Thermal properties of calcium-aluminate based materials

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Abstract. Good cementing properties, fast setting and strong thermal performance make calcium-aluminate a valuable raw material for use in the production of different types of new refractory materials, e.g., heat conductive/storage materials. The main aim of the study was to determine thermal properties of novel Nb-slag based materials with different fillers, and to clarify optimal composition and technology. Process of preparation of studied materials was following: mixing of components, casting to moulds and hardening of materials. To estimate potential application areas, we studied the following thermal properties of CA-based materials: thermal behaviour, coefficient of thermal expansion (CTE) and conductivity. For this small cylindrical specimens were cut out from produced materials, and plates sized 300 x 300 mm were used for conductivity studies. Different compositions of CA-based materials, the hardening process, and the influence of mechanical activation on the strength were analyzed. Best thermal properties similar to the analogous reference material were obtained by quartz sand and granite sand as filler materials. The thermal conductivity of the novel CA-based material is 1.5 times higher and the bending strength is about 3 times higher compared to commercial thermoplates.

1. Introduction

Slags from metallurgy composed primarily of silica with concentrations of constituents like alumina, magnesia and other components have the potential value for application, and technologies have emerged to recycle and reuse reprocessed slag in different building materials [1]. Niobium slag resulting from the aluminothermic process at Sillamäe metallurgy plant, Estonia, contains mainly calcium-consisting aluminate (CA) and due to non-full calcium-aluminothermic reduction, some amount of initial materials – mainly niobium oxide Nb2O5 (3-7%) and pure Nb up to 1% (depends on the batches) [2].

The technology of separation of pure Nb based on the disintegrator treatment of CA consists of the following steps: precrushing of big pieces, disintegrator milling and separation of milled product to fine (< 0.3 mm) and coarse fractions, followed by separative milling of coarse fraction to separate pure Nb [2, 3]. Preliminary experiments were conducted to clarify the potential application area of ground CA as the main component of heat accumulation and heat-transfer materials. Similar alumina-silica based ceramic materials are used for accumulation (slow heat release) of heat in fireplace stoves and fireplaces [4]. Due to analogous compositions of niobium slag, it may be a potential material for refractory products.

It was demonstrated by our previous experiments [2, 3] that CA-based materials have high potential of application as the main component of refractory materials, especially in the form of heat accumulation and heat transfer elements of stoves, fireplaces etc. Our preliminary experiments showed that CA-based
materials have high mechanical properties and similar heat conductive properties (about 0.34 W·m⁻¹K⁻¹ against 0.42 W·m⁻¹K⁻¹ of commercial) [2].

2. Experimental

2.1. Initial materials
Niobium slag was subjected to impact milling and a coarse ground product was subjected to separative milling in disintegrator DSL-115. Used ground slag contained mainly calcium aluminates (CA); fineness was <125 µm. Old CA (aged more than some 10 days) was used in our experiments. To have fresh mechanically activated CA, it was milled immediately before using (during the next 5 h).

The following CA based mixtures were studied (Table 1):
- Pure CA (fresh and old);
- CA with additions of granite sand (GS), CEN standard quartz sand (QS) and polarstone sand (PS). The fillers were obtained by disintegrator milling of GS gravel, standard QS and PS wastes. It was shown the same chemical compositions after milling;
- CA with addition of fly ash cenospheres of alumina-silica (AC) (lightweight, inert, hollow sphere filled with inert air or gas – a typical byproduct of coal combustion at thermal power plants (Biotecha Latvia Ltd, Riga, Latvia), mainly consisting of SiO₂ and Al₂O₃). The chemical composition of AC was studied previously in [6]. Figure 1 shows the SEM images of the used filler materials.

As a reference material, analogous Cebud thermoplate CPA-K [5] were studied and concrete (cement + standard sand) of hardened materials was prepared and tested for comparison.

![Figure 1](image1)

**Figure 1.** Filler materials: a – granite sand (GS), b – quartz sand (QS), c – polarstone sand (PS) and d – fly ash cenospheres (AC).

