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Review

A REVIEW OF THE POSSIBLE APPLICATIONS OF NANOTECHNOLOGY IN REFRACTORY CONCRETE

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Abstract. This article reviews the manufacturing nanotechnologies of modern refractory concretes and some other cementitious materials. The main part of the article focuses on the results obtained by the authors who analyzed the application of nanotechnology for manufacturing refractory concretes and examined the influence of nanostructure formation in the binding material on the properties of refractory concretes. In one case, investigations were carried out using two-component (sodium silicate solution mixed with *dicalcium silicate*) and three-component (sodium silicate solution mixed with *dicalcium silicate* plus calcium aluminate cement) binding materials, whereas in other case, multi-component material, middle cement refractory concrete with mullite aggregates, microsilica and additives of single and hybrid deflocculant (polycarboxylate ether Castament FS20 and sodium tripolyphosphate) were researched. Preliminary investigations showed that the three-component binding material under development hardens unlike the two-component material as one of the binding components (combination of sodium silicate solution and dicalcium silicate) hardens very fast and affects the hydration process of the other component, calcium aluminate cement, which has a powerful impact on the whole structure of the already hardened material. The limited amount of water in the hardening structure provides conditions for the formation of the initial nanoclusters and nanolayers of amorphous hydrates. The application of nanotechnology in manufacturing refractory concretes has enabled to increase compressive strength 3 times – from 55 MPa to 165 MPa.

Keywords: nanotechnology, refractory concrete, calcium aluminate cement, microsilica, sodium silicate solution, deflocculants.

1. Nanotechnology and Nanosized Additives in Concrete

Nanotechnology is mainly defined by size and comprises the visualization, characterizations, production and manipulation of structures which are smaller than 100 nm (Kaluza *et al.* 2008). The structures the dimensions of which range from 100 nm down to approx. 0.1 nm exhibit special mechanical, optical, electrical, and magnetic properties which can differ substantially from the properties of the same materials at larger dimensions (Nalwa 2002; Bakker 2008). Therefore, nanotechnology is a very active research field and has applications in a number of areas.

Currently, significant attention has been paid to the application of nanotechnology in the development of cementitious building materials (Sobolev and Ferrada-Gutierrez 2005). Refractory concrete with calcium aluminate cement (CAC) is one of these materials.

The application of nanotechnology is aimed at obtaining the following unique properties of cementitious materials: ultra-high compressive strength, relatively high tensile strength and ductility, more efficient cement hydration, increased aggregate-paste bond strength, control of cracks and self healing. In the case of refractory materials, the same properties as well as high resistance to thermal shock, abrasion and chemical corrosion must be obtained (Guimaraes and Lee 2007; Garbers-Craig 2008; Кузнецов *et al.* 2009).

The first papers on nanotechnology in refractories causing a big interest appeared in UNITECR (The Unified International Technical Conference on Refractories) in 2003 (Tamura *et al.* 2003; Takanaga *et al.* 2003). The researchers of these as well as later published papers (Ghosh *et al.* 2005; Mukhopadhyay *et al.* 2007; Amin *et al.* 2009) try to modify the matrix (binding phase) of advanced refractory materials with nanosized additives.

S. Mukhopadhyay proposed to use of nano spinel ($MgAl_2O_3$) precursors in alumina concrete. Nano material was synthesized via sol-gel route under laboratory conditions. The author reported that sol-gel derived spinel bonded concrete matrix showed commendable performance, especially, thermal shock and slag resistance behaviour in the corrosive environment.

The effects of using carbon black (pure elemental carbon in the form of nanoscale particles with a semi-amorphous molecular structure) on the physical and thermomechanical properties of Al_2O_3-SiC-SiO_2- graphite refractory composites were investigated by Amin *et al.* (2009).

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The investigation results showed that nanosize additive effectively improved the oxidation resistance of the material as well as its cold compressive strength.

