Science of Sintering, **42** (2010) 211-219

---

doi: 10.2298/SOS100518001M

UDK 622.785:621.742.48

Influence of the Damage Level during Quenching on Thermal Shock Behavior of Low Cement Castable

S. Martinović[1*)], J. Majstorović[2], V. Vidojković[1], T. Volkov-Husović[2]
[1]Institute for Technology of Nuclear and other Raw Mineral Materials, Franchet d'Esperey 86, 11000 Belgrade, Serbia
[2]University of Belgrade, Faculty of Mining and Geology, Djusina 4, Belgrade, Serbia,
[3]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, POB 3503, 11000 Belgrade, Serbia

---

Abstract:

In the recent decades, the use of unshaped monolithic refractories has been increasing greatly because of their significant advantages over other shaped refractory bricks of the same class. A low cement high alumina castable was synthetised and sintered at 1300°C in order to investigate thermal and mechanical properties, as well as thermal shock behavior. The water quench test was applied as an experimental method for thermal stability testing. Modification of the water quench test was performed by additional monitoring of the samples behavior during the water quench test such as implementation of image analysis and ultrasonic measurements. The image analysis program was applied on samples in order to measure the level of surface damage before and during the water quench test. Ultrasonic measurements were performed with the aim to measure the Young modulus of elasticity during the testing. Strength deterioration of the samples was calculated by the model based on ultrasonic velocity changes during the water quench test. The influence of monitoring the damage level before and during the quench experiment and its influence on thermal shock behavior will be discussed.

Keywords: *Low cement castable, Modified water quench test, Image analysis, Ultrasonic measurements, Anisotropy*

Introduction

Among unshaped refractories, castables are used especially in critical high temperature applications for complex constructions, easy applications to thin sections and regions that are difficult to reach [1,2]. Initially, conventional castables beside aggregates contained a relatively high cement content and therefore high mixing water forming high strength bonding, high open porosity (up to 20%) and low raw density. Afterwards, research was directed to the development of low cement and ultralow cement castables due to enlarged industry requirements meaning better rheology, superior physical and mechanical properties, very high thermal shock resistance, *etc*. Accordingly, different fine and ultra fillers (in the form of calcined alumina, reactive alumina, microsilica) were added to the conventional castable composition with the aim to fill the open pore space between the coarse aggregates [3,4]. Additionally, their cement content and amount of mixing water can be reduced. Because of the addition of fines and reduction on mixing water, some dispersing agents must be added to improve the rheological behavior of these castables. Addition of deffloculants and

---

[*)] Corresponding author: s.martinovic@itnms.ac.rs fillers allow simple installation of the castable with a low content of water, providing high density and low open porosity. Reduced content of cement and therefore lime induces decreased formation of low melting phases with low refractoriness. Low and ultralow cement castables have improved hot strength, higher thermal shock resistance, lower open porosity and increased corrosion resistance compared with conventional castables [1-10].

A wide range of Al_2O_3 ceramics are commercially available with strength and temperature capability depending on the Al_2O_3 content, which is usually in range of 85 to 99. Alumina is a ceramic material suitable for high temperature applications with good chemical resistance. Al_2O_3 offers good corrosion resistance to many substances including inorganic and organic acids, molten and dissolved salts, weak alkali solutions, anhydrous ammonia, hydrogen sulphide, hydrocarbons, organic and inorganic sulphides, molten Sr, Ba, Na, Be, Fe, Co, P, As, Sb, and Bi, and free molecular hydrogen. Alumina is the most widely used engineering ceramic material due to properties such as high hardness (25 GPA or 9 on the Mohs scale), high melting point (2054 ºC), good electrical, and thermal insulation [11-13]. Using nondestructive testing for characterization of refractories was increasingly used in the last decade [14-24].

The goal of this paper was to implement the modified water quench test for thermal shock behavior testing. Modification of the classical test (ICS 81.080 SRPS B. D8.308 former JUS B. D8. 306) was in additional implementation of image analysis and ultrasonic measurements for sample behavior characterization. Image analysis was used for damage monitoring at the surface and inside the sample during the water quench test. Ultrasonic measurements were applied for decreasing the Young modulus of elasticity and strength degradation during testing.

