

Article

Cement Substitution in High-Temperature Concrete

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Abstract: An alternative binder to calcium aluminate cement (CAC) was prepared by the sol-gel method. Chemically pure systems such as tetraethylorthosilicate ($\text{SiC}_8\text{H}_{20}\text{O}_4$) and nonahydrate of alumina nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as major raw materials. The manufacturing process of binder via solution is mentioned, and transitions in binder structure as a function of thermal treatment in the range between 85 and 1400 °C are described. Finally, binder efficiency was verified by its application in high-temperature concrete instead of calcium aluminate cement (CAC). Newly developed sol-gel binder was characterized by XRFS quantitative analyses, XRD diffraction, STA-DTA and TG analyses and the BET method. Samples of concrete which were based on natural bauxite raw material showed cold compressive strength of 42 MPa compared to the same material where a conventional CAC was applied, and samples reached cold compressive strength of 44 MPa.



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1. Introduction

The growing demand for the quality of high-temperature concretes forms space for the preparation of high-class binders that are excelled by chemical purity and by their manufacturing technique, which guarantees reproduction of their properties. The conventional process of production of high-temperature concretes suffers from the variability of raw materials' parameters as well as the changes in material structure parameters during their thermal treatment. A good possibility for how to prepare chemically pure material is through the sol-gel process.

The inorganic non-metallic materials such as ceramics, concrete or glass are traditionally prepared from natural solid materials in high temperatures. Usually, it is also necessary to mill raw materials or remove various impurities and unrequired substances. Very high temperatures are required for oxide and non-oxide ceramics, where the reaction is applied in a solid state without the presence of melting low-temperature components which is typical in this case. To shift the limits and to increase the possibility of applying silicates as traditional materials, this means to improve their competitiveness, it is necessary to fulfil increasing demands related to their structure, namely the final properties and application also in special branches so that it is not only known for use in porcelain cups or refractory bricks. Many branches require making products in a special shape, production at low temperatures (e.g., electronics, optics, in combination with organic or biomaterials) or what is known as “powder technology” for the production of thin layers [1,2].

Among the requirements that are placed on modern concretes and ceramics are adjustable porosity, the particular size and shape of particles, purity and composition stability of initial raw materials, etc. It is impossible to achieve improvement in the quality

of future silicate products without ensuring the above-mentioned requirements. From what was previously mentioned, it is clear that the necessity of high-temperature treatment and the use of natural raw materials which, in addition, need to be adjusted before being used, as well as the structural instability of the initial raw materials will be the main obstacles.

One possible way to produce high-temperature concrete with a reduced number of imperfections in traditional production is the sol-gel process. The formation of an oxide network is established at low temperature, usually through a solvent. Reactants are dispersed on a molecular level, which causes a short diffusional distance of reacting components and a much faster reaction under moderate conditions (compared to traditional high-temperature concrete or ceramics, where powdered precursor is used and products are formed using ionic diffusion throughout grains, sometimes with the help of melt). Additionally, very pure substances are usually used for the sol-gel processes which are prepared through chemical reaction. This is an indisputable advantage in specific applications, such as electronics, optics, biomedicine, etc. [3–5].

From a historical point of view, there was a primal and therefore today very well-known and widely used sol-gel process for the production of silica gel. However, the method was gradually familiarized for use with other metals, namely for the production of metal oxides [6].

Alumina–silicate, specifically alumina gel, can be prepared in various ways from a wide source of raw materials. For synthesis, methanol, ethanol, ethyl acetoacetate, ethylene glycol, butanol, butoxyethanol, etc., can be used as a solvent; hydrochloric acid, nitric acid, acetic acid or distilled water as a catalyst; and precursors can be tetraethyl orthosilicate, nonahydrate of alumina nitrate, colloidal silica, Pluronic P123, hydrolysed ethyl silicate, etc. [7–11].

The experiments described in this article focus on the possibility of applying the sol-gel method to produce a bonding system for basic high-temperature refractory concrete. This idea is not very common; therefore, precursors and the whole process as well were adapted to these proposals. The first stage of experiments included the development of the bonding system based on SiO_2 and Al_2O_3 . In the next stage of the research, it was necessary to verify the bonding ability of the developed SiO_2 – Al_2O_3 system. For the very first testing of binder efficiency, the bauxite-based high-temperature concrete was chosen. The main characteristic in the beginning of research, which should help to compare parameters of concretes with various type of binders, was cold compressive strength possibly achievable at 1200 °C.

2. Materials and Methods

2.1. Binder Manufacturing Method and Materials

For the production of our binder, chemically pure substances such as the resulting product alumina–silicate were chosen. The basic effective components were tetraethylorthosilicate ($\text{SiC}_8\text{H}_{20}\text{O}_4$) in concentration $\geq 99\%$ and nonahydrate of alumina nitrate p.a. ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and as supporting agents, ethanol p.a. ($\text{C}_2\text{H}_6\text{O}$) in concentration 96%, distilled water (H_2O) and hydrochloride acid p.a. (HCl) in concentration 35% were used.

The bonding system was made using the sol-gel method, where chemically pure substances were stirred in. The active components used were based on Al_2O_3 and SiO_2 as well as ethanol, hydrochloride acid and distilled water. The aim was to produce a powder product which could replace cement in application and therefore eliminate its related disadvantages.

The procedure lays in the preparation of two primary solutions and their following stirring into a final solution resulting in sol. The process of stirring was carried out in a beaker covered with watch glass and placed on Compact Direct magnetic stirrer (LAVAT a.s., Radim u Kolína, Czech Republic) with a high intensity of stirring, from 9 to 10 in scale, without additional heating. Finally, xerogel arose because of the thermal treatment of sol. Thanks to the specific procedure and raw materials as well, the way to prepare sol, namely gel, was optimized at first. In the second step, it was necessary to characterize

the product and determine its properties. The determination of the basic properties of the sol-gel synthesis product is the aim of this article.