Different investigations (Andersen 2005; Ismael *et al.* 2007) revealed that colloidal (nanoscale) silica and hydratable alumina (amorphous mesophase transition alumina) as a combined binding system also contributed to better advantages to the processing and properties of refractory concrete. The conducted investigation (Huizhong *et al.* 2002) showed that adding nano-sized alumina and silica into corundum-based refractory concrete not only increased compressive strength but also lowered calcining temperature.

Today, technologies for producing nano MgO, Al_2O_3, ZrO_2, Cr_2O_3 as well as other types exist (Changming *et al.* 2007) and the perspectives of using them in refractories also seem to be very high.

Most of the above mentioned nano additives are very expensive. Therefore, the performed investigations focused on nanostructures which were formed during hardening cementitious materials and their modifications were found to be more promising.

2. CSH Nanostructures

CSH ($CaO–SiO_2–H_2O$) is the principal hydration product and primary amorphous binding phase in Portland cement as well as a phase of refractory compositions with sodium silicate binder (Борсук, Ляс 1979).

Over the past two decades, investigations have provided a reasonably clear picture of CSH structure on the sub-nm scale, and therefore it is widely accepted that CSH is composed of nanoparticles (Richardson and Groves 1992; Taylor 1993; Richardson 2004, 2008; Viehland *et al.* 1996).

Along with Portland cement, various pozzolan additives (fly ash, silica fume) (Kosior-Kazberuk and Lelusz 2007; Boudchicha *et al.* 2007; Bai and Gailius 2009) and plasticizers (deflocculants) are used. The quantity of CSH is normally increased when pozzolans are incorporated along with cement. Differences between the nanostructures of CSH have been found in Portland cement paste with pozzollanic additives (Richardson 2004). CSH presence in the hardened Portland cement has a mean Ca/Si ratio of about 1.75. If the paste contains pozzolanic material (silica fume, fly ash, metakaolin etc.), Ca/Si ratio is often < 1 (Pellenq *et al.* 2008). It has been noted (Ремнев 1996) that the limit of the tensile strength of high alkali units C_6S_3H, C_5S_3H, C_2SH, C_3SH is 770 – 830 MPa which is less than half the strength of low-alkali calcium hydrosilicate crystals that can measure up to 2000 MPa. The calculations of the atomic scale show (Richardson 1999) that when two parallel CSH lamellae at low Ca/Si ratio are at a distance of the order of one or two water molecular diameters (1.2 nm at a distance), they are trapped in an extremely deep electrostatic potential well which may be considered as a chemical ionic bond.

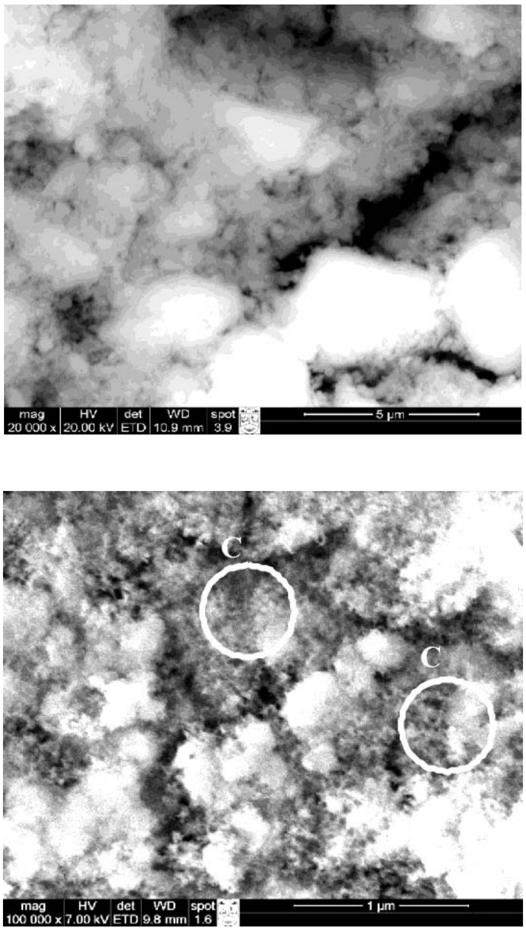
In a refractory binder consisting of sodium silicate solution (Na_2O-SiO_2-H_2O) and metallurgical slag mainly made of dicalcium silicate (γ-C_2S), calcium hydrosilicates (CSH) and sodium calcium hydrosilicates are the main final products.

