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New Insulating Raw Material for High Temperature Applications

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Abstract

A new refractory insulating aggregate, SLA-92, for high temperature applications has been developed. The product contains approximately 92 % Al_2O_3 and 7.5 % CaO; its mineralogical composition is calcium hexaluminate. The product is a homogeneous material with a high porosity of typically 75 % and a small pore radius of 0.5-2.5 µm. These characteristics result in a material with low thermal conductivity even in the temperature range above 1200 °C as well as high thermal shock resistance. Some raw material properties are presented and some applications of SLA-92 in refractory materials are discussed.

1. Introduction

Insulating materials are important products for many industrial applications. They are used to minimize heat and energy losses and to improve safety of equipment and working environment. Depending on the application, insulating products have to meet various requirements: highly efficient thermal insulation properties in order to minimize wall thickness, excellent thermal shock resistance, easy to handle and safe to install, and high durability to minimize downtimes and related costs.

Recent changes in the European legislation have started a new discussion around the health aspect of various insulating products In December 1997, the European union has classified ceramic mineral fibres as a category 2 carcinogen [1]. This has stimulated an intensive search for alternative products with similar refractoriness, low thermal conductivity, and less concerns around potential health hazards. The newly developed SLA-92 has the potential to be an excellent replacement material in many of the applications where ceramic fibres are currently used.

2. Thermal conductivity and high refractory insulating materials

The thermal conductivity properties of refractory materials are determined by their heat transport characteristics, which are conduction in solids/gases, convection, and radiation. The kinetics are explained in detail by Schulle [2]. An article by Seifert [3] specifically discusses the thermal characteristics of microporous materials.

The development of SLA-92 was targeted to obtain an insulating aggregate with high refractoriness for use at temperatures above 1200 °C. At high temperatures the major heat transfer mechanism is the radiation. The radiation emission rises with the 4th power of the temperature. Pores behave like a vacuum for radiation (so-called short circuit of pores). Thermal conductivity by radiation is proportional to the pore size, smaller pore sizes will lead to a lower radiant heat conductivity. **Fig. 1** shows an example for two products with similar total porosity, but different pore sizes. The product with the smaller pore size has the lower thermal conductivity at high temperatures.

Therefore to provide optimum insulating efficiency, the target microstructure for the new insulating aggregate was that the pore size should be as small as possible to minimize radiation, and that the total porosity should be high. To allow the use at high temperatures, the mineral phase should have a high refractoriness and a low impurity level.

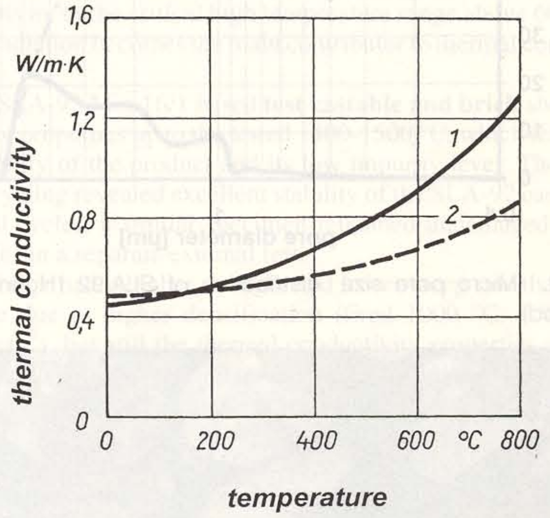

Fig. 1. The effect of temperature on the thermal conductivity of two refractory materials with similar porosity (pore size of 1 > 2) [2]

3. SLA-92

3.1. Physical product properties

The base mineral composition for SLA-92 is calcium hexaluminate (CA_6[2]). CA_6 exhibits the most excellent thermal properties of the calcium aluminate system with a melting point above 1850 °C. Several research works [4-7] report the properties of CA_6. The main findings are high thermal shock resistance, a thermal expansion and fracture toughness K_{IC} similar to alumina, moderate flexural strength due to anisotropic grain growth, and stability in reducing atmosphere. A good stability of Calciumaluminate-based material in contact with alkalioxides is also reported [8].

