

Paweł Pichniarczyk, PhD

Institute of Ceramics and Building Materials

Cementowa 8, 31-983 Kraków

COVER LETTER

PRESENTING SCIENTIFIC ACHIEVEMENTS, ESPECIALLY SPECIFIED IN THE ART. 16, PARA. 2 OF THE ACT OF 14 MARCH 2003 LAW ON ACADEMIC DEGREES AND TITLE AND DEGREES AND TITLE IN THE ARTS

1. First name and last name: **Paweł Pichniarczyk**

2. **Diplomas and scientific degrees - giving the name, place and year of obtaining, the title of the doctoral dissertation and names of people who performed the functions of the supervisor and reviewers.**

Doctor in technical sciences, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Discipline: Chemical Technology, 2000,

Dissertation: „**Hydrophobization of light, porous pastes from synthetic gypsum, obtained in the process of flue gas desulfurization**”

Supervisor: dr hab. inż. Stanisław Peukert, prof. IMMB

Reviewers: prof. dr hab. inż. Jacek Śliwiński, dr hab. inż. Jerzy Dyczek, prof. AGH.

Master, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Course: Chemical Technology, 1995

Engineer, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Course: Chemical Technology, 1994

3. **Information on previous employment in scientific entities**

Since 1995 - till now

Institute of Mineral Building Materials in Opole, Division in Krakow (currently Institute of Ceramics and Building Materials in Warsaw);

Professional experience:

1995 -2001

- Intern engineer
- Assistant

	▪ Adjunct (2001 – till now)
2001 - 2004	Manager of Gypsum Department, Institute of Mineral Building Materials in Opole, Division in Krakow (currently Institute of Ceramics and Building Materials);
2004 - 2007	Deputy Director of Institute of Mineral Building Materials in Opole (currently Institute of Ceramics and Building Materials) for Research and Development;
2007 - 2010	Deputy Director of Division of Mineral Building Materials in Krakow (currently Institute of Ceramics and Building Materials);
IV.2009 - XII2009	Director of Division of Glass at Institute of Ceramics and Building Materials – delegated by the Director of Institute to carry out the restructuration and modernization of Division of Glass due to the planned merge with Division of Mineral Building Materials;
2010 - 2017	Deputy Director of Division of Glass and Building Materials in Krakow at Institute of Ceramics and Building Materials;
2017 - 2018	Director of Division of Glass and Building Materials in Krakow at Institute of Ceramics and Building Materials;
2018 - till now	Director of Institute of Ceramics and Building Materials in Warsaw.

4. Indication of the scientific achievement obtained after receiving the doctoral degree, constituting a significant contribution to the development of the discipline of construction in accordance with art. 16 para. 2 of the Act of 14 March 2003 Law on Academic Degrees and Title and Degrees and Title in the Arts:

- a) **Influence of selected heavy metal oxides on setting process of cement and its importance in construction** - a habilitation monograph published in 2018 by the Committee of Civil and Water Engineering of the Polish Academy of Sciences, as part no. 98 of the Engineering Studies, ISSN 0137-5393, ISBN 978-939534-2-4
- b) discussion of the scientific goal of the above-mentioned work and the results achieved, together with a discussion of their possible use.

Heavy metals such as zinc, lead, vanadium and copper are retarders of cement setting, which is known at least since 1958. Since then, works on this subject have appeared, which was finally summarized by Neville in his monograph "Properties of Concrete". The importance of these metals for the construction industry is related to the possibility of their occurrence, inter alia, in aggregates,

which can cause interference in the concrete setting processes at the construction site. Therefore, Neville, based on his research, recommends determining the setting time of concrete produced from unknown aggregate to avoid the consequences.

In tests carried out at the Institute of Ceramics and Building Materials, it turned out that in cases of cements to which anhydrite II was added instead of gypsum, zinc may have the opposite effect, relying on a significant acceleration of the cement setting process. In connection with these experimental results, it was necessary to examine the factors determining the influence of the most important heavy metals on the cement setting process in concrete. Understanding these factors will allow to avoid unexpected disturbances in the concrete setting process in the future and thus eliminate the possibility of problems at construction sites. The main purpose of the dissertation was to present the results of investigation on the influence of the most important heavy metals on the Portland cement setting process, which is the binder most often used for concrete production.

The studies undertaken included the influence of three heavy metals, namely lead, vanadium and copper, on the setting process of two Portland cements CEM I 52,5N-SR3/NA and CEM I 52 NA. In these cements anhydrite II is used to regulate the setting. For comparison, classical cement CEM I 42,5R with the addition of gypsum was used. The setting of these cements, without the addition of heavy metals, was also tested to obtain the output data.

The research included mainly the phase composition of pastes from these cements during the setting and concentration of heavy metals and sulfate ions in the liquid phase in these pastes. Experiments led to a number of original results that shed new light on the mechanism of heavy metals influence on the cement setting. The results obtained allowed to draw a number of scientific conclusions, but also important for the construction practice and to propose models describing these processes.

