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85 years of the Department of Silicate Technology at Kaunas University of Technology

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The Department of Silicate Technology of the Faculty of Chemical Technology of KTU has been training specialists for the Lithuanian binder materials, ceramics and glass industries for 85 years. During that long period, there have been various periods, but the core values have remained – a benevolent attitude towards students and efforts to meet their expectations, respectful relationships between colleagues, and openness to new developments and innovations. Our primary mission is to prepare a new, highly moral and well-educated generation of Lithuanian engineering intelligentsia. At the same time, we understand very well that we must convey to our young colleagues all technological innovations and scientific achievements in our field. This would be impossible to do if comprehensive fundamental and applied research were not carried out, and novelties and innovations were not absorbed.

The past 15 years have been an intense period in the life of our department. During this period, many changes have taken place – study programs have been significantly restructured, the instrumental base of science and studies has been substantially updated, national science and studies projects have been intensively implemented, scientific services have been provided to industrial enterprises, and international cooperation has been developed.

This review presents the main research topics carried out by the department staff over the past 15 years, the main research topics and results obtained, cooperation with Lithuanian industry and international partners, and the evaluation of the department's colleagues for science and studies activities.

Keywords: Department of Silicate Technology, cement chemistry, supplementary cementitious materials, synthesis of calcium silicates and their hydrates, CO_2 utilisation

INTRODUCTION

Studies

The teachers of the Department of Silicate Technology are responsible lecturers (supervisors) of almost 40 modules of the Chemical Technology Faculty and conduct theoretical and practical classes for students of all 3 study cycles and all study programs of the faculty. However, the main program in which our lecturers work has remained Chemical Engineering. It should be noted that for almost 15 years now, there has been no separate branch of Silicate Technology in the 1st cycle (bachelor's) and it has been combined with the specialisation of Inorganic Materials Technology.

For several decades, the department staff has been actively preparing and publishing new textbooks (3 pcs) and educational books (19 pcs). In recent years, the need has decreased slightly, because most of the study literature has already been prepared and is not yet outdated, and textbooks are also used in master's and doctoral studies in English. In any case, practically every module coordinated by the department staff is fully equipped with study literature in Lithuanian. In our opinion, this

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is important, because students can study in their native language, while contributing to the maintenance and nurturing of the vitality of Lithuanian technical and engineering terminology. Recently, with the increasing number of foreign students, great attention has been paid to the preparation of study literature and other methodological materials in English.

We try to use all opportunities to involve as many students as possible in scientific research, to familiarise them with the research conducted at the department and to allow them to experience the taste of a scientist's career for themselves. Our students successfully participate in the Lithuanian Academy of Sciences' (LAS) Higher School Student Research Paper Competitions, and over the past year, 9 graduates of the department have become laureates. Over the past 15 years, as many as 48 students, who were supervised by lecturers from the Department of Silicate Technology, have participated in the Student Summer and Student R&D Capabilities Education Programmes funded by the Lithuanian Science Council (LSC), winning the competitions. Those studies not only enriched the participants' academic knowledge but also provided practical skills that were useful both in their further scientific careers and contributed to the progress of science in Lithuania. A significant number of students who participated in this programme later chose to study at our university for master's and doctoral studies, and some of them are now academic staff members of the department.

In 2010–2025, 131 bachelor's and 77 master's theses were defended which were led by the department's lecturers. It should be noted that the topics for the final theses are suggested by the academic staff of all departments and students are given complete freedom to choose both the topic of the final theses and the supervisor.

Doctoral studies

In 2011–2025, 22 doctoral students defended their doctoral dissertations in the department. Only one student did not complete her doctoral studies. They were supervised by 5 lecturers of the department: prof. K. Baltakys – 11, prof. R. Šiaučiūnas – 6, prof. R. Kaminskas – 2, assoc. prof. A. Eisinas – 2 and assoc. prof. Z. Valančius – 1. Currently, 10 doctoral students are preparing doctoral dissertations in the department. Three young Doctors of science of the department won the competitions 'Promotion of Post-doctoral Internships' under the LMT measure 'Postdoctoral Internships'. Three professors of the department are chairmen or members of the KTU Doctoral Committees of the scientific fields of Chemical Engineering, Civil Engineering and Measurement Engineering. In 2011–2025, the department's teachers participated in the work of 78 Public Defence Commissions for doctoral dissertations not only at KTU, but also at VU, VGTU, VDU and RTU. This testifies to the fact that scientists from all major Lithuanian universities fully trust our scientific and expert qualifications.

Scientific research

Over the past 15 years, the staff of the Department of Silicate Technology have published 4 monographs (1 by the international Springer publishing house, the other by national ones), registered 2 patents with the EPO Patent Office, and 5 patents with the State Patent Office of the Republic of Lithuania.

The department staff is actively preparing applications for LSC, the EU Structural Funds Human Resources Action Programme and the European Social Fund competitions. We can be proud that quite often the submitted applications received funding, which allowed us to significantly strengthen the scientific qualifications of researchers, prepare publications for high-ranking journals, involve young researchers in scientific activities and purchase modern equipment. Over the past 15 years, 3 international, 13 national and 6 institutional projects have been won. In 2011–2025, 182 articles were published in journals indexed in the Clarivate Analytics Web of Science database with a citation index (JCR SCIE), 41 articles in the peer-reviewed materials of international scientific conferences, 322 conference abstracts in publications of international databases. 6 employees of the department are experts in international and national programs. Four employees of the department are members of the editorial boards of 18 international scientific journals or Executive Guest Editors (*Journal of Thermal Analysis* and *Calorimetry and Ceramics International*). In 2011–2025, 11 employees of the department and doctoral students received as many as 44 international, national or institutional awards for their scientific achievements. Prof. R. Šiaučiūnas is a full member of the LAS, and

Assoc. Prof. A. Eisinas and Assoc. Prof. T. Dambrauskas are members of the LAS Young Academy.

