

STRUCTURE AND ENVIRONMENT

ARCHITECTURE, CIVIL ENGINEERING, ENVIRONMENTAL ENGINEERING AND ENERGY

No. 3/2010 vol. 2 PL ISSN 2081-1500 www.sae.tu.kielce.pl KIELCE UNIVERSITY OF TECHNOLOGY



Contents

structure

STIMULATING DESIGN CREATIVITY BY PUBLIC PLACES IN ACADEMIC BUILDINGS	5
HOU YUEMIN, JI LINHONG	
IMPACT OF BASALT AGGREGATE ON POROSITY AND STRENGTH OF SILICATE PRODUCTS	14
ANNA STĘPIEŃ	
ABOUT CORRECT METHOD OF ANALYTICAL SOLUTION OF MULTIPOINT BOUNDARY PROBLEMS OF STRUCTURAL MECHANICS FOR SYSTEMS OF ORDINARY DIFFERENTIAL EQUATIONS WITH PIECEWISE CONSTANT COEFFICIENTS	21
PAVEL A. AKIMOV, VLADIMIR N. SIDOROV, MARINA L. MOZGALEVA	
INVESTIGATION OF ALKALI-AGGREGATE REACTION IN CARBONATE ROCKS	25
ZDZISŁAWA OWSIAK	

environment

ENERGY SAVING USING HEAT EXCHANGERS COVERED WITH POROUS COATINGS	35
TADEUSZ M. WÓJCIK	
EVALUATION OF THE USE OF COAL FLY ASH FROM MUNICIPAL HEAT – POWER PLANT WITH REGARD TO FOREIGN EXPERIENCES	40
MARIA ŻYGADŁO, AGNIESZKA SEWERYN, MAGDALENA WOŹNIAK	
THE APPLICATION OF SELECTED ACTIVATED CARBONS TO DYE WASTEWATER TREATMENT	52
ANNA PICHETA-OLEŚ	

EDITORIAL BOARD

Main Editor Jerzy Z. Piotrowski

Editor Ludwik Śliwa

Secretary of the Editorial Board Radosław Zaborek

Sectional Editor STRUCTURE Zdzisława Owsiak

Sectional Editor ENVIRONMENT Lidia Dąbek

SCIENTIFIC BOARD

Chairmanship Tomasz Kozłowski

STRUCTURE

Tomasz Arciszewski (USA), Lesław Brunarski, Go Iwahana (Japan), Marek Iwański, Zbigniew Kowal, Jozef Melcer (Slovakia), Michail V. Nemchinov (Russia), Victor Proskuriakow, Zbigniew Rusin, Bohdan Rymaszewski, Wacław Seruga, Małgorzata Wilczkiewicz (USA)

ENVIRONMENT

Satoshi Akagawa (Japan), Elżbieta Bezak-Mazur, Dorota Chwieduk, Graham Herbertson (Scotland), Andrzej Kapłon, Andrzej Kulczkowski, Janusz Łomotowski, Paweł Purgał, Leszek Radziszewski, Anatol Stroy (Ukraine), Maria Żygadło

www.sae.tu.kielce.pl

sae@tu.kielce.pl

The quarterly printed issues of Structure and Environment are their original versions

The Journal published by the Kielce University of Technology
Faculty of Civil and Environmental Engineering

PL ISSN 2081-1500

© Copyright by Wydawnictwo Politechniki Świętokrzyskiej, 2010

25-314 Kielce, Al. Tysiąclecia Państwa Polskiego 7
tel. 41 34 24 581
www.tu.kielce.pl/organizacja/wydawnictwo



structure
structure

HOU YUEMIN¹
JI LINHONG²

¹Beijing Information Science & Technology University, 100085, Beijing, China

²Tsinghua University, 100084 Beijing, China

STIMULATING DESIGN CREATIVITY BY PUBLIC PLACES IN ACADEMIC BUILDINGS

Abstract

Design creativity is constrained by the limitations of knowledge of a given designer or even of a design team. Also, each design process is a dynamic process because novel design ideas may emerge spontaneously and their occurrence is unpredictable. One way to increase the probability that novel ideas are produced is to provide designers with additional knowledge, which will expand their design space. The other way is to create an environment stimulating generation of novel ideas. Such an environment should allow and encourage reflection, relaxation, formal and informal interaction among people, and knowledge sharing. The concept of structural hole in sociology is introduced and extended by distinguishing three classes of structural holes: domain, thinking, and working structural holes. It is postulated that an environment with abundance of structural holes can be created by proper public places. Such places should be comfortable to stay and easily accessible and they could be, for example, entrance halls, restaurants, activity centers, or corridors, which are discussed in the paper.

Keywords: Creativity, environment, structural holes, public place, campus

1. Introduction

Engineering design means to develop an artifact or a description of it to meet the desirable function with limited resources, including available knowledge and problem-specific experience, manufacturing technology, cost and time. There are no simple laws linking the structure of a system to specific functions. Therefore, each design process is like searching for an unknown artifact. A designer develops a design description, generally represented graphically, numerically, and/or by a text, to provide specified functions with available tools within limited time and cost. The designer may be knowledgeable and experienced, or not, but the specified function must be provided by the final design.

One approach to engineering design is to design a novel device, or an engineering system, automatically by a computer-aided design system. Unfortunately, such systems are still in an experimental stage. Hence, the designer must do it himself or herself. What a designer usually does is to decompose the desired function into sub-functions, then to select some known systems and devices or to invent a novel system to achieve the sub-functions, and

finally to combine these substructures into a whole system while satisfying all applied constraints and requirements (Pahl etc. 2007). This process is usually called “conceptual design”. The final design depends on the knowledge space of the designer. Creative design emerges when previously unrelated concepts, principles, functions, behaviors and structural elements are brought together and combined in a new but feasible way, which improves with respect to existing designs. Unfortunately, no single designer, or even a design team, has complete knowledge that might be potentially useful in the design being conducted. Therefore, design creativity is usually constrained by knowledge limitation.

On the other hand, the design is “situated”. According to the Heisenberg Uncertainty Principle, we cannot actually predict the position of an electron exactly; the best we can say is that the electron is mostly here and partially somewhere else. Quantum mechanics also tells us that radioactive decay occurs entirely by chance and is unpredictable except in the statistical sense. Uncertainty is ingrained in nature. It may be safe to say that novel ideas in design also usually occur by chance and are unpredictable.

One way to increase the probability that novel ideas are produced is to provide designers with additional knowledge, particularly interdisciplinary knowledge, which will extend the design space. The other way is to create an environment that may stimulate generation of novel ideas and developing creativity.

Our claim is that proper public places can create an environment promoting design creativity and increasing the probability that novel design ideas actually emerge. The concept of structural holes (Burt 1992, Gellynck et al 2007) is extended in this paper by distinguishing three specific classes of structural holes: domain, thinking and working structural holes. The three classes of structural holes are used to explain the effect of public places on design creativity. Finally, examples of public places in campus building are discussed. The paper begins with the discussion of impact of environment on creativity, which is partially based on the review of current research. Next, the analysis is provided how proper public places can promote design creativity.

2. Environment Support to Creativity

An extensive literature on creativity has been published, but very little focused on creativity-stimulating environments. "We spent an awful lot of money on how to analyze, but we do not spend much money on creating an environment for creativity (of aircraft design)" (Rutan 1996). It is known, however, that the workplace environment can have a dramatic impact on mood, motivation, creativity and productivity of employees, both positively or negatively (Lee et al 2010). For example, the open information flow, available resources, positive challenges, and negative workload pressure contribute to creativity (Amabile, 1996). The basic assumption of this paper is that a proper physical environment that suits for reflection, relaxation, interaction, and knowledge sharing may foster and stimulate creativity.

First, creativity needs quiet individual reflection. Creativity results from bringing together and combining previously unrelated ideas, and that happens only when a person has been thoroughly involved in a problem or situation for a long time, particularly in the case of engineering design, which requires knowledge retrieval, analysis, and integration.

Second, creativity needs relaxation. Creativity often takes place in a natural context. "Someone's best ideas may come while walking on a beach" (Young 2007), while someone's best ideas may be inspired by a chat with other people. Creative

process is iterative and punctuated by periods of incubation. The thoughts and ideas are incubated unconsciously or semiconsciously. Then they re-emerge as a new idea or a concept. "These periods of incubation happen best when we are engaged in relaxing, reflective or playful activity, when the mind has switched off from the problem at hand". (Lee et al 2010). One of the relaxation activities is excursion, which is considered as one of the most effective creative thinking techniques. "It's a simple 5-10 minute exercise that forces you to do something else - get out of the office, take a walk, listen to music - that sort of thing" whenever someone has design block (Leigh-Ann Bartsch 2010). In many cases, according to our personal experiences with designing many new engineering systems, relaxation is a good medicine to cure "no idea" mental state. Particularly, a short break outside the office during work helps with new ideas emergence when focusing a solution of a complex problem for a long time.