2.2. Binder Identification Methods

A chemical composition was identified by a method of energy dispersive X-ray fluorescence spectroscopy (ED-XRF) on the SPECTRO XEPOS (Spectro Analytical Instruments, Kleve, Germany). Powdered samples were shaped/pressed into tablets for the measurement.

In addition, simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were applied for the purpose of finding the temperature when volatile components leave (alcohol, water) as well as their amount and temperatures of decomposition or mineral formation using an STA 504 instrument (TA instrument, New Castle, DE, USA) in air atmosphere ($5 \text{ L} \cdot \text{h}^{-1}$) at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ between 25°C and 1400°C .

Mineralogical composition of the product was evaluated using X-ray diffraction analysis on the X-ray diffractometer MiniFlex 600 (Rigaku, Tokyo, Japan) equipped with Co tube and a D/teX Ultra 250 detector. The XRD patterns were recorded in $5\text{--}90^\circ 2\theta$ range with a scanning rate of $5^\circ \cdot \text{min}^{-1}$. Focus was placed on determining the amorphous/crystalline shape of the product and basic minerals, especially the beginning of mullite, specifically α -corundum formation. Thermal treatment is also important for product properties.

The produced gel was calcined at various temperatures and, thanks to the BET method, a specific surface area of product was determined using nitrogen physio-sorption method at temperature 77 K (3Flex Micromeritics, Norcross, GA, USA). The goal was to find out the temperature when the product achieves its highest specific surface area at the point when it is most reactive.

Furthermore, additional parameters were determined such as the porosity, size of the pores and density of the prepared gel as well.

2.3. Concrete Sample Manufacturing Method and Materials

To provide proof of the newly developed binder's efficiency, beam samples of bauxite-based concrete were formed in standard sizes $160 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$. The concrete composition is shown in detail in Table 1, where it can be seen that the major part of the mixture is created from bauxite (84, resp. $100 \text{ wt.}\%$), while a minor part is optionally reactive alumina. As binders, calcium aluminate cement (CAC) and silica-alumina sol (S-A sol) were compared to our own production. An original concrete recipe was shifted a bit for the purpose of usage to a liquid binder instead of a powder one. The mentioned shift lies in granulometry treatment, as it is shown below in Table 1. This means that it was necessary to support the finest part of concrete recipe on one side and to eliminate mixing water content on the other one. The chosen type of concrete after the binder exchange according to European standard EN 1402-1 belongs to the category of NCC, which means non-cement castable, chemically bonded.

Table 1. Concrete mixture recipe with various types of binder (powdered (CAC) and liquid (S-A sol).

Component Type	Component Amount (wt.%)	
Bauxite (3–6 mm)	27	23
Bauxite (1–3 mm)	36	29
Bauxite (0–1 mm)	10	22
Bauxite ($<160 \mu\text{m}$)	10	22
Reactive alumina	11	4
Water	5	-
Powder (CAC)	6	-
Liquid (S-A sol)	-	8.5

Beam samples were prepared by blending of dry parts of mixture together, followed by moistening thanks to the addition of binder and shaping by the vibro-cast method into metal moulds (vibration frequency 50 Hz, time of vibration 2 min). In the case of an optimal binder amount, it was possible to demould samples after 2 h of aging in laboratory conditions. In the following, thermal treatment samples were dried at 110 °C to the constant weight and after that were fired at 1200 °C (regarding the bauxite origin of concrete) in the air atmosphere.

3. Results and Discussion

3.1. Thermal Treatment, TG and DTA Analyses of Gel

Exactly because a wide scale of raw materials exists, it is also necessary to choose an appropriate course of thermal treatment for a newly formed product. The gel is often produced at an elevated temperature (50–85 °C) when the polymerization of a system is supported, which usually causes strong shortening of the whole synthesis. For the characterization of the prepared gel, it is ideal to transform the gel into the state of powder. This means that the following step is drying the gel at about 100 °C and alternatively, the next calcination.

DTA and TG analysis is usually performed to obtain a basic imagination about the behaviour and processes taking place in the gel at an elevated temperature, especially for the verification of temperature leaving the volatile components and the formation of the required minerals. The temperature range of analysis is typically between 20 and 1200 °C, speed of heating 5–10 °C·min^{−1}. At first, it is possible to observe the leaving of adsorbed water above 100 °C, at evaluation of DTA and TG curves. In this case, we can see the endothermic effect, which is a phenomenon accompanied by strong weight loss visible on the TG curve. Other observable effects can be connected with alcohol leaving the system, decomposition of böhmite and its transformation in the line of böhmite (AlOOH) and α -corundum (α -Al₂O₃), where the complete string of transformation looks like this: böhmite, γ -corundum, δ -corundum, θ -corundum, α -corundum. The next significant peak occurs at about 300 °C when böhmite decomposes (elimination of OH groups). Then, a typical endothermic peak is visible without weight loss on graphic schemes. At higher temperatures, an exothermic reaction of α -corundum transformation manifests during α -corundum transformation. The formation of stable α -corundum can already be observed from 850 °C and above, depending on the type of initial raw materials and properties of the product achieved from the synthesis. The formation of transient forms of corundum can be expected in the stage between decomposition of böhmite and crystallization of α -corundum, which means at 300 °C and higher (later at about 850, 1000, 1100 °C), when their crystallization is manifested as exothermic effect without weight loss. Typically, the transition to a stable α -corundum form can be observed from 1200 °C. However, it has already been mentioned and many authors have verified that it is possible to prepare very a fine-grained product with high specific surface as well as a very reactive product by the sol-gel method. This fact can be useful with the benefit of a decreased temperature for the formation of α -corundum more than several hundred degrees. Weight loss presents only water and alcohol leaving from the system, namely the OH groups from the structure of böhmite. It is not unusual that this loss takes 40 wt.%, and it is visible to about 500 °C [11–13].

