 1500 °C. Only a small evaporation of Na₂O could be detected, the phosphate content is virtually unchanged (see Tab. 2).

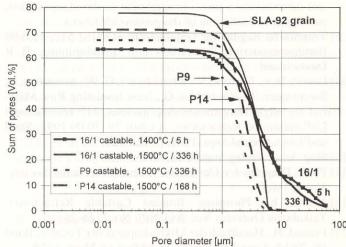


Fig. 4. Micropore size distribution (Hg-intrusion method)

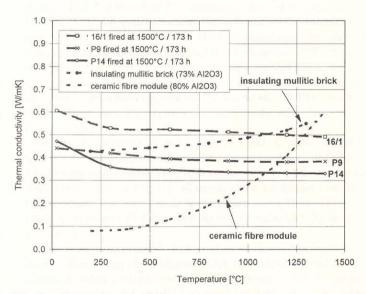


Fig. 5. Thermal conductivity

Permanent linear change of dimensions

Test temperature 1400 °C (Fig. 3a): The cement bonded mix 16/1 reaches a shrinkage after 14 days of only -0.2 %. The phosphate bonded castables show a slight expansion with increasing firing time of 0.76 % for P9 and 0.16 % for P14.

Test temperature 1500 °C (Fig. 3b): Shrinkage of mix 16/1 is very rapid in the first 29 h of firing. After about one week the future shrinkage is practically stopped and a volume stability is reached. The phosphate bonded mix P9 shows an expansion in the first 5 h, while mix P14 exhibits a slight shrinkage. After a one week hold time, both P9 and P14 show dimensional stability with a total shrinkage of about 0.25 %.

Micro pore size distribution (Fig. 4)

This study reveals that long time heating at 1500 °C does not change the pore size distribution. An interesting and not yet fully explainable phenomenon is that the phosphate bonded mixes contain only micro pores of <10 μm diameter and the overall pore size distribution is actually finer than the pore size in the SLA-92 raw material grains.

Strength

Taking into consideration the variation in fine grains and the resulting mixing water content, the results of comparing the test pieces fired for 5h and for 14 days firing do not show any significant differences in the cold crushing strength or the modulus of rupture (see Tab. 3).

Thermal conductivity (Fig. 5)

All mixes show a slowly decreasing thermal conductivity as a function of temperature up to 1400 °C. When compared to a mullitic insulating high alumina brick (73 % Al_2O_3) and a ceramic fibre module (80 % Al_2O_3), the thermal conductivity of the SLA-92 castables is lower at temperatures above 1200 °C. The phosphate bonded mix P14 shows the lowest thermal conductivity of the tested mixes in the temperature range of 1200 to 1400 °C of 0.33 W/m·K.

Because of the shrinkage of mix 16/1 at 1500 °C of 1.9 % after 1 week the thermal conductivity increases from 0.4 W/m·K, measured after firing for 5 h [5], to 0.5 W/m·K. Looking at the shrinkage curve in Fig. 3b a further shrinkage at longer firing is not expected and thus the thermal conductivity is not expected to increase above this level.

Thermal shock resistance

The air quenching method (DIN ENV 993-11) was used to evaluate thermal shock resistance up to 10 test cycles. Even after long time heating at 1500 °C no cracking of the cement bonded material 16/1 was observed even though the shrinkage reached 1.9 %. The phosphate bonded materials are destructed after 7-10 cycles. Visual evaluation of the texture of this type of finer grained castable showed that in the dried and fired material, layers were detected which originate from test specimen preparation. The formulation needs further refined to prevent these material defect. It can be deducted that a sound, layer free material will reach the same thermal shock resistance as the cement bonded mix.

Refractoriness under load

Fig. 6 illustrates that the phosphate bonded mix P9 has the same good refractoriness under load properties as the cement bonded mix 16/1. Long firing at 1500 °C stabilises the

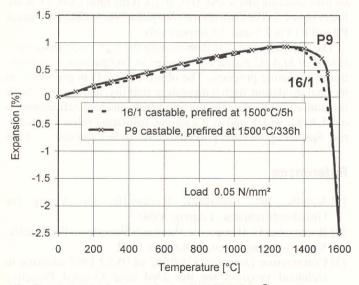


Fig. 6. Refractoriness under load (0.05 N/mm²)

microstructure of the materials, thus the beginning of "softening" is retarded. The $T_{0.5}$ values P14 and 16/1 are around 1500 °C. The test was done under a load of 0.05 N/mm².

It has to be mentioned that the practically glassy free SLA-92 materials do not soften like an alumina-silicate material. The measured subsidence is a result of the shrinkage of these high porosity materials.