Cooperation with scientific and educational institutions

The department closely cooperates with departments of VU, VGTU, LSMU, VDU, KU, FTMC and LEI in related fields, as well as with foreign partners – Technical University of Munich (Germany), Lehigh University (USA), Swiss Federal Laboratory for Materials Science and Technology EMPA, Bratislava and Brno Universities of Technology (Czech Republic), Riga Technical University (Latvia), University of Bologna (Italy), University of Split (Croatia), University of Craiova (Romania), Royal Swedish Institute of Technology (KTH), University of Palermo (Italy), University of Aveiro (Portugal), and others. Joint articles have been published in international journals and presentations have been made at conferences with scientists from these institutions in France, the United Kingdom, Ireland, Finland, Spain, Italy, Croatia, Malta, Romania, Poland, Slovakia, Slovenia, Latvia and Lithuania, and students are exchanged under the ERASMUS program. Over the past 5 years, the department's staff has given 18 lectures at 10 foreign universities.

Cooperation with industry and business

The Department of Silicate Technology is a technologically oriented university department; therefore, its activities are focused not only on studies, scientific research, but also on maintaining close and professional relations with Lithuanian industrial enterprises and business. The cooperation developed over many decades allows us to stay connected with real life, get acquainted with innovations and equipment introduced in industry, helps students find attractive internships and, ultimately, get a job and start their professional career. Over the past year, particularly close and professional relations have been established with AB Akmenės cementas (a member of the German concern Schwenk Zement Beteiligungen GmbH group), AB Silikatas, UAB Kauno stiklas, UAB Bauroc, UAB Stikloporas, AB Achema, AB Lifosa, UAB Ecostone Solutions, Heidelberg Materials Research Laboratory LT, UAB Panevėžio stiklas, and many others. Over the past 10 years, 9 scientific, technological and experimental development works, and 47 R&D services have been performed on behalf of industry.

Outreach activities

Work with gymnasiums and general education schools

The department's staff actively contributes to the popularisation of science and studies among students. In 2019–2020, 4 teachers participated in the science popularisation project 'THINK', during which they visited more than 25 Lithuanian educational institutions, presenting natural sciences and study opportunities at the Faculty of Chemical Technology of KTU. Since 2017, our staff has been giving distance lectures to students to commemorate Earth Day or on other topics, contributing to the implementation of the 'Researchers' Night' and 'Spaceship Earth' activities, actively participating in study fairs or career days organised in schools, and conducting laboratory work aimed at strengthening the practical skills of students in grades 9–10. Every year, ~10th grade students from many regional gymnasiums and general education schools in Lithuania come to perform these tasks. They contribute to the organisation of Lithuanian and global science Olympiads and the preparation of students for them, for example, the European Practical Science Olympiad. Finally, the department's staff annually prepares articles to popularise science and studies in electronic media and participates in various other studies popularisation activities.

EXPERIMENTAL PART

Instrumental analysis

Raw materials were dried in a Kambič S-25C (Slovenia) dryer, burned in a Nabertherm LV150K 1SN (Germany) furnace, mixtures were prepared using a Fritsch crusher (Germany), a Fritsch Pulverisette 9 planetary mill (Germany) and a WAB T2F homogenizer (Switzerland). The chemical composition was determined using an XRF spectrometer Bruker S8 Tiger WD (Germany), the granulometric composition was determined using a laser device Cilas 1090LD (France), the surface area by the Blaine method with CE091 (Germany), and the density by a pycnometer Ultrapyc 1200e (USA).

The mineral composition was determined by XRD with a Bruker X-ray D8 Advance (Germany) for quantitative evaluation, supplemented by Rietveld refinement (Diffrac.Topas 4.2), and the nature of the bonds was determined by FT-IR with a PerkinElmer FT-IR Spectrum (USA). Thermal transformations were studied with a STA analyzer Linseis PT1000 (Germany) and a DSC calorimeter Netzsch DSC 214 Polyma (Germany). Calcium silicate hydrates were synthesised in Parr Instrument autoclaves (USA, models 4621 and 4751). The specimens (EN 196-1) were formed with a Controls L12 shaker (Italy) and cured in an automatic climatic chamber Rumed 3001 (Germany), and in a CO_2 environment, in a Parr Instrument 4555 reactor (USA). The mechanical properties of the samples were determined with a FORM+TEST MEGA 10-400-50 press (Germany), the linear and volumetric shrinkage with a Linseis 75PT 1600 dilatometer (Germany), their operating temperature in a Nabertherm LHT 08/16 furnace (Germany, up to 1600°C), and the pore volume and shape by the BET method with a Costech Instruments KELVIN 1042 (Italy). The porosity and pore size distribution of the samoles were measured by the Mercury porometry method with AutoPore III, Micrometrics (USA). Laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS) was performed using an ESI NWR 213 (ESI New Wave Research, USA) laser providing 10 lines, each 60 μm wide and 20000 μm long, and a NexION 300D Perkin Elmer (USA) spectrometer with the NexION ICP MS software. Solid-state ^{29}Si NMA analysis was performed using a Bruker Advance 300 spectrometer (Germany). The latter 3 studies were performed at the Technical University of Munich. The heat flux released during hydration was measured using a TAM Air III calorimeter (USA), and the frost resistance and abrasion were measured according to the standard EN 1338:2003+AC:2006. The CO_2 content was determined using an automatic calcimeter FOGL (Greece). SEM and TEM studies were performed at Center for Physical Sciences and Technology (Vilnius, Lithuania) with a Helios Nanolab 650 FEI.