The product chemistry (**Tab. 1**) of SLA-92 is – compared to pure CA_6 (91.6 % Al_2O_3, 8.4 % CaO) – on the alumina-rich side in order to suppress the formation of hydratable calcium aluminate phases (CA, CA_2). The impurity level is low, SiO_2 and Fe_2O_3 contents are max. 0.1 %. The bulk density is around 0.65-0.7 g/cm^3.

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[2] C=CaO, A=Al_2O_3

Tab. 1. Product data of SLA-92

SLA-92	unit	typical	min	max
Chemical Composition				
Al_2O_3	%	92.5-93.5	91	
CaO	%	6-7		8
Na_2O	%	0.2-0.4		0.5
SiO_2	%	0.05-0.07		0.1
Fe_2O_3	%	0.03-0.04		0.1
MgO	%	0.05-0.3		0.4
Bulk Density	g/cm³	0.65-0.7		0.75

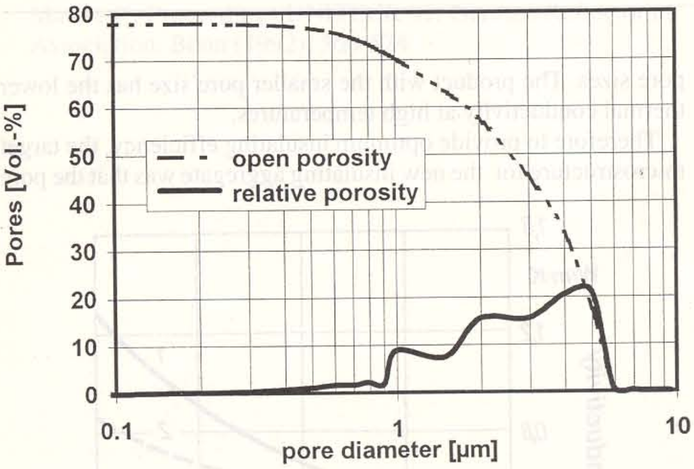

Fig. 2. Micro pore size distribution of SLA-92 (Hg-intrusion method)

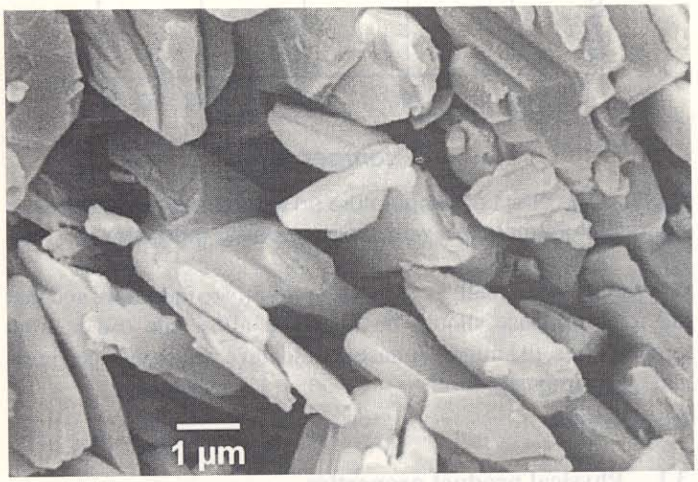

Fig. 3. Scanning Electron Microscope Picture of SLA-92 (broken surface)

The micro pore size distribution in **Fig. 2**, as measured by Hg-intrusion method, shows a narrow range of 1-5 µm with an average pore size of 3-4 µm. The scanning electron microscope image in **Fig. 3** shows the microporous, homogeneous internal structure of SLA-92. The interlocking nature of the platelet-shaped CA_6-crystals results in a high level of internal porosity (typically 75 %), as well as enhancing the strength of the aggregates. The free distance between the CA_6-platelets determines the small pore diameter.

SLA-92 is produced via a wet chemical process which includes sintering of the final product at high temperatures. Its performance has been evaluated at temperatures up to 1500 °C. SLA-92 is produced in four sizes, three closed sizes (1-3, 3-6, 6-10 mm) and one open (0-1 mm). The loose bulk density is around 400 kg/m³ for the closed sizes and around 700 kg/m³ for the fine fraction.