Third, creativity needs both formal and informal interaction. Creative ideas may occur at conscious, semiconscious, and subconscious mental sorting, grouping, and matching (Leonard and Sensiper 1998). On the other hand, open information flow is one of important environment components when creativity is concerned (Amabile et al 1996). The interactions between an individual and other human beings stimulate and enhance creative activities (Johnson and Carruthers 2006). Formal interactions such as workshops and seminars are likely to provide information at conscious level, while talks or chats between two people, or between two groups from different domains, help to channel information at semiconscious and subconscious level. In the case of engineering design, the first important thing is to produce a design concept, which requires integration of advanced theories, methods, tools and technology with existing similar products. The behavior of any perceiving individual depends on the information available (Gibson 1972, Neisser 1976). Interactions between two people that do not belong to same specific domain group help with information exchange, and particularly help with acquiring interdisciplinary knowledge, which will likely lead to new products or new engineering systems. Not only a complex engineering system but also even a simple mechanical device may require a team to work out a solution by interaction. In an example of designing a device for mounting and transporting a hiker's backpack on a mountain bicycle, a three-person team developed

a design concept during a short discussion (Cross 1997). Figure 1 illustrates how the design concept was developed by evolution from a concept of bag to the product ideation of a tray-like device. I, J and K in the Figure 1 represent the three members of the team. The process begins with an idea of a bag proposed by I, then the bag is modified as something like a tray by J. The idea of snaps, stapes, and rails are emerged when the talk continues. The final ideation of the device to mount and transport the hiker's backpack is a device that snaps the rails into the tray there. The dash line in the figure 1 shows how the talk continues among the members.

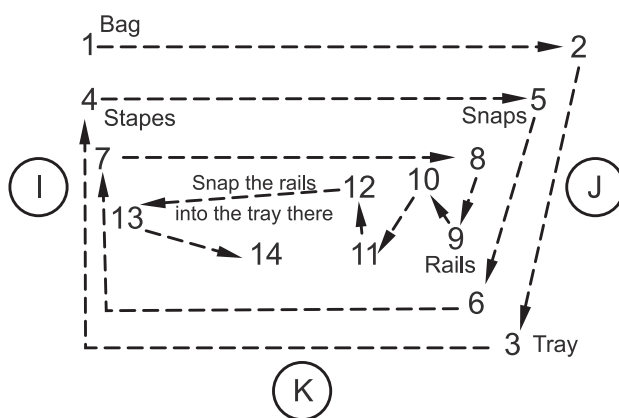


Fig. 1. Idea flow initiated by interaction

Fourth, creativity often occurs as a collective creativity. Creativity likely occurs when distant analogies are discovered (Hargadon and Bechky 2006), which likely emerges when a bisociation is shared by two or more people, called collective creativity (Sanders 2001). Creativity happens in the interaction between a person's thoughts and a socio-cultural context (Csikszentmihalyi 1996) or emerges in interactions (Hargadon and Bechky 2006). Collective creativity can promote creativity by (1) helping to seek assistance of others; (2) helping to make time and attention commitment to assist others; (3) helping to reflectively reframe the comments and actions of others; (4) reinforcing activities that support individuals engaged in the process (Hargadon and Bechky 2006).

Finally, creativity needs knowledge sharing. Creativity most typically happens when people share their knowledge and opinions. Knowledge becomes meaningful in interactions with others and in combination with others' knowledge in order to create new knowledge (Lee et al 2010).

To summarize, an environment that supports reflection, relaxation, social interaction, formal and

informal interaction, and knowledge sharing will foster and promote creativity.

3. Structural Hole

The concept of the structural hole is used in this paper to explain the environment impact on creativity. The term structural hole is coined to refer to a social gap between two groups (Burt 1992). Structural holes mean the weak connections between clusters of densely connected individuals (Granovetter 2005). The structural hole can be also understood as weak ties between the two shortest nodes of two networks and they are more likely to be bridges (Borgatti 2010). The bridges connect people not otherwise connected who are in the adjacent communities (Burt 2002). A simple analogy of a structural hole to an insulator in an electric circuit may help with understating the concept. People on either side of a structural hole are focused on their own activities such that they do not know about activities of people in the other group (Burt 2001). Hence, structural holes can be understood as weak ties between two distant groups or communities, and the weak ties are likely formed by informal links or indirect contacts, e.g. having or overhearing a conversation, or catching a glimpse of something. If all ties between two groups are strong, then there are no structural holes between the two groups.

Structural holes are an opportunity to initiate the flow of information between people from the opposite sides of the holes (Burt 2001). An individual whose network spans the structural holes has an opportunity to access richer information than an individual who only communicates with people within his/her group. An abundance of structural holes creates opportunities for the new combinations and recombinations of ideas (Gellynck et al 2007). Also, structural holes create opportunities to extend knowledge and information space, see Figure 2. Hence, structural holes potentially promote creativity.

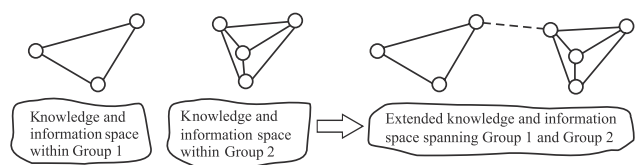


Fig. 2. Extended knowledge and information space

4. Creating an Environment to Promote Design Creativity

We use the concept of structural holes to explain the effect of environment on design creativity. As discussed in Section 3, structural holes potentially

promote creativity. Then it raises a question: is it possible to create structural holes by means of a proper physical environment?

We need an environment that supports reflection, relaxation, social interaction, formal and informal interactions, and knowledge sharing, as discussed in the Section 2. Our assumption is that a proper environment may create structural holes so that it may lead to stimulation of human creativity, particularly design creativity, which requires broad range of engineering knowledge. We will demonstrate this by distinguishing three classes of structural holes and linking them with specific environments.

A structural hole is understood as a weak connection between two different groups. This kind of connection can be reached in various ways, depending on the difference between the two groups. The two groups may differ in their professional backgrounds, in thinking styles, or in locations. For example, the faculty of an aerospace engineering department and the faculty of a biology department belong to different disciplines; one person has a global thinking style while the other person has a local thinking style; people living in one community and people living in a far distant community may have different information space. Furthermore, when we consider a person as a system, he/she will have different mental states in different places. For example, he/she may be in a relaxed state at home or in holiday, and in a focused state in office.

Therefore, we extend the concept of structure hole by distinguishing three classes of structural holes: domain, thinking and working structural holes. The domain structural hole refers to the disciplines gap between two groups; the thinking structural hole refers to the thinking style gap between two groups; and the working structural hole refers to the space gap between working place and home as well as between the working state and non-working state.

A domain structural hole creates opportunities for knowledge sharing and integration across traditional borders, which will leads to an extended knowledge space. A thinking structural hole creates opportunities for distant analogies and new interpretations to promote collective creativity. A working structural hole creates opportunities for unpredictable fresh ideas through formal and informal interaction, quiet individual reflection at conscious, semiconscious, and subconscious levels, as well as relaxation.

An environment with abundance of structural holes can be created by public places. The term “Public places” refers to places or areas that are open and

accessible to community members and that are not owned or controlled by private interests (<http://ct4ct.com>). “Public spaces are an inseparable part of the urban fabric. Such spaces function mostly as passageways from place to place, or for short term activities” (Dekel A et al, 2005).

We focus on public places in a campus building. Proper public places in campus building may be an entrance hall, a restaurant, an activity center, or simply a corridor. All such have potential to create domain, thinking and working structural holes.

A proper public place means a place that is comfortable to stay for chat, rest, and thinking, even for doing nothing, just relaxing. No reason is needed for coming or leaving. Such a places should only take one or several minutes to get there. And the place itself should be a spacious and enjoyable physical space and should always have something to attract visitors, such as information board, newspapers and magazines, snacks and drinks, various models such as machine models or architecture models, photos, sculptures, paintings, posters, plants and flowers, long tables and long benches, a beautiful scene, fresh air, even computers and internet access. Several examples of such spaces are discussed next.

(1) Entrance hall

Entrance halls provide thinking and working structural holes. They are places where faculty members and students meet frequently every day. They say “hello” to each other and have brief talks whenever they meet. They may discuss news or current issues or talk about a poster or a conference flyer. They may exchange ideas regarding a specific event or activity. People learn and understand different thinking styles and learn from each other unconsciously. Therefore, thinking holes can be provided by an entrance hall. An individual may watch a machine model, a painting, a sculpture, or an evolving scene outside the glass wall or doors while he/she takes drinks. What to see is important because one can get relaxed only if he/she sees something enjoyable. However, the most important is that the models, sculptures and the like switch his/her mind from his/her work, but not far away. In this way, he/she is in neither at work nor at home so that his/her mental state would be neither entirely relaxed nor fully focused on work, a state in which novel ideas will likely emerge. Hence, working structural holes are provided.

Figure 3 shows the entrance hall in the Aerospace Building at TU Delft, the Netherlands. It is a large space with front and back doors as well as several

other entrances to connect several sections of the building and a small restaurant. A big model of a rocket is located in the lobby at the entrance hall of the building. There are big photos of famous scientists that are also alumni on the wall across from the staircase. The stairs face the entrance and there is a large space between the front door and the stairs, which is often used for reception lectures with speakers standing on the stairs, like speakers in ancient Rome. The entrance hall is also used for receptions, meetings, lectures, exhibitions, dinner parties, and concerts.

