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The ageing effect of raw materials on the final properties of high alumina refractory grog

D Zemánek[1] and L Nevřivová[1]

[1] Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components, Veveří 331/95, 602 00 Brno, Czech Republic

E-mail: zemanek.d@fce.vutbr.cz

Abstract. High alumina ceramics is a part of the refractory ceramics in SiO_2-Al_2O_3 binary system. The aim of this paper is to characterize the effect of ageing raw materials and its influence on final properties of fired refractory grog. Refractory grog is very important component in production of refractory materials, such as fireclay, mullite and andalusite bricks. Refractory grog is manufactured generally from clay, claystone and kaolin, nowadays is mainly burnt in rotary and shaft kilns. The primary objective of this article is to determine an influence of ageing effect, which has impact on mineralogical composition of raw material which obviously results in different mineralogical composition of fired grog. Raw material with different age was used for the mixtures and properties of fired samples were investigated, considering the influence of the raw materials mixtures. Specifically, the apparent porosity, water absorption, bulk density, apparent porosity, mineralogical composition and pore distribution were investigated.

1. Introduction

Refractory grog is a basic component of ceramic products and has a major influence on the final properties. Very important component in refractory manufacturing is chamotte and high alumina grog. These grogs are manufactured from suitable sources, especially from clays, claystones and shales. Nowadays, the firing process is carried out in shaft and rotary kilns at temperatures between 1350 °C and 1550 °C. [1] High temperatures leads to changes of mineralogical composition. The minerals mullite, cristobalite and amorphous phase are formed during this process. Mullite is in these types of refractory grog a main carrier of refractory properties, therefore presence of mullite is required at the expense of other minerals. Chemical formula of mullite is $3Al_2O_3{\cdot}2SiO_2$, and its occurrence in nature is very rare.[2]

Current requirements on high quality of ceramic products leads to decreasing of natural sources. At the same time waste or secondary raw materials, which are not directly applicable in the required applications.[3] Ageing is spontaneous or intentionally controlled process by which the properties of raw materials are improved when are stored in stockpiles. In particularly, plasticity, viscosity and other rheological properties are improved. During the ageing, water, additives and chemical and biological processes in material are evenly distributed.

It is common practice in the ceramic industry to land freshly mined clays or their sieve-passing fractions and eventually expose them to external influences before entering the production process. In the past, clays and kaolins intended for the preparation of fine ceramics were left to rest in moist pits.

A small amount of biological plant waste was added to the surface of the deposited material. This activity aimed to create an environment that is natural for clay materials. The action of microorganisms on the clay material has a positive effect on flexural strength and other physical and mechanical properties. [4]

Natural raw materials are becoming rare, while millions of tons of inorganic wastes are produced daily in the mining and processing industries worldwide. However, some wastes with their composition resemble the original raw materials or are beneficial in other parts of the production process. Thus, the use of waste as an alternative to raw materials deserves particular emphasis in terms of economics and ecology. Processing wastes from the mining and treatment of natural raw materials has been used for landfill for decades or stockpiled near plants.

The current state of the mining industry, when new deposits opening is complicated and takes more than 20 years and the old ones are almost mined, leads to the need to deal with materials that were previously unwanted in manufacturing processes and were considered waste. Finding suitable ways to use them involves a reduction in production costs, alternative products or new products for other industrial applications. [5]

In Czech Republic, over the decades, the sieve-passing fractions of W claystone have been stockpiled. The reason was their difficult processing and the negative effect on firing process in the shaft kilns. There are several thousand tons of high-quality raw material available. The way that has been developed in recent years is the briquetting of mentioned sieve-passing fractions. By compressing the raw material, it is possible to form bodies corresponding to the appropriate claystone fraction and to utilize the material that was previously considered as waste. [6]

Because the material is stockpiled for different periods of time, its age is divided as follows:

- W claystone freshly mined F – without ageing (0)
- W claystone charcoal piles C – ageing 5 years (5)
- W claystone matured M – ageing 10 years (10)

The different ageing time may have an impact on the mineralogical properties of the sieve-passing fractions of claystone, but also on the resulting mineralogical composition of the fired ceramic body. In Table 1 are presented chemical compositions of materials used for the experiment.