According to Korneev (Корнеев, Данилов 1991), hardening may be expressed by the following reaction:

$$Na_2O\cdot nSiO_2 + 2CaO\cdot SiO_2 + H_2O \rightarrow CaO\cdot mSiO_2\cdot aq + SiO_2\cdot aq + (Ca,Na_2)O\cdot SiO_2\cdot aq. \quad (1)$$

SEM investigations into such binder demonstrated (Antonovič *et al.* 2009) that its structure was composed of conglomerates (Fig. 1a), i.e. partially dissolved particles of dicalcium silicate and other admixtures of metallurgical slag coated by the clusters of the products formed during a reaction of sodium silicate solution and dicalcium silicate. Fig. 1b clearly indicates that the nanosized structures (< 50 nm) are dominant among the amorphic products that create the clusters. As the reaction between the components of composition is very fast (setting time 20–50 min.) (Goberis, Antonovič 1998), hardening products make certain networks with big voids (Fig. 1a). Unfortunately, in respect of microstructure, the mechanical properties of such refractory binder as well as concrete are not high (Antonovič, Goberis 2001; Goberis *et al.* 2002).

The usage of complex binding materials with effective additives and the possibilities of modern laboratory equipment have provided new ideas for improving the micro and nanostructures of materials.



a)

b)

Fig. 1. The structure of a sodium silicate binder: a) x 20 000; b) x 100 000; C – clusters

Further, this paper analyzes several examples of nanotechnology for refractory materials with applied CAC currently developed by the authors of this paper.

3. Investigation into CAC Based Complex Binder for Refractory Concrete

Studies on nanostructures in refractory materials using CAC have not been examined as widely as those on Portland cement systems.

During the hydration of CAC, various hydrates may appear, develop from the nano level (gel) and transform at the macro level into crystalline calcium aluminate hydrates (i.e. CAH_{10}, C_2AH_8, C_3AH_6 together with AH_3 gel) (Majumdar *et al.* 2001; Middendorf, Singh 2006). V. Lamour observed that during the induction period of CAC hydration and at the beginning of massive precipitation of hydrates, the size of amorphous size hydrates reached approximately 30 nm (Lamour *et al.* 2001).

The size of crystalline calcium aluminate hydrates in the end of the hydration process can grow up to 1–20 μm (Taylor 1993; Rivas-Mercury *et al.* 2003). When water and cement ratio is very high (W/C = 20), the size of the hexagonal prisms of hydrates reaches approx. 40 μm (Fig. 2) (Kalpokaitė-Dičkuvienė *et al.* 2009).

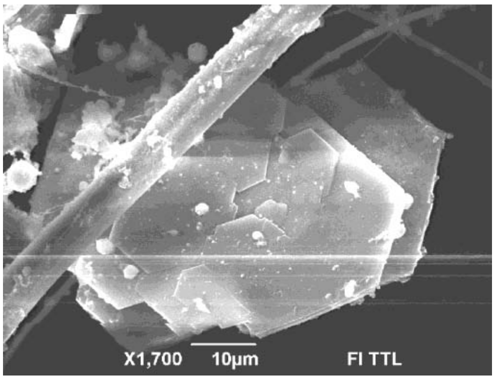
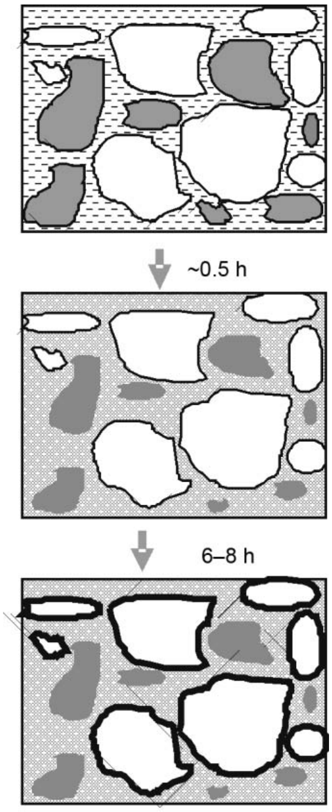