3.2. Thermal conductivity of SLA-92 grains

The thermal conductivity of 1-3 and 3-6 mm SLA-92 grains was tested in the form of beds with packed density. Testing was done up to 1400 °C according to the hot wire method (parallel wire) (DIN EN 993-15). The packing density of the grain bed was achieved by densification of the loose fill trough tapping.

Fig. 4 presents the test data of SLA-92 as compared to the thermal conductivity data for commercially available bubble alumina, insulating fireclay grains, and ceramic fibre blanket. At 25 °C, SLA-92 has a thermal conductivity of 0.15 W/m·K which gradually rises up to 0.5 W/m·K at 1400 °C. The curve of the ceramic fibre blanket crosses the curves of the SLA-92 grain beds at 1200 °C and shows a higher thermal conductivity up for 1400 °C.

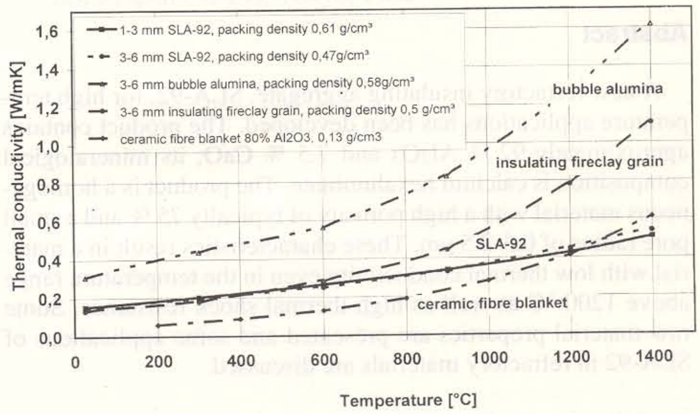

Fig. 4. Thermal conductivity of SLA-92 grains

Both the bubble alumina as well as fireclay grain bed have a rapid rise of thermal conductivity from 600 °C up to 1400 °C. The thermal conductivity of the bubble alumina bed is much higher than that of SLA-92 over the entire temperature range.

The data illustrates the large effect that pore size has on thermal conductivity. The pore size of bubble alumina is nearly equivalent to the grain diameter which is in the mm-range, whereas SLA-92 shows microporosity in the µm-range. This leads to much lower thermal conductivity of SLA-92 especially in the high temperature range where the conductivity is dominated by radiation. The different packed densities of SLA-92 1-3 and 3-6 mm (0.61 vs. 0.47 g/cm³) have no effect on the thermal conductivity.

4. SLA-92 in insulating products

SLA-92 is currently under evaluation in several applications, where low weight of the castables, refractoriness and thermal insulation properties are key factors. High purity is essential in applications such as petrochem and ammonia industry to give CO- and alkali resistance [9,10]. Industrial scale trials for fibre replacement are in progress.

Brick pressing trials at Laeis Bucher, Trier, showed that the grain crushing strength is sufficient for insulating brick production. The relatively high grain strength also provides grain stability when the mix casting is helped by ramming or poking. Ease of installation as well as of destruction leads to shorter downtimes and helps to reduce costs. The porosity of SLA-92 provides good stickiness for gunning.

5. SLA-92 castable and brick test pieces – Preparation and testing

The tests described in chapter 5 and 6 are designed to give some examples for the application of SLA-92 aggregate in castables or bricks and show the physical and insulating properties of the refractory products produced from this aggregate.

5.1 Test Mix 16/1 - Vibration Castable

The composition of the Test Mix 16/1 castable is shown in **Tab. 2.** Preparation and treatment of the test pieces and testing followed the European standard DIN ENV 1402 "Unshaped refractory products", Part 5 and Part 6.

Tab. 2 Composition of theSLA-92 Mix 16/1 castable .