RESULTS AND DISCUSSION

A brief overview of scientific research conducted in the Department of Silicate Technology in 2015–2025

The main research topics are the development of alternative binding materials for Ordinary Portland cement (OPC); the research and application of various technogenic and natural raw materials in silicate systems; modern hydrothermal, microwave and high-temperature synthesis processes, which include the peculiarities of the formation of silicate and related materials; research on their properties, structure and use in advanced production technologies of low carbon dioxide emissions and energy consumption cements and other functional inorganic products.

In this topic, the main attention is paid to the study of the topics listed below.

Topic 1. To increase the reactivity of calcium silicates and the stability of their active forms by mechanochemical-thermal activation and to obtain a new promising hydraulically hardening binding material – nanocement from calcium silicate hydrates.

It was found that the precursor of this cement – dibasic calcium silicate hydrate α-$Ca_2(SiO_4H)OH$ (α-C_2SH) – can be synthesised both from the reagents CaO and SiO_2, and from natural raw materials – Žemaitkiemis-Stoniškės deposit opoka and Juodžiai deposit chalk marl or Karpėnai deposit limestone and Anykščiai deposit sand. Before use, carbonate rocks must be calcined: a mixture of opoka and chalk marl for 2 h at 825°C, and limestone for 2 h at 1000°C. It was studied that α-C_2SH must be synthesised from all these raw materials in an environment of saturated water vapour at a temperature of 200°C, only the duration of isothermal treatment differs: 8 h from reagents, and 4 h from mixtures of opoka and chalk marl and limestone and sand. It is recommended to additionally add 5% Na_2O to the latter. α-C_2SH is obtained in mixtures with a molar ratio of $CaO/SiO_2 = 1.5–2.0$ [1].

It has been proven that the tribochemical activation of α-C_2SH can provide hydraulic properties, as the hydrogen and Si–OH bonds stabilising the compound are broken. The properties of the product depend on the composition of the α-C_2SH–quartz mixture, the additives used, the grinding method, its intensity, duration and temperature. During the ribochemical activation, the structure of the compound is broken, and crystal water is released, but it remains in the product. For this reason, it must be supplemented with a 0.5 h heat treatment at 450°C. In this way, the nanocement obtained from the α-C_2SH–quartz mixture (optimal component ratio 1:1) has a very good hydraulic activity, and the amount of heat released during the second exothermic reaction (3.01 mW/g) is close to that of OPC (3.62 mW/g), so it can be used to produce a hydraulic binder [2].

The work examined and explained the processes occurring during hydration and identified the resulting compounds. The data showed that nanocement from calcium silicate hydrates is characterised by an intense hydration reaction and its microcalorimetric analysis curves are analogous to OPC. In the initial hydration period, the greater the amount of heat released, the more α-C_2SH is in the mixture, and its duration is ~12 min. During this period, the solution is saturated with Ca^+, OH^- and SiO_4^{2-} ions. The second, induction period is shorter than that of OPC: approximately 46–60 min and 1.5 h, respectively. The acceleration period lasts ~4 h and during this period the maximum amount of heat is released, as the C–S–H phase crystals grow intensively. The intensity of the hydration reaction is directly proportional to the amount of α-C_2SH. The deceleration period is much shorter than that of OPC, approximately 10 and 25 h, respectively. This is due to the fact that the nanocement from calcium silicate hydrates does not contain calcium aluminates and calcium aluminoferrites. Thus, the hardening rate of nanocement from calcium silicate hydrates is ~2 times higher than that of conventional OPC.

It was found that after 3 days of hardening in water, the compressive strength of nanocement from calcium silicate hydrates is 11.5 MPa, and with increasing hydration time, the strength of the samples increases consistently and reaches 24 MPa after 28 days. In accordance with the Standard EN 206:2013+A1:2016, concretes of class C20/25 (medium strength) can be produced from this binder, and their composition should be 25% of calcium silicate hydrates obtained during hydrothermal synthesis (mainly α-C_2SH), 25% of quartz sand ground together with α-C_2SH during tribochemical activation and 50% of standard sand or other analogous filler. This composition corresponds to the standard samples (1 part of binder and 3 parts of filler) used to determine the strength properties of concretes made from OPC [3].

Topic 2. To investigate the suitability of reagents and industrial raw materials (Karpėnai limestone, Žemaitkiemis-Stoniškės deposit opoka, Anykščiai quartz sand, granite grinding waste, and AlF_3 production waste–silica gel) for the synthesis of calcium silicate hydrates, as well as the influence of hydrothermal synthesis parameters on the sequence of compound formation and spontaneity of reactions, their stable state intervals, product purity, dispersity, and crystal lattice parameters.