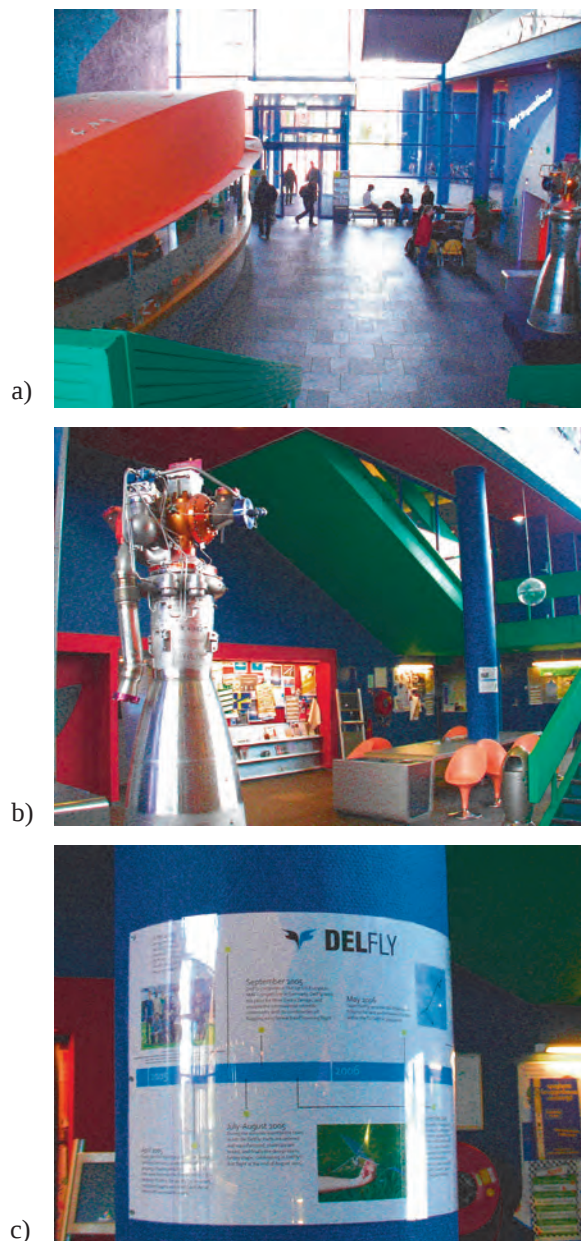


Fig. 3. a) The entrance hall of the Aerospace Building, TU Delft, the Netherlands, b) the back entrance to the same building, c) the recruitment poster of an e-dragonfly design team in the entrance hall, the same building

Figure 4 shows the entrance hall in the School of Architecture Building at the Technische Universität Berlin, Germany. It is spacious, bright, and warm in winter. Outside the glass wall is a garden, to which people can go through a glass door to enjoy trees, flowers, sunshine, fresh air, as well as sculptures. So it is easy for anyone to go to the garden for a walk and a moment of relaxation. In this way, working structural holes are provided. Along the glass wall is a row of heaters, which are also designed to serve as seats. So, people can seat there and have a chat, or a discussion. The entrance hall is also used for receptions, dinner parties, and lectures.

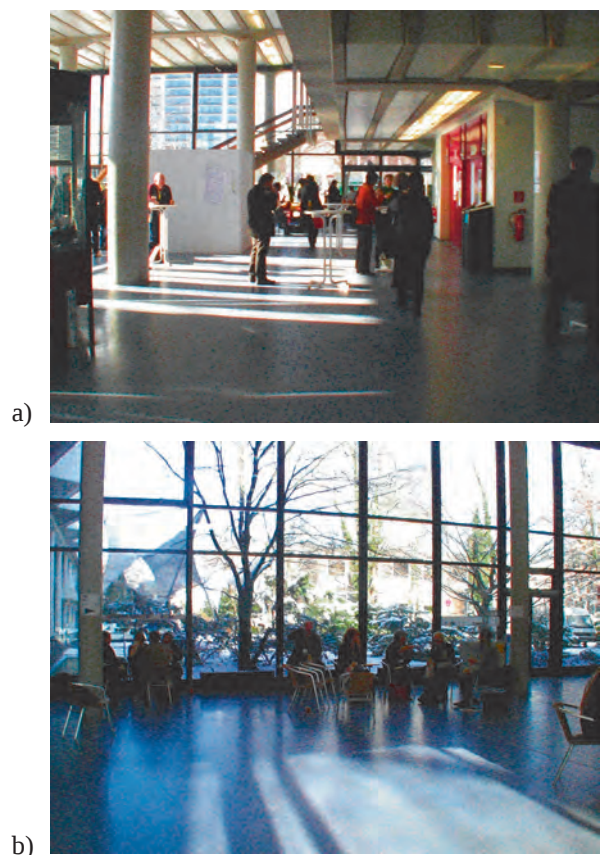


Fig. 4. a) The entrance hall of the Architecture Building, the Technische Universität Berlin, Germany; b) the back door of the entrance hall, the same building

(2) University restaurants

Restaurants in a campus building provide thinking and working structural holes. They generally serve lunches, snacks and drinks. Faculty and students from different departments with differentiated research background and thinking styles meet there every day for lunch and also for a chance of talk. In this way, they learn from each other unconsciously. Therefore, thinking holes are provided. Obviously,

not all restaurants are proper places for thinking and working structural holes. A preferable restaurant is located within the faculty building or very close to that building. Besides, it should be comfortable to stay as discussed above and it should serve delicious food so that people really enjoy the stay there both for lunch and for social activities. When people are there, their minds are forced to turn away from their professional activities either by lunch, by talk or by the involving scene outside the low windows. In this way, working structural holes are provided. However, a restaurant will not provide any structural holes if it is far from the faculty building, crowded, hot in summer and cold in winter, and uncomfortable to stay.



a)



b)

Fig. 5. a) University restaurant in the Aerospace Building, TU Delft, The Netherlands; b) University restaurant at GMU, USA

Figure 5a is a small restaurant in the Aerospace Building at TU Delft, the Netherlands. The university restaurant is located on the ground floor of the main building and has four entrances, two on the ground floor of the main building, one on the first floor of the main building, one on the first floor of the other building, so it is easily accessible from both buildings.

A model of an airplane is hanging from the ceiling of the hall in this restaurant. Outside the glass wall of the restaurant, there is a small pond with plants, fountain, and swimming ducks. The sky and grass all are visible through the glass wall. The restaurant is a nice place to talk, and also for small meetings and exhibitions. Figure 5b shows a university restaurant at George Mason University in Fairfax, USA. The restaurant is located on the first floor of a building called “Johnson Center”, which is located in the center of the campus and has five entrances from all directions so that it is easy to go into this building from any building on the campus. Also, it functions as passageways from one place to another place since it provides a short cut between several buildings. The restaurant is spacious, with nice setting, and serves lunches, drinks and snacks (also providing computers and access to the Internet) and it opens from the early morning to midnight. Therefore, visit to this restaurant becomes an everyday activity for many peoples of the university.

(3) Activity centers

Activity centers provide domain, thinking and working structural holes. Events, conferences, and various activities frequently take place in activity centers. People from various departments, disciplines, and countries, and also at different professional levels (e.g. students, professors, experts, scientists, engineers, managers, administrators and the like) meet here to work together for several days or weeks, or simply meet here for discussions. They learn new knowledge from various domains and different thinking styles from other people. In this way, domain structural holes are provided. Besides academic activities, an activity center is usually used as performance center (usually with free entrance) too, particularly for students’ bands. Concerts, drama performances, movies, and dance parties can be held here. People can participate in such activities easily, just leaving their offices, laboratories or classrooms and taking a short walk to the activity center. In this way, working structural holes are provided.

Figure 6 shows the Johnson Center, which is used for various activities at the George Mason University, including social, cultural, and political activities, such as meeting, conference, opening ceremony, performance, concert, and students activities. It is also has a restaurant, a commercial bank, a library, a news center, many meeting and computer rooms as well as multimedia rooms.



Fig. 6. Johnson Centre at the GMU: a) The commercial center, bank, and news centre in the first floor and meeting rooms, computer rooms and multimedia rooms in the second and third floor of the building; b) the news centre in the first floor of the building; c) the library in the second floor of the building

(4) Corridor space

The corridor space also provides working structural holes. This space is special since it provides a short and easy transition from work to relaxation at any time. When people get tired with their regular works and it is not the end of their regular working hours, they need a short break, five or ten minutes. In this

case, the corridor space is an ideal place for a short relaxation. Drink a cup of coffee, have a chat with a person happening to be there, or just be there for a change. On the other hand, it also provides a flexible space to involve a dynamic team working together, whenever needed. People from different offices can arrange brief meetings there. The meetings are informal, so they may not think they are working. In these ways, working structural holes are provided.

Figure 7 shows the corridor of the engineering building of the Università Politecnica delle Marche, Italy. The corridor is also used as study space, discussion space and an information board. Figure 8 shows space for discussion and relaxation in the corridor of the aerospace building of TU Delft. Several aircraft models are exhibited, and printers, automatic vending machines and hot drinks machines are placed in the corridor of each floor of the building. People can take a drink, talk to someone happening to be there when they use the printer or simply take a rest in a chair.