Mix 16/1 castable	
SLA-92 grain	70 %
cement CA-25R	30 %
Additives	+1 %
0,5 % cellulose solution	+60 %

The dry ingredients were mixed for 1 minute. After addition of 60 % of a solution with 0.5 % cellulose (Blanose ex 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:

- 230 mm x 64 mm x 54 mm for testing the conventional properties (DIN ENV 1402-6)
- 230 mm x 114 mm x 64 mm for testing thermal conductivity (hot-wire (parallel) method DIN EN 993-15)
- 150 mm x 25 mm x 25 mm for testing the hot modulus of rupture (DIN EN 993-7)

The vibrated test pieces were cured at room temperature in the mould for 24 h and after demoulding for another 24 h in air with a relative humidity of ≥90%. The pieces were dried for 24 h at 110 °C and fired from 850 °C up to 1500 °C with a soaking time of 5 h.

5.2 Test Mix 16/1 – Pressed Brick

For the brick preparation the same composition as for the vibration castable (Tab. 2) was used, but only 30 % of the cellulose solution was added.

Bricks (250 mm x 100 mm x 65 mm) and plates (250 mm x 100 mm x 30 mm) were pressed without problems on an industrial hydraulic press (Laeis Bucher, Trier) with an applied pressure of 2 kN/cm². Edges and corners of the pressed pieces are strong enough for an automatical transport. The modulus of rupture of the green pressed plates is about 0.8 N/mm².

5.3 Properties of Mix 16/1 castable and brick

The physical properties of the prepared test pieces after drying and firing up to 1500 °C are compiled in **Tab. 3**.

5.3.1 Permanent linear change of dimension

The drying shrinkage of the Mix 16/1 is about 0.05 % and the firing shrinkage at 1400 °C/5 h reaches about 0.4 % for both castable and pressed brick. The firing temperature of 1500 °C results in a shrinkage of 0.95 % for the castable and 0.77 % for the pressed brick.

5.3.2 Bulk density and apparent porosity

There is practically no change in bulk density and open porosity at firing temperatures from 850 up to 1400 °C. In this temperature range the castable has a bulk density of about 1.1 g/cm³, the pressed brick of about 1.28 g/cm³. The apparent porosity is about 70 % for the castable and 66 % for the pressed brick.

The slightly higher shrinkage at 1500 °C results in a small increase of bulk density and decrease in porosity.

5.3.3 Pore size distribution

Results of micro pore size distribution are shown in **Fig. 5**. The sum of the microporosity is roughly 60 %. Even at firing at 1500 °C the median pore diameter of the Mix 16/1 material remains at about 3-5 µm similar to that of the SLA-92 grain, but the castable and the brick contain a small amount of larger pores up to 60 µm.

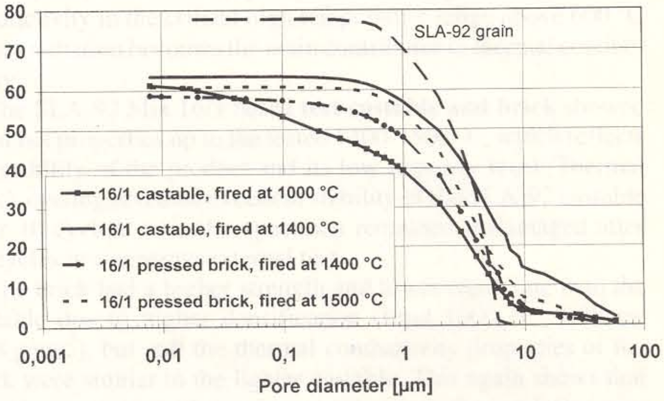

Fig. 5. Micro pore size distribution of SLA-92 Mix 16/1 castable and brick (Hg-intrusion method)

5.3.4 Gas permeability

The gas permeability of the fired 16/1 castable and pressed brick at 1400-1500 °C is in the range of about 5.5 nPm, a relatively low value for these high porous materials. The low value is the effect of the very small pore size.

5.3.5 Cold modulus of rupture and cold crushing strength

Up to a firing temperature of 1000 °C, the flexural strength remains at about 0.3 N/mm² for the castable and about 1 N/mm² for the pressed brick because of its higher bulk density. Firing temperature of 1500 °C increases strength about a factor of three.