In our case, the whole process of gelation took place at an ambient temperature, and after that, the prepared sol was left to age. The time of curing to the point of gelation depends on temperature of the sol stirring (see above). During experiments while tracking the effect of temperature on gelation, the final sol solution gelled after 1 h of stirring at an elevated temperature of 85 °C. In a simplified procedure, which means stirring at ambient temperature, gelation was delayed about 2 weeks.

In the next step, after observing gelation, the gel dried at 85 °C for 12 h, which is the minimal necessary thermal treatment and thus is suitable for a laboratory sample of gel. In the case of the preparation of a bigger amount of gel (future binder), it had shown

even more comfortable calcinate gel at 500 °C. Even just staying at this temperature for a minimal time causes the elimination of volatile components and thus the stabilization of gel and loss of its hygroscopicity, as it is declared in Figure 1 below.

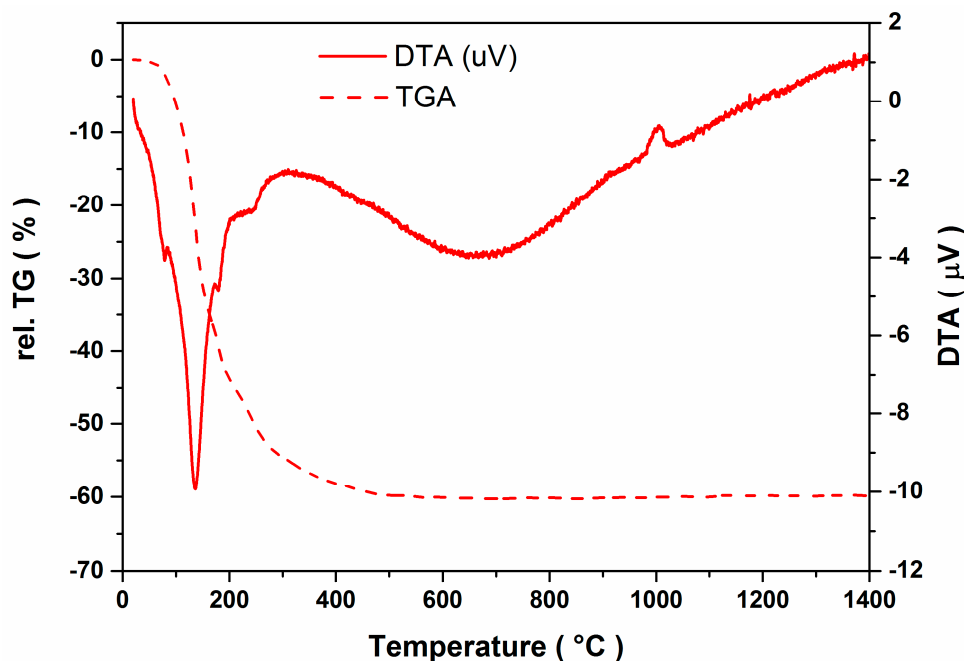


Figure 1. DTA and TG curve of gel dried at 85 °C, 12 h.

Other authors when manufacturing aluminium gel usually only focus on the formation of α -corundum as a required mineral. However, for our purposes, it is also useful to determine the temperature when mullite mineral is formed. This should occur at about 1200 °C, while α -corundum around 1500 °C. In Figure 1, the typical behaviour of the sol-gel method product is visible, when the aim is to create a product containing at least some mullite and alternatively also corundum. In the zone of up to 300 °C, it is possible to observe an endothermic effect. This is caused by water and alcohol leaving. In this stage, a decrease in weight of about 55% is recorded. The decrease in weight continues up to 500 °C, with 60% loss in total. In the range between 300 and 800 °C, another endothermic effect is manifested. The presented expression can be explained as the transformation of the amorphous phase into crystalline. The first evident exothermic peak manifests at 1000 °C. According to measured results from the XRD phase analysis, this peak belongs to the formation of mullite. The maximum temperature of the STA device did not enable measurement at a higher temperature; nevertheless, according to the XRD analysis, the formation of α -corundum was at first described at 1400 °C. Related to that, we can talk about a significant decrease in temperature of the beginning of the formation of both required minerals.

3.2. XRFs and X-ray Diffraction of Gel

The concrete chemical composition of the bonding system was determined on a sample of gel calcined at 500 °C by the XRFs method. The sample of gel contained after recounting on oxides only 41.2 wt.% of Al_2O_3 and 58.8 wt.% of SiO_2 . The total amount of minor components (CaO , Na_2O , K_2O , Fe_2O_3) was in sum less than 0.02 wt.%.

From a mineralogical point of view, the resulting minerals and their character depend on raw materials, so results from individual authors can significantly differ. For example, some authors concluded that a dried Al product showed amorphous character, but with an increasing water coefficient, increasing intensity of peaks can be observed, which indicates progressive development of böhmite structure. On a calcined sample, forming γ -corundum

structure with increasing water coefficient was observed, which corresponds to the fact that böhmite is a precursor for γ -corundum [14].