Fig. 7. a) The corridor of the Engineering Building, the Università Politecnica delle Marche, Italy; b) one of the entrances to the building

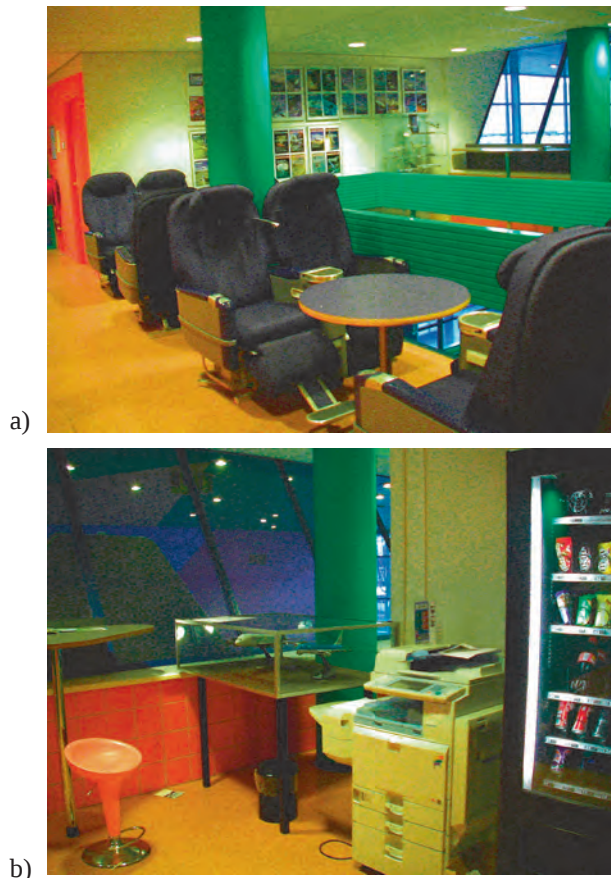


Fig. 8. a) The discussion and rest space in the corridor, the Aerospace Engineering Building, TU Delft; b) the aircraft models and facilities, same building

(5) Discussion

A better understanding of the concept of a structural hole may be developed using an analogy to a gap on the ground and a bridge across the gap. The difference between a gap and a structural hole lies in the bridge that may emerge naturally across the gap. Such a bridge may possibly emerge naturally through communication, contemplate, or incubating. We want bridges since they inspire or promote creativity, but we cannot build them with steel, concrete, or stone. What we can do is to create many gaps to facilitate an environment in which many bridges may emerge. Domain and thinking structural holes provide more and wider gaps to cross, while working structural hole provides more gaps to cross. Particularly, in the case of this paper, the concept of structural holes may be simply understood as the mental state gap between working place and home, the thinking style gap between different groups, and the domain gap between different disciplines and backgrounds.

The fundamental assumption of this paper is that bridges may possibly emerge naturally when structural

holes are created through formal or informal interaction and unconscious or semiconscious incubation, which can be supported by the studies on the environmental support to creativity. Hence an expanded knowledge space is achieved and the probability of design creativity is increased when structural holes exist.

Structural holes are used here as a theoretical framework to analyze the impact of environment on creativity. The analysis can also be done under a historical framework and psychological framework, as discussed in the book “Successful Education” (Arciszewski 2009). In the book, “Medici Effect” is introduced to illustrate the environment factor in engineering creativity; “Engineering Village” and “Design Studio” are proposed to practice “Da Vinci Seven Principles” in order to develop student’s creativity. The book investigates complex factors that will influence the development of creativity, including management, psychology, economics, politics, public policy, education paradigm, teaching style, thinking style, and architecture etc. The research presented here focuses on explaining how proper public space can promote creativity.

5. Summary

An environment supporting reflection, relaxation, formal and informal interaction, and knowledge sharing will foster and promote design creativity. The concept of structural hole is extended in this paper by distinguishing three classes of structure holes: domain, thinking and working structural holes. The domain structural hole refers to the disciplines gap between two groups; the thinking structural hole refers to the thinking style gaps between two groups or two persons; and the working structural hole refers to the space gaps between the working state and non-working state as well as relaxed mental state and focused mental state.

The domain structural holes create opportunities for knowledge sharing and integration across traditional borders so that the knowledge space can be expended. The thinking structural hole creates opportunities for distant analogies and new interpretations to promote collective creativity. The working structural hole creates opportunities for unpredictable fresh ideas through formal and informal interaction, individual reflection as well as relaxation.

An environment with abundance of structural holes can be created by proper public places. The proper public places in campus buildings create domain, thinking and working structural holes. A public place means a place that is comfortable to stay, takes only several minutes to get there, and it is a large and

enjoyable physical space that always has something to attract visitors. Proper public places in campus building may be an entrance hall, a restaurant, an activity center, or simply a corridor space.

A better understanding of the concept of structural hole may be achieved by comparing it to a bridge across a gap. The bridge can possibly emerge naturally through communication, contemplation, or incubation when gaps (structural holes) are created.

The next step of this research is to establish a design framework of creativity-oriented public spaces.

Acknowledgements

The research presented in this paper is partially supported by a key grant from Beijing Information Science and Technology University. The paper is a revised and extended version of an initial paper, which has been partially presented at the Third Design Creativity Workshop, Stuttgart, July 10, 2010. We would like to thank professor Arciszewski of George Mason University for his valuable suggestions regarding this paper and, particularly, for his careful revisions and editing of the manuscript to make the paper easier to read and comprehend.

References

- [1] Amabile, T.M. et al: 1996, *Assessing the Work Environment for Creativity*, Academy of Management Journal, 39(5), pp. 1154-1184.
- [2] Arciszewski, T.: 2009, *Successful Education: How to Educate Creative Engineers*, Successful Education LLC.
- [3] Bernus, J.S. and Chase, M.A.: 1990, *Decision making in a networked environment*, in H. Eschenauer, J. Koski and A. Osyczka (eds.), Technology and Communication, Springer-Verlag, Berlin, pp. 376-396.
- [4] Borgatti, S.: 2010, *Strength of Weak Ties, Structural Holes, Closure and Small Worlds*. www.analytictech.com/mgt780/slides/swt.pdf
- [5] Burt R.S.: 1992, *Structural Holes: The Social Structure of Competition*, Cambridge, Mass., Harvard University Press.
- [6] Burt R.S.: 2001, *The social capital of structural holes, in New directions in economic sociology*, ed. By Guillen MF et al. New York, Russell Sage Foundation.
- [7] Burt R.S.: 2002, Bridge Decay, *Social Networks* 24: pp. 333-363
- [8] Burt R.S.: 2004, *Structural Holes and Good Ideas*, *American Journal of Sociology*, Volume 110 Number 2, pp. 349-99
- [9] Gellynck, X.; Vermeire, B.; and Viaene, J.: 2007, *Innovation in food firms: Contribution of regional networks within the international business context*, *Entrepreneurship & Regional Development*, 19, pp. 209-226.
- [10] Gibson, J.J.: 1972, *A Theory of Direct Visual Perception*. In J. Royce, W. Rozenboom (Eds.). *The Psychology of Knowing*. New York: Gordon & Breach.
- [11] Gellynck, X.; Vermeire, B.; and Viaene, J.: 2007, *Innovation in food firms: Contribution of regional networks within the international business context*, *Entrepreneurship & Regional Development*, 19, pp. 209-226.
- [12] Granovetter, M.: 2005, *The impact of social structure on economic outcomes*, *Journal of Economic Perspectives*, 19(1), pp. 33-50.
- [13] Cross, N.: 1997, *Descriptive models of creative design: application to an example*, *Design Studies*, 18(4), pp. 427-455.
- [14] Csikzentmihalyi, M.: 1996, *Creativity. Flow and the psychology of discovery and invention*. New York: HarperCollins.
- [15] Dekel A. et al: 2005, *Adding Playful Interaction to Public Spaces*, M. Maybury et al. (Eds.): INTETAIN, LNAI 3814, pp. 225-229.
- [16] Hargadon, A.B. and Bechky, B.A.: 2006, *When Collections of Creatives Become Creative Collectives: A Field Study of Problem Solving at Work*, *Organization Science*, 17(4): pp. 484-500.
- [17] http://ct4ct.com/index.php?title=Public_Space
- [18] Lee, S et al: 2010, *The impact of environment*, <http://www.creativityincubator.com>
- [19] Leigh-Ann Bartsch: 2010, listen to your heart, lmbartsch.com/design/images/ListenToYourHeart.pdf
- [20] Leonard, D. and Sensiper, S.: 1998, *The role of tacit knowledge in group innovation*, *California Management Review*, 40 (3), pp. 112-132.
- [21] Johnson, H. and Carruthers, L.: 2006, *Supporting creative and reflective processes*, *Int. J. Human-Computer Studies*, 64, pp. 998-1030.
- [22] Minsk, M.L.: 1990, *Process models for cultural integration*, *Journal of Culture* 11(4): pp. 49-58.
- [23] Neisser, U.: 1976, *Cognition and reality: principles and implications of cognitive psychology*, WH Freeman.
- [24] Pahl, G. and Beitz, W. et al: 2007, *Engineering Design: a Systematic Approach*, Springer-Verlag, Berlin.
- [25] Sanders, L.: 2001, *Collective Creativity*, *LOOP: AIGA Journal of Interaction Design Education*, 3, pp. 1-6.
- [26] Smythe, J.S. (ed.): 1990, *Applications of Artificial Intelligence to Communication*, CMP and Springer-Verlag, Berlin.
- [27] Rutan, B.: 1996, Scaled composites, in a documentary interview.
- [28] Sanders L.: 2001, *Collective Creativity*, *AIGA Journal of Interaction Design Education*, 3, pp. 1-6.
- [29] Young, T.M.: 2007, *Aircraft design innovation: creating an environment for creativity*, *Proc. IMechE* Vol. 221 Part G: J.
- [30] Van Der Merwe, R., *Structural Holes and Online Social Networks*.
- [31] <http://ezinearticles.com/?Structural-Holes-And-Online-Social-Networks&id=744899>

IMPACT OF BASALT AGGREGATE ON POROSITY AND STRENGTH OF SILICATE PRODUCTS

Abstract

This paper presents the key features of calcium silicate products modified by basalt aggregate. The special focus is on porosity and compressive strength of the products discussed. From a practical point of view, these features are particularly important in building materials technology. The primary objective of the conducted research is to identify and analyze the porous structure of traditional and modified products as well as to determine an impact of the basalt aggregate on their compressive strength.