Material

A low cement castable (LCC) was prepared by tabular alumina (T-60, Almatis) used as an aggregate with maximal particle size of 5 mm, and matrix composed of fine fractions of tabular alumina, 5 wt. % of calcium-aluminate cement (CA-270, Almatis), reactive alumina (CL-370, Almatis), and dispersing alumina (ADS-3 and ADW-1, Almatis). The castable was mixed with 4.67 wt. % of water (dry basis) dispersed with citric acid.

Particle size distribution was adjusted to a theoretical curve based on a modified Andreassen's packing model, with a distribution coefficient (*q*) of 0.375. The castable mixture was cast in steel moulds with vibration. Prepared samples were cubes of 40 mm edge length for mechanical strength and prisms of 40 mm x 40 mm x 15 mm for ultrasonic measurements. After demoulding, the samples were cured for 24 hours at room temperature and dried at 110˚C / 24 h. Then, they were sintered at 1300 ˚C and cooled down to the room temperature inside the furnace. In this paper, the behavior of the sintered samples during thermal shock will be discussed.

Chemical composition of the samples is given in the Tab. I. and relevant mechanical properties are shown in the Tab. II.

Tab. I. Chemical composition and physical properties of raw materials

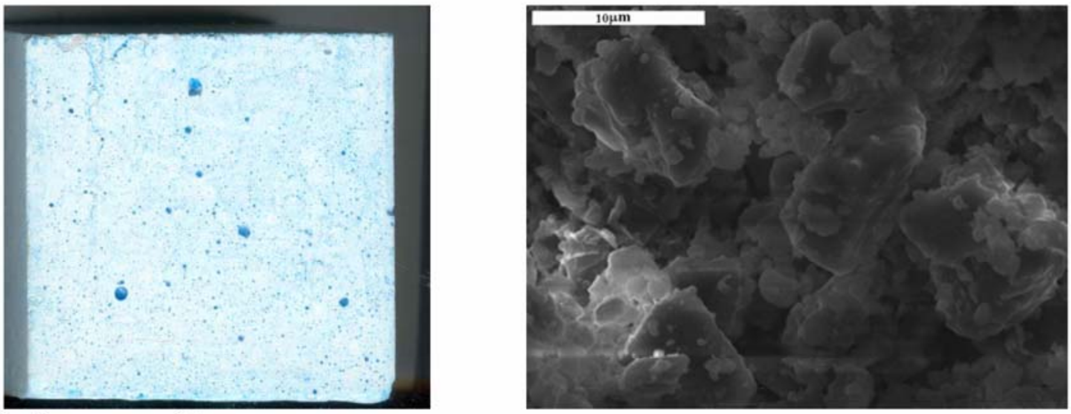
	Chemical analysis (wt.%)			Physical properties		
	Al_2O_3	CaO	Na_2O	Bulk density (g/cm^3)	BET (m^2/g)	Porosity (%)
Tabular alumina	≥99.4	0.02	≤0.38	3.79	-	≤ 5
Reactive alumina	99.7	0.02	0.098	3.9	3	-
Cement	73	24	≤0.3	3	2	-

*All components are from Almatis

Tab. II. Relevant mechanical, physical and thermal properties of the reference samples

Property	Value
Compressive strength after drying on 105ºC/24h	84.37 MPa
Compressive strength after sintering on 1300ºC/3h	171.55MPa
Flexural strength after drying on 105ºC/24h	16.09 MPa
Bulk density	3.12 g/cm^3
Water Absorption	3.2 %
Apparent Porosity	9.9%
Modulus of Elasticity	44.95 GPa
Refractoriness	SK>35 (1780°C)
Refractoriness under load	Ta, Te > 1780°C

The structure of samples after sintering at 1300 °C is given in the Fig. 1.