Fig. 2. Hexagonal prisms of CAC hydrates

The essence of the technology under development is to retard the formation and development of large crystalline hydrates and to stimulate the generation of nanoscale amorphous hydrate structures as the binding component for refractory concretes.

For this purpose, the use a complex binder composed of sodium silicate solution, dicalcium silicate and CAC is proposed.

The mechanism of complex binder hardening can be illustrated by the scheme presented in Fig. 3. In such binder sodium silicate solution mixed with dicalcium, silicate (metallurgical slag) hardens very fast (~0.5 h) and the hydration reactions of the other component, CAC, take place in the structure of the already hardened material (Goberis *et al.* 2002; Goberis and Antonovich 2004). Water for the partial hydration of cement is released during the reaction between sodium silicate solution and dicalcium silicate as well as from silicate gel. The limited amount of water in the hardening structure provides the conditions for the formation of the initial nanoclusters and nanolayers of amorphic hydrates.



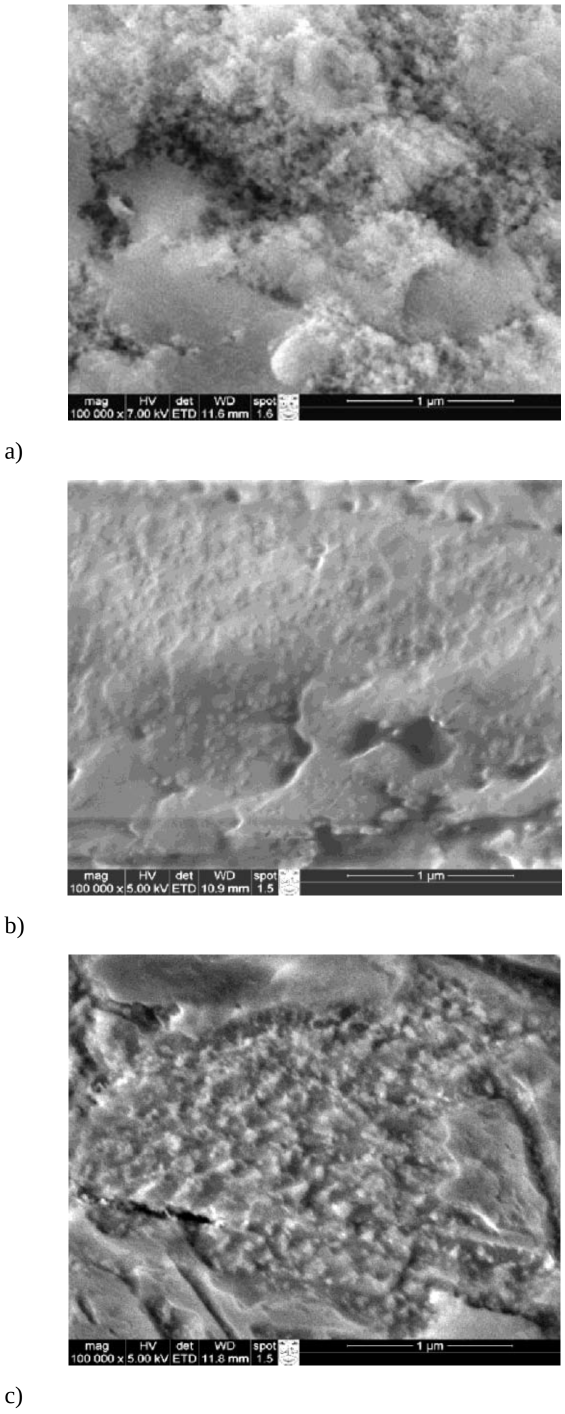
▤ – sodium silicate solution; ☐ – particles of alumina cement; ■ – dicalcium silicate; ▨ – products of the reaction between sodium silicate and dicalcium silicate; ▬ – layers of nanometric hydrates