Keywords: silicate, mercury porosimetry, porosity, strength, basalt

1. Introduction

Silicate products are a completely natural building material consisting of sand, lime and water, so they are environment-friendly. Silicate products are characterized by their high strength. Furthermore, they show high resistance to weather conditions, to the process of biological corrosion and owing to their ability to accumulate heat and humidity, silicates have good properties for regulation of interior heat and humidity conditions.

Their unquestionable advantage is also a large mass, which gives them a high acoustic insulation which is of major importance in modern times. They are widely used in many European countries as well as on other continents, though to a smaller degree [1, 2].

The analysis of various filling materials in respect of suitability pointed out to basalt aggregate as the most suitable. Basalt is characterized by high density of 2700 to 3200 kg/m³, which can considerably improve the physical and mechanical properties of a product as well as its acoustic properties [4].

Though widely used, sand-lime products are still scarcely known from a scientific point of view. Knowledge of structural and textural properties of silicate products (i.e. their specific surface area and volume and size of pores) is of key importance in many processes, especially those connected with catalysis and adsorption and in testing physical and mechanical

properties. While scientists succeeded in casting some light on such features of silicate products such as: strength, absorbability and absorption, investigations related to adsorption still are open to many questions. Adsorption is the process causing accumulation of molecules on the surface in a condensed form [5] (of a solid i.e. silicate). The adsorbed substance is called an adsorbate and the substance on which this process occurs is called an adsorbent or substrate [3] (silicate is an adsorbent). An adsorbent's active surface consists also of various pores and ducts. Depending on the degree of adsorbent's fragmentation, its specific surface area enlarges.

Widely-used adsorbents include inter alia different kinds of prepared activated charcoal.

Apart from adsorption [i.e. concentration of adsorbent on a surface], there is a simultaneous occurrence of absorption [i.e. the smooth assimilation of an adsorbate by a silicate product]. The process of adsorption and absorption is generally called sorption [6, 7]. Large specific surface area, porosity and the size of pores are some of the factors influencing adsorbents' sorbed capacity. In order to specify the textural properties of solids, the most-frequently used methods are based on the measurement of the amount of adsorbed adsorbate on the surface of the tested material. The obtained data makes it possible to calculate the specific surface area and porosity of

the analysed product. Silicates are porous materials, therefore they were examined by means of mercury porosimetry. This method enables measurement of volume, distribution and size of macro and mezo pores of solids. It uses one of mercury characteristics that is the non-wetting of surfaces of the most solids, thanks to which mercury under lowered pressure does not automatically penetrate into the pores. When pressure is increased, mercury intrudes into the sample's pores. Knowing the amount of mercury loaded into the pores under given pressure, we can determine the volume and size of pores [8].

2. Methodology of experimental examinations

Tests were conducted in accordance with the previously-assumed methods. Experiments concerned traditional silicate products as well as the products modified by basalt aggregate of a specific fraction and size. Three kinds of tests were made. They contributed to the knowledge and systematization both of structure and texture of traditional (standard) and modified sand-lime products. The content of basalt aggregate of a given fraction (2-4 mm) in the modified elements was: 10, 20 and 30% of an addition in proportion to the product mass, respectively.

The following tests were made:

- strength of modified silicate products,
- absorption caused by capillary rising,
- mercury porosimetry.

The tests results were compared with the results of traditional sand-lime products.

The strength test was performed on traditional and modified silicate elements, the size of 180 x 250 x 220 mm.



Fig. 1. Absorption of traditional (B) and modified (A) silicate products

Sand-lime products underwent tests that aimed to determine their water absorption. Absorption is a smooth assimilation of an adsorbate (here: water) by the entire mass of a silicate product, through capillary rising. Tests concerned traditional and modified silicate products. The process of water absorption through capillary rising by the sample consisted in submerging face sides (220 x 250 mm) of the analysed elements in water at a given depth [(in millimeters)] and for a given time (Fig. 1). The test was conducted in accordance with the standard PN-EN 772-11 [10].

The method of mercury porosimetry enables determining the size of pores which minimal radius depends on maximal pressure achieved during a measurement. Samples of 4 x 4 x 2 cm were used. The pore volume of the tested silicate product is determined on the basis of the known amount of mercury intruded into the pores as a result of the applied pressure. This amount is specified by the capacity method. It was done by measuring changes in capacity of the condenser whose covers include an outer, motionless electrode (put on a dilatometer) and the moveable mercury column in a calibrated dilatometer pipe. The length of the mercury column decreases proportionally to the pressure increase. It is due to the compressibility of mercury and its intrusion into the pores of the tested material. Knowledge of the relationship between the current pressure and the compressibility of mercury makes possible to determine the amount of mercury which penetrated the material pores, and consequently the volume of these pores [8].

Every porous material, including silicates, can be characterized by basic parameters which describe its structure. For determining the porous structure of a solid body these include:

- a) average radius of pores R . It's an average pore radius for a given porous material. Therefore we can state that we face a certain distribution of pore sizes with respect to the radius R . It is denoted in literature as PSD (Pore Size Distribution);
- b) specific surface area S of a solid body. It is equal to the total sum of external surface (S_e) and internal surface (S_i). The external surface corresponds to geometric surface area of porous grains per gram of adsorbent. It is reversely proportional to the grain size. Pore walls form the internal surface area. According to definition, pores have to be open. Thus the S_i value does not concern the area of closed pores.

Generally, the Si value considerably exceeds the Se value. The larger specific surface area S the smaller values of pore radii R. Large specific surface area ($S > 500 \text{ m}^2/\text{g}$) indicates the existence of narrow pores. The small specific surface area ($S < 10 \text{ m}^2/\text{g}$) is characteristic of macroporous solids;

- c) total pore volume V_p which corresponds to the volume of liquid adsorbate that fills in pores contained in a unit of sorbent mass [11].

During performance of mercury porosimetry it is also necessary to determine three values. These are: the bulk and apparent density and percentage share of pores in the tested element.

3. Results of experiments

Compression of the tested elements is shown in the photographs below.



Fig. 2. Strength test of a traditional silicate product



Fig. 3. Strength test of a modified silicate product

The test showed increased strength of modified silicates. The analysis results are shown on the below chart.

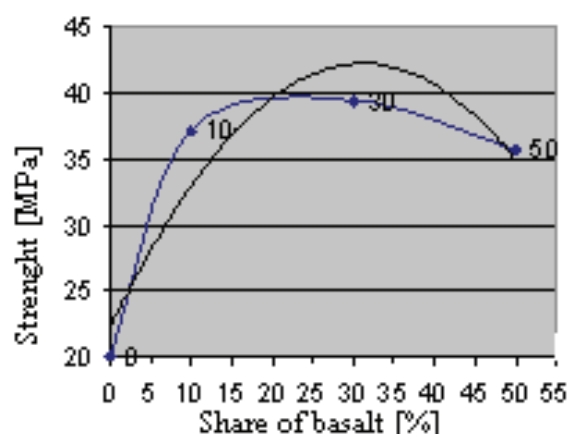


Fig. 4. Dependency of compression strength on the percentage share of aggregate

Figure 4 shows a chart of dependency of the silicate strength on its composition. The strength of a traditional product was about 20 MPa, while silicates modified by basalt aggregate gained far greater compression strength. The application of basalt aggregate of high density increased the density of modified elements. Consequently, increased their compressive strength. The strength optimum ranges from 25 to 35% of the share of aggregate in proportion to the product mass. However, a further increase in the share leads to the decrease in strength. An excessive interference in the sand-lime product structure may also lead to the worsening of other physical and mechanical characteristics.

The presently-applied classification of pores (micro-, mezzo- and macro pores) is based on the different adsorptive and capillary reactions IUPAC classifies pores according to their size in the following way:

- micro pores $d_p < 2 \text{ nm}$,
- mezzo pores $2 \text{ nm} \leq d_p \leq 50 \text{ nm}$,
- macro pores $d_p > 50 \text{ nm}$ [12].

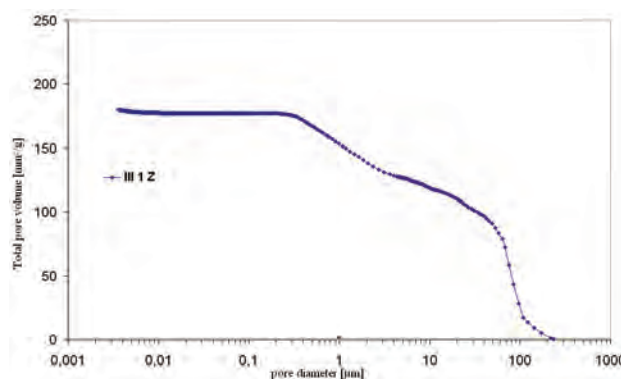


Fig. 5. Dependency of the volume of pores on their diameter in a traditional silicate

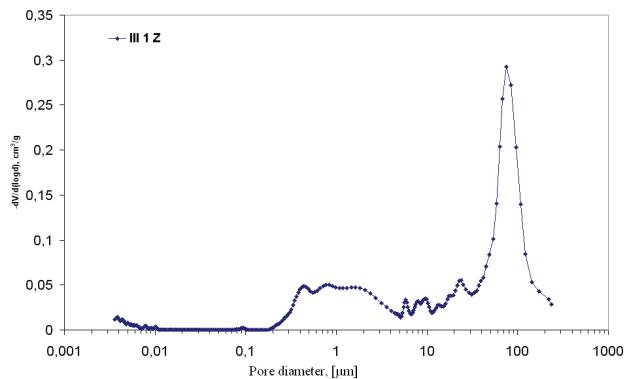


Fig. 6. Distribution of pore volume in a traditional silicate

The charts below (Figures 5 and 6) present dependencies between the diameter of pores and their volume in traditional sand-lime products. The below curves shows, that the smaller diameter of pores in a product, the larger their total volume. The volume of mezo pores is even in a given range (2-50 nm) and has the form of a straight line; while the macro pores are distributed in a more varied and non-uniform way.