As shown in the studies, the process of cement setting depends to a large extent on the content of tricalcium aluminate and the type of sulfate used, which regulates its course. With normal C_3A content, i.e. around 9%, ettringite is involved in the entire cement setting process and influences the initial and final setting times. For this reason, on the classic schematic of changes in the paste phase composition during this process, proposed by Locher and Richartz, the ettringite content curve should show some increase in the period from one hour to 6 hours. This would be the way to change this scheme based on the results of my experiences.

In the case of cements with the addition of anhydrite II, with the classical composition of clinker, despite the much lower concentration of sulfate ions in the liquid phase of paste, ettringite also crystallizes and its effect is comparable to that of C-S-H. However, the influence of this last phase is dominant. However, as my experience has shown in the case of CEM I 52,5N-SR3/NA special cement,

of low C_3A content, ettringite only affects the final setting time. This is due to the low concentration of not only sulfate ions, but also aluminate ions in the liquid phase in the paste pores.

As shown in the studies, the delaying effect of zinc and lead, or their oxides, on the setting depends on the concentration of sulfate ions in the liquid phase in the cement paste. Normal concentration of sulfate ions typical for gypsum and equal to about 0,7 moles/L causes the delaying effect of both heavy metals: zinc and lead. This delay effect is caused by the formation of a continuous layer of zinc hydroxide, as demonstrated in the case of zinc by Arligu and Grandet and lead sulfate, as demonstrated in my research.

Low concentration of sulfate ions has the opposite effect; it causes acceleration of cement setting in the case of lead and zinc. This very fast setting, lasting about 20 minutes is due to ettringite crystallization, which I have shown experimentally. This is also a proof that in these conditions a continuous ettringite film on C_3A crystals is not formed. This accelerating effect of lead and zinc is different than in the case of vanadium, the addition of which does not prevent the formation of an impermeable film of ettringite on the tricalcium aluminate. Therefore, beginning of the cement setting with the addition of this metal does not change significantly. However, the hydrolysis of the alite is significantly delayed, which causes a significant increase of final setting time. The conclusions from the conducted research can be summarized as follows:

1) the concentration of sulfate ions in the paste liquid phase is the decisive factor that determines the influence of heavy metals on the setting process,

2) decisive role is also played by the dissolution rate of heavy metal oxides, or also those metals in the case of zinc and copper,

3) in the case of low dissolution rate of heavy metals, i.e. their low concentration in the solution during the cement setting period, an impermeable ettringite film is formed on C_3A crystals and the effect of these metals on the initial setting time is negligible. Practically they do not affect the beginning of cement setting. These are cases of vanadium and copper,

4) if this dissolution rate is very low, such a metal also has no effect on the final setting time that will start earlier. It is a case of copper.

Copper has a completely different influence on cement setting compared to other metals tested. Due to the low dissolution rate, it does not prevent the formation of impermeable coatings on C_3A crystals or an alite. Copper, therefore, does not have much impact either on the beginning or on the end of Portland cement setting. Even increasing the concentration of sulfate ions in the paste liquid phase does not cause major changes during the end of the setting.

At the end, it should be repeated that in order to avoid complications in the production of concrete or at the construction site with the setting of concrete, if unknown aggregates are used it is

necessary to examine their influence on the cement setting time. This is what Neville expresses in the introduction to his monograph.

5. Discussion of the applicant's other scientific and research achievements, demonstrating the significant scientific activity of the postdoctoral researcher

I studied at the AGH University of Science and Technology in Kraków, at the Faculty of Materials Science and Ceramics, Chemical Technology, which I graduated in 1995 with a Master's degree. In the same year, I started working at the Institute of Mineral Building Materials, in division in Krakow. For one year I was an intern engineer and in October 1996 I was appointed by the Director of Institute for the position of assistant in the Gypsum Department. At the same time, it was the beginning of my scientific activity, which mainly concerned the possibility of using gypsum from flue gas desulfurization for the production of semi-hydrated calcium sulfate and derivative binders. The results of these works were the content of two two-author publications in Journal Cement Lime Concrete [Cement Wapno Beton, CWB]. Simultaneously, in 1995 I started a five-year doctoral thesis at AGH at the Faculty of Materials Science and Ceramics. At that time, I was also involved in the start-up of the first flue gas desulfurization plant in Poland at the Bełchatów Power Station.

