

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Refractory Materials for Biofuel Boilers

Valentin Antonovič, Jacek Szczërba,
Jadvyga Kerienė, Rimvydas Stonys and Renata Boris

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65550>

Abstract

The energy equipment usable for solid biofuel incineration usually operates upon aggressive conditions. The internal structures (lining) of the equipment are made of refractory materials that are affected by combined loads: thermal, mechanical and chemical (i.e. high temperature—up to 1200°C, chemical impact of alkaline compounds and slag, repeating thermal shocks, abrasive effect caused by solid particles and so on). A majority of traditional refractories usable for lining in such equipment are not durable. Upon certain conditions of use (such as high local temperatures, influence of alkaline biofuel combustion products and so on), durability of the traditional materials is 1–2 years only. The opportunities of new refractory materials application should be set upon taking into account the conditions of operation for biofuel boilers of specific types. In this section - the data on the peculiarities of using refractory materials in biofuel boilers are reviewed, and the impact of aggressive operating conditions of such thermal equipment on the properties of refractory materials is discussed. In addition, the investigations results of refractory castables alkali resistance and its explosive spalling are discussed. The recommendations for use of refractory materials in biofuel boilers are also presented.

Keywords: biofuel boiler, refractory materials, refractory castables, alkali resistance

1. Introduction

Biofuel boilers are used in modern fuel combustion systems, with the function to ensure high energy conversion efficiency and comply with environmental standards applied on such devices. Despite the fact that energy equipment may have different designs, their operation is based on a standard three-level process diagram (**Figure 1**) [1].

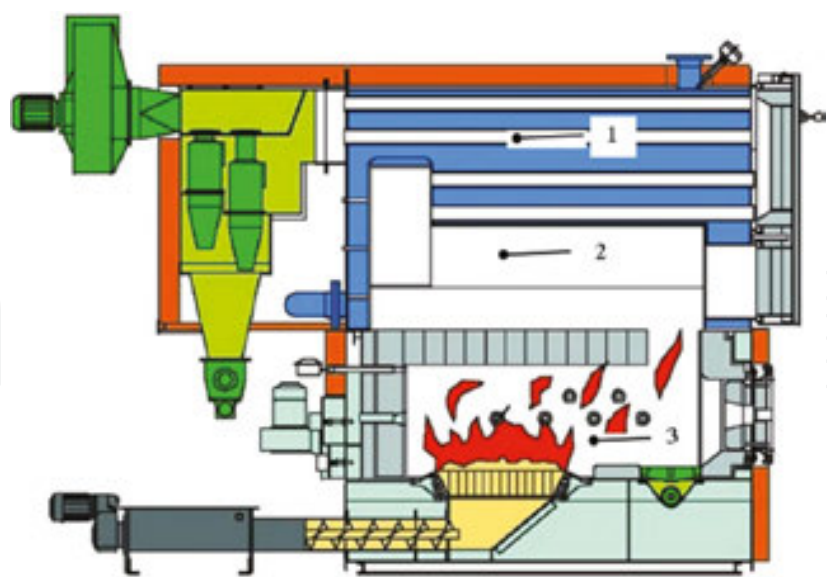


Figure 1. Solid biofuel incinerator scheme: 1—primary combustion chamber with fuel feeding system; 2—secondary combustion chamber; 3—exhaust gas and the heating system [1].

Refractory materials are used for biofuel boilers’ internal structures (lining). These materials are non-metallic inorganic materials, which do not melt and do not decompose at high temperatures (600–2000°C). Main elements of lining (**Figure 2**) are made of shaped (bricks, blocks, etc.) and unshaped (concrete, mortar, coatings, etc.) refractories. They can be classified by general (chemical or mineral composition, refractoriness, porosity, etc.) and specific (type of binder and main raw material, forming method, etc.) features.



Figure 2. Biofuel boiler lining made of (a) fired bricks and (b) castables.

One of the most important groups in the unshaped materials classification is refractory castables. These are mixtures of refractory aggregates and bond(s), mainly supplied dry and

used after addition and mixing with water or another liquid. They are placed by casting with vibration, by casting without vibration (self-flowing), by rodding, by shotcreting or when necessary by tamping. Based on the standard EN ISO 1927-1:2012, they can be dense or insulating and divided into chemically and hydraulically bonded; the latter are then divided into regular and deflocculated. The above-mentioned standard contains reference castable classification scheme (**Figure 3**), which can be used when reviewing the variety of refractory castables.

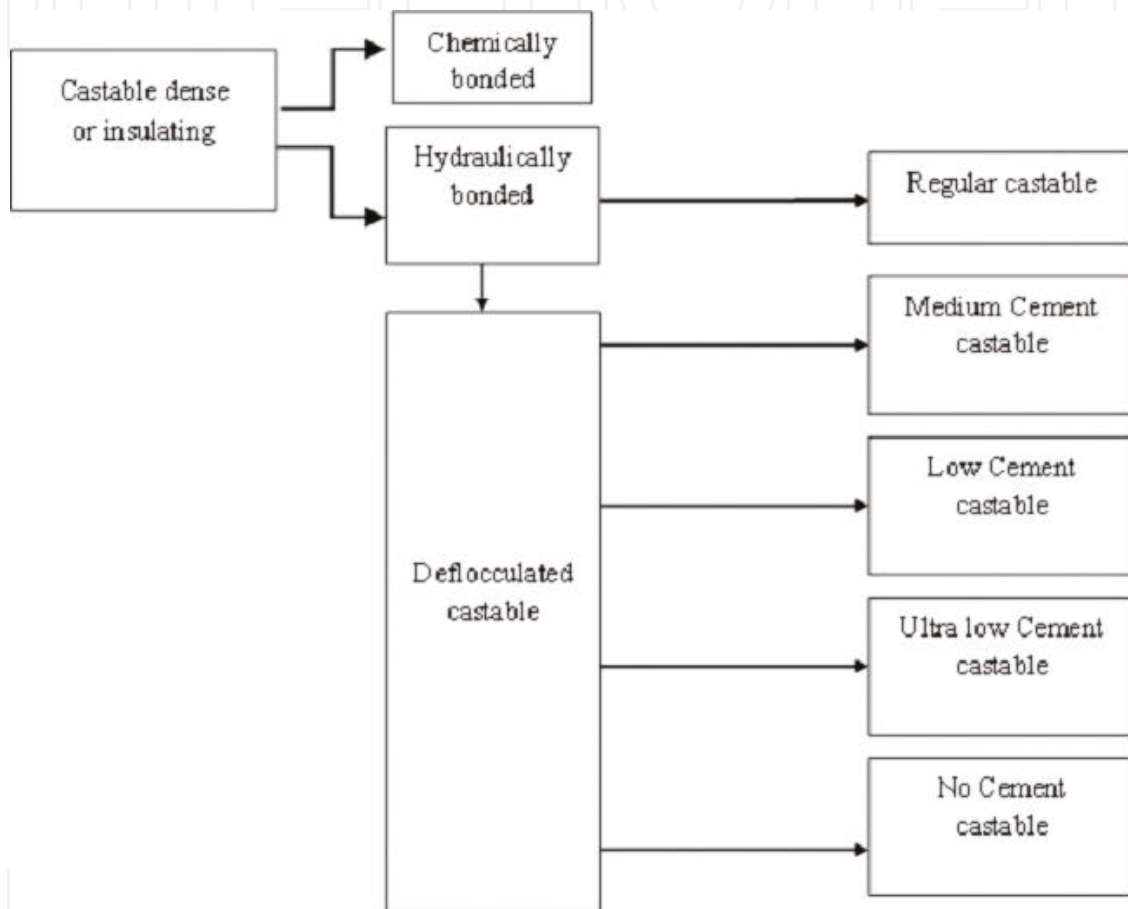


Figure 3. General classification scheme of dense or insulating castables according to standard EN ISO 1927-1:2012.