Fig. 3. The scheme of hardening the complex binder

The structure of the complex binder (Fig. 4a) versus that of the one-component binder of sodium silicate (Fig. 1a) is more compact (Antonovič *et al.* 2009). The separate zones of the structure indicate that in the composition, the particles of metallurgical slag and cement are joined by the nanostructures (Fig. 4a) of the reaction products between sodium silicate solution and metallurgical slag. When proving the scheme of hardening (Fig. 3), SEM investigations showed that the surface of cement particles was coated by the nanostructures of certain orientation and with the particles sized from 30 up to 100 nm (Fig. 4b, c).

The density of sodium silicate solution is the tool for controlling the hydration of CAC and the properties of the complex binder. One can see (Fig. 5) (Antonovič *et al.* 2007) that the lowest value of exothermic (EXO) temperature during hydration is achieved when the density of sodium silicate solution is about 1250–1330 kg/m^3.

The highest compression strength was recorded for a binder's composition containing 1250 kg/m^3 dense sodium silicate solution (Fig. 5) (Antonovič *et al.* 2007). It must be noticed that the compression strength of such material is 2–3 times higher than that of the one-component materials (~50 MPa for cement stone and 30 MPa for the hardened binder of sodium silicate solution and dicalcium silicate).



a)

b)

c)

Fig. 4. The structure of the complex binder: a) products of the reaction between sodium silicate solution and slag, b, c) the surface of alumina cement particle coated by nanoparticles. Please, find in the text a more detailed description. Magnification x 100 000

The performed investigations (Antonovič and Goberis 2001) revealed that the mechanical properties and thermal durability of refractory concrete with the complex binder were very high. A comparative analysis of the physical-mechanical characteristics of concrete showed that the cold crushing strength of concrete with the complex binder after its setting, drying and firing at a temperature of (500–600) °C was 1.5–3 times higher than that of the concrete with a conventional binder. The thermal shock resistance of conventional concrete reaches only 16 cycles while in case of concrete with complex binders, it amounts to 40–45 cycles.

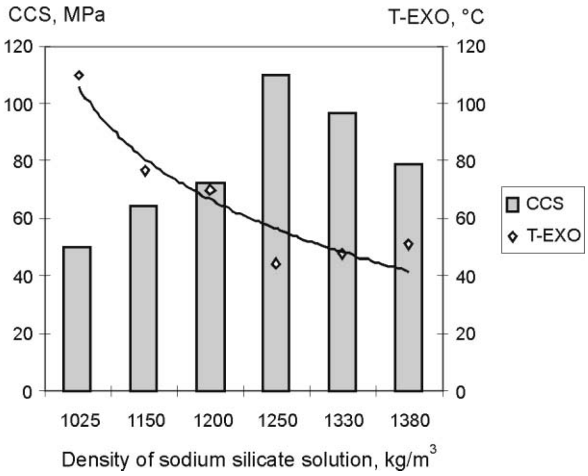


Fig. 5. The dependence of complex binder hydration exothermic temperature (T-EXO) values and hardened complex binder cold compression strength (CCS after 3 days of curing at a temperature of 50 °C) upon the density of sodium silicate solution

4. Refractory Concrete Produced Using Microsilica Hybrid Deflocculant

A semi-amorphous submicrocrystalline CASH (CaO–Al_2O_3–SiO_2–H_2O) phase (zeolitic structure) appears during the interaction between hydrating CAC and microsilica (silica fume) that is the ultra-fine dispersal of tiny spheres average size ~150 nm with some less than 20 nm (Fig. 6) (Pundene *et al.* 2009). This additive is effective in forming nanostructures during cement hydration.