Phase analysis of our product was performed on a gel sample prepared at 85 °C (which is the temperature of gelation). Our gel was dried to a powder product at 110 °C for XRD purposes and calcined at 500, 800, 1000, 1200 and 1400 °C. The gel showed just amorphous character up to 800 °C, which is a welcomed variety from the point of system reactivity. The first recorded crystalline phase was mullite at 1000 °C, and at 1200 °C, the expected mullite and the initial α -corundum were registered. At a temperature of 1400 °C, the presence of α -corundum could be observed with no doubts. From the nature of input materials, phases containing SiO₂ in the bonding system also exist there. This phase was also registered on a pattern at first independently, later as a part of mullite and finally as a cristobalite. In Figures 2–7, the above-mentioned comment is declared about the development of the gel structure we prepared with an increasing temperature of calcination.

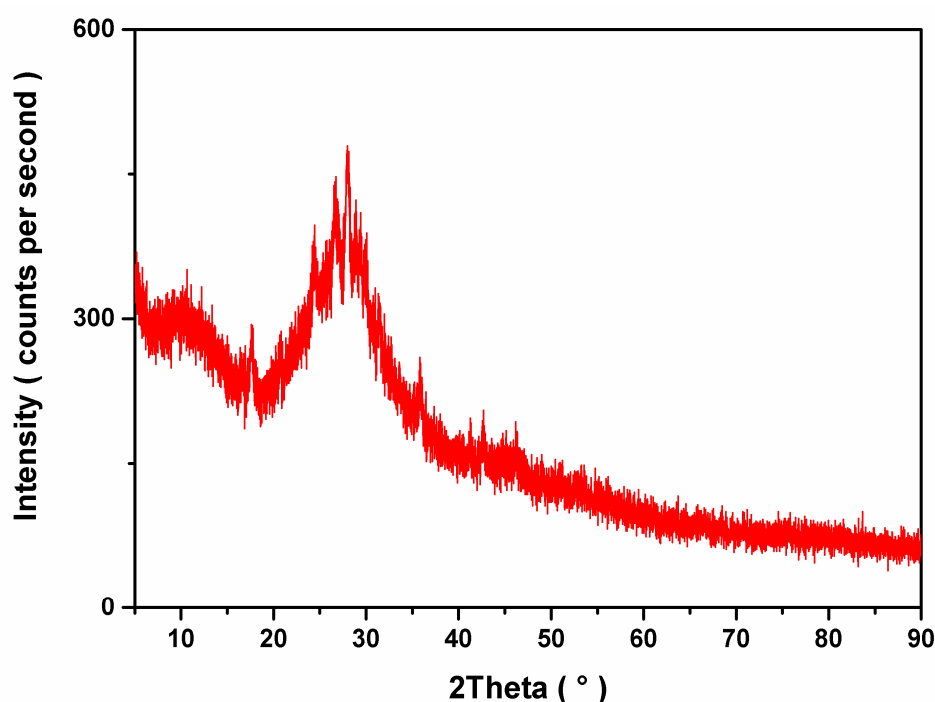


Figure 2. XRD patterns of a gel sample dried at 110 °C—amorphous character.

Figures 2–4 show the typical wavy shape of diffraction pattern in the initial part between 0 and 30° on 2 θ scale at temperatures up to 800 °C. It can be also seen raising the intensity of the “future” characteristic on the cristobalite peak. According to the listed patterns, cristobalite arose in the gel structure first at 1400 °C. A more interesting change was recorded at 1000 °C, shows Figure 5, where mullite occurred for the first time. In ceramic high-temperature concrete technology, a significant shortening of time (at least 200 °C) can be observed when the structure of material usually fails, as in the case of using CAC as a binder. As a bonus, Figure 6 shows start of formation of the next important mineral α -Al₂O₃ at a much lower temperature (1200 °C) than typical 1550 °C. The reason of the existence of the above-mentioned minerals at lower temperatures can be assigned to chemically pure raw materials without impurities and to the colloidal character of material. In Figure 7, there is a clearly visible existence of mullite, cristobalite and α -corundum which developed from the initial colloidal solution due to its thermal treatment. The following results from BET analyses support the idea that except for mineral formation above temperatures of 800 °C, the sintering of material also occurs.

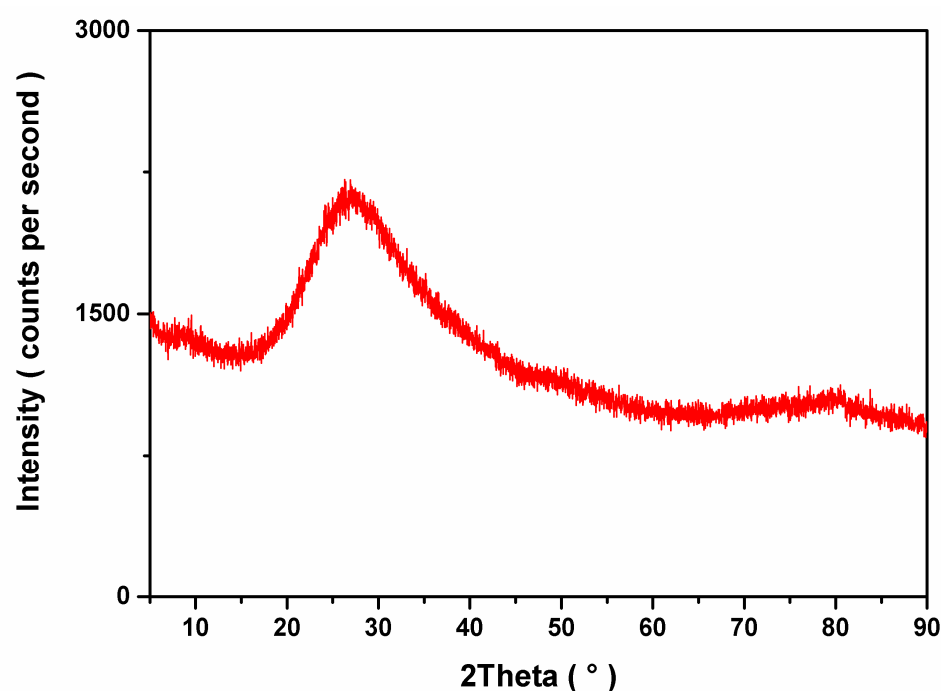


Figure 3. XRD patterns calcined at 500 °C—amorphous character.