In **Figure 3**, refractory castables with hydraulic binders (calcium aluminate cement) are divided into groups according to the scheme depending on the amount of cement. Regular castable (RC) group includes castables with calcium aluminate cement content of up to 15–30%, medium cement content (MCC) group—8–15%, castables with low amount of cement (LCC) group—4–8%, castables group with ultra-low content of cement (ULCC)—1–3% and no cement group includes cast castables without cement (NCC). MCC, LCC and ULCC types of castables, compared with RC, contain special ultra-fine particles (less than 1 μm), and various deflocculants (soluble compound (usually an electrolyte) which, when added even in very small quantities, will reduce the water content in castable). Hydraulically bonded castables set and harden at ambient temperatures.

The manufacture of modern LCC or ULCC refractory castables with very low cement content often involves a number of process difficulties. Among them the problem of the loss of workability of castables, since these castables are sensitive to environmental temperature changes during manufacture, water quantity and quality, mixing parameters and other factors. For example, increase in water content by 2% in LCC and ULCC type of castable with chamotte filler reduces the cold crushing strength (CCS) of those castables after drying at 110°C and firing at the temperature of 1100°C from 80 and 90 MPa to 60 and 20 MPa, respectively [2]. MCC type refractory castables with performance characteristics much better than the traditional concrete are not as “sensitive” to the conditions of production; they are attractive to use in a variety of thermal equipment linings.

Not only castables with hydraulic binders, but also with other types of binders as well as gunning and ramming materials can be used in biofuel boilers. Another bond may be:

- a ceramic bond with hardening by sintering during firing;
- a chemical bond (inorganic or organic-inorganic) with hardening by chemical, but not hydraulic, reaction at ambient temperature or at a temperature lower than that of a ceramic bond; and
- an organic bond with binding or hardening at ambient temperature or at higher temperatures.

When choosing refractory linings for biofuel boiler, it is necessary to know the effect of loads attributable to the material during operation and to adapt it to the service properties of the materials [3] (**Table 1**). Before selecting the material, it is also important to check the material bond, in order to know about the need of special heat treatment. This will help to avoid discussions about setting times, progress of work, and the date of taking the boiler into operation [4].

Type of load	Properties
Thermal	Pyrometric cone equivalent (refractoriness), refractoriness under load, thermal expansion under load (creep), hot modulus of rupture, thermal expansion, reheat change (after shrinkage and after expansion) and thermal shock resistance
Thermo-technical	Thermal conductivity, specific heat, bulk density, thermal capacity and temperature conductivity
Mechanical	Crushing strength, abrasion resistance, cold modulus of rupture and deformation modulus, porosity and density
Chemical	Chemical composition, mineralogical composition and crystal formation, pore size distribution and types of pores, gas permeability, resistance to slag, glass melts, gases and vapours

Table 1. Important service properties of refractory materials [3].

Information about properties of refractory materials and their determination methods can be found in various works that are subject to EN or ASTM standards [4, 5]. Some of these information will be presented in this chapter.

2. Influence of operation conditions of biofuel boilers on durability of refractory materials

It is noted that thermal equipment that use solid biofuel experience significant increase in thermal and mechanical loads and chemical effects on lining and refractory materials. In some cases, sudden spalling of lining is observed in biofuel boilers as soon as after 1–2 years of use. The observation of the lining and the investigations of refractory materials used in various biofuel boilers show that the cause of poor durability of refractory materials is a combined impact of negative factors, such as high temperatures, an aggressive chemical effect of alkali compounds, an abrasive effect caused by solid particles, repeating thermal shocks and mechanical loads. It is noted that the risk of failure of materials highly increases with the increase in alkali when changing the type of fuel.

In biofuel boilers, depending on the type and sort of firewood used, different levels of ash and alkali metals (Na, K) are produced during combustion that adversely affects refractory materials. **Table 2** shows the content of alkaline oxides in different types of wood ashes [6]. Wood ash contains much more potassium than sodium; moreover, potassium diffusion to refractory material is faster than that of sodium. Therefore, while investigating the lining materials that spall in solid biofuel combustion devices, potassium compounds are found in corrosion products.

Types of wood	Ash content, %	Chemical composition of ash, %					
		SiO ₂	CaO	Na ₂ O	K ₂ O	MgO	P ₂ O ₅
Oak	0.51	0.01	0.37	0.02	0.05	0.02	0.03
Birch	0.26	0.01	0.15	0.02	0.03	0.02	0.02
Beech	0.55	0.03	0.31	0.02	0.09	0.06	0.03
Pine	0.29	0.04	0.14	0.01	0.04	0.03	0.02
Larch	0.25	0.01	0.07	0.02	0.04	0.07	0.03

Table 2. Various types of wood ash chemical composition (of total dry mass of wood) [6].

Although ash content in wood fuel or other solid fuels is low (up to several per cent), ash fusion characteristics have an impact on the properties of refractory materials because ash melt easily penetrates to the structure of the material. Ash melting behaviour depends on the type of fuel. With the ASTM D1857 standard, the changes in the shape of a standard ash cone by burning it in acidifying (oxidizing) environment are defined: initial deformation—IT; softening temperature—ST; the point of hemisphere formation—HT; and flow temperature—YP.

Table 3 presents fusibility characteristics of ash of some wood types [7]. As we can see, pine sawdust ash may adhere to the material of lining when the boiler's operating temperature reaches the ash ST of around 1180°C. Such ash begins to melt and flow at temperature of 1225°C. This means that pine sawdust fuel greatly increases the chemical effects on the

refractory materials given the boiler operation if the local temperature (e.g. in the secondary combustion chamber) is around 1200°C.

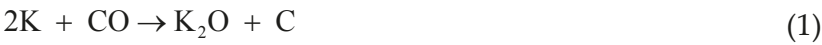
Fuel	Values of melting characteristics, °C			
	IT	ST	HT	YP
Woodchips total, pine	1210	1225	1250	1275
Slashings	1175	1205	1230	1250
Sawdust, pine	1150	1180	1200	1225
Bark, spruce	1405	1550	1650	1650
Bark, pine	1340	1525	1650	1650

Table 3. Fusibility characteristics of wood ash [7].

2.1. Alkali effects at high temperatures

In the combustion chamber, under reducing environment alkali metals react with the refractory lining material. There are two different types of alkaline reactions with refractory materials: in dry conditions under the influence of alkali vapour or in humid environment, when melt ash is formed on the surface of the refractory material.

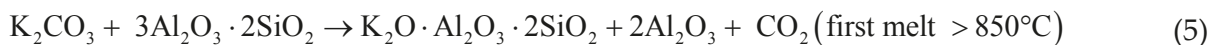
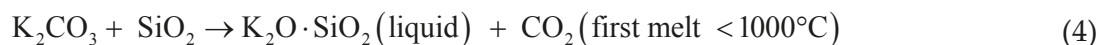
Potassium or sodium released during combustion reacts with CO gas [8]:



Potassium vapour over time can penetrate into the refractory material to the depth of more than 100 mm [8].