It is believed (Wohrmeyer *et al.* 1999) that the hydration process of CAC and microsilica at a temperature of 20 – 25 °C follows the reaction sequence:

$$CAH_{10}+CAS_mH_n+S,$$

$$CA+H+S \rightarrow C_2AH_8+AH_3+CAS_mH_n+S, \quad (2)$$

$$C_3AH_6+2AH_3+CAS_mH_n+S.$$

CASH structures are extremely difficult to identify. During investigations into low cement castable (LCC-cement content 4–8%) having microsilica and deflocculant additives, only CSH and C_2ASH_8 (stratlingite) are identified (Chakraborty 2004). In combination with CAC, microsilica and deflocculant (sodium sulfate) the formation of stratlingite is also observed (Ding *et al.* 1995). There is no doubt that the latest research will enable scientists to achieve more exact data about the structure of the hydration products of these compositions.

A new generation of refractory concretes the manufacturing technology of which was created using microsilica MCC (middle cement castable having 8–15% of cement) LCC (low cement castable having 4–8% of cement) and ULCC (ultra low cement castable having 0.5–

4% of cement) are significant for very high (in comparison with conventional castable) thermal, physical and mechanical properties. CCS and strength under loading after heating at 1500 °C are 2–3 times higher and density is up to 2 times higher. It is necessary to note that these types of concrete are highly sensitive to manufacturing conditions such as environmental temperature, mixing parameters, water quality etc., and therefore manufacturers sometimes fail to make a high quality product (Myhre 2005). This shows difficulties in controlling the hydration process of new cementitious materials and regulating the formation of micro and nano-scale phases. One of the ways to produce a more homogenous dispersed product (slurry) and improve the overall hydration reactions is to use a hybrid deflocculant (plasticizer).

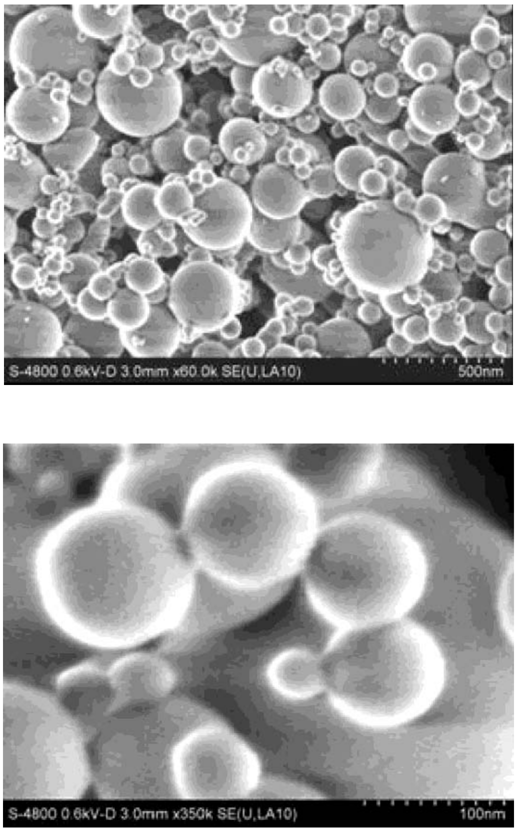


Fig. 6. A scanning-electron-microscope image of microsilica

Earlier used different materials (proteins, lignosulfanates, polyphosphates, polyacrylates etc.) as deflocculants are still in use nowadays. The most recent development in deflocculants is the so-called polycarboxylate ethers (PCE) which are not only very efficient in terms of water reduction but also in improved workability (Hommer, Wutz 2005). It also influences the hydration process of CAC. PCE are polyelectrolytes with the main chain (length is 3–20 nm) bearing negatively charged functional groups and additional side chains (3–40 nm).