Table 1. Chemical composition of input materials.

material	Al_2O_3 [%]	SiO_2 [%]	Fe_2O_3 [%]	TiO_2 [%]	CaO [%]	MgO [%]	Na_2O [%]	K_2O [%]	LOI [%]
W claystone F	42.15	53.19	1.03	1.68	0.38	0.17	0.45	0.85	14.24
W claystone C	41.71	54.02	1.23	1.67	0.28	0.14	0.10	0.75	14.63
W claystone M	41.72	53.51	1.58	1.80	0.34	0.17	0.10	0.68	14.77
Mullite MOTIM	76.04	23.00	0.26	0.05	0.32	0.05	0.10	0.12	0.19

2. Experimental

Three types of undersize W claystone fractions were used for specimen preparation. Physical and chemical properties are mentioned above. In the first phase, the claystone moisture was found to be 12 % for W claystone C and M and 9 % for W claystone F. Claystone was dried and then mixed with mullite MOTIM in proportion 90:10 to achieve content of alumina higher than 45 %.

Table 2. Designed mixtures with different type of W claystone.

Mixture ID	type of W claystone	W claystone [%]	mullite MOTIM [%]
0	F – freshly mined	90	10
5	C – charcoal piles	90	10
10	M - matured	90	10

Mixtures were homogenized in mull mixer. There were prepared three mixtures of high alumina grog, each contained same amount of mullite MOTIM and different type of W claystone, average designed chemical composition is shown in Table 3.

Table 3. Average designed chemical composition of high alumina grog.

material composition	Al_2O_3 [%]	SiO_2 [%]	Fe_2O_3 [%]	TiO_2 [%]	Na_2O+K_2O [%]
90 % W claystone + 10 % mullite MOTIM	46.20	49.31	1.81	1.82	0.99

Prepared mixtures were uniaxially pressed in a cylindrical steel mold using 20 MPa, 25 MPa and 30 MPa of pressure. The green bodies were dried in a laboratory drier at 110 °C and then fired at temperatures 1300 °C, 1400 °C and 1500 °C with a heating rate of 3,5 °C/min and soaking time of 2 hours at the maximum temperature in a laboratory furnace.

After firing the apparent porosity, bulk density, water absorption and apparent porosity were determined by the official standard EN 993-1:1995 [7] (vacuum water absorption). Pore structure was determined by mercury intrusion porosimetry test. Phases were identified by X-ray diffraction (PANALYTICAL Empyrean XRD) with Cu Kα as the radiation source, accelerating voltage 45 kV, beam current 40 mA in the range from 5° to 80° with a step scan of 0.01°. The obtained X-ray diffraction patterns were compared with the Crystallography Open Database (COD). [8]

3. Results and discussion

The most important properties of high alumina grog are apparent porosity and bulk density, along with final chemical and mineralogical composition suitable for the intended use. Higher linear shrinkage is appropriate but may be caused by higher content of fluxes. For example, in case of anode bake furnaces is suitable content of flux lower than 1 %.

Apparent porosity and bulk density of mixtures are presented in Table 4, 5 and 6. Increasing of firing temperature is associated with decreasing of apparent porosity, also with increasing bulk density. Increasing of pressure provides us diverse results.

Table 4. Apparent porosity and bulk density of Mixture 0 based on W claystone F at different firing temperatures and variable pressure.

firing temperature [°C]	pressure [MPa]	apparent porosity [%]	bulk density [$kg \cdot m^{-3}$]
1300	20	18.5	2230
	25	18.1	2220
	30	17.5	2200
1400	20	14.7	2300
	25	14.2	2300
	30	14.5	2290
1500	20	5.6	2440
	25	6.4	2410
	30	7.6	2390

Table 5. Apparent porosity and bulk density of Mixture 5 based on W claystone C at different firing temperatures and variable pressure.

firing temperature [°C]	pressure [MPa]	apparent porosity [%]	bulk density [$kg \cdot m^{-3}$]
1300	20	17.8	2210
	25	19.2	2240
	30	18.4	2230
1400	20	12.8	2260
	25	13.3	2290
	30	14.4	2280
1500	20	9.7	2370
	25	10.9	2360
	30	9.4	2420

Table 6. Apparent porosity and water absorption of Mixture 10 based on W claystone M at different firing temperatures and variable pressure.

firing temperature [°C]	pressure [MPa]	apparent porosity [%]	bulk density [$kg \cdot m^{-3}$]
1300	20	21.3	2160
	25	20.2	2160
	30	19.4	2180
1400	20	16.3	2190
	25	17.4	2250
	30	17.0	2230
1500	20	10.3	2340
	25	10.7	2360
	30	9.8	2380

The addition of mullite MOTIM affected the physical properties when fired. After firing the aluminium oxide content was higher than 45 % as designed.