For the study of mechanical properties, bending strength specimens sized 40 x 40 x 160 mm were prepared. For the study of thermal properties, cylindrical specimens with ø7 mm from mechanical test pieces were cut out. For the study of thermal conductivity, the plates sized 300 x 300 x 25 mm were produced. Prepared mixtures of CA with fillers and addition of water (about 33%) were casted to molds and densified by vibration. The procedure was as follows: preparation of components → mixing of mixtures → hardening at air 24 h → drying at 100 °C for 24 h. Density of CA-based materials with filler GS and QS was about 2.0 g/cm³, with PS was about 1.5 g/cm³ and with AC was about 1.3 g/cm³.

2.2. Characterization of mechanical properties
Prismatic specimens were tested on a universal testing machine according to standard EN 196-1 [7]. Bend strength of the specimens at three-point bending was determined. Universal testing machine P-5 (50 kN) was used and distance between the points of support was 100 mm.

2.3. Characterization of thermal properties
The thermomechanical characteristics of the samples from heat-conductive materials were determined on Setaram Setsys 1750 CS Evolution dilatometer. Cylindrical specimens with a diameter of 7 mm and a height of 15-16 mm in corundum sample holder were heated up to 1000 °C at a heating rate of 5 °C per minute and cooled down at the same rate in an Ar atmosphere. The diagrams DTDA – T and Δl% – T were plotted.
Thermal conductivity was measured according to the standard EVS-EN 12667 [8] using LaserComp FOX-304 heat flowmeter. The average heat flux was used to calculate the thermal conductivity (\( \lambda \)) and thermal resistance (R) according to Fourier’s Law.

For thermal plates the optimal composition of CA : Filler (50:50) was selected keeping in the mind as technological as well strength properties of studied materials.

### Table 1. Composition of studied materials.

| Composition [wt%; conditions; fraction size] | Post-treatment |
|--------------------------------------------|----------------|
| CA\(^a\) [100; fresh and old] | – |
| [66, 50 and 34; fresh] | granite sand (GS) [34, 50 and 66; milled; < 125 \( \mu \text{m} \) ] |
| [66, 50 and 34; fresh] | quartz sand (QS) [33, 50 and 66; milled; < 125 \( \mu \text{m} \) ] |
| [66, 50 and 34; fresh] | polarstone (PS) [33, 50 and 66; milled; < 125 \( \mu \text{m} \) ] |
| [75 (vol% 50); fresh] | ash cenospheres (AC) [25 (vol% 50); < 300 \( \mu \text{m} \) ]; |
| – | portland cement [25] + standard sand [75; 2÷0 mm] |
|  | Hardening at 20 °C / up to 54 days |
|  | Hardening at 20 °C / 7 days |

\(^a\) – fraction size < 125 \( \mu \text{m} \)

### 3. Results and discussion

#### 3.1. Thermal Analysis

As it follows from the DTDA-diagram belong to old CA (Figure 2), changes up to 100 °C are connected with the emission of physically bound water. Changes in the range from 200 up to 400 °C are probably connected with thermo-oxidation of the matter contained in Nb-slag as remains of the reduction process and change at 970 °C caused probably with formation of liquid phase.

The contraction-expansion behavior of samples of the studied materials by heating up to 1000 °C at the heating rate of 5 °C/min is presented in Figure 3.

As the graphs show, up to 180 – 200 °C, low shrinkage (up to −0.1%) can follow. Then, around 260 °C, deep shrinkage of bodies at 340 – 380 °C follows, which is most significant for pure CA (fresh -1.03%, old −0.85%). Starting from 400 °C, stabilization takes place.

Behavior of composites (except CA+QS) differs from the behavior of pure CA; shrinkage is less and more dependent on the temperature. Shrinkage increases up to 360 °C (up to −0.5%) and then stabilizes.

Composition containing quartz sand (CA+QS) behaves in a slightly different way: shrinkage is low (−0.2%) up to temperature 480 °C and then expansion up to 580 °C (up to +0.5%) follows and it is stabilized. The thermal behavior of CA+AC body is characterized in an analogous way: starting from 550 °C notable elongation (+0.6%) and stabilize from 600 °C up to 1000 °C.