My research continued to use gypsum from flue gas desulfurization for the production of various types of gypsum binders. The results of these experiments allowed me to prepare a doctoral dissertation entitled: "Hydrophobization of light, porous pastes from synthetic gypsum, obtained in the process of flue gas desulfurization". Dr hab. Stanisław Peukert, prof. IMMB was my supervisor and professors Jacek Śliwiński (Cracow University of Technology) and Jerzy Dyczek (AGH University of Science and Technology) were my reviewers. I presented my doctoral dissertation in June 2000 at the AGH to the Council of the Faculty of Materials Science and Ceramics, obtaining a PhD in technical sciences, in the chemical technology discipline. On the basis of this achievement, I was appointed by the Director of Institute to the position of adjunct in July 2000. The results of these tests were used in a building application. In Gdynia, Sewaco Sp. z o. o. built a housing estate of single and multi-family buildings in the technology described in the doctoral dissertation. The walls of these buildings were erected from hydrophobic and porous gypsum blocks, for production of which gypsum from the Flue Gas Desulfurization Installation using the wet lime method from Bełchatów Power Station was used.

At the end of 2000, the Director of Institute entrusted me with the duties of Acting Manager of Gypsum Department. My positively evaluated scientific and organizational activity in this Department prompted the Director of Institute to entrust me with the position of the Manager of Department from January 1, 2001.

It was an extremely difficult time, because Polish mineral building materials industry was completely taken over by western concerns. However, it was possible to establish cooperation with leading companies in this industry (Knauf, Lafarge, Norgips, Rigips) by carrying out research and development, engineering and expert works. The next task that the Director set for me was to prepare the laboratory of the department to obtain the status of accredited laboratory by the Polish Center for Accreditation, which was also achieved after two years.

My doctoral research continued to focus on issues related to the use of gypsum binders in construction. The first, which was published in Cement Wapno Beton (CWB) in 2001, and co-authored with Malata, concerned the influence of the morphology of β calcium sulfate semi-hydrate crystals on the durability of technological properties of gypsum binder. Studies under the scanning electron microscope showed that the crystal size of the β $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ phase in the original samples did not exceed several dozen microns. Short-term grinding up to 5 minutes causes a significant reduction in fluctuations in the properties of gypsum binder. This is due to the removal of surface cracks occurring on the crystals. This causes the stabilization of the properties of gypsum binder, which is very important in the construction industry in case of its use for making gypsum plasters. The more important it was that it was a time of big development of this part of the building materials industry related to the production and use of gypsum finishing materials on a large scale. They gained more and more popularity.

In connection with the above and my numerous contacts with manufacturers of gypsum binders and the implementation of research projects ordered by them, it allowed me to learn about the problems associated with the sale of these products in Poland. On this basis, I developed and published in CWB [issue 5 in 2002, the paper "The Gypsum Market in Poland" [annex 4, p. II A, row 3], which to my surprise achieved very high readership. The difficulty of its development has paid off in full.

Another research concerned the durability of gypsum plasters on a concrete substrate [authors Pichniarczyk, Malata, Sobala, CWB, issue 5, 2002] [annex 4, p. II A, row 4], and it was caused by frequent cases of plasters falling off. One of the reasons is the low porosity of the concrete substrate layer, however, experiments have shown that the application of gypsum plaster should take place under air-dry conditions, and the concrete substrate should be previously "primed". Observance of these principles ensures adhesion of gypsum plaster exceeding 3 MPa and its durability. Appropriate preparation of the concrete substrate allows elimination of adverse chemical and physical reactions at the gypsum-concrete interface, which are related to the crystallization of ettringite, $\text{Ca}(\text{OH})_2$ carbonatization or crystallization of secondary gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. These processes are related to the increase of the crystallization pressure due to the increase in the volume of crystals formed, which leads to the physical separation of the plaster from the concrete substrate.

In 2004, as a result of staff changes at the Institute of Mineral Building Materials, the Director, appreciating my scientific development and organizational skills, appointed me as the Deputy Director of the Institute for Research and Development. In those years I was probably the youngest member of the management in research institutes in Poland. It allowed me to participate in wider research teams implementing other issues related to the industry of mineral building materials.

Subsequent research carried out together with Malata concerned the influence of barium and strontium chlorides on the properties of gypsum products [publication in CWB, issue 2, 2009] [annex 4, p. II A, row 5]. The study investigated the effect of barium and strontium chlorides on the strength of hardened gypsum pastes. As a result of hydrating gypsum samples by strontium chloride, especially in the case of earlier hydrating them with potassium sulfate, the strength of gypsum bars increases and the softening factor increases too. However, barium chloride does not affect the properties of gypsum samples. Both ions form sulfates in gypsum samples: baryte and celestine. Hydrating gypsum bars with K_2SO_4 aqueous solution causes the formation of syngenite, which is located mainly in the surface layer of the samples.