The development of cold crushing strength is similar to the changes in the cold modulus of rupture. After firing at 1500 °C, the cold crushing strength reaches 6.5 N/mm² for the castable and 11.5 N/mm² for the pressed brick.

5.3.6 Hot modulus of rupture

The test results indicate that the modulus of rupture from room temperature up to 1500 °C testing temperature remains constant at about 1 N/mm², emphasising that no melting phase in the material develops.

Tab. 3. Physical properties of SLA-92 Mix 16/1castable and pressed brick

	unit	Pre-Treatment [2]) [°C]	Mix 16/1 castable	Mix 16/1 brick
Permanent linear change	%	110 850 1000 1400 1500	-0.05 -0.04 -0.08 -0.44 -0.95	-0.02 -0.04 -0.06 -0.40 -0.77
Bulk density	g/cm^3	110 850 1000 1400 1500	1.19 1.10 1.08 1.07 1.12	1.42 1.29 1.28 1.27 1.32
Open porosity	Vol.%	110 850 1000 1400 1500	62.7 70.9 71.3 68.6 66.8	55.5 65.8 66.0 62.0 60.6
Cold modulus of rupture CMOR	N/mm^2	110 850 1000 1400 1500	0.33 0.27 0.24 0.6 0.98	1.1 0.9 1.2 2.2 2.6
Cold crushing strength CCS	N/mm^2	110 850 1000 1400 1500	2.2 3.1 3.7 3.7 6.5	8.7 8.5 8.9 10.3 11.5
Hot modulus of rupture HMOR	N/mm^2	1400 1500	1.0 0.9	n.d.
Thermal expansion at 1000 °C	%	1500	0.79	0.76
Refractoriness under Load $T_{0,5}$ (0.05 N/mm^2)	°C	1500	1485	1495
Thermal shock resistance (air)	cycles	1400 1500	>10 >10	10 n.d.
Gas permeability	nPm	1400 1500	– 5.4	5.1

[2]) firing time 5 h

5.3.7 *Refractoriness under load and creep in compression*

Fig. 6 shows the refractoriness under load curves (DIN EN 993-8) of prefired specimen of Mix 16/1 castable and brick.

The pressed brick prefired at 1400 °C reaches practically the same high $T_{0,5}$ value as the 1500 °C prefired castable of about 1490 °C.

From the creep curves (DIN EN 993-9) in **Fig. 7** the test results as given in **Tab. 4** were calculated. They demonstrate the good creep resistance of SLA-92 materials up to 1400 °C.

5.3.8 *Thermal shock resistance*

The air quenching method, according to DIN ENV 993-11 was used.

The thermal shock test was stopped after 10 cycles and the strength measured in comparison to the untreated material. The results (**Tab. 5**) show that the Mix 16/1 castable fired at 1000 °C up to 1500 °C shows no sign of cracks and no strength decrease after 10 cycles.

The pressed brick fired at 1400 °C failed at 10 cycles by one crack passing through the material, probably due to the higher density of the material or not yet optimised pressing parameters when forming the brick (laminations).