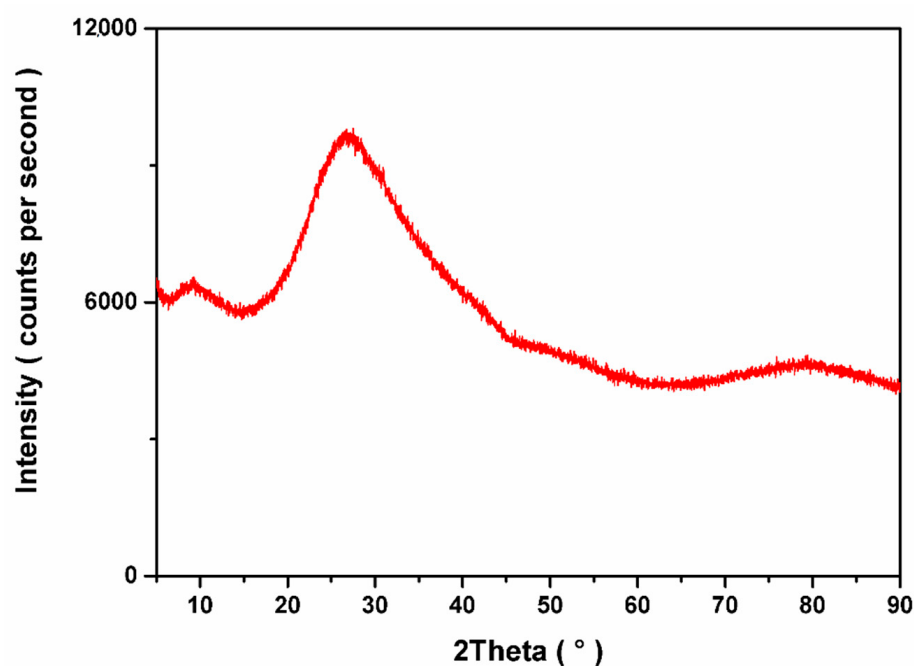


Figure 4. XRD patterns calcined at 800 °C—amorphous character.

3.3. BET, Porosity and Density

Most authors mention grinding and determination of granulometry before the TA, XRD or BET analyses are applied and the same also before the use of the product. Samples are usually treated after drying on a particle size of 44, 40, which are 37 μm [13,15]. The specific surface of sol-gel products is typically high, around 400 m^2/g . This fact makes their later successful application unsure in cases where it should work as a catalyst, or where, as in our case, it should react with its surroundings and sinter at a much lower temperature. The typical characteristic of a sol-gel product is its constant specific surface with a relatively uniform size of pores.

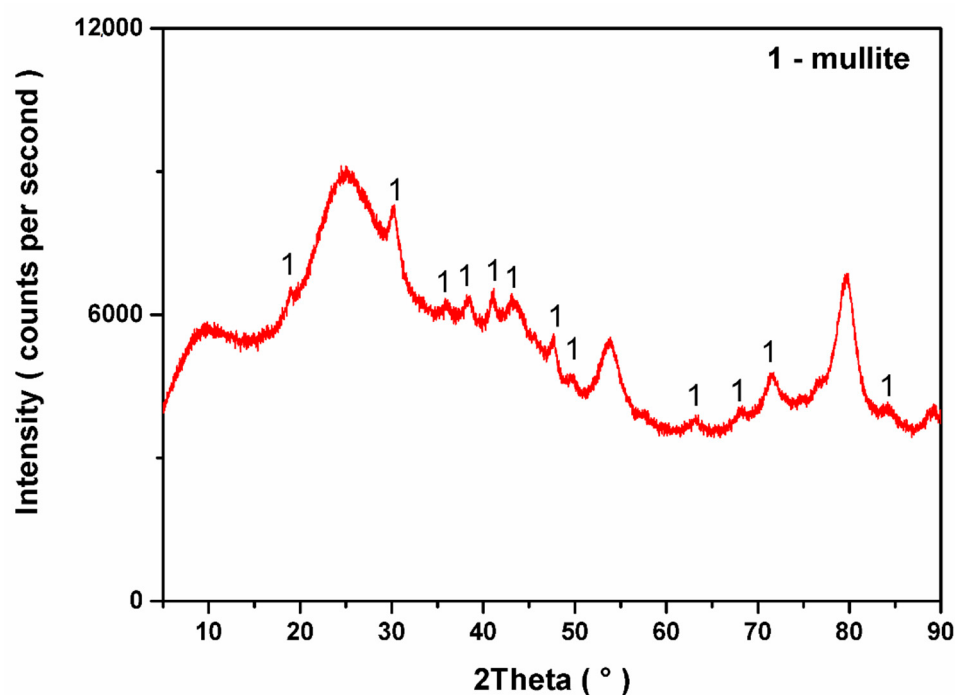


Figure 5. XRD patterns calcined at 1000 °C—start of mullite formation.