When refractory material is exposed to alkali vapour or melt, it may form the following compounds: kalsilite ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$), leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$), feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$) and others [9]. Formation of this type of minerals in the refractory material increases its volume by 15–30% and sometimes even 55%, compared to the initial volume of the material. This promotes the formation of porous structure (**Figure 4**) [10], micro-cracks in refractory material and the spalling degradation due to alkali effects.

Under wet conditions when the melt forms on the surface of the refractory material, it can lead to reactions that reduce the temperature of melt formation [11]:



Further, $4\text{K}_2\text{O} \cdot \text{CaO} \cdot 10\text{SiO}_2$ first melt $< 950^\circ\text{C}$.

Thus, spalling of refractory material due to the effect of alkali may be intensive even with reduced operating temperature of the boiler.

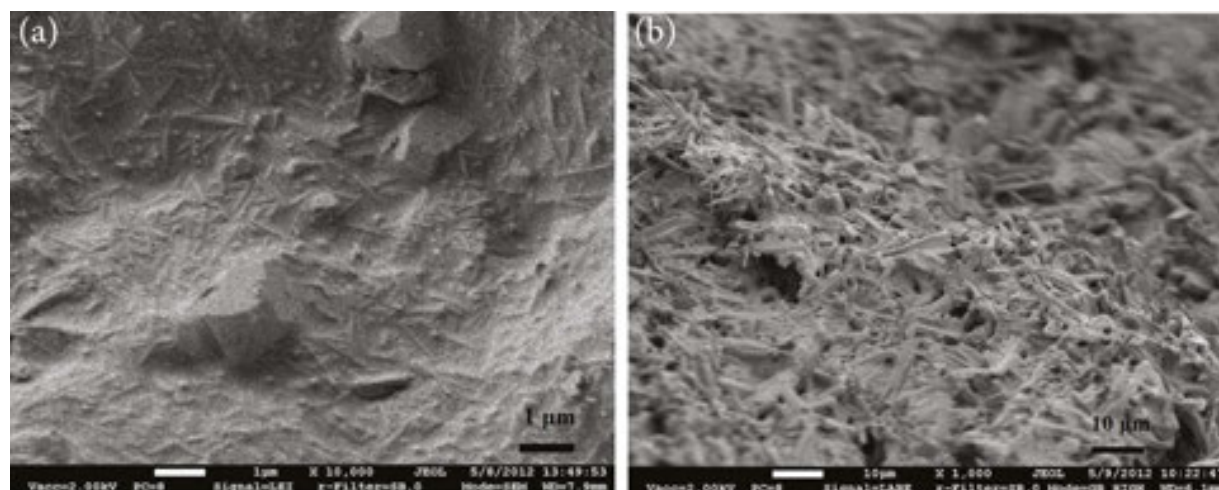


Figure 4. Mullite brick structure: (a) undamaged layer and (b) porous layer affected by alkali [10].

It should be noted that the possibilities of the melt penetration into the structure of the material depend on the porosity of refractory materials, effective potential of pores and capillaries, etc. Thermal expansion coefficient of melt is significantly different from the thermal expansion coefficient of the refractory material. Therefore, with cooling material (e.g. when the boiler is stopped), expansion differences of unaffected refractory materials and its areas saturated with melt, cause stresses leading to the layering, crumbling and destruction of the product. **Figure 5** shows characteristic nature of disintegration of shaped refractories when affected by ash melt [12].

Resistance of refractory materials to alkaline compounds is often measured with the crucible method [9, 13]. When analysing, the alkali resistance of castables or fired bricks with test samples with a cylindrical cavity are made. The cylindrical cavity is filled with certain alkali salt (K_2CO_3 , K_2SO_4 , etc.), and the samples are heated for some time at the temperature of $\geq 1000^\circ\text{C}$. After multiple tests (each time anew by adding a fixed amount of salt), the samples are visually inspected, capturing the occurrence of micro-cracks. Some of the specimens are cut along the cylindrical axis into two parts, and the depth of the material affected by alkaline substances is evaluated.

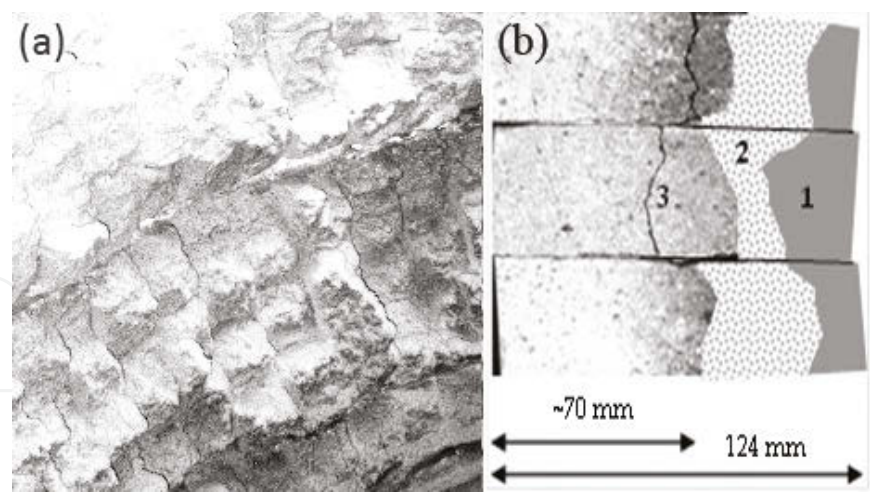


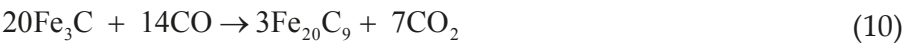
Figure 5. Typical fragmentation of bricks affected by ash melt (a) and scheme of a bricks' step-by-step degradation (b): 1,2,3—steps of degradation.

2.2. Resistance to the impact of carbon monoxide (CO)

Incompletely burned carbon compound products, the main of which is carbon monoxide (CO) can penetrate (diffuse) in the material and react with refractory materials containing iron oxide. In such a case, four-step reaction occurs in which one of the end-products is Fe₃C [3]:



Fe₃C can react with CO:



If the refractory material contains metallic iron and/or iron oxides, CO in the temperature interval of 400–800°C produces carbon: 2CO → CO₂ + C. Mechanical stresses caused by crystallization of carbon deposited in local areas may cause complete disintegration of the

material. It has been found [14] that degradation of certain types of aluminosilicates due to CO exposure is a result of two interrelated processes: reduction in iron oxides and volume changes and carbon formation and its accumulation in the material structure.

It has been observed that when excessive CO has been formed in the boiler for extended periods (disrupted boiler operational mode), disintegration of refractory castable with high iron oxide content (>4.4%) due to the general effect of CO and alkali occurred already after 8 months of operation (**Figure 6**) [15].

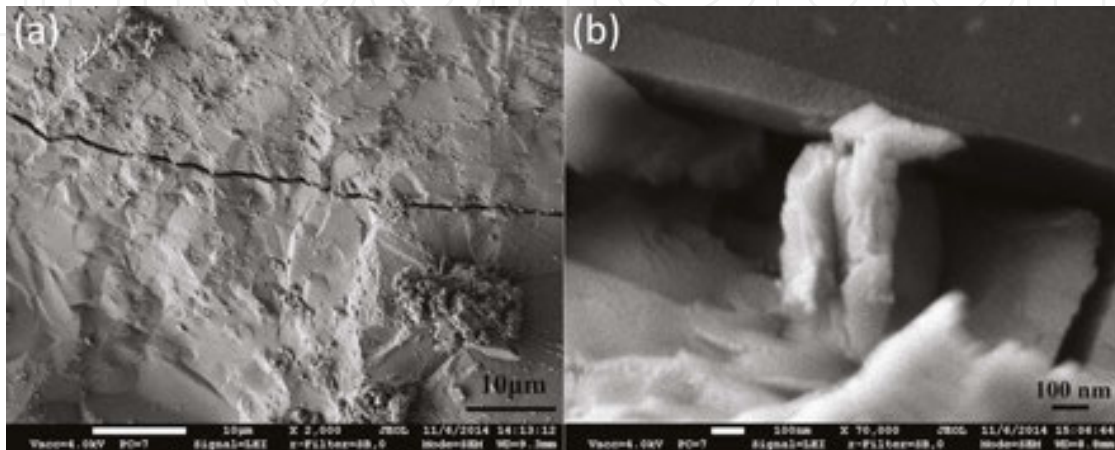


Figure 6. Cracking (a) and degradation of aluminosilicate materials due to the formation of new compounds (carbon and leucite) in its structure (b) [15].