The experiments carried out together with Najduchowska regarding the addition of hydrophobic compounds had a great cognitive significance on the properties of gypsum and cement mortars [the work was published in CWB, issue 3, pp. 141-148, 2010] [annex 4, p. II A, row 7]. They were primarily intended to increase the resistance of gypsum binders and cement mortars to water. The influence of a whole range of silico-organic compounds was investigated. A small addition of these compounds, equal to 0,2% of the binder mass, caused a delay in the reaction of the gypsum with water which was revealed by a shift of initial and final setting time. On the other hand, on the curves of heat of hydration, the prolongation of the induction period and the decrease in the amount of heat. A particularly beneficial influence on the microstructure of gypsum pastes and mortars was obtained by the use of polydimethyl siloxane. As a result of the addition of this admixture, mortars with very low surface wettability and very low capillary water uptake were obtained. These mortars showed reduced absorption and increased resistance to freezing - thawing. On the other hand, the use of a methyl silicone resin solution resulted in a reduction in water absorption and increased strength in the state of full moistening of hardened gypsum pastes, while maintaining favorable physical properties in the dry state. The beneficial effect of this admixture is related to the reduction of the mortar porosity and the change in the shape and size of the gypsum crystals.

One of the research focused on fibrous gypsum composites in a polymer matrix as an alternative to traditional thermal insulation materials. Studies conducted over two years have shown that waste raw materials, including synthetic gypsum, can be used to obtain fibrous gypsum by recrystallization. The composite of gypsum and anhydrite obtained in the solution of sulfuric acid is impregnated by a polymeric binder, mainly silicone resins. The obtained gypsum-polymer materials have properties

comparable to traditional mineral wool. Their density, in the case of the Sil 1 polymer, is equal to $0,20 \text{ g/cm}^3$, while in the case of mineral wool is $0,25 \text{ g/cm}^3$; thermal conductivity with the same Sil 1 polymer = $0,046 \text{ W/mK}$, while mineral wool $0,035 \text{ W/mK}$. The obtained type of mineral wool combines the specifically advantageous properties of gypsum products:

- Thermal and acoustic insulation properties with the possibility of obtaining it at relatively low temperatures of about 100°C , in contrary to existing types of mineral wool, produced at temperatures of $1000\text{-}1400^\circ\text{C}$.
- The possibility of using chemical gypsum in the production of composites, formed as a by-product in industrial processes or in the desulfurization of flue gases. Due to technological reasons, currently the Polish industry is not processing many of these raw materials.

The results of the research were published in CWB, issue 4, 243-249, 2012. Co-authors were Malata and Szeląg [annex 4, p. II A, row 9]. The presented research was financed under the grant MNiSW N507 330 936 "Gypsum fiber composites".

Gypsum Department in the Krakow Division of the Institute of Ceramics and Building Materials also dealt with the production technology of adhesives for ceramic tiles. Due to the fact that there were large differences in the properties of cement adhesives, this problem became the subject of another series of research.

The first work in this series concerned the influence of methylcellulose on the properties of cement adhesives [CWB, No. 6 pp. 359-365, 2010, co-authors: Sobala and Nosal] [annex 4, p. II A, row 6]. Experiments have shown that cement mortar without the addition of methylcellulose does not meet the requirements of PN-EN 12004: 2008 and does not provide adequate adhesion of ceramic tiles to the concrete substrate. However, the addition of methylcellulose with a viscosity of $70 \text{ Pa}\cdot\text{s}$ has a very beneficial influence on the physical properties of these mortars. The use of methylcellulose with lower viscosity, i.e. 40 and $15 \text{ Pa}\cdot\text{s}$, does not provide good properties of mortars. Investigations of the microstructure of the hardened mortar indicated a high influence of methylcellulose, first of all on the C-S-H phase morphology, which is known to determine the strength of the paste. Simultaneously there are gypsum crystals that have not reacted with calcium aluminates. The explanation of this phenomenon required further examinations.

In order to better understand the influence of methylcellulose on the properties of cement adhesives, I undertook research on the addition of this admixture in the hydration of tricalcium aluminate [CWB, No. 2, pp. 65-73, 2013; annex 4, p. II A, row 11]. Experiments have shown that despite the very small addition of methylcellulose, equal to about $0,3\%$ of the cement mass, these changes are extensive. They concern primarily maintaining a significant gypsum content in the paste,

practically until the completion of hydration process. As the result of hydration, mainly monosulfate and hydrated hexagonal aluminate C_4AH_{14} are formed.

The next work from this series was the study of the influence of methylcellulose on the reaction of alite with water [CWB, 4, pp. 245-252, 2013; annex 4, p. II A, row 12]. The addition of methylcellulose reduces the reaction rate of the alite with water, while the simultaneous addition of gypsum significantly reduces effect of this admixture. However, in both cases the induction period is longer and the main maximum on the curve of heat evolution rate is much smaller.

Subsequent studies focused on the influence of methylcellulose addition on the C_3S and C_3A reaction with water, and completed experiments on the effect of this admixture on the hydration of the alite mixture with tricalcium aluminate. Investigations have shown that the addition of methylcellulose significantly reduces the rate of reaction of this mixture with water, whereas the influence is significantly lower in the case of gypsum addition [CWB, 2014, No. 6, p. 405-415; annex 4, p. II A, row 13].