It was found that of all the SiO_2-containing raw materials mentioned above, the most suitable one is opoka calcined at a temperature of 775°C. When using its mixture with calcined limestone, 1.13 nm tobermorite, xonotlite, α-C_2SH, and other calcium silicate hydrates are formed incomparably faster in a hydrothermal environment (saturated water vapour temperature 180–200°C) than in the CaO and $SiO_2{\cdot}H_2O$ reagent system. In our opinion, the activity of opoka under hydrothermal conditions is greatly influenced by its chemical composition, especially 2.53% Al_2O_3 and 0.83% K_2O. Al^{3+} ions promote mutual reactions between amorphous SiO_2 and CaO, therefore the formation of 1.13 nm tobermorite occurs faster in the early stage of hydrothermal synthesis. K^+ ions accelerate the dissolution of crystalline SiO_2 varieties (quartz, tridymite and cristobalite), destroying the particle surface and increasing the concentration of SiO^{4-} ions. The obtained results provide the prerequisites for producing low-density (120–200 kg/m^3) effective heat-resistant (up to 1000°C) thermal insulation materials from tobermorite and xonotlite [4]. To obtain the target compounds by hydrothermal synthesis, mixtures with a molar ratio $CaO/SiO_2 = 0.83$ and 1.0 were prepared from lime and granite grinding screenings. It was found that 1.13 nm tobermorite is formed quite slowly at 180°C. The situation changes when the synthesis temperature is increased to 200°C, because 1.13 nm tobermorite becomes the dominant compound after 8 h of hydrothermal treatment. Such temperatures and durations are common in the silicate products industry, so granite grinding waste can be used in their production.

It was found that in the $CaO–SiO_2{\cdot}nH_2O–H_2O$ system, when the molar ratio of the mixture $CaO/SiO_2 = 1.5$, α-C_2SH was formed after 24 h at 175°C. Based on TG analysis, it was estimated that ~55% of this compound is formed in the synthesis product.

A positive influence of Na^+ ions on the solubility of quartz in the $CaO–SiO_2–H_2O$ system was established, since its amount decreased significantly after 4 h of synthesis, and after 8 h reacted completely. The Na_2O additive had a significant influence on the formation and stability of intermediate and final products: together with α-C_2SH, a new calcium silicate hydrate – killalaite $Ca_3(Si_2O_7)\cdot 0.5H_2O$ – was formed after 12 h of synthesis. It was demonstrated for the first time that Na^+ ions do not interfere with the crystal structure of α-C_2SH and reduce the temperature of their transition to wollastonite (~50°C). Summing up the results, it can be stated that alkaline additives change the mineral composition of calcium silicate hydrates, as well as the duration of the existence of intermediate compounds and their structure.

Topic 3. Synthesise Ca/Si composite compounds from Lithuanian natural and industrial technogenic raw materials and activate them.

The possibility of using silica gel, a waste product of the aluminium fluoride AlF_3 production process, contaminated with fluoride ions, was investigated. A single-stage synthesis was performed in a temperature range of 800–950°C, while a two-stage synthesis involved hydrothermal treatment of the initial mixture (200°C, 4–72 h) and subsequent calcination of the resulting synthesis products in a temperature range of 800–950°C. It was found that during solid-phase synthesis, the reaction of CaO and silica gel waste mixtures with molar CaO/SiO_2 ratios of 0.75 or 1.0 proceeds slowly, since only a small amount of wollastonite is formed when the mixture is calcined at 950°C.

The products of hydrothermal synthesis of CaO and silica gel waste suspension after 4 h at 200°C were dominated by cuspidin and semi-crystalline C–S–H(I). By extending the synthesis time to 24 h, C–S–H(I) becomes metastable and recrystallises into gyrolite ($CaO/SiO_2 = 0.75$) or 1.13 nm tobermorite ($CaO/SiO_2 = 0.83$). After calcination of the products of hydrothermal synthesis at 850°C, cuspidin remains stable, and 1.13 nm tobermorite recrystallises into wollastonite. The experimental results are confirmed by thermodynamic calculations [5].

A method for producing a prosopite $CaAl_2F_6(OH)_2$ – calcium fluoride CaF_2 target composite under hydrothermal conditions has also been proposed, which differs in that it includes the following steps: a) an initial CaO/Al_2O_3 mixture with a molar ratio from 0.857:1 to 6:1 is prepared; b) the initial mixture is poured with a saturated AlF_3 solution, where the water to solids ratio is ~32:1; c) the resulting suspension is placed in an autoclave and hydrothermal synthesis is carried out at a pressure of 10 bar; d) the suspension is kept at a temperature of 110–150°C at a pressure of 13–15 bar. To implement this patent, an aluminium fluoride solution was produced by AB Lifosa according to the methodology proposed by us [6].

The influence of the pozzolanic activity of the SiO_2 raw material on the synthesis processes of calcium silicate hydrates was also studied. It has been shown that the formation of crystalline calcium silicate hydrates and the sequence of intermediate phases are influenced not only by the activity of the SiO_2 component, but also by other factors. When using mixtures of the highest activity with $SiO_2\cdot nH_2O$, the z-phase $9CaO\cdot 6SiO_2\cdot H_2O$, C–S–H(I) and gyrolite $NaCa_{16}(Si_{23}Al)O_{60}(OH)_8\cdot 14H_2O$ are formed very quickly, which are difficult to recrystallise into a thermodynamically stable mineral – xonotlite. Despite the moderate activity, calcined opoka is an excellent raw material for the synthesis of crystalline calcium silicate hydrates. First, the amorphous SiO_2 contained in it begins to react, followed by tridymite and cristobalite. The combination of different SiO_2 modifications and the balanced content of compounds containing K^+ and Al^{3+} ions in the opoka allows the synthesis of xonotlite and 1.13 nm tobermorite with a very high degree of crystallinity [7].