Risks of refractories degradation due to CO can be reduced by using materials with as low amount of Fe_2O_3 as possible (<1%).

2.3. Thermal shock resistance

This indicator shows the ability of refractory materials to resist thermal stresses in its structure from temperature gradients. Such temperature gradients cause degradation of refractory materials when boiler is often stopped (material is cooled) and start to operate (material is heating up). Burning of solid biofuels generates a lot of fly ash that cause fouling of heat transfer surfaces. As a result, boilers must be frequently stopped for cleaning and therefore linings experience repeated thermal shocks. Different countries apply different methods [16] to determine thermal shock resistance (number of cycles) of refractory materials, which vary by sample size, heating temperature and sample cooling method (water, air, water-cooled panels). It is noted that the thermal shock resistance of the refractory material may differ depending on the selected method [17]. Where it is difficult to evaluate test results obtained in one or another method, thermal shock resistance criteria R_4 and R_{st} are calculated [18, 19].

The thermal shock resistance of refractories can be evaluated not only by calculating the thermal shock resistance criteria, but also by the refractory material surface appearance after thermal shocks—test sample heating and cooling cycles. In the case of a low thermal shock resistance refractory castable, a network of long cracks appears on the surface (**Figure 7a**).

Meanwhile, in the case of high thermal shock resistance refractory castable, a network of short cracks is formed (**Figure 7b**). Such fragmental structure of the castable compensates its thermal extensions and relaxes its stress. Therefore, when the number of cycles was increased the cracks slightly widened but the castable did not collapse.

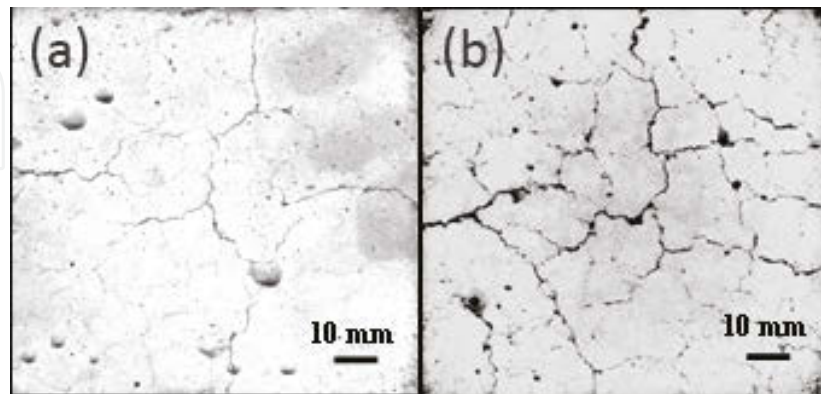


Figure 7. Surface of castable before break up of sample: (a) which withstood 9 cycles (water—800°C) [20] and (b) 45 cycles [21].

Refractory materials that have structures with built-in micro-cracks show better thermal shock resistance than rigid systems. In some refractory materials, the bond possesses micro-structural defects or cracks that provide better thermal shock resistance [4].

2.4. Abrasion resistance

Abrasion resistance is a feature of material to its surface that resists external mechanical effect when solid particles fly at a high speed and mechanically rubs the material surface.

Refractory materials used in chemical and cement plants, when process products intensively circulate and rubs the surface of refractory material, must have a high abrasion resistance. Abrasion resistance is determined according to standard ASTM C-704:1999. The abrasion resistance rate of materials used under the above-mentioned conditions must not exceed 5–6 cm³.

In biofuel combustion plants, abrasion resistance of refractory materials is relevant when the fluidized bed system (movement of a mixture of sand and fuel) is used in the technology and also when during boiler pipe blowing off (clean procedure) ash particles fly at a high speed. **Figure 8** shows a fragment of cross section of a fireclay brick where the surface in the bottom part of the picture has been exposed to high speed particles flying at the direction marked with the arrow.

Abrasion resistance and compressive strength are correlated with each other: the higher the compressive strength, the greater its abrasion resistance. In this regard, strength characteristics of refractory materials used in biofuel combustion equipment must be maximally high.

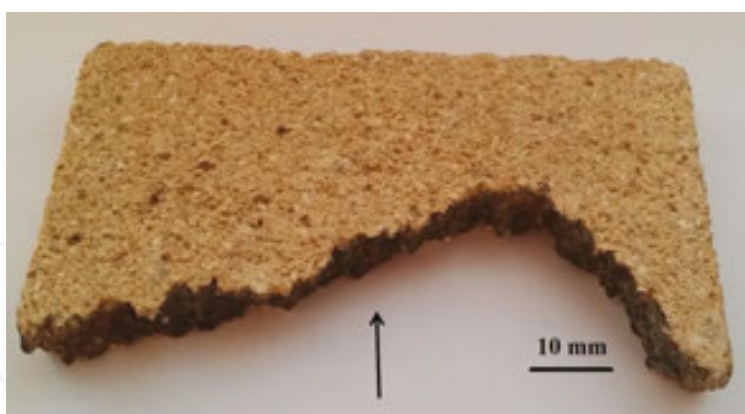
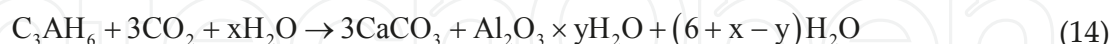
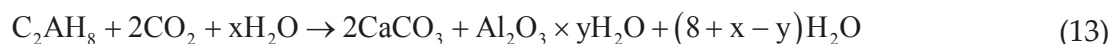
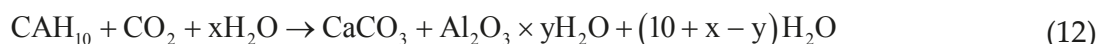


Figure 8. Sectional fragment of fireclay brick after 3 months of exploitation in solid biofuel combustion lining. Particles flying at the direction marked with the arrow mechanically affected the brick surface in the bottom part of the picture.

2.5. Carbonation of calcium aluminate cement-bonded regular refractory castable

The observations showed that the lining of domestic boilers made by using regular castables do not have long durability. Having been exploited for some time, it destructs. One of the reasons that cause this destruction might be the so-called “carbonation” of calcium aluminate cement hydration products. It is known that the main hydration products formed during the reaction between calcium aluminate cement and water are as follow: CAH_{10} (forms at the temperature $<21^\circ\text{C}$), C_2AH_8 and AH_3 ($21\text{--}35^\circ\text{C}$) and C_3AH_6 and AH_3 ($>35^\circ\text{C}$) [22]. The carbonation of calcium aluminate cement hydration products is thought to occur by the following reactions [23]:



Carbonation causes a large-scale destruction of calcium aluminate cement materials [24] when Na^+ , K^+ ions participate in the so-called “alkaline hydrolysis” [25]. CO_2 , alkalis and H_2O environment is typical for domestic boilers during often stopping and starting of operations. After the calcium aluminate cement hydration products dehydration at the temperature of $500\text{--}800^\circ\text{C}$, C_{12}A_7 is formed, which, after heating at 1000°C is converted to CA , CA_2 . If the operation temperature is less than 1000°C (usually in domestic boiler), C_{12}A_7 in humid environment (in moment of stopping and starting of boiler operation) is repeatedly hydrated. Then carbonation of hydrates occurs (**Figure 9**), and the destruction of castable will start. It was established that the additive of micro-silica (SiO_2) in regular castable increases its resistance to the carbonation [25].