The firing temperature has a strong impact on the density of the fired high alumina grog samples. Apparent porosity does not decrease at higher pressures for all samples and some results have opposite trend, but the results are in range lower than 1 %. Best results in case of apparent porosity at temperature 1500 °C are achieved with the Mixture 0, final apparent porosity is between 5,6 % and 7,4 % depending on applied pressure. Apparent porosity results of the Mixture 5 and Mixture 10 at this temperature are higher than Mixture 0 at pressure 20 MPa and 25 MPa.

XRD analysis did not proved significant differences among three types of raw W claystone in case of mineralogical composition.

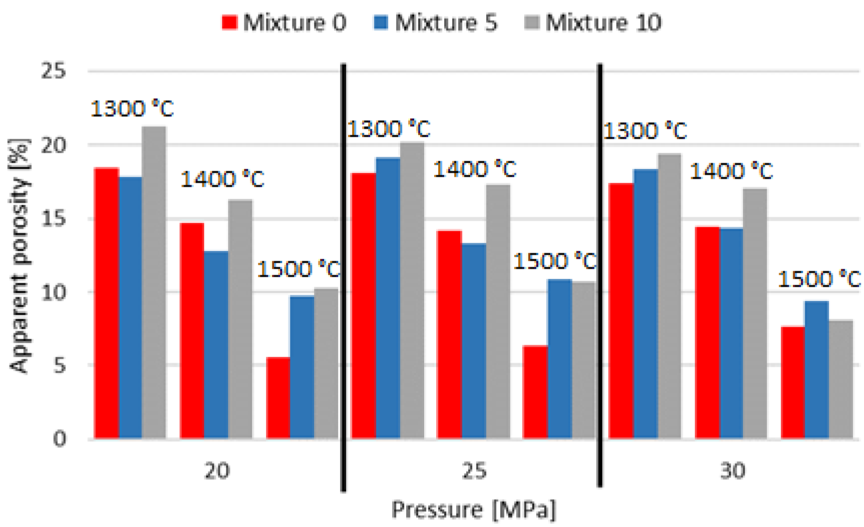

Figure 1. The influence of pressure and firing temperature on apparent porosity.

The result of XRD analysis of fired samples is shown in Figure 2. Enlarged section between 2Θ angle 25° and 27° is shown in Figure 3.

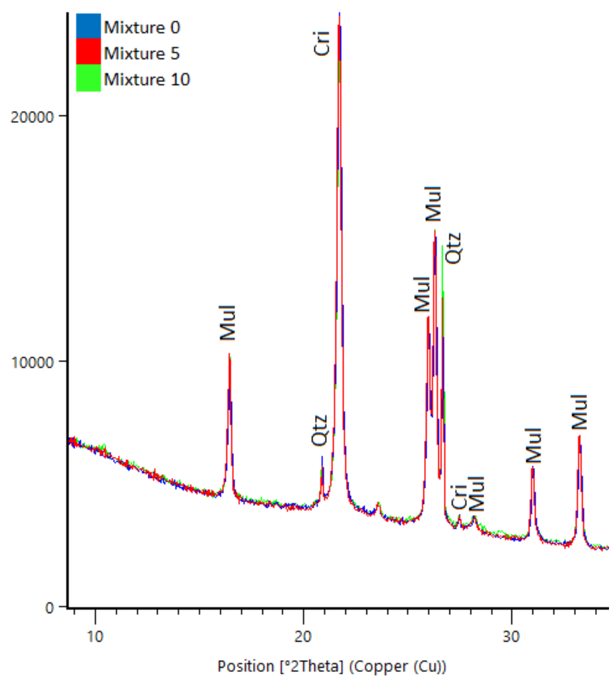

Figure 2. Influence of different W claystone age on mineralogy of high alumina grog at temperature 1300 °C.

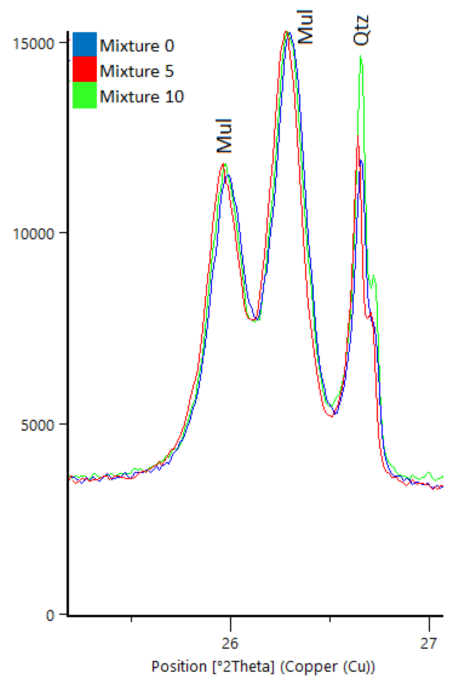

Figure 3. Influence of different W claystone age on residual quartz presence at temperature 1300 °C.