Our last investigation (Пундене *et al.* 2009) analyzed the influence of different types of deflocculants (PCE and sodium tripolyphosphate) and their combinations (hybrid deffloculant) upon a structural formation during hardening MCC-type refractory concrete with mullite aggregates using the ultrasonic method. Fig. 7 presents the data on these investigations.

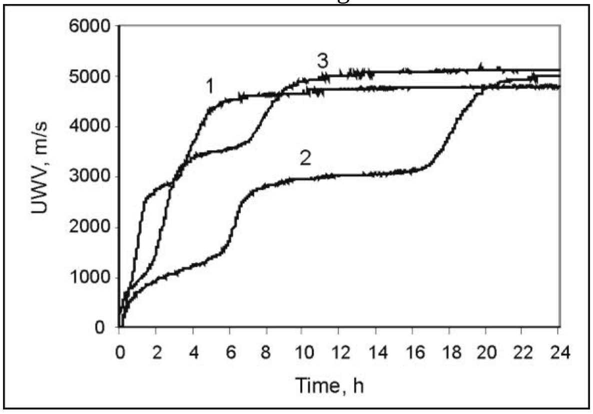


Fig. 7. Ultrasonic wave velocity (UWV) in the sample of MCC type concrete during hardening: 1 – with sodium tripolyphosphate; 2 – with PCE; 3 – with hybrid deflocculant

It was established that the structure of concrete formed at two stages when sodium tripolyphosphate deflocculant was used. At the first stage, the speed of ultrasound reached approximately 2500 m/s while at the second stage it was approximately 5000 m/s. With PCE (Castament FS 20), as many as three stages were detected in the formation of concrete. The speed of ultrasound at every stage was 1000 m/s, ~2500 m/s and ~5000 m/s respectively. In case of a hybrid deflocculant, three stages of the structural formation remained, however, at the second stage, the speed of the ultrasound impulse exceeded 3500 m/s.

The CCS results of investigations into mechanical properties show (Fig. 8) (Пундене *et al.* 2009; Антонович *et al.* 2010) that when the hybrid deflocculant was used, the CCS of concrete after the hardening process ranged within 58–65 MPa. It did not differ much from the CCS of concrete with the additives of sodium tripolyphosphate or PCE (about 55 MPa). Nonetheless, after drying castable at 110 °C and its firing at a temperature of 800–1000 °C, the CCS of concrete with the hybrid deflocculant was twice higher than that of the CCS of concrete where only sodium tripolyphosphate or PCE deflocculant was used (Fig. 8).

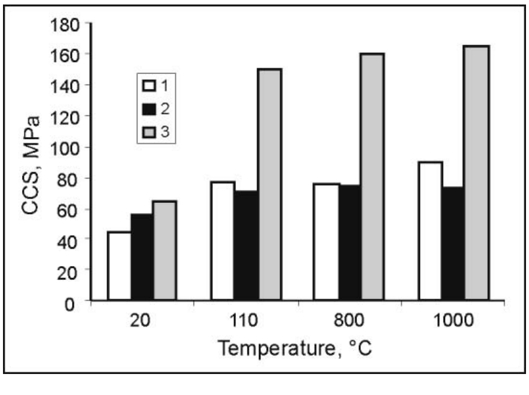


Fig. 8. The CCS of MCC concrete with a mullite aggregate: 1 – with sodium tripolyphosphate; 2 – with PCE; 3 – with hybrid deflocculant

The reason for such a result lies in the structures formed at the second step of UWV change. At the second stage of formation, nanostructures are formed and their maximal amount is reached with the hybrid deflocculant. The formed nanostructure of the dried and fired concrete gets compacted and the skeleton of large crystalhydrates undergoes transformation and disintegrates at a temperature of up to 400 °C. Therefore, the skeleton formed by nanostructures has a decisive influence on the CCS of concrete after firing.