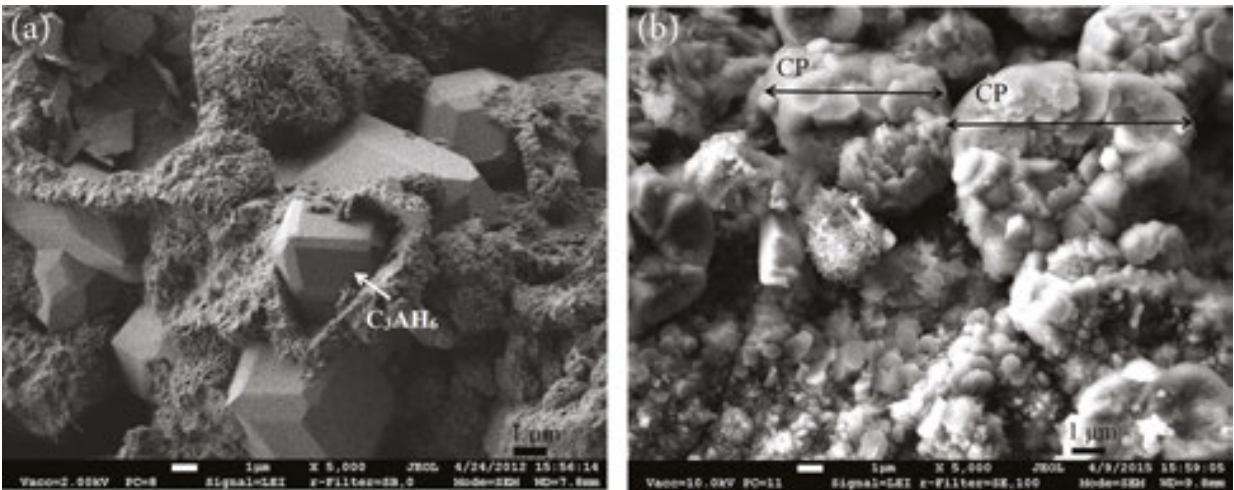


Figure 9. C₃AH₆ hydrates (a) and its carbonation products (CP) (b).

2.6. Destruction of SiC-based refractory materials

Studies have shown that castables with SiC filler resist much better the effects of alkali compounds than those with aluminosilicate filler (fireclay and mullite) [13]. It should be noted, however, that in the oxidizing atmosphere at >900°C SiC castable filler can oxidise resulting in the formation of SiO₂ and higher volume of minerals. The reaction takes place according to the following scheme [26]:



Reverse reaction in castable with SiC may occur under reducing environment [11]:



Because of mineralogical changes of structural elements of refractory material with SiC, the strength is critically reduced.

3. Materials for working layer of linings of biofuel boilers and its investigations

Over the last decade it has been noted that the use of shaped products is reducing, while the use of unshaped materials such as refractory castables is constantly growing. This is due to the shortcomings of shaped products: long duration of installation of the lining in thermal equipment, complex repairs, complex design and manufacturing technologies of thermal equipment from shaped products and higher cost of production of shaped products.

Research shows [9, 13] that in alkali-resistant castables, under the influence of alkali on the surface of the material, a layer of glass of high viscosity is formed, which prevents further penetration of alkali into the material.

The aim of investigations [26] was to evaluate the resistance to potassium compounds' attack on refractory castables, modified and unmodified, by additive of milled quartz sand (SiO_2). The findings are presented below.

Unmodified commercial fireclay castable (B0) and unmodified clinker castable (B1) and modified clinker castables (B2, B3), in which ground quartz sand was used to increase alkali resistance, were tested. Chemical composition (mass %) of castables B0, B1, B2, B3 was as follows: B0— Al_2O_3 45.7; SiO_2 43.6; CaO 7.6; Fe_2O_3 1.50; B1— Al_2O_3 42.9; SiO_2 25.5; CaO 27.3; Fe_2O_3 1.77; B2— Al_2O_3 41.8; SiO_2 27.3; (2.5% of this quantity has ground quartz sand additive); CaO 26.6; Fe_2O_3 1.79; B3— Al_2O_3 40.9; SiO_2 29.0 (5.0% of this quantity has quartz sand additive); CaO 26.0; Fe_2O_3 1.80 [26]. **Table 4** presents technical characteristics of castables used in alkali tests with potassium carbonate salt by crucible method.

Characteristics	The mark of the castables			
	B0	B1	B2	B3
Cold crushing strength, MPa	53	115	115	114
Open porosity, %	27.4	14	14	14
Bulk density, kg/m^3	2070	2460	2450	2420
Shrinkage, %	0.2	0.28	0.28	0.28
Thermal shock resistance (950°C —water), cycles	19	13	10	8

Table 4. Technical characteristics of fireclay and clinker refractory castables after firing at the temperature of 1100°C [26].

Macroscopic assessment of samples is presented in **Table 5**. It was found that the samples of commercial fireclay castable B0, affected by K_2CO_3 , cracked after 1 cycle (**Figure 10a**) and after 2 cycles split into multiple fragments. The analysis of the surface view of the sample cut along the cylinder bore axis (**Figure 10b**) shows changed zones because of alkaline impact (penetration depth ~ 11 mm) [26].

Clinker-based castable B1 without additives during the alkali test split into separate fragments after 3 cycles (**Table 5**), while clinker castable with ground quartz sand additive (B2, B3), depending to its quantity, split after 6–8 cycles.

The analysis of the surfaces of sawn samples of clinker castable B1 without additives and B3 with ground quartz sand additive (**Figure 11**) shows that decomposition products of potassium carbonate salt already in the first cycle are easily penetrated into the structure of castable without additive (similar as with commercial fireclay castable, **Figure 10b**). Potassium carbonate salt decomposition products penetrated the structure of the castable B3, modified with ground quartz sand additive, with more difficulty. After 3 cycles, a protective layer of 2–

3 mm was observed (in some places up to 8 mm), capturing the penetration of potassium carbonate salt decomposition products into the material (deeper) (**Figure 11b**). This increased the resistance of castable samples to alkaline compounds—samples cracked just after 8 cycles [26].

Macroscopic assessment	The mark of the castables			
	B0	B1	B2	B3
The number of cycles that caused appearance of cracks of a width over 0.4 mm	1	1	3	5
The number of cycles that caused disintegration of the specimen to two or more fragments	2	3	6	8

Table 5. Macroscopic assessment of fire clay and clinker refractory castables, affected by K_2CO_3 [26].