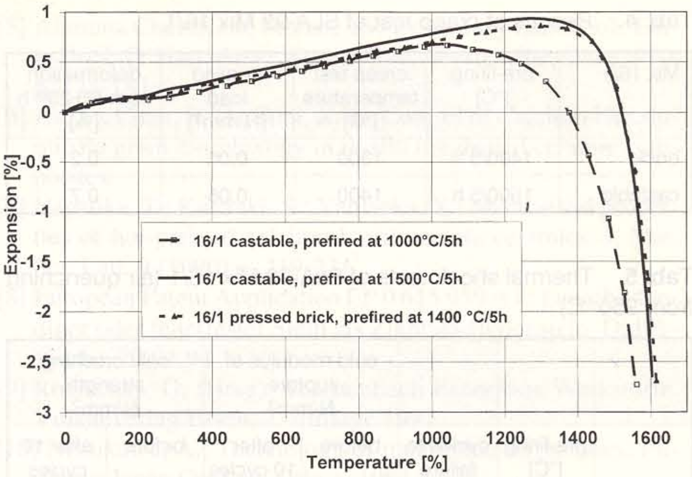

Fig. 6. Refractoriness under load 0.05 N/mm^2 of SLA-92 Mix 16/1

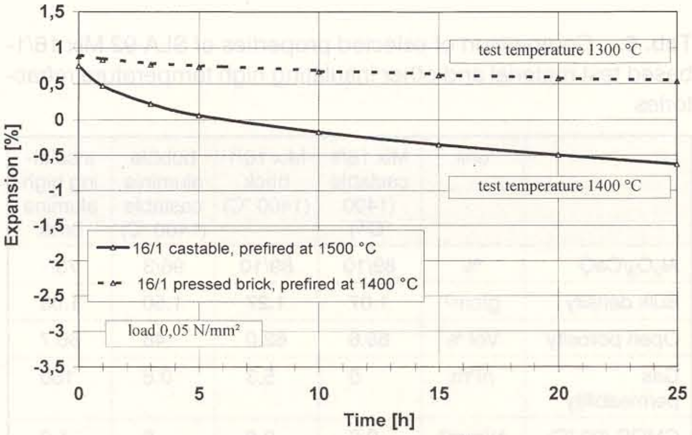

Fig. 7. Creep in compression 0.05 N/mm^2 of SLA-92 Mix 16/1

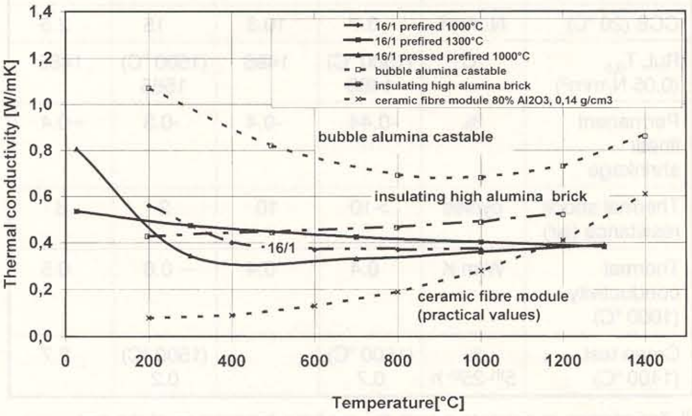

Fig. 8. Thermal conductivity of SLA-92 Mix 16/1

5.3.9 *Thermal conductivity*

Fig. 8 presents the thermal conductivity of Mix 16/1 castable and pressed brick.

For the materials pre-fired to 1000 °C, the thermal conductivity decreases from 25 °C down to 500 °C and then levels out in the temperature range from 800 °C to 1300 °C at about 0.4 W/m·K.

Pre-firing at 1300 °C results in a steady decrease of thermal conductivity from 0.5 W/m·K to 0.4 W/m·K. The differences of thermal conductivity between castable and brick are small, even though the brick has a higher bulk density.

Tab. 4. Results of creep test of SLA-92 Mix 16/1

Mix 16/1	pre-firing [°C]	creep test temperature [°C]	applied load [N/mm²]	deformation from 5th-25th h [%]
brick	1400/5 h	1300	0.05	0.2
castable	1500/5 h	1400	0.05	0.7

Tab. 5. Thermal shock tests of SLA-92 Mix 16/1 (air quenching from 950 °C)

			cold modulus of rupture N/mm²		cold crushing strength N/mm²	
	pre-firing [°C]	cycles to failure	before	after 10 cycles	before	after 10 cycles
Mix 16/1 castable	1000	>10	0.24	0.30	3.7	3.5
	1400	>10	n.d.	n.d.	n.d.	n.d.
	1500	>10	0.6	1.1	6.5	6.1