Legend: Mul-mullite, Qtz-quartz, Cri-cristobalite

The addition of mullite powder or fine-grained aluminium oxide impacts the mineralogy of the fired clay as mentioned in previous paper.[9] In Figure 2 there is no significant difference among mixtures based on three types of W claystone. In Figure 3 there is zoomed section, which shows different quartz content of tested mixtures. Different amount of quartz indicates that W claystone age effects mineralogical composition of fired grog. Mixture 0 based on freshly mined W claystone has lower content of quartz, and this amount is increasing with the age of W claystone. Mullite content strongly depends on firing temperature and soaking time, increasing temperature causes higher mullite content and decreasing of residual quartz and cristobalite content.

The fact that apparent porosity increases with the addition of fine particles was confirmed in previous paper. [10] Figure 4 shows results of mercury intrusion porosimetry test of Mixture 0 and Mixture 5 at different temperatures. The lowest apparent porosity and pore volume at all tested temperatures was measured in Mixture 0, which is based on W claystone freshly mined. Obtained results show increasing porosity and pore volume together with age of W claystone. Increasing temperature causes pore volume decreasing and increasing the density of high alumina grog.

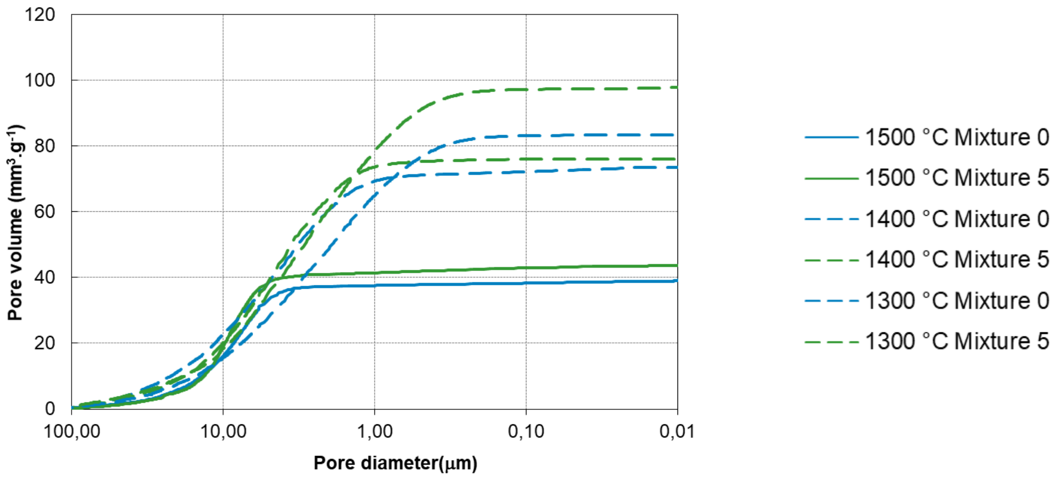

Figure 4. The influence of temperature on pore size distribution on Mixture 0 and Mixture 5, samples were pressed at 30 MPa.

4. Conclusion

This article successfully determined differences among three types of W claystone. The ageing effect of the raw materials was analyzed in terms of mineralogical composition, physical properties and mercury intrusion porosimetry test.

Mixture 0 was based on W claystone freshly mined, Mixture 5 was based on W claystone charcoal piles, Mixture 10 was based on W claystone matured. All three mixtures contained 10 % of mullite MOTIM to achieve content of Al_2O_3 higher than 45 %. Ageing effect of grog based on W claystone was determined in case of mineralogical composition. Increasing W claystone age results in higher content of residual quartz in grog, while mullite content was in all three mixtures almost identical.

Using higher pressure did not show noticeable decrease of apparent porosity in case of all three mixtures. Therefore, the use of higher pressure does not seem to be appropriate, the higher the pressure is related to the higher financial costs and demands on the briquetting press machine. It was proved by mercury intrusion porosimetry test that W claystone with increasing age has higher content of pores in fired grog. In case of future application in dense bricks would be suitable to use sintering additives to achieve lower porosity of fired grog.

The results from the study determined that it could be possible to utilize all three types of W claystone. Influence of ageing effect of raw materials in fired grog is determined particularly in different content of quartz and pore volume.

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