Figures 7 and 8 present dependencies between the diameter of pores and their volume in modified sand-lime products.

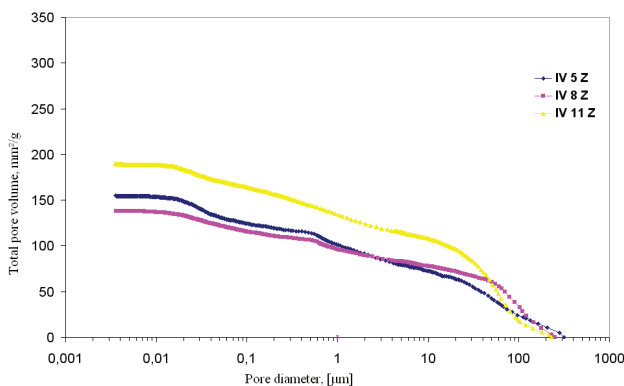


Fig. 7. Dependency of the volume of pores on their diameter in a modified silicate

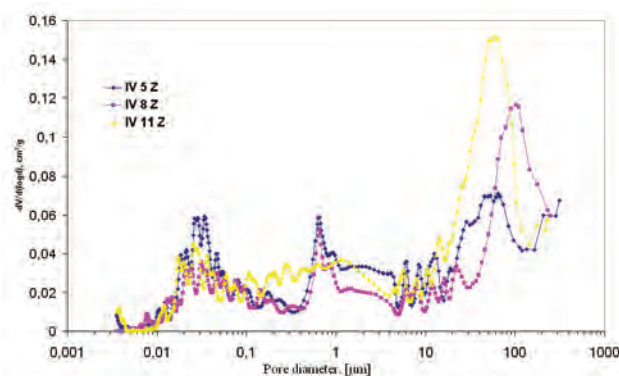


Fig. 8. Distribution of pore volume in a modified silicate

Figure 7 shows dependency between the volume of pores and their diameter in products modified by basalt aggregate. The blue curve (IV 5 Z) indicates a product with 10% of aggregate, the yellow curve (IV 11 Z) shows a product with 30% of aggregate, and the pink curve (IV 8 Z) symbolizes a product with 50% of basalt aggregate. Traditional silicate products consist of sand and lime with a small amount of water. The insertion of bigger grain-size aggregate into a product resulted in formation of additional pores of different diameters. In mercury porosimetry the best result was obtained by the product with 10% of basalt aggregate. Curve IV 5 Z has the smoothest distribution. The charts show that the occurrence both of mezo and macro pores is similar. However, the comparison of the results of mercury porosimetry with the strength test of the product of the identical content of basalt aggregate gave less optimistic results. The silicate product with 30% of aggregate turned out poorly though it is characterized by the best compression strength. The chart showing the pore distribution is, in this case, uneven and abrupt. The content of macro pores considerably exceeds the content of mezo pores in the tested product. Curve IV 8 Z contains the smallest total volume of mezo pores of the smallest diameter that occurs here while the distribution and volume of macro pores approximates curve IV 5 Z.

Summarizing of the above facts we may state that: indicates curve IV 5 Z as the best. The blue curve (IV 5 Z) shows the least anomalies and runs in the smoothest way in relation to the remaining two. For the purpose of better understanding of the obtained dependencies it's necessary to conduct an additional test on the Scanning Electron Microscope (SEM).

Data obtained as a result of the test related to absorption caused by capillary rising of silicate products showed the following dependencies.

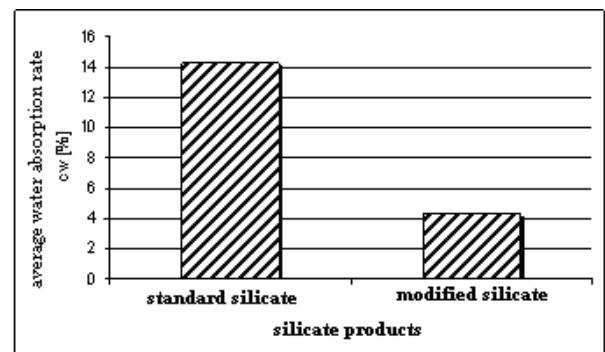


Fig. 9. Difference in water absorption in traditional and modified silicate products

The above chart presents water absorption ability by two types of the tested elements. Each material is characterized by a specific absorbability and humidity. Due to its microporous (microcapillary) structure, the silicate brick absorbs water very quickly, but it stops after a maximum saturation of 16%. Such water rising does not lower other properties of the silicate. The present tests aim at improving physical and mechanical properties of this type of products. The experiment has shown that traditional (standard) silicates are characterized by the considerably greater water absorption than their modified equivalents (Fig. 9). Thus, in the tested products, the change in material structure contributed to considerable percentage decrease in water absorption with the simultaneous increase in strength. Summarizing it up we may state, that standard silicates have been entirely moistened by water through capillary rising while modified products have been damped a little above the half of their height (where $h=17$ cm per 22 cm of the product height).

4. Conclusions

1. The change in the structure of silicate products modified by basalt aggregate improved compression strength of the products.
2. The application of an addition in the form of basalt aggregate of high density led to the increase in density of the product itself.
3. The increase in density of the product modified by basalt aggregate reduced absorbability caused by capillary rising of the new silicate product.
4. The introduction of bigger grain-size basalt aggregate into the sand-lime product caused formation of additional pores of different diameters. Consequently that brought about a change in the structure and texture of the modified product.
5. It has been proved that the increase in density of a traditional product modified by appropriate aggregate may lead to improvement of some assumed physical and mechanical properties, without changing the element's volume.
6. The introduction of 30% content of basalt aggregate into the sand-lime product proportionally to the product mass caused the increase in compression strength of the silicate product.
7. The most optimal distribution of pores manifests itself at 10% content of aggregate in the product.

References

- [1] Parker Philip M., Lilly E., *The 2006-2011 World Outlook for All Silica*. Brick and Shapes Excluding Semi-Silica. INSEAD (Singapore and Fontainebleau, France) ICON Group International, Inc. 2005.
- [2] Dachowski R., Linczowski C., *Comparison of the Most Popular Wall Building Materials Used in Detached Houses*. Przemiana. Kielce, 1998.
- [3] Stypuła B., *Adsorption – Process Occurring on the Surface of Condensed Bodies*. Laboratory tests, Akademia Górniczo-Hutnicza in Cracow.
- [4] Dachowski R., Stępień A., *Examination of Physical Characteristics of the Modified Sand-Lime Products*. Transcom 2009, pp. 35-38, Slovak Republic.
- [5] Ościk J., *Adsorption*, PWN Warsaw, 1979.
- [6] Atkins P.W., *Basics of Physical Chemistry*, PWN, Warsaw 2001.
- [7] Pigoń K., Ruziewicz Z., *Physical Chemistry*, PWN, Warsaw 1980.
- [8] *Porous Structure of Solids – Mercury Porosimetry*, Industrial Laboratory of Chemical Technology, Politechnika Wrocławska.
- [9] Imielińska K., Wojtyra R., *Impact of Water Absorption on Properties of Vinyl Ester Laminates Strengthened by Aramid and Glass Fibre*. COMPOSITES 3 (2003) 7.
- [10] PN-EN 772-11 *Methods of Wall Elements Testing*.
- [11] Szymański E., *Laboratory Tests in Physical Chemistry - Measuring Equipment*, UMCS Lublin, 1991.
- [12] Maresz K., *Occurrence and Characteristics of New Mezo-porous Proton Catalysts and their Application in Esterification Reaction*. Ph.D. thesis, Institute of Chemical Engineering of Polish Academy of Sciences in Gliwice.

Anna Stępień

Wpływ kruszywa bazaltowego na porowatość i wytrzymałość wyrobów silikatowych

1. Wprowadzenie

Wyroby silikatowe są całkowicie naturalnym materiałem budowlanym, składającym się z piasku, wapna i wody, są więc przyjazne dla środowiska naturalnego. Cechą charakterystyczną silikatów jest ich znaczna wytrzymałość. Ponadto odznaczają się wysoką odpornością na działanie czynników atmosferycznych, odpornością na proces korozji biologicznej, a dzięki zdolności do akumulacji ciepła i wilgoci silikaty posiadają bardzo dobre właściwości do regulacji warunków cieplno-wilgotnościowych w pomieszczeniu.

Ich niewątpliwą zaletą jest również duża masa, która sprawia, że cechują się wysoką izolacyjnością akustyczną, co ma niebagatelne znaczenie w dzisiejszych czasach. Na szeroką skalę stosuje się je w wielu krajach europejskich, jak również na pozostałych kontynentach, choć w mniejszym stopniu [1, 2].

Analiza różnorodnych wypełniaczy, przeprowadzona w celu doboru najbardziej odpowiedniego, wskazała na kruszywo bazaltowe.