A group of experiments on the influence of methylcellulose on the hydration of C_3A and C_3S closed the study of this process by means of calorimetry, which provided original new data. There have been no measurements of such a system so far and the course of curves of heat evolution rates, which modified the main peak, indicating the accelerating effect of tricalcium aluminate on the hydrolysis of synthetic alite, was very interesting. It can be assumed that the formation of hydrated calcium aluminates by binding calcium ions accelerates the hydrolysis of alite. I published this work together with Malata in the Journal of Thermal Analysis and Calorimetry, vol. 126, no. 3 in 2016 [annex 4, p. II A, row 21].

A further series of studies, including cement adhesives for ceramic tiles with various additions of methylcellulose, was a work published together with Niziurska in Construction and Building Materials 77, 227-232 (2015) [annex 4, p. II A, row 15]. The most important conclusions from the research results were as follows. Once again it was confirmed that cement mortars without the addition of methylcellulose do not meet the requirements of EN 12004 standard and do not ensure adequate adhesion of ceramic tiles to the substrate. On the other hand, the addition of methylcellulose with a plastic viscosity of 70 Pa·s cement mortars has very good physical properties. Methylcellulose with lower viscosity does not provide such a favorable effect on the mortar properties. If the correct w/c ratio for mortar is established, the addition of methylcellulose has no adverse effect on the viscosity and density of these mortars. The addition of methylcellulose delays cement hydration, which I have already stated in previous works. Methylcellulose also affects the microstructure of hardened mortars and the increase in its viscosity also increases the content of C-S-H with gel morphology. Simultaneously, gypsum crystals appear which have not reacted with

aluminate ions. Thus, the results of my studies of simplified systems containing only C_3A or its mixture with alite were confirmed.

I also carried out supplementary studies on the influence of methylcellulose on cement hydration [CWB, No. 3, pp. 186-192 2015; annex 4, p. II A, row 16] , in which I put a special emphasis on the investigation of the microstructure of the hardened paste. The paper presents the results of studies on the influence of methylcellulose addition on the reaction rate of cement with water, which is an important supplement to the author's earlier work related to the influence of this admixture on the reaction of tricalcium aluminate, alite and a mixture of these phases. CEM I 52.5N-HSR/NA cement and hydroxypropyl methylcellulose with a plastic viscosity of 70 Pa·s were used for the tests. Studies have shown that the addition of methylcellulose has a large effect on the hydration course of cement in the initial hours of hydration. The results of XRD examinations and observations of the microstructure under the SEM confirm the presence of gypsum after 24 hours of hydration of cement with the addition of methylcellulose. Moreover, the addition of methylcellulose not only inhibits the formation of ettringite but also monosulfate. The above observations confirm my previous research on the hydration of basic cement phases in the presence of methylcellulose.

In addition, I examined the influence of methylcellulose on the formation of composition gradient in cement mortars [unpublished work]. Two known effects, the ability of methylcellulose to move with the mixing water and the effect of this admixture on the transport properties of porous liquid in mortars, cause an uneven distribution of components in hardening and drying cement mortars. The paper presents an analysis of the spatial distribution of methylcellulose in cement mortar and an attempt to link it with the distribution of mortar components and cement hydration products. The tests were performed using DTA/QMS techniques supplemented with IR, XRD, SEM and Raman tests. In a study of model cement mortar with methylcellulose, the effect of local methylcellulose concentration in the contact zone with the substrate discussed for adhesives was confirmed. Due to the different application characteristics, the lack of coverage with an impermeable layer intensifies the movement of the liquid to the free surface. The outer zone of the product is definitely more modified. The changes in the organic phase (MC) distribution are accompanied by an analogous change in mineral components, however, it is limited to the newly formed hydration and carbonation products. This disproportion has two parallel causes - mass transport with MC solution (remarkable by comparing the even distribution of anhydrite with the surface concentration of hydrated gypsum) and uneven access to migrating moisture (observed as changes in the degree of belite reaction, increasing at the outer surface of the mortar layer). In the XRD investigation, the effect of migration of solid particles - grains of admixture - was not observed. This effect is only noticeable by filling the substrate macropores in the SEM observations, which means that the obtained microstructure is too tight to allow the transport of such grains. Therefore, it is likely that

the transport of the hydrating material occurs in a dissociated form in the solution, and the hydration products only precipitate in the near surface zone of drying or concentration of the liquid phase.

My research interests also included glass technology, which I could develop after taking over the function of the Deputy Director of Institute for Research and Development, which I held in the period from June 2004 to September 2007. This year, the Institute was reorganized by merging with the Institute of Ceramics in Warsaw. However, due to my duties as the Deputy Director of the Institute's Division in Krakow, I continued to provide scientific care for the Glass Department. The Division in Krakow covered departments related with technology of cement, gypsum and glass.