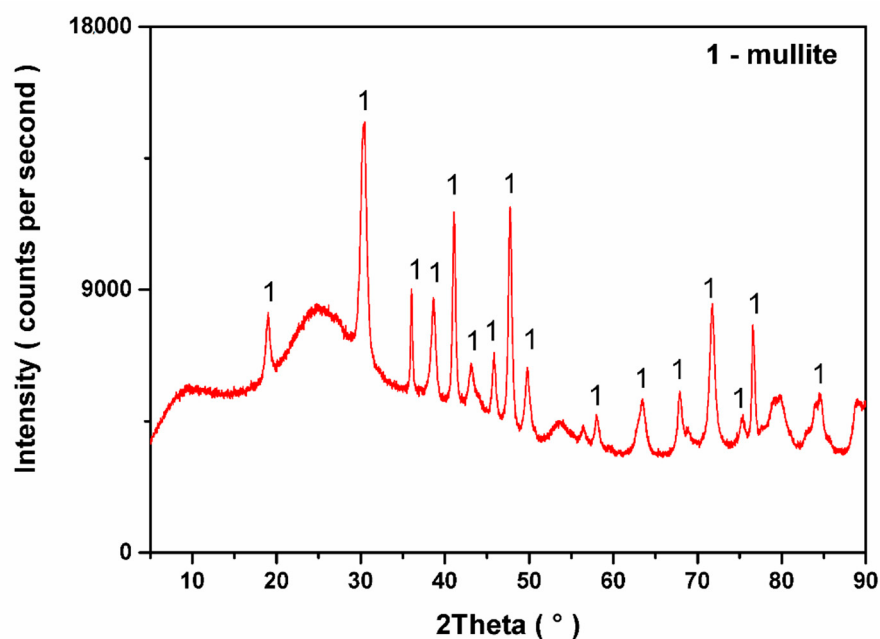


Figure 6. XRD patterns calcined at 1200 °C—mullite, start of α - Al_2O_3 formation.

For more detailed examination of pores in a structure for the determination of their distribution, size and shape, the method of nitrogen adsorption is typically used, based on the BET theory or easier Blain method. For example, other authors proved, by using the BET method, that Al powder developed by them and prepared by the sol-gel method has a relatively uniform size of pores and the average size of pore diameter is between 3–9 μm . Different authors, in turn, proved that in manufacturing Al powder by the sol-gel method, it is possible to prepare a product with a high specific surface in a narrow range of pore size and with a pore diameter 6–8 μm [14].

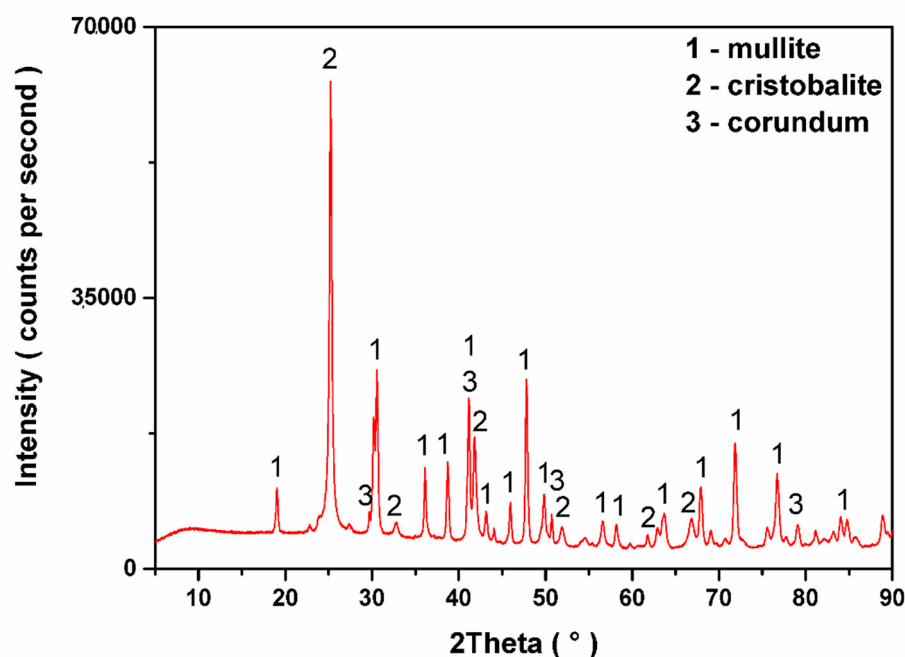


Figure 7. XRD patterns calcined at 1400 °C—mullite, α -Al₂O₃, cristobalite.

Considering the fact that the size of a specific surface area of material affects its reactivity at later application the most, in our case, the development of the size of a specific surface of a prepared product was observed with temperature. The BET method was used for the determination of its specific surface. Changes in a specific surface were observed on the gel after its thermal treatment at 85, 500, 800, 1000 and 1200 °C. In Figure 8a–g, the measured adsorption-desorption isotherm of nitrogen on individual samples of gel at given temperatures is documented.

Figure 8a–f shows the total volume and pore distribution in gel samples. The specific surface of individual samples was evaluated according to BET theory. Its size and the size of pores are listed in summary in the following Table 2.

Table 2. Textural properties of gel samples at different temperatures of thermal treatment.

Temperature (°C)	Character of Gel	S_{BET} (m ² /g)	V_{net} (mm ³ /g)	$D_{pore,max}$ (nm)
85	non-porous	0.98	1.6	-
500	mesoporous	98	108	4
800	mesoporous	72	87	5
1000	meso-macroporous	2	5	14.5
1200	macroporous/non-porous	0.6	2	-

From both previous tables, it is obvious that the temperature of thermal treatment of materials has a significant impact on the size of a specific surface. The sample after drying (85 °C) can be considered as a non-porous, with a very small specific surface, as well as a sample after calcination at higher temperatures (1000 and 1200 °C) when the material already gradually sinters. Based on achieved results, it can be said that a product had a maximal specific surface after the leaving of volatile components from its system above 500 °C. It is also evident that when this temperature product loses 60 wt.% of its weight, it creates total loss in whole temperature interval. A very good result was still achieved at 800 °C, but at higher temperatures, sintering occurs as well as the repeated decrease in porosity, the number of pores and the size of specific surfaces.