before quenching

Fig. 1. Structure of a sample sintered at 1300 °C

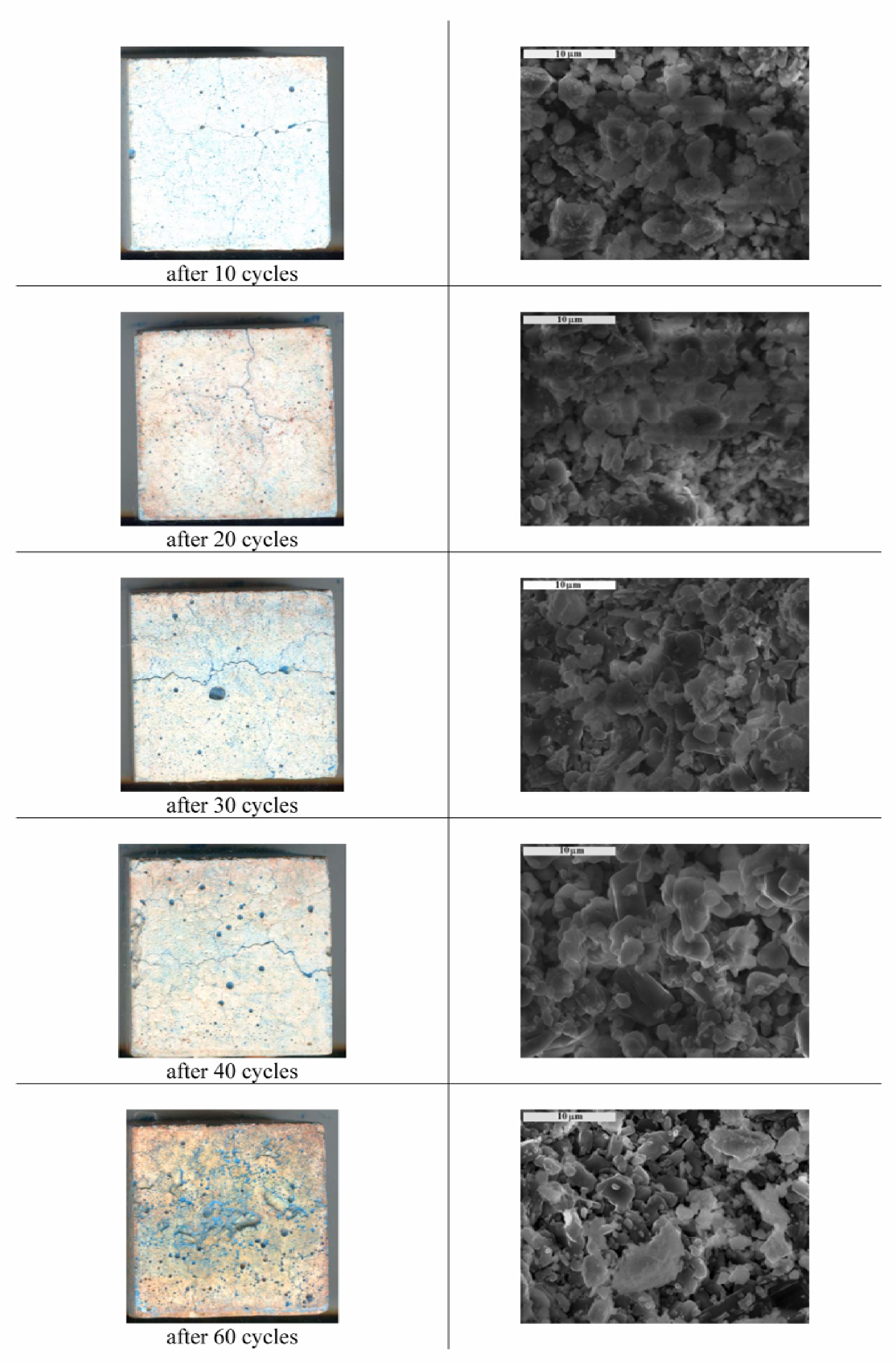
Water Quench Test

Thermal shock behavior of the samples was investigated using the water quench test as the experimental method (ICS 81.080 SRPS B.D8.308 former JUS B. D8. 306). Samples were cubes 4 x 4 x 4 cm. Each thermal shock cycle consisted of several consequent steps. Slow heating up by a nominal heating speed of 10°C/min to the quench temperature set at 950 °C, holding at this temperature for 30 minutes to reach thermal equilibrium in the whole specimen volume and finally quenching into a water bath at the temperature of 23 °C. The experimental method is similar to the procedure described in PRE Refractory Materials Recommendations 1978 (PRE/R5 Part 2). The material exhibited excellent resistance to rapid temperature changes. Samples did not exhibit total destruction during the test procedure till 110 cycles. In this paper results up till 60 cycles will be presented.