One of the most important works concerned the influence of TiO_2 and ZrO_2 as nucleation additives that facilitate the production of glass-ceramic materials. The study covered the influence of these additives, in the form of individual oxides and their mixture, on the possibility of obtaining glass-ceramic materials from glass waste from cathode ray tube (CRT) for TV sets. The main goal was to obtain barium-titanium glass-ceramics as a result of surface crystallization. The tests showed that the addition of ZrO_2 increases the glass transition temperature and the glass viscosity, which is caused by a decrease in the content of non-bridging oxygen ions in the glass network. TiO_2 shows the opposite effect and by increasing the content of bridging oxygen ions reduces the viscosity of the glass and facilitates its crystallization. The use of the TiO_2 additive allowed the crystallization of the barium-titanium silicate on the surface of the waste glass, and thus it has been presented that this method can be used for the production of glass-ceramics containing barium-titanium silicate. The size of dendritic barium-titanium silicate crystals is increased when the titanium oxide content in the glass increases. These examinations were carried out by a five-member team consisting of employees of Institute and Department of Glass of Faculty of Materials Science and Ceramics at AGH. Co-authors of the work: Reben, Kosmal and Olejniczak. The results of this work were published in the Journal of Non Crystalline Solids pp. 118-123, in 2015 [annex 4, p. II A, row 14].

A similar work, also related to the glass-ceramic material, concerned studies of a network of silica glass modified by the addition of strontium and barium. The waste glass also came from cathode ray tubes for televisions. Blast furnace slag as well as cement dust were added to this glass. It was found that aluminum occurs only in tetrahedral coordination, whereas increasing the content of CaO and Al_2O_3 caused by these admixtures increases the glass transition temperature and heat of this transformation. The research was carried out by a team of scientists from AGH and Division of Glass and Building Materials. The work was published in the Journal of Molecular Structure, 2016 pp. 265-274 [annex 4, p. II A, row 20].

This experimental series also included research over the crystallization of glass waste from CRT for televisions. Observations of the influence of the chemical composition of these glasses by means of infrared spectroscopy, differential thermal analysis and XRD indicated that increasing

aluminum content only shifts the position of Si-O-Si and Si-O-Al bridges in the infrared spectrum towards the lower frequency band. This shift confirms that even a small addition of CaO has a greater impact on reducing the proportion of Si-O-Si bridging oxides in the glass network in favor of aluminum containing bridges Si-O-Al. Simultaneously, it has been shown that a low content of modifiers ions, especially Ca^{2+} and Mg^{2+} , decreases the crystallization tendency of glass. The authors Kosmal, Reben and Pichniarczyk published the results in the Journal of Thermal Analysis and Calorimetry, in 2016 pp. 353-361 [annex 4, p. II A, row 22].

Another work was related to the influence of additives in the form of glass cullet and slag, and most of all ion modifiers namely sodium sulfate and a mixture of As_2O_3 , Sb_2O_3 , NaNO_3 in a 1: 1: 1 ratio, on a glass transition. The thermal differential analysis was chosen as the basic method. The obtained results allowed to draw the following conclusions:

- a) addition of glass cullet decreases the decomposition temperature of dolomite and limestone, due to the influence of active silica,
- b) comparing to glass cullet the addition of slag decreases by 20°C to 40°C the temperature of the eutectic being created and accelerates this process, increasing the alloy content,
- c) introduction of modifiers mixture into the blend significantly reduces the binding process of silicon ions in the glass.

The work was published in the Journal of Thermal Analysis and Calorimetry, co-authors of the work Kuśnierz, Kosmal, Środa, volume 130, pp. 229-247, 2017 [annex 4, p. II A, row 24].

The last published paper concerning glass and its transformations were experiments on glass-ceramics crystallization with the chemical composition of the $\text{BaO-SrO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ system. It has been indicated that addition of TiO_2 to waste glass from CRT reduces the glass transition temperature and glass crystallization temperature. This is due to the weakening of the glass network as a result of the increase in the content of nonbridging oxygen ions, which decreases viscosity of the glass. This makes it possible to control the surface crystallization process of the glass. Ti (IV) ions play the role of heterogeneous nucleation agents of crystallization; the combination of several research methods, primarily XRD and DTA, made it possible to establish that the crystallization process begins on the surface of the glass and then goes into the deeper layers. The research was performed by: Kosmal, Reben, Pichniarczyk, Ziąbek and Skrzypek, and was published in the Journal of Thermal Analysis and Calorimetry, Vol. 130, No. 1. pp. 221-228, 2017 [annex 4, p. II A, row 25].