![Figure 2. Heating curve (DTDA-diagram) of CA.](image-url)
3.2. Behavior of CA in the hardening process

It was demonstrated in our preliminary experiments that in the hardening process, a notable increase of the temperature of hardenable specimens takes place, first, with CA just milled.

For this propose, a special study with pure CA with particles size <125 µm was carried out: old (early milled and aged) and fresh (just milled) CA were used. Hardening time was 16 h.

Figure 4a shows that the temperature at the hardening of specimens made from fresh materials increases up to 100 °C whereas with specimens from old CA, the temperature is not significantly increased. It reveals mechanical activation in the high velocity impact milling process. The mechanical activation of materials due to the disintegrator milling was demonstrated in our earlier work [9, 10]. It causes a notable increase in the mechanical properties as well as the bending strength; materials made from fresh milled CA demonstrated up to 2 times higher strength (Figure 4b). It takes about two days to achieve the necessary minimal strength level, e.g., 4 MPa with old CA, while with fresh CA, only 10 h are required. One of the ways to suppress this phenomenon is using ballast materials, i.e., inert fillers. Using fillers noticeable heating of cast mixture was not observed and was similar to old CA.

3.3. Optimization of composition

To suppress the high activity of fresh CA, the inert filler materials like granite sand (GS), polarstone sand (PS) and CEN standard sand – quartz sand (QS) were used. The studied mixtures consisted of filler materials from 33 to 66%. Materials were made by the same technology: mechanical mixing of components, casting of mixtures to molds and hardening at room temperature for 24 h, followed by drying at 100 °C for 24 h. Three prismatic specimens were subjected to the bend load at the three-point test. Results of the bending test are given in Figure 5.
At all studied compositions, increase of the filler content causes a decrease in the bending strength. With fillers GS and QS content over 50%, a deep increase in the strength can be seen (Figures 5a and 5b). Up to that point, at the increase of the filler content, flexural strength decreases proportionally. At the same time, the strength of materials increases with the use of fresh immediately disintegrator milled filler materials, being 30% higher (GS and QS) except for PS.

Figure 5. Dependence of flexural strength on the amount of filler in the mixture: a – granite sand (GS), b – quartz sand (QS) and c – polarstone (PS)

Notable influence of hardening time on the strength was observed. Samples gained half of their strength in the first 14 days of hardening. Over time (42 and 56 days), the rate of increase in the flexural strength slowed down.

Adding polarstone (PS) as a filler has a strong effect on to the strength. The dependence of the decrease in strength on the amount of filler has a pronounced linear character (Figure 5c). Better strength was observed when using non-milled PS filler. It can be explained with a change of morphology of PS particles as a result of milling. Due to the lamellar structure of PS particles, we obtained flake powder (Figure 5c).

3.4. Thermal conductivity of CA based materials

Results of the thermal conductivity study are given in Figure 6. The figure shows that the CA+QS material has better conductivity, about 55% higher than the reference material CPA-K, followed by CA+GS material (about 29% higher) and CA+PS (10% higher).

Taking into account the mechanical and thermal properties and the economic aspect, CA-based materials with a quartz sand filler are more prospective.

Figure 6. Thermal conductivity of CA based materials.
4. Conclusions

1. Novel Nb-slag based materials were obtained and prospective of application as heat conductive materials were demonstrated.

2. Based on the study of mechanical and thermal properties of calcium aluminate (CA) materials of different compositions and conditions, we can draw the following conclusions:
   - With mechanical milling of CA, activation of ground material is accompanied due to the fresh surfaces formed. As a result, this hardening process is more intensive, accompanied by higher strength (up to 2 times). At the same time, an increase in the temperature accompanied in the hardening process results in the decrease of density and distortion of material. It can be suppressed by optimizing the composition by the use of fillers.
   - Optimal CA: filler proportion in fresh CA based materials is 50:50 percentage. Increase of strength using a filler is about 10 – 15% (by GS) and 25 – 30% by QS and PS.
   - In view of thermal properties, the composition of CA with a granite and quartz sand fillers is favorable. The thermal conductivity properties is 30-50% higher and strength properties about 3 times higher than that of the reference thermoplates.

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