Results and discussion

Image analysis

Image analysis using the Image Pro Plus Program was applied to the samples for determination of the level of sample destruction. Samples were photographed before and during testing, in order to measure the level of deterioration. The results of image analysis are given in Fig. 2. as a function of the number of cycles of the water quench test.



after 10 cycles

after 20 cycles

after 30 cycles

after 40 cycles

after 60 cycles

Fig. 2. Samples during quenching

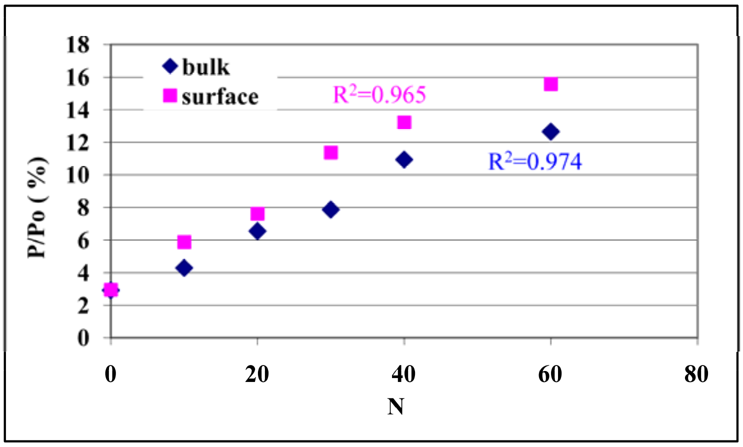


Fig. 3. Level of degradation of samples (P/Po) versus the number of cycles (N),
(P is the damaged surface area before testing and Po is the non-damaged surface area)

As seen on Fig. 3., the level of destruction is defined as P/P_0 (P-damaged surface and P_0-non-damaged surface, surface before quenching) and increases with the number of quench experiments (N). It is very important to observe that a certain level of destruction was observed in samples before quenching (3.22 %). This level of destruction will affect thermal shock behavior of the samples, as a higher level of destruction will lead to lower thermal stability. Decreasing the damage level is faster at the surface of the sample, than inside the bulk.

Samples were experimentally investigated till 110 cycles. This high level of thermal shock pointed out that the samples exhibited the excellent thermal stability behavior. In this paper results for 40 cycles will be discussed. The level of destruction was below 8 % after 40 cycles.

Ultrasonic determination of dynamic Young modulus of elasticity

Ultrasonic pulse velocity testing (UPVT) [8-13] was first reported being used on refractory materials in the late 1950's. Various publications have dealt with the practical application of UPVT to characterize and monitor the properties of industrial refractory materials non-destructively. The UPVT method has been considered in detail in [8-14,16-24]. Briefly, pulses of longitudinal elastic stress waves are generated by an electro-acoustical transducer that is held in direct contact with the surface of the refractory under test. After travelling through the material, the pulses are received and converted into electrical energy by a second transducer. Most standards describe three possible arrangements for the transducers:
1) the transducers are located directly opposite each other (direct transmission),
2) the transducers are located diagonally to each other; that is, the transducers are across corners (diagonal transmission),
3) the transducers are attached to the same surface and separated by a known distance (indirect transmission).

The velocity, *V*, is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$V(m/s) = \frac{L}{T} \qquad (1)$$

where *L* is the path length (m) and *T* is the transit time (s).

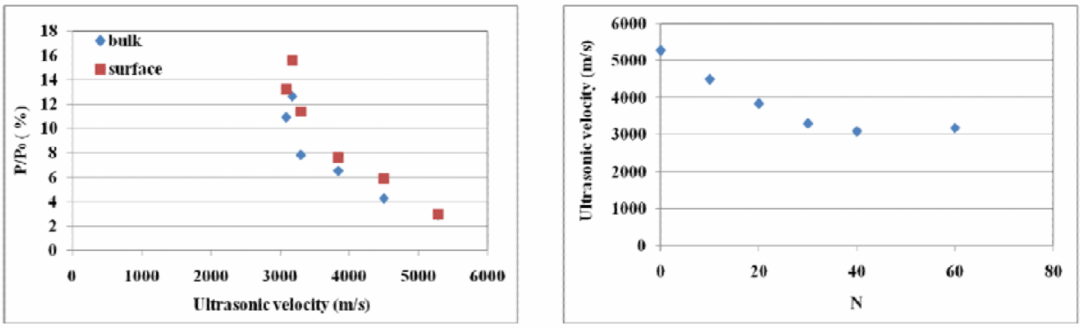
By determining the bulk density, the Poisson's ratio and ultrasonic velocity of a refractory material, it is possible to calculate the dynamic modulus of elasticity using the equation below [7,12,13,16-24]:

$$E_{dyn} = V^2 \rho \left(\frac{(1+\mu_{dyn})(1-2\mu_{dyn})}{1-\mu_{dyn}} \right) \qquad (2)$$

where V is the pulse velocity (m/s), ρ is the bulk density (kg/m^3) and μ_{dyn} is the dynamic Poisson ratio.

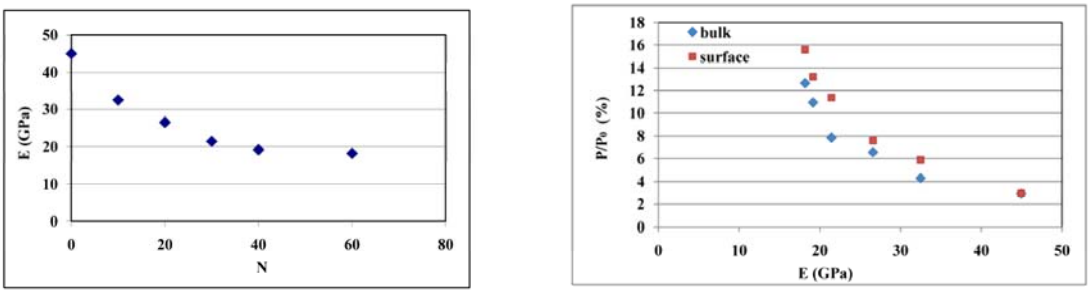
The measurement of ultrasonic velocity was performed using the equipment OYO model 5210 according to the standard testing procedure (SRPS D. B8. 121. former JUS. D. B8. 121.). The transducers were rigidly placed on two parallel faces of the cylindrical sample having 1 cm diameter and 1 cm height by using Vaseline grease as the coupling medium. The ultrasonic velocity was then calculated from the spacing of the transducers and the wave from time delay on the oscilloscope.

Results for the changes of ultrasonic velocity and Young modulus of elasticity are given in the Figs 4. and 5.



a) b)

Fig. 4. Changes of ultrasonic velocity during testing versus a) number of quench experiment (N) and b) level of degradation (P/P_0)



a) b)

Fig. 5. Changes of Young modulus of elasticity during testing versus a) number of quench experiment (N) and b) level of degradation (P/P_0)

Strength degradation

Results for the velocity change in samples suggest that materials were very stable during testing, as decrease of the velocity was not too significant from the velocity through the sample before water quench test. These results indicate that number of nucleated cracks and crack propagation did not resolute in rapid degradation of strength and Young modulus of elasticity, and samples exhibited excellent thermal shock behavior.

The following expression for strength degradation, based on the decrease in ultrasonic velocity was used [7-9,13,16-23]:

$$\sigma = \sigma_0 \left(\frac{V_L}{V_{L0}} \right)^n \qquad (3)$$

where σ_o is compressive strength before exposure of the material to the thermal shock testing, V_L is longitudinal or ultrasonic velocity after testing, V_{L0} is longitudinal or ultrasonic velocity before testing and n - material constant (n = 0.488, ref. [7]). This equation was used for calculation with both longitudinal and transversal ultrasonic velocity.

The obtained results for the strength degradation based on results of ultrasonic measurments, and calculated using Equation (3) respectively were presented in the Fig. 6.