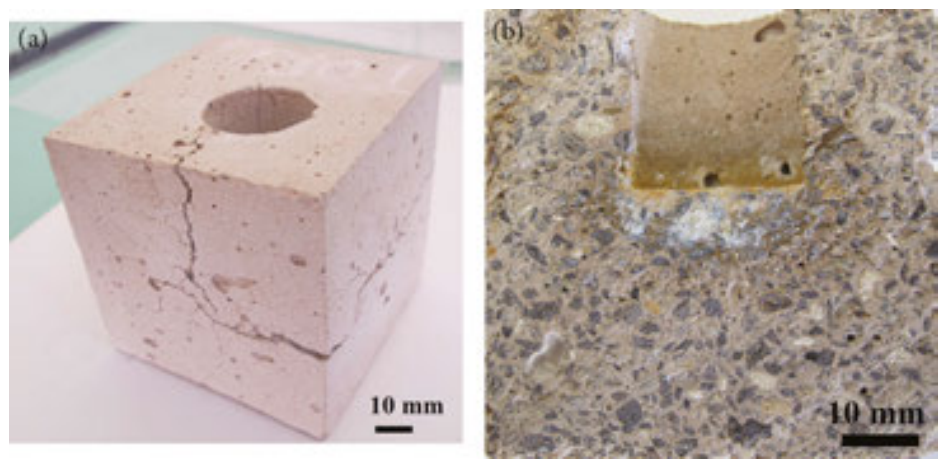


Figure 10. The view of specimens of commercial fireclay castable after the tests with alkali compounds: (a) appearance of over 0.4 mm wide cracks and (b) the section view of the specimens after one cycle [26].

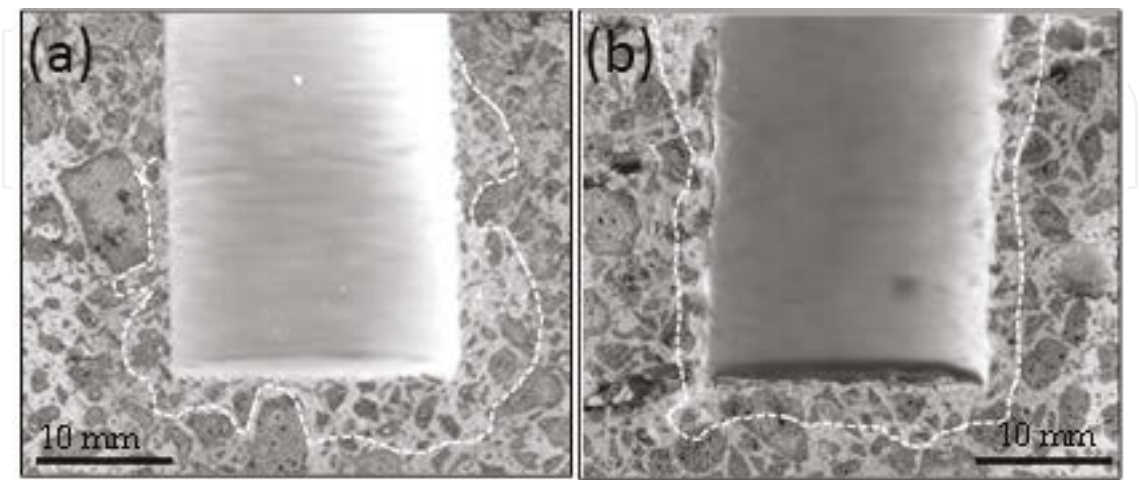


Figure 11. The view of sections of castable specimens after firing at the temperature of 1100°C with K_2CO_3 : (a) B1 after 1 cycle and (b) B3 after 3 cycles [26].

The phase composition of substances formed during the reaction with K_2CO_3 was found with the tablet method [13]. The results are provided in **Table 6**. For comparison, the table also contains the phase composition of products formed in fired castables at the temperature of $1100^{\circ}C$ in the absence of the effect of K_2CO_3 . These data show that commercial fireclay castable B0 contains the following minerals after firing at the temperature of $1100^{\circ}C$: gehlenite (C_2AS), mullite($3Al_2O_3 \cdot 2SiO_2$) and quartz (SiO_2). The resistance test to alkaline compounds allowed to identify new products in this castable—feldspars and leucite. In clinker castables, without additive (B1) and with ground quartz sand additive (B2, B3), a new product leucite was also identified. Test results of the tablet method suggest that in all cases, both in absence and presence of quartz sand additive in clinker castable, during the reaction of its compounds with K_2CO_3 decomposition products, leucite is formed. However, the tablet method, which allows to identify the chemical composition of compounds occurring from the reaction, does not allow to assess a very important factor of castable corrosion—diffusion rate of corrosion-causing substances deeper into the castable. So, a comparison of the penetration depth of fireclay castable B0 without ground quartz sand additives (**Figure 10b**) and clinker B1 (**Figure 11a**), with the penetration depth of castable with quartz additives B3 (**Figure 11b**) shows that in the case of castable B3, diffusion was stopped. Apparently, the reaction of grounded quartz with decomposition products of K_2CO_3 resulted in a viscous layer of this reaction product inhibiting the penetration of alkaline compounds deeper into the sample. Therefore, a destruction and disintegration of the specimens caused by formation of corrosion products and different thermal expansion coefficients of the initial material and zone saturated with the melt in the castable with ground quartz sand additive appeared considerably later.

The mark of composition	The treatment method	The phase identified
B0	$1100^{\circ}C$	Gehlenite, mullite, quartz, hematite
	After test	Gehlenite, mullite, quartz, hematite, feldspars, leucite
B1	$1100^{\circ}C$	Gehlenite, CA_2 , CA , anorthite, corundum
	After test	Gehlenite, CA_2 , CA , anorthite, corundum, leucite
B3	$1100^{\circ}C$	Gehlenite, CA_2 , anorthite, corundum
	After test	Gehlenite, CA_2 , anorthite, corundum, leucite

Table 6. The phase composition of fireclay and clinker refractory concretes before and after test with K_2CO_3 upon applying the tablet method and firing at the temperature of $1100^{\circ}C$ [26].

The above test results show that often traditional fireclay materials used in biofuel boilers are not resistant to the effects of alkaline compounds. Refractory materials recommended for biofuel boiler lining should be examined in laboratories to evaluate the alkaline salt penetration into the material.

3.1. Explosive spalling of refractory castable

Calcium aluminate cement-based refractory castable should be dried and heated up after curing for moisture removal. In the process of heating, the temperature is gradually raised until the operational temperature (1000–1200°C) of the boiler is achieved. During heating up of the castable, chemical and physical processes causing the removal of chemically bound water and formation of new crystalline phases take place. All these processes also cause great changes in the micro-structure of a castable and pose a threat of its explosive spalling [27, 28]. In **Figure 12**, part of the structure of the heating unit used in oil refinery, damaged by explosive spalling, is shown.



Figure 12. The part of the combustion zone structure in the heating unit used in oil refineries damaged by explosive spalling (metal anchors can be seen on the photograph) [29].

Explosive spalling is usually caused by water vapour pressure, which builds up when chemically bound water is turned into free water. The risk of explosion of the structure is greatly increased, if the following types of castable are used: MCC, LCC and ULCC. To avoid explosive spalling of refractory castable due to the pressure of water vapours developed at the initial stage of heating, new produced linings of thermal equipment are dried and heated up for the first time in a very careful way [29]. But in the case of biofuel boilers, in practice, it is hardly technically possible to perform the procedure of castable drying accurately. Therefore, in order to reduce a risk of explosive spalling, when castable drying and the initial heating modes are not rigorously controlled, various additives (e.g. aluminium powder, polymer fiber, etc.), which increase castable permeability by forming a capillary system for removing water vapour without damaging the castable, are used. Aluminium powder reacts with water in the alkaline medium, releasing hydrogen, which causes the formation of open porosity in castable and makes it more easily permeable to water vapours. However, though the addition of aluminium powder increases castable permeability to water vapours, a loose structure is formed; therefore, the mechanical properties of the castable is decreased.