In order to replace the traditional burning additive, sawdust, in the production of porous CaO/SiO_2 composite compounds with another, but no less effective substitute, the influence of buckwheat hulls and their ashes on the changes in the mineral composition of micaceous fusible clay and the physic mechanical properties of the ceramic body was studied. Buckwheat hulls reduce the glass phase formation temperature in the samples by ~100°C and accelerate the decomposition of the crystal lattice of clay minerals. As a result, anorthite $CaAl_2Si_2O_8$ begins to crystallise at a temperature ~60°C lower and its amount in the ceramic body increases. Buckwheat hull ash promotes the formation of leucite $KAlSi_2O_6$. These changes in the mineral composition, among other factors, have a positive effect on the compressive strength of the samples. Buckwheat hulls can be successfully used in the production of porous ceramic products, since the technological process does not change, and the compressive strength values are close to or even better than those of samples without additives [8].

Topic 4. In order to reduce CO_2 emissions, the synthesis characteristics of hydraulically inactive, but hardening calcium silicates or their hydrates in a CO_2 environment and the physical and mechanical properties of cement stone and concrete obtained from them should be investigated.

For the synthesis of anhydrous calcium silicate, rankinite binder, a stoichiometric ($CaO/SiO_2 = 1.5$) mixture of local raw materials – opoka and burnt limestone – was used, and the firings were carried out in a temperature range of 900–1275°C. The optimal conditions for the synthesis of nano-sized rankinite are 45 min solid-phase sintering at a temperature of 1250°C. In a range of 900–1100°C, a lot of unreacted CaO and SiO_2 remain. At 1200–1225°C, other Ca/Si composite derivatives with foreign ions intercalated into their structure prevail – larnite, wollastonite, akermanite $Ca_2Mg(Si_2O_7)$ and bredigite $Ca_7Mg(SiO_4)_4$. At a temperature of 1275°C, the mineral composition no longer changes, and later the material begins to melt. Meanwhile, it is recommended to produce wollastonite in a two-stage process – 8 h hydrothermal synthesis of precursors at a temperature of 130°C and their combustion at a temperature of 900°C. It has been established that the rankinite binder is a suitable alternative to OPC cement in the production of very strong and durable carbonised products – the strength of dough samples exceeds 100 MPa. Concrete with a compressive strength of ~45 MPa can be produced from rankinite mixtures with sand. Under the same conditions, the compressive strength of concrete hardened from conventional OPC is lower and reaches ~36 MPa. It was investigated that the degree of carbonation of the samples depends on the binding material layer in the microstructure. Only about 40% of the volume of the binding material particles must be carbonised for the dough sample to reach the maximum degree of carbonation. This is explained by the fact that during carbonisation, a dense layer of reaction products formed on the binder particles hinders further CO_2 diffusion – first, an amorphous SiO_2 ring is formed, and then a $CaCO_3$ layer is formed, which fills the pores, densifies the microstructure and thus affects the increase in compressive strength [9].

The synthesis temperature of rankinite is 1250°C, and wollastonite precursors are burned at ~900°C. Thus, the formation temperature of anhydrous calcium silicates is quite high. In order to avoid this operation, we conducted research to produce concrete hardening in a CO_2 environment, in which the binding material would not be anhydrous calcium silicates, but their hydrates synthesised under hydrothermal conditions. To our knowledge, no one in the world has yet studied this. It has been shown that α-C_2SH, as well as its mixture with kilchoanite, are binding materials that harden in a CO_2 atmosphere [10]. They were synthesised from lime-burnt opoka mixtures (molar ratio $CaO/SiO_2 = 1.5$) at 200°C within 8–16 h. The pressed samples were treated in a CO_2 gas environment at a pressure of 1.5 MPa and a temperature of 45°C for a period of 8 to 48 h. After 8 h of curing, the compressive strength of the samples was ~10 MPa. With increasing treatment time, it consistently increased and reached ~35 MPa after 24 h, and ~60 MPa after 48 h. The majority of α-C_2SH carbonises within the first 8 h. Subsequently, the amount of $CaCO_3$ formed gradually but consistently increases up to 48 h. SEM and ^{29}Si solid state nuclear magnetic resonance have shown that the strength gain is more influenced by the growth of calcite crystals than by the polymerisation of SiO_2. In accordance with the Standard EN 206:2013+A1:2016, from these binders and a standard sand mixture (component ratio 1:3), it is possible to produce C20/25 class (medium strength) concretes. Compared to OPC products, the production of concrete from α-C_2SH or its mixture with kilchoanite has a significantly lower negative impact on the environment: CO_2 emissions, energy and fuel consumption are reduced, CO_2 is combined in the concrete structure in the form of stable carbonates. It should be noted that the more kilchoanite in the mixture, the less CaO is needed for the synthesis of the binding material, and at the same time, carbonate rocks.