3. Stability of SLA-92 Based Materials Based on Phase Diagram Evaluation and Testing

3.1 Evaluation of refractoriness of phosphate-bonded SLA-92 mixes

The influence of phosphate bonding (Na-Phosphate) on the high temperature behaviour of SLA-92 mixes has been evaluated with respect to the ternary phase diagrams C-A-P1), N-C-P, N-C-A [6, 7]; the ternary diagram N-A-P and the quaternary diagram N-C-A-P are not available.

The C-A-P system shows no ternary phase. The A-P binary shows the well known bonding phase AP with a melting temperature of 1450 °C. The melting temperatures of binary calciumphosphates are decreasing with increasing phosphate content from >1700 °C for C₄P and C₃P to 1350 °C for C₂P and <1000 °C for CP, C₂P₃, and CP₂. A similar behaviour shows the ternary system N-C-P, which contains several ternary phases. Melting temperatures of >1500 °C for phase compositions with <50 % P₂O₅ are decreasing sharply to <1000 °C with P₂O₅ contents >50 %.

With respect to N:C:P-ratio the compositions of the SLA-92 mixes P9 and P14 correspond to the phase triangle C-NC₂P-N₃CP with a temperature of onset of melting of 1630 °C, which explains the high temperature stability of the phosphate bonded SLA-92 mixes. Taking into account the Al₂O₃-content of the mixes P9 (89 %) and P14 (86 %), CaO is replaced by Hibonite (CA₆). Electron microprobe analysis confirmed the existence of NC₂P (solid solution (ss) with C₃P) in contact with CA₆. NC₂P has a high melting temperature of 1830 °C and is reported by Yorita [8] as the binder phase in phosphate bonded basic castables.

X-ray analysis of the P14 and P9 compositions fired at temperatures >1400 °C shows CA₆, α-alumina, and β-alumina (Na₂O·11Al₂O₃). Due to overlapping peaks, NC₂P and AP phase can not be identified. The phase diagram N-C-A [6] shows a dotted line between CA₆ and β-Alumina at 1200 °C, indicating a compatibility between both phases. However, formation of solid solutions and phase compatibility in this part of the system need to be investigated more in detail.

3.2. Evaluation of contact reaction with Al₂O₃-SiO₂ insulating bricks

Contact reactions between SLA-92 based insulating refractory materials and Al_2O_3 -SiO₂ insulating bricks have been evaluated theoretically by the ternary phase diagram CaO-Al₂O₃-SiO₂ [6]. The composition of a 1:1-mixture of SLA-92 Mix 16/1 and insulating brick has been drawn in the diagram and the corresponding phase triangle and temperature of onset of melting have been evaluated.

For mixtures of ASTM class 26, 28, and 30 insulating bricks (40 %, 60 %, 73 % Al_2O_3) with material 16/1 (89 % Al_2O_3), 11 % CaO) the stable phase composition is Corundum-Anorthite-Mullite with an onset of melting at 1512 °C. During the reaction with such insulating bricks Hibonite (CA₆), the main phase of mix 16/1, will be transformed to Anorthite and Mullite, but with-

¹⁾ With Al₂O₃=A, CaO=C, P₂O₅=P, Na₂O=N; K₂O=K, SiO₂=S

out formation of phase compositions melting below 1512 °C. Experimental investigation of creep behaviour at 1400 °C of a contact sample from mix 16/1 and an ASTM class 30 brick (JM 30) confirmed the phase diagram conclusion and showed only a 0.5-1 mm thin reaction layer between the different insulating materials.

On the other side, combination of mix 16/1 with a lower grade insulating brick of ASTM class 23 (35 % Al₂O₃) has, according to the phase diagram, a stable phase composition of Mullite – Anorthite – Cristobalite with an onset of melting at 1345 °C. With respect to the higher amount of impurities (i.e. alkalis) contained in this type of insulating bricks, a much more severe contact reaction could be expected at temperatures above 1300 °C, but this is above the classification temperature of 1260 °C for a class 23 brick.

3.3 Evaluation of contact reaction with alkalis

By the reaction of Mullite insulating brick JM 30 with K_2CO_3 at 1250 °C Mullite is decomposed under formation of Leucite (KAS4) and Kalsilite (KAS2) with melting points of 1686 °C and >1750 °C according to the ternary phase diagram K-A-S [6]. This change of mineralogical phase composition is related with a large specific volume increase, which causes the observed crack formation of the sample cup and is known as alkali bursting [9]. Due to the high melting temperatures of the formed phases no melting could be observed, but a pulverised reaction layer was apparent.