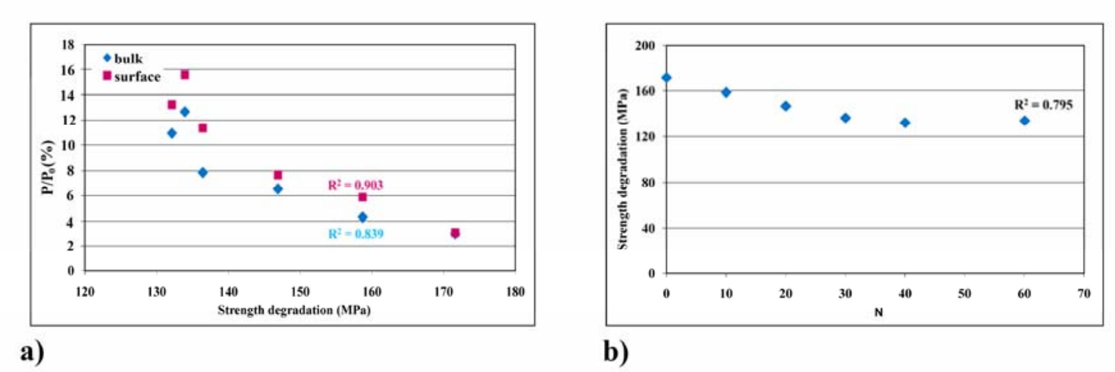


Fig. 6. Strength degradation during testing versus a) number of quench experiment (N) and b) level of degradation (P/P_0)

Image analysis was applied in order to measure the damage level at the surface and inside the samples. Results presented in Fig.3. show the existance of a certain level of degradation before quenching. This level was around 2.9 %, and similar values were observed for the sample surface and bulk. During the water quench test, the level of destruction increased, but surface damage was faster than inside the sample. An excellent correlation was observed between the level of destruction (P/P_0) and number of quench experiment (N).

Monitoring of the changes in ultrasonic velocity during thermal shock stability testing was performed using the UPVT method. Changes of longitudinal waves (V_L) were from 5050 m/s at the beginning to 2050 m/s after 40 cycles and the transversal velocity range was between 2500 and 1000 m/s. Very good correlation between ultrasonic velocity degradation and number of cycles was observed (Fig.4.). Similar results were observed when the Young modulus of elasticity was monitored (Fig. 5.). Decreasing of the Young modulus of elasticity versus number of cycles was observed, from 49.95 to 18.16 MPa, after 60 cycles.

Results for the strength degradation calculated from Eq. (3) based on results for longitudinal velocities showed a similar correlation with the number of cycles, as with the level of destruction, which is presented in Fig. 6. After 60 cycles the strength degradation was 22 %, which could explain very good thermal stability results of the water quench test.

4. Conclusion

Synthesis of low cement high alumina castable and its thermal stability characterization was the goal of this work. Material preparation was discussed, and the sintering temperature of 1300°C was chosen for samples preparation. Obtained conclusions were as follows:

- The material exhibited very good thermal stability, as the maximal number of quench experiment was 110 cycles.
- A modified water quench test was applied; nondestructive evaluation of surface and bulk degradation during testing was performed in order to monitor the level of destruction using the Image Pro Plus Program and UVPT for monitoring changes in ultrasonic velocity, Young modulus of elasticity and strength degradation.
- Very good results for correlation of ultrasonic velocity, Young modulus of elasticity and strength degradation during testing with the number of quench experiment (N) and level of degradation (P/P_0) were observed.

On the basis of the obtained results and conclusions it is our opinion that low cement high alumina castable sintered at 1300°C exhibited very good thermal shock resistance, and future application of this material could be expected in conditions where rapid temperature changes will be included or expected.

Application of nondestructive methods (image analysis and UPVT) showed their advantages in monitoring sample behavior during thermal stability testing. The results obtained by nondestructive measurements give better possibility of monitoring sample behavior during testing. It is very convenient to measure the level of degradation, and calculate strength degradation, in order to achieve better prediction of material behavior, as well in optimum design of materials for specific applications where thermal stability is included.

Acknowledgements

The authors wish to express their sincere gratitude to PhD Andreas Buhr, Almatis, Germany and the Netherlands for supplying the raw materials used in the experiments. This research has been financed by the Ministry of Science and Environment of the Republic of Serbia as a part of the projects OI 142016, TR16004 and TR 19016.