So, it can be stated that alternative to OPC binders for the production of high/medium-strength durable carbonised concretes can be obtained from rankinite, wollastonite, α-C_2SH and kilchoanite. By isolating CO_2 in the form of stable carbonates in their structure, the emission of these gases is significantly reduced. Non-traditional layered Ca/Si composite compounds, kilchoanite and hydroxyledgrevite, as well as α-C_2SH and wollastonite, due to their structural features, can be used as adsorbents for the removal of heavy metal ions, catalysts in the oxidation reactions of organic compounds, fillers in the production of plastics and other areas.

Topic 5. To investigate the influence of supercritical and gaseous CO_2 on the hardening mechanism of calcium silicates, the distribution of chemical elements in the resulting stone, its structure and properties.

The process of carbonisation of a rankinite binder with supercritical CO_2 was investigated. Samples formed from the resulting rankinite binder and sand mixture were cured in a CO_2 environment using gaseous (5 and 50 bar) and supercritical (100 and 150 bar) CO_2 at temperatures of 20 and 50°C. When curing the samples with supercritical CO_2, the samples achieved a similar strength as those cured with gaseous CO_2. For this reason, it can be stated that carbonisation under supercritical conditions is economically unprofitable.

Continuing the study of the carbonisation process of the rankinite binder, the conditions for curing in a CO_2 gas environment were optimised. The influence of these parameters was studied – CO_2 pressure, duration, temperature, compaction, water/binder and binder/sand ratios. It was found that the strongest samples were obtained by curing for 24 h at a temperature of 45°C at a CO_2 pressure of 15 bar when the water/binder ratio was 0.25 and the binder/sand ratio was 1:3. The strength of the samples cured under those conditions exceeded 45 MPa.

After performing the XRD analysis, it was observed for the first time that samples consisting of only the binding material and a mixture of the binding material and sand, carbonise differently – different polymorphic varieties of $CaCO_3$ are formed. In samples consisting of only the binding material, three varieties of crystalline $CaCO_3$ were identified, i.e. calcite, vaterite and aragonite, and in samples consisting of a mixture of the binding material and sand, only calcite. In samples consisting of a mixture of the binding material and sand, the density of the structure is lower, and the binding material particles cover the surface of the sand particles with a significantly smaller layer. In samples with sand, the binding material requires more water during the hardening reaction, because quartz (sand) particles do not participate in the reaction. It is also assumed that quartz itself, which, like calcite, belongs to the trigonal crystal shape class, may have a significant influence on the formation of carbonates, and therefore determines the formation of this stable polymorphic variety of $CaCO_3$.

The carbonisation kinetics of the rankinite binder was studied by varying the carbonisation duration from 2 to 48 h and the temperature from 25 to 55°C. It was found that the strongest samples were those cured at 45°C for 24 h – more than 100 MPa. After conducting studies of the microstructure and mineral composition of the specimens, it was found that the samples cured for 24 h and longer at a temperature lower than 35°C were completely carbonised, and the formed carbonates were evenly distributed in the cross-section of the specimens. These results are consistent with the compressive strength results, which indicate that the strength of samples cured for a shorter time or at a lower temperature is lower.

It was observed that the strength of the samples is determined not only by the formation of carbonates, but also by the degree of polymerisation of the relaxed amorphous SiO_2. By ^{29}Si nuclear magnetic resonance has been found that by extending the treatment time to 24 h, the polymerisation of silica gel increases almost twice – the Q^3/Q^4 ratio, which characterises the polymerization of SiO_2, decreases.

After performing the chemical analysis of the samples using laser ablation with inductively coupled plasma mass spectrometry, as well as SEM studies, it was observed that the carbonisation process occurs in two stages – the formation of an initial layer of carbonates on the surface of the particle and diffusion into the inner layers. When the layer of reaction products reaches a certain thickness, further reactions proceed very slowly or stop completely, because CO_2 can no longer penetrate through the dense layer of products and reach the unreacted part. Thus, although conventional instrumental analysis methods indicate that the sample is completely carbonised, in fact, only ~40% of the particle volume has reacted. It has been established that the layer of binder particles in the microstructure of the sample determines the course and degree of carbonisation. For this reason, mixtures of binder and sand carbonise more easily and faster, because here the binder particles cover the sand particles with a thinner layer – forming a lower density microstructure, which facilitates the carbonisation process [11].

The main technological property of cement pastes or pressing powder is the water content in it. It was found that by increasing the water/binder ratio w/c in the moulding mixture from 0.15 to 0.25, the compressive strength of rankinites samples hardened in a CO_2 environment increases almost twice – from ~24 to ~45 MPa. With a further increase in the w/c ratio, the compressive strength of the samples begins to decrease consistently and at w/c = 0.4 it drops to ~23 MPa. In contrast, the compressive strength of OPC sample increases consistently up to w/c = 0.35 but remains lower than that of rankinite – the maximum value is ~41 MPa. Determining the optimal moisture content of the moulding mixture is very important, because when it is too low, it is difficult to form high-quality samples, and the carbonation rate also decreases, because there is not enough water in the pores to form a sufficient amount of carbonic acid. When the moisture content of the mixture is too high, the carbonation rate also decreases, because CO_2 diffusion through pores completely filled with water is difficult. It has been determined that the optimal w/c = 0.25 for the rankinite binder, ensuring excellent technological properties and saturation of the pores for the carbonation reaction.