Tab. 6. Comparison of selected properties of SLA-92 Mix 16/1-based test material and other insulating high temperature refractories

	unit	Mix 16/1 castable (1400 °C[3]))	Mix 16/1 brick (1400 °C)	bubble aluminia castable (1400 °C)	insulating high alumina brick
Al_2O_3/CaO	%	89/10	89/10	96/3	73/-
Bulk density	g/cm³	1.07	1.27	1.50	1.08
Open porosity	Vol.%	68.6	62.0	48	66.7
Gas permeability	nPm	5	5.3	0.8	160
CMOR (20 °C)	N/mm²	0.6	2.6	5	1.6
HMOR (1400 °C/5 h)	N/mm²	1	n.d.	4.9	0.4
CCS (20 °C)	N/mm²	3.7	10.3	15	2.5
RuL $T_{0,5}$ (0.05 N/mm²)	°C	(1500 °C) 1485	1495	(1500 °C) 1565	1485
Permanent linear shrinkage	%	-0.44	-0.4	-0.3	+0.4
Thermal shock resistance (air)	cycles	>10	10	2	6
Thermal conductivity (1000 °C)	W/m·K	0.4	0.4	~ 0.6	0.5
Creep test (1400 °C)	% 5th-25th h	(1500 °C) 0.7		(1500 °C) 0.2	2.7

[3]) Temperature in brackets equals the pre-firing temperature of the test pieces.

The Mix 16/1 material competes with the thermal conductivity of high temperature insulating bricks. The increasing thermal conductivity of ceramic fibre modules (data from practical use) leads at 1200 °C and above higher as of the Mix 16/1 material.

6. Comparison of the properties of Mix 16/1 materials

6.1 Comparison of selected properties

In **Tab. 6** selected properties of the Mix 16/1 castable and pressed brick are compared to two just available refractory materials for high temperature insulating applications: a bubble alumina castable and an insulating mullite brick (Group ASTM 30).

It has to be mentioned, that the two other products can only give a rough comparison because of the wide variety of the properties of these two refractory product types.

7. Discussion

The SLA-92 concept of an optimised insulating aggregate for high temperatures with a high porosity and a small pore size, has shown to give the targeted low thermal conductivity up to 1400 °C.

Tests with SLA-92 as a **grain bed** showed a slow rise in thermal conductivity up to 1300 °C, an effect of its microporosity. A similar slow rise in thermal conductivity was seen for the ceramic fibre blanket but above 1200 °C ist conductivity is higher then that of the SLA-92 grain bed. This finding could indicate some future potential. – The tested bubble alumina and fireclay grain beds had a distinctly higher and steeper rising thermal conductivity in the critical high temperature range above 600 °C where radiation becomes the main contributor to thermal conductivity.

The SLA-92 Mix 16/1 based **test castable and brick** showed good hot properties up to the tested 1400-1500 °C, which reflects the stability of the product and its low impurity level. Thermal shock cycling revealed excellent stability of the SLA-92 castable after 10 cycles, a similar specimen remained undamaged after 20 cycles in a separate external test.

The brick had a higher strength and lower creep rate than the castable due to higher densification (fired 1000 °C: 1.08 vs. 1.28 g/cm³), but still the thermal conductivity properties of the brick were similar to the lighter castable. This again shows that the microporosity is the major contributor to the insulating properties.

An important characteristic of the SLA-92 Mix 16/1 materials is the constant low thermal conductivity level with little or no rise up to 1300 °C, where an average value of 0.4 W/m·K is found. This indicates competitiveness of its properties to high temperature insulating bricks. The increasing thermal conductivity of ceramic fibres modules at 1200 °C and above lead to values higher as the Mix 16/1 material, a finding which again could open up some future potentials for SLA-92.

8. Outlook

SLA-92 presents a new concept for insulating aggregates with a high potential for high performance, innovative insulating products. It could be the key to new solutions for technical requirements like decreased lining thickness, longer lifetime, increased volume/capacity, higher operating temperatures, or higher energy savings.

This new insulating aggregate can be an alternative material for existing insulating products. Its benefits include high creep resistance, high thermal shock resistance, high purity, and low thermal conductivity at temperatures above 1200 °C. It seems to have a potential to be a replacement material in many applications that currently use ceramic fibres. SLA-92 could assist in alternative products solutions with similar refractoriness, low thermal conductivity, and less concerns around potential health hazards.

SLA-92 performance for higher application temperatures will be explored. The option for the development of an SLA-family of insulating raw materials with different chemistries is under evaluation for the future.

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9. Literature

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