References

1. I.A. Altun, Cem. Concr. Res., 31 (2001) 1233.
2. N. M. Khalil, M. F. Zawrah, M. A. Serry, Ind. Ceram. 25 2 (2005) 104.
3. F. A. Cardoso, M. D. M. Innocentini, M. F. S. Miranda, F. A. O. Valenzuela, V. C. Pandolfelli, J. Eur. Ceram. Soc. 24 (2004) 797.
4. C. Parr, B. Valdelièvre, C. Wöhremeyer, Refractories Applic. News 7 3 (2002) 17.
5. G. W. Меетхам & M. H. Van de Voorde, Materials for High Temperature Engineering Applications, Springer, 2000.
6. M. Bengisu, Engineering Ceramics, Springer, 2001.
7. online http:// www. matweb.com
8. C. E. Semler, Interceram 5 (1981) 485.
9. F. Aly, C. E. Semler, Am. Ceram. Soc. Bull. 64 (1985) 1555.
10. S. K. Nyiogi, A. C. Das, Interceram 43 (1994) 453.

11. R. O. Russell, G. D. Morrow, Am. Ceram. Soc. Bull. 63 (1984) 911.
12. G. E. Lockyer, E. A. Proudfoot, Am. Ceram. Soc. Bull. 46 (1967) 521.
13. D. N. Boccaccini, M. Romagnoli, E. Kamseu, P. Veronesi, C. Leonelli, G. C. Pellacani, J. Eur. Ceram. Soc. 27 (2007) 1859.
14. J. M. Auvray, C. Gault, M. Huger, J. Eur. Ceram. Soc., 27 (2007) 3489.
15. A. Kovalčíková, J. Dusza, P. Šajgalík, J. Eur. Ceram. Soc., 29 (2009) 2387.
16. D. N. Boccaccini, M. Romagnoli, P. Veronesi, M. Cannio, C. Leonelli, G. Pellecani, T. Volkov Husovic, A. R. Boccaccini, Int. J. Appl. Ceram. Technol. 4 (2007) 260.
17. S. Marenovic, M. Dimitrijevic, T. Volkov Husovic, B. Matovic, Ceram. Int. 34 (2008) 1925.
18. D. N. Boccaccini, M. Cannio, T. D. Volkov-Husović, I. Dlouhy, M. Romagnoli, P. Veronesi, C. Leonelli, J. Eur. Ceram. Soc. 28 (2008) 1941.
19. M. Posarac, M. Dimitrijevic, T. Volkov-Husovic, A. Egelja, A. Devecerski, B. Matovic, J. Optoelectron. Adv. Mat. 10 (2008) 883.
20. D. N. Boccaccini, E. Kamseu, T. D. Volkov-Husovic, M. Cannio, M. Romagnoli, P. Veronesi, C. Leonelli, I. Dlouhy, A. R. Boccaccini, J. Mat. Sci. 43 (2008) 4079.
21. M. Posarac, M. Dimitrijevic, T. Volkov-Husovic, A. Devecerski, B. Matovic, Ceram. Silik. 32 (2008) 115.
22. M. Posarac, M. Dimitrijevic, T. Volkov-Husovic, A. Devecerski, B. Matovic, J. Eur. Ceram. Soc. 28 (2008) 1275.
23. M. Dimitrijevic, M. Posarac, T. Volkov-Husovic, A. Devecerski, B. Matovic, Ceram. Int. 35 (2009) 1077.
24. S. Martinovic, J. Majstorovic, V. Vidojkovic, T. Volkov-Husovic, Proc. & Applic. Ceram., 3 (2009) 191.

Садржај: *Последњих деценија необликовани монолитни ватростални материјали имају све ширу примену због бројних предности у односу на обликоване ватросталне опеке исте класе. У овом раду испитиване су термичке и механичке особине и понашање при термошоку нискоцементног високоалуминатног ватросталног бетона који је синтетизован, а затим синтерован на 1300ºC. Као експериментални метод за испитивање термостабилности бетона примењен је модификован тест класичне методе испитивања наглим хлађењем у води који се састојао у додатном праћењу понашања узорака приликом термошока имплементацијом анализе слике и ултразвучних мерења. У циљу праћења степена оштећења површине пре и током теста на термостабилност, коришћен је софтверски програм за анализу слике, а ултразвучним мерењима промена Јунговог модула еластичности. Пад чврстоће узорака израчунат је помоћу модела на бази промене брзине ултразвука током тестирања узорака на термошок. У овом раду биће дискутован утицај праћења степена оштећења на понашање материјала пре и током тестирања узорака на термошок.*

Кључне речи: *Нискоцементни бетон, тодификовани тест каљења у води, анализа слике, илтразвучна мерења, анизотропија.*