Wyroby wapienno-piaskowe choć tak powszechnie stosowane z naukowego punktu widzenia są jednak wciąż mało znane. Znajomość właściwości strukturalnych (tj. powierzchni właściwej oraz objętości i rozmiaru porów) wyrobów silikatowych, ma kluczowe znaczenie w wielu procesach, szczególnie związanych z katalizą i adsorpcją, jak również przy badaniu właściwości fizyko-mechanicznych. O ile naukowcom udało się rzucić nieco światła na takie cechy wyrobów silikatowych jak: wytrzymałość na ścislenie, nasiąkliwość i absorpcja, o tyle badania nad adsorpcją wciąż pozostawiają szereg pytań. Adsorpcja to proces powodujący nagromadzenie się cząstek na powierzchni fazy skondensowanej [5] (ciała stałego, czyli silikatu). Substancję, która ulega adsorpcji nazywana jest adsorbentem, a substancja na której ten proces zachodzi – adsorbentem lub podłożem [3] (adsorbentem jest silikat). Powierzchnię czynną adsorbentu tworzą również różne pory i kanaliki. Zależnie od stopnia rozdrobnienia adsorbentu zwiększa się jego powierzchnia właściwa. Do często stosowanych adsorbentów należą między in-

nymi różne gatunki specjalnie preparowanego węgla aktywnego.

Obok adsorpcji, polegającej na powierzchniowym zagęszczaniu adsorbentu, występuje równoległe zjawisko absorpcji, które polega na równomiernym pochłanianiu adsorbentu przez wyrób silikatowy. Zjawisko adsorpcji i absorpcji nazwano ogólnie sorpcją [6, 7]. Duża powierzchnia właściwa, porowatość oraz rozmiar porów są jednymi z czynników wpływających na zdolność sorpcyjną adsorbentów. W celu określenia właściwości teksturalnych ciał stałych stosowane są najczęściej metody polegające na pomiarze ilości adsorbentu zaadsorbowanego na powierzchni badanego materiału. Na podstawie otrzymanych danych możliwe jest obliczenie powierzchni właściwej i porowatości wyrobu poddanego analizie. Silikaty to materiały porowate, dlatego też zostały poddane doświadczeniom z zastosowaniem porozymetrii rtęciowej. Wykorzystuje się w niej jedną z cech rtęci, jaką jest brak zwilżalności powierzchni większości ciał stałych. Zwiększenie ciśnienia powoduje „wepchnięcie” rtęci do wnętrza porów. Znajac ilość rtęci wtłoczonej pod danym ciśnieniem do wnętrza porów możliwe jest określenie objętości porów oraz ich rozmiarów [8].

2. Metodyka badań eksperymentalnych

Badania wykonano według wcześniej przyjętej metodyki i w oparciu o normę PN-EN 772-11. Doświadczeniom poddano tradycyjne wyroby silikatowe, jak również te modyfikowane kruszywem bazaltowym o określonej frakcji i wymiarach. Wykonano trzy rodzaje badań, które pomogły w poznaniu i usystematyzowaniu zarówno struktury, jak i tekstury wyrobów wapienno-piaskowych tradycyjnych oraz modyfikowanych. Zawartość kruszywa bazaltowego o określonej frakcji (2-4 mm) w modyfikowanych elementach wynosiła odpowiednio 10, 20 i 30% dodatku w stosunku do masy wyrobu.

Wykonano następujące badania:

- wytrzymałość modyfikowanych wyrobów silikatowych,
- absorpcję spowodowaną podciąganiem kapilarnym,
- porozymetrię rtęciową.

Uzyskane w wyniku doświadczeń dane zestawiono z wynikami tradycyjnych wyrobów wapienno-piaskowych.

3. Wyniki badań eksperymentalnych

Rysunek 4 przedstawia wykres zależności wytrzymałości silikatu w odniesieniu do jego składu. Wytrzymałość tradycyjnego wyrobu wyniosła około 20 MPa, podczas gdy silikaty modyfikowane kruszywem bazaltowym uzyskały znacznie większą wytrzymałość na ściskanie. Zastosowanie kruszywa bazaltowego o dużej gęstości doprowadziło do zwiększenia gęstości elementów modyfikowanych, a tym samym do podniesienia ich wytrzymałości na ściskanie. Optimum wytrzymałościowe znajduje się w przedziale 25-35% udziału kruszywa w stosunku do masy wyrobu. Dalsze zwiększanie udziału tego rodzaju kruszywa w wyrobie powoduje jednak spadek wytrzymałości. Nadmierna ingerencja w strukturę wyrobu wapienno-piaskowego może doprowadzić również do pogorszenia się innych cech fizyko-mechanicznych tych elementów.

Obecnie stosowana klasyfikacja porów (mikropory, mezopory i makropory) oparta jest na różnicy zachodzących w nich zjawisk adsorpcyjnych i kapilarnych. Pory klasyfikowane są przez IUPAC ze względu na ich rozmiar.

Wykresy (rys. 5 i 6) przedstawiają zależności między średnicą porów a ich objętością w tradycyjnych wyrobach wapienno-piaskowych. Z poniższych krzy-

wych można odczytać, że im mniejsza jest średnica porów występujących w wyrobie, tym większa jest ich objętość sumaryczna. Objętość mezoporów jest równomierna w określonym przedziale (2-50 nm) i przybiera postać prostej, natomiast rozkład makroporów jest bardziej zróżnicowany i niejednorodny.

Na rysunek 7 przedstawiono zależność pomiędzy objętością porów a ich średnicą w modyfikowanych kruszywem bazaltowym wyrobach. Najkorzystniej w porozymetrii rtęciowej wypadł wyrób z 10% zawartością kruszywa bazaltowego. Na wykresach widać, że występowanie zarówno mezo- jak i makroporów jest zbliżone.

Wyrób silikatowy z 30% zawartością kruszywa wypadł niekorzystnie, choć odznacza się on najlepszą wytrzymałością na ściskanie.

4. Wnioski

1. Zmiana struktury wyrobów silikatowych modyfikowanych kruszywem bazaltowym korzystnie wpłynęła na poprawę wytrzymałości na ściskanie powstałego wyrobu.
2. Zastosowanie dodatku w postaci kruszywa bazaltowego o dużej gęstości spowodowało tym samym zwiększenie gęstości samego wyrobu.
3. Wzrost gęstości wyrobu modyfikowanego kruszywem bazaltowym ograniczył absorpcyjność powodowaną podciąganiem kapilarnym nowego wyrobu silikatowego.

PAVEL A. AKIMOV¹
VLADIMIR N. SIDOROV²
MARINA L. MOZGALEVA³

Moscow State University of Civil Engineering
26, Yaroslavskoe Shosse,
129337, Moscow, Russia

¹e-mail: pavel.akimov@gmail.com

²e-mail: sidorov.vladimir@gmail.com

³e-mail: marina.mozgaleva@gmail.com

ABOUT CORRECT METHOD OF ANALYTICAL SOLUTION OF MULTIPOINT BOUNDARY PROBLEMS OF STRUCTURAL MECHANICS FOR SYSTEMS OF ORDINARY DIFFERENTIAL EQUATIONS WITH PIECEWISE CONSTANT COEFFICIENTS

Abstract

This paper is devoted to correct method of analytical solution of multipoint boundary problems of structural mechanics for systems of ordinary differential equations with piecewise constant coefficients. Its major peculiarities include uni-versality, computer-oriented algorithm involving theory of distributions, computational stability, optimal conditionality of resultant systems and partial Jordan decomposition of matrix of coefficients, eliminating necessity of calculation of root vectors.

Keywords: correct analytical solution, multipoint boundary problem, discrete-continual methods, structural mechanics, system of ordinary differential equations, piecewise constant coefficients

1. Formulation of the Problem

Piecewise invariability of physical and geometrical parameters in one dimension exists in various problems of analysis of structures and their mathematical models. We should mention here in particular such vital objects as beams, strip foundations, thin-walled bars, deep beams, plates, shells, high-rise buildings, extensional buildings, pipelines, rails, dams and others [1, 2, 3]. Analytical solution is apparently preferable in all aspects for qualitative analysis of calculation data. It allows investigator to consider boundary effects when some components of solution are rapidly varying functions. Due to the abrupt decrease inside of mesh elements in many cases their rate of change can't be adequately considered by conventional numerical methods while analytics enables study. Another feature of the proposing method is the absence of limitations on lengths of structures. Hence it appears that in this context so-called discrete-continual methods of structural analysis

(especially discrete-continual finite element method) are peculiarly relevant [1, 2, 3]. Generally, discrete-continual formulations are contemporary mathematical models which currently becoming available for computer realization.

Discrete-continual methods are reduced at some stage to the solution of multipoint boundary problems of structural mechanics for systems of ordinary differential equations with piecewise constant coefficients. Conventional formulation of multipoint boundary problem of this type has the form

$$\bar{y}^{(1)} - A_k \bar{y} = \bar{f}_k, \quad x \in (x_k^b, x_{k+1}^b), \quad k = 1, 2, \dots, n_k - 1; \quad (1.1)$$

$$B_k^- \bar{y}(x_k^b - 0) + B_k^+ \bar{y}(x_k^b + 0) = \bar{g}_k^- + \bar{g}_k^+, \quad k = 2, \dots, n_k - 1; \quad (1.2)$$

$$B_1^+ \bar{y}(x_1^b + 0) + B_{n_k}^- \bar{y}(x_{n_k}^b - 0) = \bar{g}_1^+ + \bar{g}_{n_k}^-, \quad (1.3)$$

where

$$\bar{y} = \bar{y}(x) = [y_1(x) \ y_2(x) \ \dots \ y_n(x)]^T$$

is the desirable vector function;

$$x_k^b, \quad k=1, \dots, n_k$$

are coordinates of boundary points;

$$A_k, \quad k=1, 2, \dots, n_k-1$$

are matrices of constant coefficients of order n ;

$$\bar{f}_k = \bar{f}_k(x) = [f_{k,1}(x) \ f_{k,2}(x) \ \dots \ f_{k,n}(x)]^T$$

$$k=1, 2, \dots, n_k-1$$

are right-side vector functions

$$B_k^-, B_k^+, \quad k=2, \dots, n_k-1 \quad \text{and} \quad B_1^+, B_{n_k}^-$$

are matrices of boundary conditions of order n at point

$$x_k^b; \quad \bar{g}_k^-, \bar{g}_k^+, \quad k=2, \dots, n_k-1 \quad \text{and} \quad \bar{g}_1^+, \bar{g}_{n_k}^-$$

are right-side vectors of boundary conditions at point

$$x_k^b; \quad \bar{y}^{(1)} = \bar{y}^{(1)}(x) = d\bar{y} / dx.$$

Solution of multipoint boundary problem of this type in structural mechanics is accentuated by numerous factors. They include boundary effects (stiff systems) and considerable number of differential equations (several thousands). Moreover, matrices of coefficients of a system normally have eigenvalues of opposite signs and corresponding Jordan matrices are not diagonal. Special method of solution of multipoint boundary problems for systems of ordinary differential equations with piecewise constant coefficients in structural mechanics has been developed. Not only does it overcome all difficulties mentioned above but its major peculiarities also include universality, computer-oriented algorithm, computational stability, optimal conditionality of resultant systems and partial Jordan decomposition of matrix of coefficients, eliminating necessity of calculation of root vectors.