When studying the influence of technological parameters on the physical and mechanical properties of concrete hardened in a CO_2 environment, it was found that all of them, i.e. binder/sand ratio, water/binder ratio, specimen pressing pressure, CO_2 pressure, carbonation duration and temperature, have their own optimal values, under which the strongest concretes are obtained. Concrete with the highest compressive strength exceeding 45 MPa was obtained under the following conditions: ratio of rankinite binder/sand 1:3, water/binder ratio 0.25, samples forming pressure 12.5 MPa, CO_2 pressure 15 bar, carbonation duration 24 h and temperature 45°C. Under the same conditions, the compressive strength values of concrete hardened from OPC are lower and amount to ~36 MPa. The presence of Mg-impurities in raw materials on the synthesis of rankinite clinker and the strength of mortar hardening in CO_2 environment has a negative impact [12].

An equally important performance characteristic of concrete is its durability. It is usually assessed by the number of freeze-thaw cycles. It has been established that the frost resistance of concrete made from a rankinite binder is significantly higher than that of OPC: after 100 freeze-thaw cycles, the mass loss of its samples did not exceed 1 g/m^2, while that of those made from OPC was 5.6 g/m^2. Additionally, durability was assessed by performing an abrasion test using corundum as an abrasive, and it was established that the width of the groove formed after 70 cycles was less than 20 mm. All these indicators not only meet, but also significantly exceed the requirements of the EN 1338:2003+AC:2006 standard.

In order to use wollastonite as an alternative binding material, the process of its solidification in a CO_2 environment was studied. The compressive strength of the samples increases with increasing the amount of binding material in them, the forming pressure, and the duration of curing in a CO_2 environment at a pressure of 15 bar and a temperature of 45°C – after 24 h it reaches 18.3 MPa. The degree of carbonisation consistently increases with increasing the duration of CO_2 treatment and reaches 100% after 24 h. Significant amounts of cuspidin $Ca_4Si_2O_7F_2$ were identified in all calcined hydrothermal synthesis products together with wollastonite. After treatment of pure cuspidin in a CO_2 environment, it was determined (to our knowledge, for the first time) that it reacts with these gases, forming calcite, vaterite and fluorite. Thus, the waste product of AlF_3 production, silica gel, can be used to produce a binding material that hardens in a CO_2 environment, since both main minerals formed during the two-stage synthesis, wollastonite and cuspidin, participate in the carbonisation process.

Topic 6. To propose a *new method for producing anhydrous calcium silicate – kilchoanite – under hydrothermal synthesis conditions.*

It was previously known that kilchoanite $Ca_3Si_2O_7$ with a small amount of other calcium silicate hydrates could be prepared only using finely ground quartz and at high pressure (50–100 MPa) and temperature (280–600°C). The department's researchers synthesised this compound by hydrothermal synthesis at a temperature of 200°C within 24 h, and its purity after 48 h reaches as much as 96%. When studying the crystallisation of calcium silicates and their hydrates in a mixture with a molar ratio of CaO/SiO_2 = 2.25 (200°C; 4–72 h), a compound previously found only in nature was synthesised for the first time – hydroxyledgrevite $Ca_9(SiO_4)_4\cdot(OH)_2$, the purity of which exceeded 93% [13]. The temperature and duration limits of the existence of this compound have been determined, the sequence of formation of intermediate compounds has been studied. A method for the synthesis of an environmentally friendly binder, the compressive strength of which after 28 days of hydration (24 MPa) meets the requirements for belite and special low-temperature cements, has been proposed.

It has been proven that synthetic calcium silicate hydrates – α-C_2SH and hydroxyledgrevite – are mesoporous materials, while calcium silicate – kilchoanite – is a non-porous solid. It has been studied that heat treatment has a significant effect on the structure of α-C_2SH, hydroxyledgrevite and kilchoanite samples, since after burning not only the specific surface area decreases, but also the shape of the pores and crystals changes [14].

The influence of heavy metal ions (Cd^{2+}, Zn^{2+}, etc.) and hydrothermal synthesis parameters on the crystallisation processes of phyllosilicate group compounds has been studied. The influence of heavy metal ions introduced into the structure of calcium silicate hydrated on their texture and specific surface area, pore volume and their distribution by radius, crystal size and shape has been studied. Optimal values of technological parameters have been proposed.

Samples of calcium silicate hydrates with disordered and ordered crystalline structures ($CaO/SiO_2 = 1.5$) were synthesised and it was found that they can be used as chemo sorbents for the removal of Cu^{2+}, Co^{2+} and Cr^{3+} ions both in adsorption processes and during hydrothermal synthesis [15]. The synthesised and fired samples with intercalated ions of the mentioned metals can be used as catalysts in propanol oxidation reactions, since at temperatures below 175°C the compounds function as adsorbents, and at higher temperatures catalytic oxidation occurs.