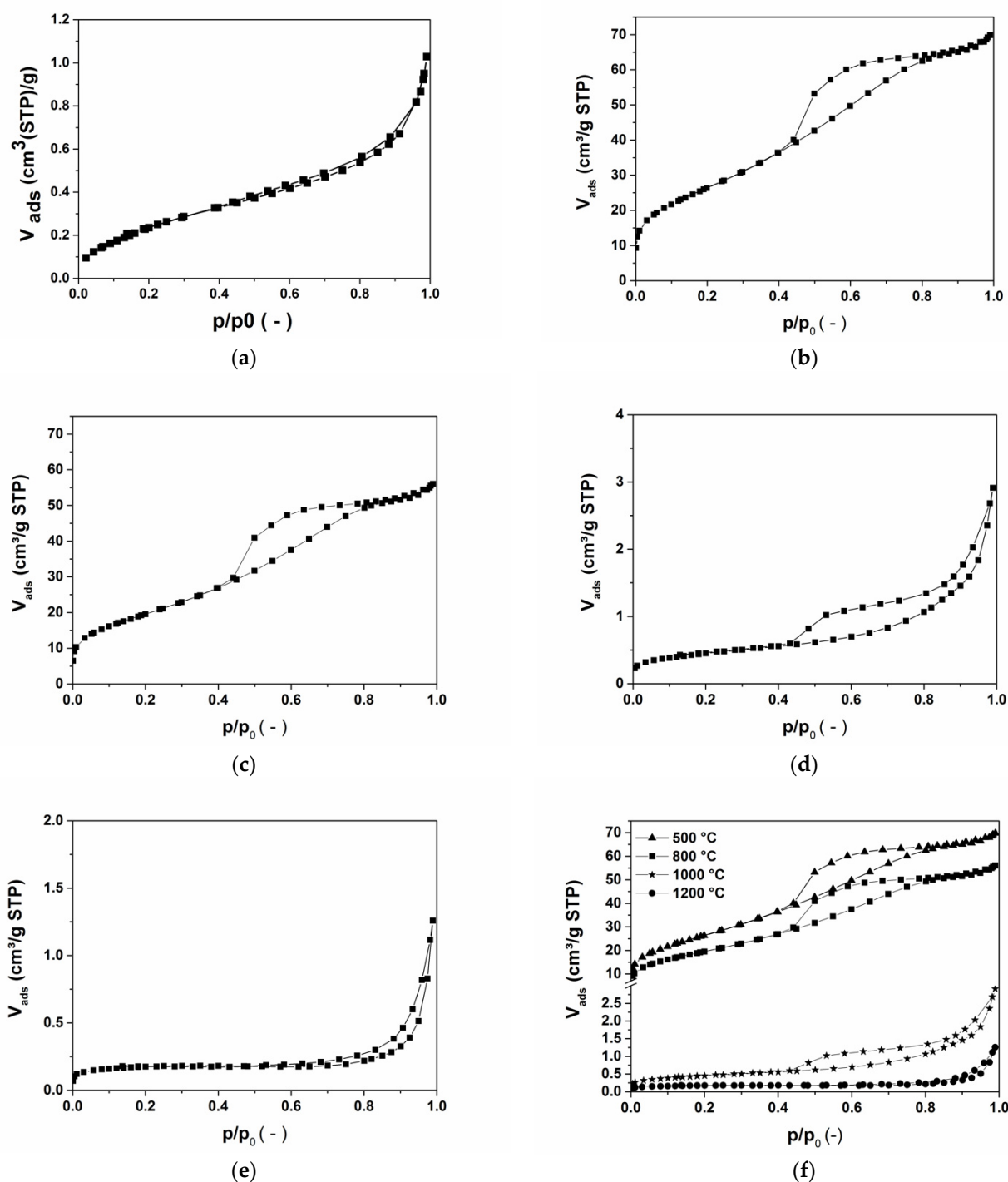


Figure 8. Adsorption–desorption isotherm of nitrogen for samples of gel at temperature 85–1200 °C; (a) Gel dried at 85 °C; (b) Gel dried at 500 °C; (c) Gel calcined at 800 °C; (d) Gel calcined at 1000 °C; (e) Gel calcined at 1200 °C; (f) Interrelation of measured isotherms.

The type and size of pores were roughly determined again from parameters gained at physisorption analysis. Density was determined on automatic pycnometer Pycnomatic ATC in an inert atmosphere of helium.

The following summary of pore size distribution in Figure 9 proves the character of pores that the gel contained at different stages depending on if it was porous or non-porous. Analyses showed that it was always non-porous material or material with bigger pores in a narrow interval of their size.