Reaction of SLA-92 mixes with K₂CO₃ at 1350 °C results in decomposition of Hibonite and formation of K-β-Alumina and KA, which is a strongly hydratable phase. The phase changes are related with an increase of specific volume causing the sample cups to crack. Using a 1:1-mixture of NaCl+K₂SO₄ the reaction at 1250 and 1350 °C is less severe. At 1250 °C some β-Alumina is formed, at 1350 °C Hibonite is decomposed and β-Alumina and CA₂ are formed, but with only little crack formation of the sample cups. A more detailed discussion of the reactions and phase compatibility is not possible due to a lack of suitable phase diagrams. For the N-A-S system as well as for the K-A-S system a conode between Hibonite (CA₆) and K-β-Alumina (KA₁₁) is indicated at 1100 °C, but no conode between K-β-Alumina and CA₂ [6].

4. Comparison of the Properties of SLA-92 Based Materials to Conventional High Temperature Insulating Materials

The *low thermal conductivity* from 300 °C up to 1400 °C is a distinct advantage of SLA-92 based refractory products. This is a result of the high level of microporosity which keeps the dominant heat transfer mechanism (radiation) at increasing temperatures, at low levels. Fibre based products or insulating bricks with comparable refractoriness show an increase in thermal conductivity with rising temperatures [1,2,10].

The tested SLA-92 based materials show high volume stability with shrinkage being well below 2 % after 14 days at 1400 or 1500 °C and all materials reaching a stable dimension after 7 days. Comparable insulating alumina-silicate bricks, castable or ramming mixes of ASTM class 28-30 or EN 1094 class 150-160 show continuous growth over time due to mullite formation [11], while lower class materials (ASTM 26) tend to shrink over long holding times (200 h) at 1400 °C due to formation of melting phases [10].

Insulating alumina-silicate ceramic fibres blankets or modules for these application temperatures show significant changes in structure during use at high temperatures.

Alumina silicate fibres (Al₂O₃-contents of 40-60 %) are vitreous products. After prolonged use at high temperatures they will gradually devitrify to crystalline phases of mullite (at 900 °C) and of crystalline silica (at 1200 °C), the later being a hazardous material. The recrystallisation process results in volume contraction, increase of density, sintering of the fibres, continuous crystal growth, brittleness, destruction of the structure and thus the loss of the inherent insulating characteristics of the fibre materials [1, 12-14].

Fibres show an exponential increase of thermal conductivity at increasing temperatures due to the permeability for radiation of glass (in case of vitreous fibres) and their very high porosity [1].

5. Discussion & Outlook

The evaluated SLA-92 based castable materials showed high thermal stability at the tested temperatures of 1400 and 1500 °C after 14 days. All mixes reached a stable level of permanent linear change (PLC) of less than 2 % shrinkage after 7 days exposure at 1500 °C. The phosphate bonded mixes P9 and P14 exhibited volume stability at 1500 °C with 0.25 % shrinkage; the cement bonded castable 16/1 showed a stable shrinkage of 1.8 % which is still below the limit of 2 % as requested by ASTM C 155 or EN 1094. At 1400 °C mix 16/1 and P14 showed very low shrinkage after 14 days holding time of -0.2 % and +0.2 % PLC, respectively, while mix P9 expanded continuously over time up to +0.8 %.

The *micro porosity* after 14 days at 1500 °C remains stable with 65-70 % open porosity and an average pore size of 1-3 μm. The low *thermal conductivity* reflects the effect of the small pore size: After 7 days at 1500 °C all mixes show a constant low thermal conductivity over a wide temperature range from 300 up to 1400 °C, with mix P14 showing the lowest value of 0.33 W/m·K at 1400 °C.

The *strength* decreased slightly after 14 days. *Thermal shock* testing after 14 days heat treatment for 10 cycles revealed for the cement bonded castable 16/1 no failure whereas the phosphate bonded castables P9 and P14 showed cracking and failed after 10 tests, likely due to lower matrix phase bonding strength.

Based on thermochemical phase equilibrium, little *contact reactions* can be expected between SLA-92 based materials and alumina silicate insulating bricks >40 % in alumina content at temperatures below 1400 °C, and with bricks <40 % in alumina content at temperatures below 1250 °C. The addition of *Na-Phosphate binder* to SLA-92 mixes results in formation of *high melting bonding phase* (NC₂P-C₃P _{ss}), if the ratio (N+C):P is not lower than 1.2. The ratio for the phosphate bonded SLA-92 mixes P9 and P14 is 7.5 and 3.7 respectively.

The described test data demonstrate the *high performance potential of SLA-92 based refractories* in comparison to conventional insulating products. The observed excellent properties in thermal insulation, high temperature stability, and thermal shock resistance are based on the micro porosity and high refractoriness of SLA-92, which makes it a unique insulating refractory material. Further application potentials have to be explored. (F 106)

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