In addition, for the last few years I also dealt with the production technology of cements and their properties, especially cements with mineral additions. The research team: Baran and Pichniarczyk published in Construction and Building Materials, 150, pp. 321-332, 2017 [annex 4, p. II A, row 26], tests results of common and special cements. As it is known, the heat of hydration of cement depends on the phase composition of the clinker and on the fineness. The latter factor

primarily influences on the heat of hydration, and on the paste strength primarily in the initial hardening period. Due to the fact that both the heat of hydration and the strength of paste are affected mainly by two phases; tricalcium aluminate and alite. However, after a longer period of time, most of all after 28 days of hardening, which determines the standard strength, the other phases, generally belite, are also of importance. The addition of gypsum also influences on the heat of hydration and strength. In order to clarify what correlation occurs between heat of hydration and mortar strength, an appropriate series of tests was carried out. It was found out that on the basis of the known heat of hydration after 24 hours the strength of the mortar from this CEM I cement after 28 days can be relatively accurately estimated using linear correlation. This correlation is particularly strong and allows for more accurate estimation when it concerns cements produced by one plant. Each plant produces a clinker with a slightly different phase composition. However, in the case of other types of cements which contain various mineral additions, the correlation between the heat of hydration and the 28 days compressive strength of the standard mortar was weaker, which is due to the high properties variations of these additions.

Other studies on this subject were examinations determining influence of fly ash on the properties of cement and concrete. The research team of Baran, Drożdż and Pichniarczyk published in Cement Wapno Beton in 2012, No. 1, pp. 50-56 [annex 4, p. II A, row 10], a paper on the possibility of using calcareous fly ash from lignite, as well as fly ash and slag mixtures in many fields of construction. Currently, one of the most important ways of utilization of these fly ashes is to use them in the production of binding materials and for the production of concrete. Calcareous fly ash samples from Bełchatów Power Station were used for the tests. It has been stated that they indicate high variations of both chemical composition and basic properties, important from the point of view of production of cement and concrete, primarily of fineness and CaO content. The usefulness of these fly ashes in cement production is determined, among other, by high, over 25%, content of reactive silica. Simultaneously, the addition of calcareous fly ash to cement increases its water demand, significantly in the case of sample with the highest loss on ignition. 30% addition of calcareous fly ash to cement can positively influence on the strength after longer hardening period, namely after 90 and 180 days. However, due to the much lower specific surface area of some fly ash samples, which was equal to $2600 \text{ cm}^2/\text{g}$, in many cases the strengths were significantly lower than the reference cement samples.

In the case of fly ash-slag mixtures, the tests showed a very high variation in the content of fraction higher than $0,045 \text{ mm}$, which ranged from 35,2% to 78,6%. However, the chemical composition is typical for siliceous fly ash V, used in the cement industry as a pozzolanic addition to cement. This applies to both the main oxides as well as the content of alkali, SO_3 and MgO. Regarding the loss on ignition, 50% of the samples met the requirements for category A, and 50% met the

requirements for fly ashes of category B. Samples of fly ash-slag mixtures were characterized by high reactive silica content, exceeding 31%, which significantly exceeded the required minimum of 25% for siliceous fly ash. The experiments confirmed the good activity of fly ash-slag mixtures. Activity indexes after 28 and 90 days of hardening, exceed the required values, from 83 to 92% after 28 days and from 87 to 101% after 90 days. For the activity index after 90 days, which was 101%, this meant that the cement with 25% addition of this mixture achieved higher strength than the reference cement. High diversity of the waste was noted, which indicates the necessity of its treatment for the needs of the concrete industry. This applies to high material moisture and fineness that does not meet the requirements for category N.

The calcareous fly ash and fly ash-slag mixtures examinations allow to state that calcareous fly ash may be a valuable mineral addition for the production of cement and concrete after appropriate treatment and that fly ash-slag mixtures may be used as pozzolanic addition for cement production, because they meet the requirements of PN-EN 197-1 standard for siliceous fly ash. However, it should be noted that according to PN-EN 450-1 calcareous fly ashes cannot be added to concrete, in contrary to e.g. US regulations. This is mainly due to the quality of calcareous fly ashes from combustion of other fuels.

In a paper published in *Cement Wapno Beton* in 2015, No. 5, pp. 284-294 [annex 4, p. II A, row 17], the research team of Baran, Pichniarczyk and Gawlicki presented investigations on the influence of fly ashes obtained from the simultaneous combustion of hard coal and secondary fuel on the properties of cement and concrete.

Fly ashes collected from pulverized coal-fired furnaces of four power plants using a differentiated share of biofuel of plant origin, equal up to 35% of thermal equivalent were the subject of the analyzes.

Chemical composition examinations have shown that the content of some components of siliceous fly ash from the simultaneous combustion processes; Na_2O_e , MgO , SO_3 , CaO and P_2O_5 may exceed the acceptable requirements given in PN-EN 450-1. Simultaneous combustion of hard coal and secondary fuels not only leads to changes in the chemical composition of fly ashes, but also affects their phase composition, changing in particular the composition of glass, which is one of the basic component of siliceous fly ash from pulverized coal-fired furnaces. The particle size distribution of fly ashes and the morphology of fly ash particles also change. In addition to the dominant oval grains in the siliceous fly ash, there are irregularly shaped grains and wood splinters with lengths of up to about 3 mm may appear. It was shown that the highest strength after 2 and 7 days of hardening had cement with the addition of fly ash with the highest estimated amount of biomass, also in this case the setting time of cements is increased, especially in the case of CEM II/B-V Portland-fly ash cements.