It has been found that the additive of polypropylene fibres (PPF) (**Figure 13a**) is well suited for decreasing the risk of explosive spalling of refractory castables [29]. A positive effect of this additive, with regard to its ability to decrease the risk of explosive spalling, is explained by the fact that PPF disintegrates at the temperature of 150–180°C, leading to the formation of micro-channels (**Figure 13b**), allowing water vapours to pass through, and help to avoid a dangerous rise of pressure.

The testing of cylindrical MCC-type castable specimens, for their resistance to explosive spalling [29], has shown that the MCC-type specimen without of PPF additive explode at the temperature of 600°C under the conditions when temperature is raised to 1000°C at a rate of 40°C/min (**Figure 14a**). The specimen with PPF additive does not explode when the temperature is raised at the same range in heating up to 1000°C (**Figure 14b**).

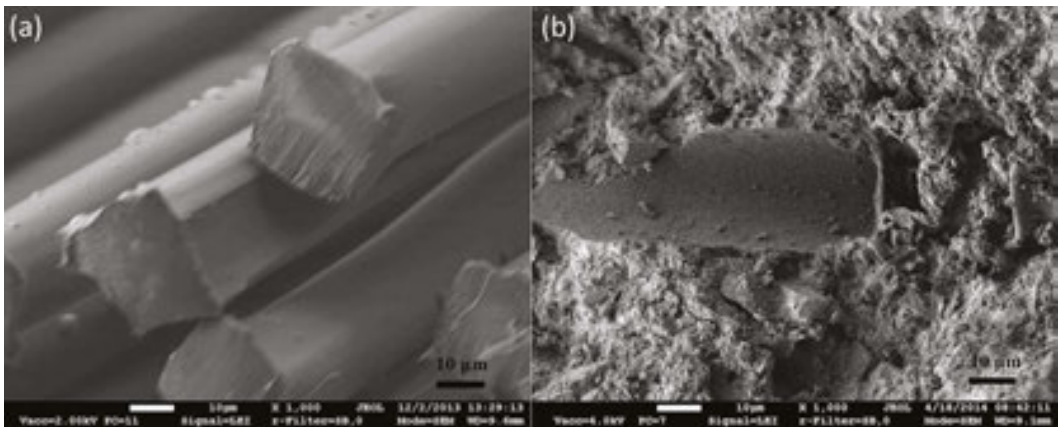


Figure 13. SEM micrographs of the PPF (a) and the micro-structure of refractory material with burned PPF after heating at 170°C (b) [29].

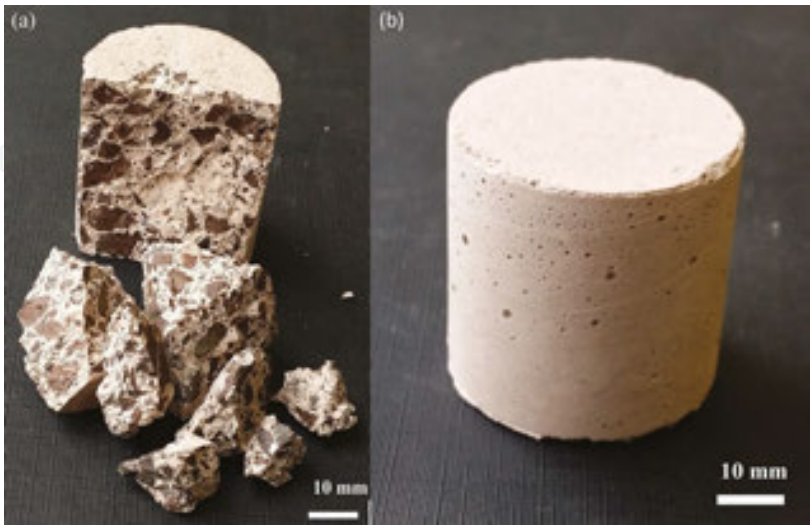


Figure 14. Castable specimens tested for explosive spalling, when the temperature was raised at the rate of 40°C/min: (a) castable sample without PPF additive exploded, when the temperature was raised to 600°C and (b) castable sample with PPF additive that did not explode, when the temperature was raised to 1000°C.

In order to simplify the drying and the first heating procedure, and to reduce the risk of explosive spalling, expensive NCC-type castables [30] are used. Such castables considerably reduce the time of drying and the first heating procedure.

3.2. Recommendations for use of refractory materials in biofuel boilers

Due to the aggressive operating conditions in biofuel incineration plants, manufacturers of refractory materials use the following specific shaped and unshaped materials: fireclay with a small amount of iron oxide, silicon carbide (SiC), mullite, zirconia, andalusite and chrome (Table 7) [11]. Fireclay, mullite and andalusite materials belong to the Al₂O₃–SiO₂ (aluminosilicate) system.

Material base	Castables					Fired bricks				
	Fireclay	Alumina, mullite, SiC	Alumina- Zirconia-Silica		Mullite	Alumina Chrome	Andalusite	Alumina- Zirconia- Silica	Alumina Chrome	
Recommended application, °C	≤1000	≤1300	≤1200	≤1200	≤1200	≤1600	≤1200	≤1300	≤1400	≤1600
SiO ₂ , %	<40	6	16	16	13	<4	36	18	6	1.3
Al ₂ O ₃ , %	>50	60	27	56	58	>90	61	>50	87	>90
Fe ₂ O ₃ , %	<1	<1	<1	<1	<1	<0.5	<1	<0.5	<0.5	<0.5
ZrO ₂ , %	–	–	–	26	–	–	–	28	–	3.5
Cr ₂ O ₃ , %	–	–	–	–	–	5	–	–	5	5
SiC, %	–	30	>55	–	>25	–	–	–	–	–
Bulk density, kg/m ³	2200	2800	2500	3000	2800	3100	2600	3100	3000	3200
CCS, MPa	60	80	55	110	90	60	100	140	100	100
Thermal shock resistance DIN 51068/1	30	120	120	100	120	30	120	100	120	120
CO resistance ASTM C 288 always A, not relevant for alumina-chrome materials.										

Table 7. Lining recommendations for biomass combustion furnaces [11].

It is stated [11] that refractory materials, suitable for use in biofuel boilers installations, should be dense ($>2200 \text{ kg/m}^3$), with CCS of at least 50 MPa, thermal shock resistance >30 cycles (under DIN 51068-1:1976 standard) and iron oxide content less than 1%.

However, it should be noted that the recommended high-grade materials with zirconium and chromium fillers are considerably more expensive than with fireclay and andalusite fillers. These materials are very dense ($\geq 3000 \text{ kg/m}^3$), their heat transfer coefficient is high and reaches up to $1.6\text{--}2.5 \text{ W/(m}\cdot\text{K)}$; therefore, the lining increases the need for insulating materials. After the lining operation time, refractory materials containing chromium oxide must be disposed of in hazardous waste landfills because their processing is complicated.

In practice, up till now the most widely used materials in solid biofuel combustion plant linings are bricks and castables with aluminosilicate fillers such as fireclay and andalusite. Selection of this type of material for biofuel boiler linings must belong to the alkali resistance class of materials and their general characteristics should be no less than that specified in Table 7. In Figure 15(a), a view of lining made of non-alkali resistance fire clay bricks, damaged by alkali attack after 6 months of boiler operation, is shown, and in Figure 15(b), a view of non-damaged lining made of alkali resistance fire clay bricks after 8 months of boiler operation is shown. The main reason of the difference between resistance of these linings was the different alkali resistance class of the materials used for their production.