It was found that the waste from AlF_3 production – silica gel modified using the constant water flow technology – is suitable for use as a mineralizer. However, this leaching technology is a complex process, since F^- ions can be removed from silica gel (up to 5%) only with a very large excess of water (when the water/solids ratio is >100). For this reason, a method for the hydrothermal synthesis of calcium silicate hydrates has been proposed, combining the utilisation of the waste from AlF_3 production – silica gel and the immobilisation of F^- ions in stable synthesis products. A technology for the neutralisation and (or) utilisation of this waste using compounds containing a calcium component has been developed, according to which the concentration of fluoride ions in silica gel can be reduced to 1.5% and the yield of the target product (aluminium fluoride) can be increased [16]. It has been proven that by changing the processing conditions (static, dynamic and mechanical activation) and alkaline compounds (NH_4OH, $Ca(OH)_2$, NaOH and Al_2O_3) it is possible to reduce the concentration of fluoride ions in the silica gel from 8.0 to 1.5%. It has been established for the first time that in the liquid medium separated by mechanical treatment or washing with alkaline solutions from the waste of AlF_3 production – silica gel, compounds containing Al^{3+} and F^- ions – aluminium fluoride, calcium fluoride and/or katoite $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ (where $x = 1.5$) crystallise. Based on the results obtained, additional equipment was installed in the industrial aluminium fluoride production line of SC Lifosa, and production tests were carried out.

Topic 7. The possibilities of using secondary products and waste generated during the production of various products.

When examining the use of phosphogypsum in the production of white water-based emulsion paints, it was found that it cannot fully replace TiO_2. An extended investigation with lime-modified phosphogypsum demonstrated that it may positively affect the quality of the paint not only by increasing such important characteristics as the pH of the paint medium, its gloss, whiteness, coverage, viscosity and density but reduced the film formation time, thereby protecting the substrate from external attacks and damage. It is noteworthy that this additive allows a 40% reduction in the amount of TiO_2 in the paint, while still maintaining a higher quality than that of the reference sample [17].

The following technogenic products as supplementary cementitious materials were examined in detail: waste from the edible oil bleaching process – smectite clay (SCW), waste from biofuel combustion in boilers – fly ash (FA) and waste from expanded clay production – expanded clay combustion dust (ECD).

It was determined that SCW consists of montmorillonite, quartz, anorthite, calcium sulphate and an amorphous phase. The pozzolanic activity of SCW is 117 mg CaO/g. Thermal activation of

SCW samples at 600°C increases their pozzolanic activity threefold. The activated SCW additive accelerates the hydration of calcium silicates, since an intensive pozzolanic reaction occurs in OPC samples with the SCW additive. Up to 15% by weight of OPC, without reducing its compressive strength class, can be replaced with a SCW additive calcined at 600°C [18].

A new method of processing FA formed during biofuel combustion is proposed – hydrothermal synthesis. The CaO/SiO_2 molar ratio in FA varies from 0.67 to 1.56. It mainly contains heavy metals Ti, Zn, Mn and Ba, and the concentration of carcinogenic elements (chromium, nickel, cobalt and lead) is small and fluctuates within 0.03% – 21.2 ppm. The optimal parameters of curing have been determined: CaO/SiO_2 = 1.0 and 1.5, temperature 200°C, time 2 h. The resulting product consists of calcium silicate hydrates, hydrogarnets, quartz and calcite. The heavy metals present in the fly ash are stable and practically insoluble, and during hydrothermal synthesis, mainly non-toxic components – SO_3, K_2O, Na_2O and CaO – pass into the liquid medium. The synthesised additive accelerates the initial hydration of OPC by acting as crystallisation centres. The composition of the liquid medium of the samples with additives, in which the samples were cured for 28 days, does not differ from the composition of the OPC medium without additives, which confirms that all heavy metals are immobilised in the structure of the synthesis products. FA after their hydrothermal treatment can replace 5–10% of conventional OPC and thus sustainably use a large part of this waste [19, 20].

It has been found that expanded clay kiln dust is a suitable cement additive. The dust collected in electrostatic precipitators consists of clay minerals (kaolinite, illite and muscovite), impurities (anorthite, calcite, anastase, quartz, magnesite and olivine) and amorphous compounds. Its pozzolanic activity is 626 mg CaO/g. Thermal activation at 600°C increases the pozzolanic activity and the content of amorphous compounds of ECD. Thermally activated and non-activated additives have a dual effect on OPC hydration – the pozzolanic reaction and accelerated calcium silicate hydration occur simultaneously. When using this production waste in the cement industry, it can replace up to 25% of the OPC mass, with the same amount of CO_2 reduction [21].

CONCLUSIONS

The research staff of the Department of Silicate Technology employs comprehensive experimental and theoretical studies in silicate and cement chemistry. The methodological framework is grounded in chemical engineering, materials science and environmental engineering, aiming to generate both fundamental insights and applied outcomes relevant to sustainable chemical technologies.

Over the past few decades, our department has accumulated extensive experience in the synthesis, identification and application of calcium silicate hydrates and their derivatives with other inorganic oxides, characterised by targeted and controlled properties, in the development of innovative products – heat-resistant insulating materials, adsorbents, catalysts, fillers for plastics, and others.

An important research topic in the last decade has been the use and development of alternative binders with a lower CO_2 footprint compared to conventional cement. The influence of accelerated carbonation parameters on the hardening kinetics of non-hydraulic calcium silicates and blended cements, the physical and mechanical properties, durability of the resulting concrete products, the mineralogical composition, structure and the amount of absorbed CO_2 is being investigated.

An equally important area of research is the development of environmentally friendly, sustainable binding materials, and the processing of waste and by-products into supplementary cementitious materials.

We also want to mention that scientists from other Lithuanian Universities and Science institutions do not study the previously mentioned research topics.

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Raimundas Šiaučiūnas

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