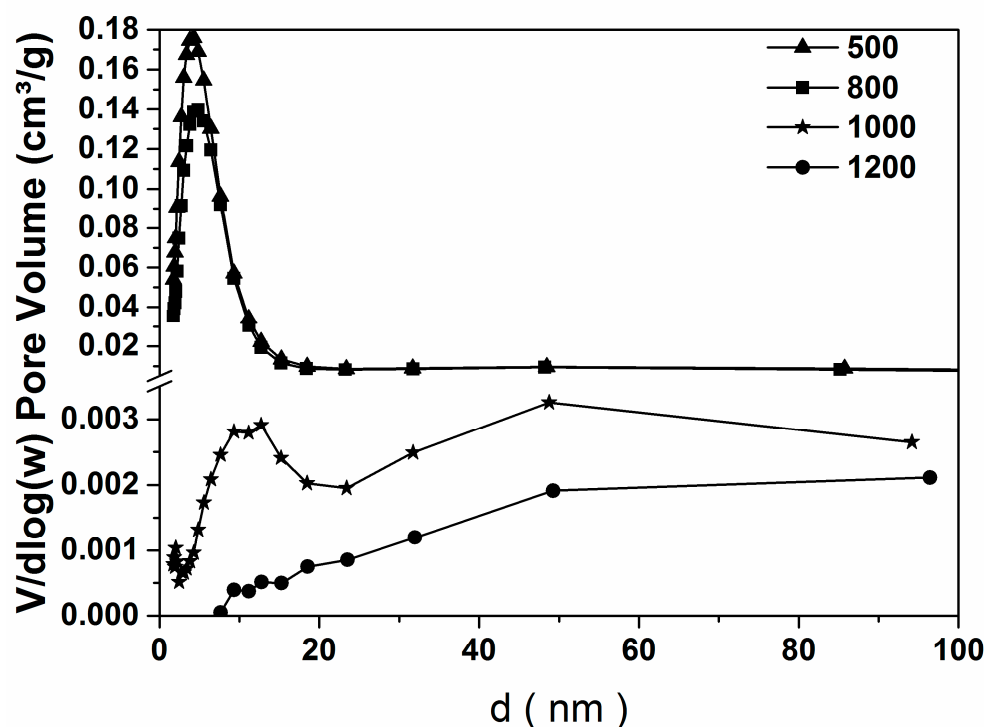


Figure 9. Size distribution of meso- and macro-pores of studied gel samples.

Based on specific surface determination, the most reactive and of course the best one for further application was evaluated a sample calcined at 500 °C. Because of that, not only phase analyses but also its density was measured at a value of $2.32 \text{ g}\cdot\text{cm}^{-3}$.

3.4. Efficiency Verification of Developed Binder

The application ability of a prepared bonding system was verified in bauxite high-temperature concrete, into which our product was applied. Related to the initial parameters of a commercial binder, the sol-gel product was also treated by grinding and sieving under $45 \mu\text{m}$ after drying and calcination at 500 °C.

Concrete samples were evaluated especially according to compressive strength. Testing was performed on an LLB1 hydraulic press (Brio Hranice s.r.o., Hranice, Czech Republic) according to the standard ČSN EN 1402-5.

The values of individual properties proved the bonding ability of the gel; however, comparable properties were not achieved such as in the case of the use of the calcium aluminate cement. Therefore, the use of binder in gel form (as well as powder form after its thermal treatment) was abandoned. Consequently, a variety of sol binders (liquid form) were tested. This variety was tested successfully. From the view of mechanical properties, an example of bonding ability can be given on a mix prepared from sol binder and bauxite with the size of particles below $160 \mu\text{m}$, where the compressive strength was measured as 42 MPa. Compared to the same sample prepared with CAC instead of sol, the measured compressive strength was 44 MPa. Table 3 below demonstrates the difference in the compressive strength that was reached by samples with all three types of concrete (with various binders—CAC, powdered gel, liquid sol). The table shows the resulting average value from seven sample pieces of each set. The reason why a powdered form of sol-gel reaction product did not fill expectations is still under investigation. It is probable that its sintering occurred earlier than the powder could become a part of concrete structure. Compared to that, it can be stated that very small particles in colloidal solution will react in shorter distances willingly and easily at much lower temperatures before sintering.

Table 3. Compressive strength of concrete samples with various type of binder.

Type of Binder	Compressive Strength (MPa)	Standard Deviation
CAC	44	2.49
Powdered gel	13	3.15
Liquid sol	42	6.16

4. Conclusions

In the presented research it was proved that the sol-gel method is suitable for the preparation of a silica–alumina system which can substitute conventional cement in high-temperature concrete. The newly developed product was characterized by various methods such as chemistry, mineralogy, specific surface or high-temperature behaviour. The changing properties of the product with increasing temperature were recorded and described. The efficiency of new product was tested on high-temperature concrete which commonly uses cement as a binder. Finally, different forms of sol-gel product next to cement-based concrete were tested and compared according to their compressive strength.

The achieved results showed that a newly developed product is chemically defined as silicate–aluminium, with a ratio of S/A 59/41 wt.%. According to the mineralogy of the system, the product showed amorphous character up to 800 °C, the formation of mullite was recorded from 1000 °C and higher and the formation of corundum later was from 1200 °C and above. The temperature of the formation of final minerals was reduced significantly. A 500 °C temperature of calcination provided a product with amorphous structure and with high enough and thus reactive specific surface.

The prepared silicate–alumina system was tested in powdered and liquid form as a binder in bauxite-based high-temperature concrete. The bonding ability of both forms of the sol-gel product was verified. However, only the liquid form (sol) proved competitiveness compared to the cement effectiveness that the measured values of compressive strength declared. Cement-based concrete showed a compressive strength value of 44 MPa, the powdered form of sol-gel product displayed only 13 MPa, and 42 MPa was the determined value in the liquid form of the sol-gel product.

To summarize the paper, it can be stated that the use of the sol form of binder (liquid form) was proven as more effective. The use of sol as a binder primarily brought about a reduction in the necessary amount of mixing water and a decrease in the temperature of formation of the required minerals—mullite and α -corundum, simplifying the thermal treatment process of high-temperature concrete, and it also led to a reduction in the decrease in product strength at middle temperatures.

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