Figure 15. View of lining made of not alkali resistance fire clay bricks after 6 months of boiler operation (a) and made of alkali resistance fire clay bricks after 8 months of boiler operation (b).

It is also necessary to note that not only quality, but also suitability for high durability lining of used materials is of great importance. The correct installation of lining is very important as well. Especially in the case of installation of monolithic lining such key quality control elements such as installation monitoring, as-installed testing, pre-dryout inspection, dryout monitoring and post-dryout inspection are necessary. Some standards [31, 32] can be useful for organization of quality control for the installation of biofuel boilers lining.

Author details

Valentin Antonovič^{1*}, Jacek Szczerba², Jadvyga Keriene¹, Rimvydas Stonys¹ and Renata Boris¹

*Address all correspondence to: valentin.antonovic@vgtu.lt

¹ Vilnius Gediminas Technical University, Vilnius, Lithuania

² AGH University of Science and Technology, Kraków, Poland

References

- [1] Firewood and wood chips for heating. Available from: <http://www.carmen-ev.de/files/informationen/hackschn.pdf>. [Accessed 2016-07-19].
- [2] Parr C, Bier T A, Bunt N E, Spreafico E. Calcium aluminate cement (CAC) based castables for demanding applications. Proceedings of the 1st International Conference on monolithics, Tehran, Iran 1997: 11 p.
- [3] Didier-Werke AG. Refractory materials and their properties. Germany: Vulkan Verlag GmbH; 1989: 103 p.
- [4] Schacht CA. Refractories handbook. Florida, USA: CRC Press, Taylor and Francis Group; 2004: 520 p.
- [5] Routschka G, Wuthnow H. Refractory materials: structure, properties and testing methods: directory. Essen, Germany: Vulkan Verlag GmbH; 2010: 392 p.
- [6] Polubojarinov OI. The density of wood. Moskva: Lesnaja promyshlennost; 1976: 160 p.
- [7] Vares V, Kask U, Muiste P, Pihu T, Soosaar S. Manual for biofuel users. Manual. Tallinn, Estonia: TUT Press; 2005: 178 p.
- [8] Riedl R, Dahl J, Obernberger J, Narodoslawski M. Corrosion in fire tube boilers of biomass combustion plants. Proceedings of the China International Corrosion Control Conference. Paper Nr. 90129. Beijing, China 1999: pp. 1–5.
- [9] Alibasic E, Oldin J, Kannabiran S, Yiakoumi A. Design of castables and their relevance to alkali resistance applications. 57th International Colloquium on Refractories: September 24th and 25th, EUROGRESS, Aachen, Germany. ECREF; 2014 pp. 67–69.
- [10] Antonovič V, Keriene J, Stonys R, Boris R, Škamat J. Study of the Structure and Phase Composition of the Refractory Comprising the Lining of a Boiler Operating on Solid Biofuel, Refractories and Industrial Ceramics. New York: Springer International Publishing; 2015, Vol. 56(2): pp. 188–193.

- [11] Klinger W, Weber W, Zimmermann H. Application concepts of shaped and unshaped refractories for combustion plants. Proceedings of the Unified International Technical Conference on Refractories (UNITECR). Dresden, Germany; 2007: pp. 440–443.
- [12] Goberis S, Antonovič V. The monolithic refractory lining of boiler fired by wood fuel. *Novye Ogneupory* 9; 2003: pp. 13–15
- [13] Szczerba J, Boczon A, Studencka B. Studies of impact of alkali salts on alumina based castables without additives and with them. *Ceramika* 88; 2005: pp. 158–172.
- [14] Pitac NV, Shapalov VS, Azarenkova LE, Privalova NG. Influence of carbon monoxide and its decomposition catalysts on the destruction of blast-furnace aluminosilicate refractories. *Refractories* 1991; 32: pp. 578–584.
- [15] Keriene J, Boris R, Antonovič V, Stonys R, Škamat J. Action of the products of biofuel combustion on the phase composition and structure of refractory material, glass and ceramics. New York: Springer; 2016, Vol. 72(9–10): pp. 345–350.
- [16] Goberis S. Thermal stability of unshaped refractory materials. *Refractories and Industrial Ceramics* 2003; 44(62): pp. 427–430.
- [17] Antonovič V, Šukšta M, Pundiene I, Stonys R. Procedural elements in estimation of the thermal shock resistance of different types of refractory concrete based on chamotte filler. *Refractories and Industrial Ceramics* 2011; 52(1): pp. 70–74.
- [18] Hasselman DPH. Unified theory of thermal shock fracture initiation and crack propagation in brittle materials. *Journal of the American Ceramic Society* 1969; 52(11): pp. 600–604.
- [19] Kingery WD, Bowen HK, Uhlmann DR. Introduction to ceramics. New York: John Wiley; 1979: 1032 p.
- [20] Goberis S, Antonovič V. Properties of refractory castable based on the Portland cement and with the addition of microsilica, *Novye Ogneupory* 5; 2002: pp. 33–36.
- [21] Antonovič V, Goberis S. The properties of refractory concrete with liquid glass binder and chamote aggregate. *Materials Science* 2002; 8(2): pp. 189–192.
- [22] Majumdar SD, Sarkar R, Vajifdar PP, Narayanan S, Cursetji RM, Chatterjee AK. User friendly high refractory calcium aluminate cement. Proceedings of the International Conference of Calcium Aluminate Cements; 2001: pp. 467–476.
- [23] Sakamoto S, Kudo E. Carbonation of alumina cement-bonded castable refractories. *Journal of Technical Association of Refractories* 2000; 20(1): pp. 18–23.
- [24] Pundiene I, Goberis S, Antonovič V, Špokauskas A. Carbonation of alumina cement-bonded conventional refractory castable in fireplace. *Materials Science* 2006; 12(4): pp. 333–337.
- [25] Garcia Alcocel E, Garces P, Chinchon S. General study of alkaline hydrolysis in calcium aluminate cement mortars under a broad range of experimental conditions. *Cement and Concrete Research* 2000; 30: pp. 1689–1699.

- [26] Boris R. The investigation on the structure and properties of medium cement refractory castable with clinker aggregate (doctoral dissertation). Vilnius: Technika; 2016: 105 p.
- [27] Vadasz P, Kamoda O, Čipkova I. Corrosion of refractory concrete monoliths on the basis of $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-SiC}$ in the process of municipal waste incineration. *Interceram Refractories Manual* 2009; 3: pp. 41–46.
- [28] Gitzen WH, Hart LD. Explosive spalling of refractory castables with calcium aluminate cement. *American Ceramic Society Bulletin* 1961; 40(8): pp. 503–507.
- [29] Boris R, Keriene J, Antonovič V, Madej D. Characterization of microstructural evolution and mechanical properties of refractory composite. In: *Composite Structures*. Oxford: Elsevier; 2015. Vol. 134: pp. 811–819.
- [30] Luz AP, Braulio MAL, Pandolfelli VC. Refractory castable engineering. Leipzig: Deutsche Bibliothek; 2015: 734 p.
- [31] Standard specification 3-24-4: Vibracast refractory lining V?anchors. UOP LLC. Illinois, USA; 2011: 38 p.
- [32] API Standard 936: Refractory installation quality control. Inspection and testing. Monolithic refractory linings and materials, Third Edition. American Petroleum Institute. Washington, USA; 2008: 49 p.