It can be clearly seen that the application of nanotechnology (modification of nanostructures formed during hydration) for constructional cementitious materials and refractory concretes reveal new perspectives in creating materials with new characteristics.

5. Conclusions

Applying nanotechnology in manufacturing refractory concretes creates a possibility that during the process of hardening binding material, nanostructure would be formed to determine a significant increase in compressive strength and thermal durability. When using the materials of nano-particle composition (sodium silicate solution, amorphous SiO_2) as binding materials for refractory concretes and in parallel with respectively selected deflocculants (superplasticizers), it is possible to increase the compressive strength and thermal durability of concrete up to 2–3 times.

According to the obtained results, as described earlier in the paper, it could be concluded that a) a three-component refractory binder consisting of sodium silicate solution, dicalcium silicate and calcium aluminate cement can be used to simulate the generation of nano-particle-sized amorphic hydration structures in the refractory material; b) the compressive strength of concrete with a hybrid deflocculant after hardening slightly differs from that of concrete with sodium polyphosphate or polycarboxylate ether additive (about 55 MPa). After drying at 110 °C, firing at 800–1000 °C and due to the formation of nanostructures, the compressive strength of concrete with a hybrid deflocculant is higher up to two times (110–165 MPa) than that of concrete with polyphosphate or PCE (70–90 MPa) only.

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NANOTECHNOLOGIJŲ NAUDOJIMO UGNIAI ATSPARIŲ BETONŲ GAMYBAI GALIMYBIŲ APŽVALGA

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Santrauka

Straipsnyje apžvelgiamos per pastarąjį dešimtmetį sukurtos ugniai atsparių betonų ir kai kurių kitų cementinių medžiagų gamybos nanotechnologijos, kurios padeda nagrinėti nanostruktūrų, susidariusių kietėjant šių betonų rišamajai medžiagai, įtaką fizikinėms betonų charakteristikoms.

Detaliau apžvelgiami rezultatai, gauti šio straipsnio autorių, nagrinėjusių nanotechnologijų taikymą ugniai atsparių betonų gamyboje tiriant nanostruktūrų susidarymo, kietėjant ugniai atsparių betonų rišamajai medžiagai bei ugniai atspariems betonams su mulito užpildu, įtaką šių medžiagų savybėms. Autorių tyrimai atlikti naudojant dvinkomponentę (natrio silikato tirpalo ir dikalcio silikato) bei trikomponentę (natrio silikato tirpalo, dikalcio silikato ir aliuminatinio cemento) rišamąją medžiagą bei vidutinio cemento kiekio ugniai atsparų betoną su SiO_2 mikrodulkių ir hibridinio deflokulianto (natrio tripolifosfatu ir polikarboksilato eteriu) priedu. Preliminarūs tyrimai parodė, kad trikomponentis rišiklis kietėja kitaip nei dvikomponentis, nes viena iš rišamųjų dalių (natrio silikato tirpalo ir dikalcio silikato kompozicija) kietėja labai greitai ir veikia kito komponento (aliuminatinio cemento) hidratacijos eigą, o tai turi didelę įtaką visai kietėjančiai struktūrai. Ribotas vandens kiekis kietėjančioje struktūroje padeda šalia amorfinių hidratų formuotis nanoklasteriams ir nanosluoksniams. Pritaikius nanotechnologiją ugniai atsparių betonų gamyboje, pavyko gerokai padidinti jų terminį atsparumą (beveik tris kartus) ir gniuždomąjį stiprį (nuo 55 MPa iki 165 MPa).

Reikšminiai žodžiai: nanotechnologija, ugniai atsparus betonas, aliuminatinis cementas, SiO_2 mikrodulkės, natrio silikato tirpalas, deflokuliantai.

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