During my scientific work I also conducted research on the industrial processing and use of chalcedonite, as a member of the research team: Naziemiec, Pichniarczyk and Saramak, who published the results of their research in 2017 in Journal – Inżynieria Mineralna No. 1, pp. 89-96 [annex 4, p. II A, row 23]. and Mineral Resources Management No. 33 (3), pp. 163-178 [annex 4, p. II A, row 27]. Chalcedonite, as a unique raw material, has been the subject of many studies and implementations carried out by the Institute of Ceramics and Building Materials in Krakow (the former name - Institute of Mineral Building Materials). Chalcedonite is a natural silica sedimentary rock. The only chalcedonite mine in Poland is located in Inowódz, where open-cast mining is carried out from the Teofilów deposit. Chalcedonite from this deposit is characterized by high lithological variability and variability of quality traits. A wide range of its potential applications includes the construction and road industry, sanitary engineering (filter material in treatment of municipal wastewater and water treatment) and the cement industry. In the introduction of presented articles, the previous directions of using chalcedonite have been discussed. In the production process the large number of small chalcedonite fractions is a big problem, which are difficult to industrial use. The articles present the results of phase and chemical composition tests of various fractions of chalcedonite raw material, as well as the results of research on chalcedonite aggregates and fine chalcedonite fractions directed to earth traps. After the analysis of the research results, attention was paid to the particularly significant problems of chalcedonite processing. An important issue is the process of rinsing chalcedonite and the exact grain classification of products. The separated grain classes were characterized by diversified chemical and mineralogical composition. Particular attention has been paid to the new possibilities of effective treatment of chalcedonite through the use of densimetric separation. The results of the separation of chalcedonite aggregate in a pulsation jig and in a heavy liquid showed that the obtained products were characterized by different density and water absorption. Separation of chalcedonite into products of different densities enables their more efficient use. Aggregates with lower density also have higher porosity and are more suitable for the production of filter grits. In turn, aggregates with higher density and lower water absorption are more suitable as concrete aggregates. It is worth noting that at present, the separation of mineral aggregates into products of different density is not applied. Pulse presses are used in the aggregate industry only for separating light impurities. An equally important issue is the possibility of using fine chalcedonite fractions in the ceramic industry. This is facilitated by the crystalline form of occurrence of silica and the content of clay minerals, mainly kaolin. The porous structure of chalcedonite allows obtaining durable colored aggregates (e.g. by iron compounds). Another issue is the possibility of thermal processing of chalcedonite (e.g. production of cristobalite) and the production of lightweight aggregate based on waste chalcedonite fractions and sewage sludge from wastewater treatment plants. New possibilities of using chalcedonite were supported by the presented research results.

My last publication in JTAC, 131/3, 2018 pp. 2321 [annex 4, p. II A, row 28] concerned the influence of heavy metals on the Portland cement setting process, which was related to a certain extent to the presented habilitation monograph. The authors of experiments presented the effect of PbO and V₂O₅ addition on the setting time of industrial Portland cement with addition of anhydrite as setting regulator. They drew several important conclusions. They stated that delaying or accelerating influence of addition of lead and vanadium oxides on the setting time of Portland cement depends on the concentration of sulfate ions in the cement paste liquid phase. Standard concentration of sulfate ions, typical for gypsum, therefore equal to about 0,67 of SO₄²⁻ mole per liter, ensures the delaying effect of heavy metals: lead and vanadium. The authors are of opinion that delaying mechanism relies on the impermeable layer formation on alite crystals, composed probably of compounds of these heavy metals, however, it requires further investigations. Low concentration of sulfate ions gives opposite effect, i.e. setting of cement is accelerated and relies on the crystallization of ettringite. Probably PbO and V₂O₅ are adsorbed also on C₃A crystals, which is preventing the ettringite layer formation on this phase, especially in the case of Pb. Thus, it makes possible the ettringite crystallization in the space between cement grains. Finally, it was stated that accelerating effect of these two heavy metals on the cement setting process is different, because of high vanadium sulfate solubility which is causing the high concentration of SO₄²⁻ ions in solution linked with vanadium. Examinations in that scope were extended in the monograph discussed in p. 4b.

I can describe the research work discussed above as closely connected with my scientific activity and scientific care of works carried out at the Institute of Ceramics and Building Materials focused on materials such as glass (including building glass) and mineral building materials, which are widely used in construction. It gave me the opportunity to learn about the operation and functioning of the building materials industry in terms of production technology as well as applications. The Institute, which I now have the pleasure to manage, is primarily active in the field of material technologies used in construction, as well as control of production and products. Institute of Ceramics and Building Materials is the only scientific, research and implementation entity in Poland that focuses on the fields of science and industry related to the processing of non-metallic raw materials, the technology of ceramic and glass materials, refractory materials, mineral building materials, mineral binders and concrete products. That is why the area of my interests is extensive, as I presented in the subsequent annexes.

.....
Signature 