2. Jordan Decomposition of Matrices of Coefficients

Jordan decomposition of matrix A_k has the form

$$A_k = T_k J_k T_k^{-1}, \quad (2.1)$$

where

$$J_k = \{J_{k,1}, J_{k,2}, \dots, J_{k,u_k}\}; \quad (2.2)$$

T_k is the matrix of order n , which columns are eigenvectors and root vectors of matrix A_k ; J_k is Jordan matrix of order n ; $J_{k,p}$ is Jordan cell corresponding to eigenvalue $\lambda_{k,p}$; $\dim J_{k,p} = m_{k,p}$.

As we have already mentioned above, specificity of problems of structural mechanics comprises in presence of multiple eigenvalues of matrix A_k and

consequently in necessity of calculation of root vectors. However at the present time there are no effective numerical method of calculation of Jordan decomposition in the general case [4]. Meanwhile the number of multiple eigenvalues in the considering type of problems is normally limited. Besides these multiple eigenvalues are generally zeros. In this connection special alternative approach to solution has been developed.

3. Partial Jordan Decomposition

Partial Jordan decomposition is based on computation of right and left eigenvectors of matrix A_k .

$$A_k = A_{k,1} + A_{k,2}; \quad (3.1)$$

$$A_{k,1} = T_{k,1} J_{k,1} \tilde{T}_{k,1}; \quad A_{k,2} = A_k - A_{k,1}; \quad (3.2)$$

$T_{k,1}$ is the matrix containing right eigenvectors corresponding to non-zero eigenvalues of matrix A_k ; $\tilde{T}_{k,1}$ is the matrix containing left eigenvectors corresponding to non-zero eigenvalues of matrix A_k ; $J_{k,1}$ is diagonal Jordan matrix corresponding to non-zero eigenvalues of matrix A_k ; $A_{k,2}$ is the part of matrix A_k corresponding to prime and multiple zero eigenvalues. It is necessary to note here that matrices $T_{k,1}$ and $\tilde{T}_{k,1}$ in general case are rectangular.

4. Construction of Projectors

Eigenvalues $\lambda_{k,p}$, $p=1, \dots, u_k$ are renumbered according to the condition

$$\left. \begin{aligned} \forall \lambda_{k,p}, \quad p=1, \dots, l_k \quad \exists m_{k,p} = 1 \\ \forall \lambda_{k,p}, \quad p=l_k+1, \dots, u_k \quad \exists m_{k,p} > 1 \end{aligned} \right\}, \quad (4.1)$$

where

$$l_k = \sum_{p=1}^{u_k} \delta_{1,m_{k,p}}, \quad (4.2)$$

where $\delta_{i,j}$ is Kronecker delta.

Due to distinctive procedure, we should properly modify matrices $T_{k,1}$, $\tilde{T}_{k,1}$ and $J_{k,1}$.

Let $P_{k,1}$ and $P_{k,2}$ be projectors to subspaces of left and right eigenvectors and root vectors of matrix A_k corresponding to non-zero and zero eigenvalues. They may be denoted as

$$P_{k,1} = T_{k,1} (\tilde{T}_{k,1} T_{k,1})^{-1} \tilde{T}_{k,1}; \quad P_{k,2} = E - P_{k,1}, \quad (4.3)$$

where E is identity matrix.

5. Construction of Fundamental Matrix-function of System of Equations

After sorting and biorthogonalization of eigenvectors and eigenvalues fundamental matrix-function $\varepsilon_k(x)$ of system from Eq. (1.1) for arbitrary k is constructed in the special form convenient for problems of structural mechanics

$$\varepsilon_k(x) = T_{k,1} \tilde{\varepsilon}_{k,0}(x) \tilde{T}_{k,1}^T + \chi(x, 0) [P_{k,2} + \sum_{j=1}^{m_{k,\max}-1} \frac{x^j}{j!} A_{k,2}^j], \quad (5.1)$$

where

$$m_{k,\max} = \max_{1 \leq i \leq u_k} m_{k,i}; \quad (5.2)$$

$$\chi(x, \lambda_{k,p}) = \begin{cases} \text{sign}(x) \theta(-\text{Re}(\lambda_{k,p})x), & \lambda_{k,p} \neq 0 \\ 0.5 \cdot \text{sign}(x), & \lambda_{k,p} = 0; \end{cases} \quad (5.3)$$

$$\text{sign}(x) = \begin{cases} 1, & x > 0 \\ -1, & x < 0; \end{cases} \quad (5.4)$$

$$\theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0; \end{cases} \quad (5.5)$$

$$\tilde{\varepsilon}_{k,0}(x) = \text{diag} \{ \chi(x, \lambda_{k,1}) \exp(\lambda_{k,1}x), \dots, \chi(x, \lambda_{k,l_k}) \exp(\lambda_{k,l_k}x) \}. \quad (5.6)$$

It should be stated that the sum in the right side of Eq. (5.1) contains four or lower components and corresponds to so-called “beam” part of solution of system.

6. General Solution of the Problem

Solution of considering problem (Eq. (1.1), Eq. (1.2), Eq. (1.3)) on the interval (x_k^b, x_{k+1}^b) is defined by formula

$$\bar{y}_k(x) = (\varepsilon_k(x - x_k^b) - \varepsilon_k(x - x_{k+1}^b)) \bar{C}_k + \varepsilon_k * \bar{f}_k, \quad x \in (x_k^b, x_{k+1}^b), \quad (6.1)$$

where $\bar{C}_k$ is the vector of constants of order n ; $*$ is convolution notation;

$$\bar{f}_k(x) \equiv f(x) \theta(x, x_k^b, x_{k+1}^b); \quad (6.2)$$

$$\theta(x, x_k^b, x_{k+1}^b) = \begin{cases} 1, & x \in (x_k^b, x_{k+1}^b) \\ 0, & x \notin (x_k^b, x_{k+1}^b). \end{cases} \quad (6.3)$$

We can rewrite Eq. (6.1) in the form

$$\bar{y}_k(x) = E_k(x) \bar{C}_k + \bar{S}_k, \quad x \in (x_k^b, x_{k+1}^b); \quad (6.4)$$

$$E_k(x) = \varepsilon_k(x - x_k^b) - \varepsilon_k(x - x_{k+1}^b); \quad (6.5)$$

$$\bar{S}_k(x) = \varepsilon_k * \bar{f}_k. \quad (6.6)$$

Substituting Eq. (6.4) in Eq. (1.2) and Eq. (1.3) and taking into account that

$$\bar{y}(x_k - 0) = \bar{y}_{k-1}(x_k - 0), \quad k = 2, \dots, n_k; \quad (6.7)$$

$$\bar{y}(x_k + 0) = \bar{y}_k(x_k + 0), \quad k = 1, \dots, n_k - 1; \quad (6.8)$$

$$E_{k-1}(x_k^b - 0) = \varepsilon_{k-1}(h_{k-1}^b) - \varepsilon_{k-1}(-0), \quad k = 2, \dots, n_k; \quad (6.9)$$

$$E_k(x_k^b + 0) = \varepsilon_k(+0) - \varepsilon_k(-h_k^b), \quad k = 1, \dots, n_k - 1; \quad (6.10)$$

$$h_k^b = x_{k+1}^b - x_k^b, \quad k = 1, \dots, n_k - 1 \quad (6.11)$$

we have the following system of linear algebraic equations for $\bar{C}_k$, $k=1, \dots, n_k - 1$

$$K \bar{C} = \bar{G}, \quad (6.12)$$

where matrix K can be divided into so-called main K^0 and additional K^1 members,

$$K^0 = \begin{bmatrix} K_{1,1}^0 & 0 & 0 & \dots & 0 & K_{1,n_k-1}^0 \\ K_{2,1}^0 & K_{2,2}^0 & 0 & \dots & 0 & 0 \\ 0 & K_{3,2}^0 & K_{3,3}^0 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & K_{n_k-1,n_k-2}^0 & K_{n_k-1,n_k-1}^0 \end{bmatrix} \quad (6.13)$$

$$K^1 = \begin{bmatrix} K_{1,1}^1 & 0 & 0 & \dots & 0 & K_{1,n_k-1}^1 \\ K_{2,1}^1 & K_{2,2}^1 & 0 & \dots & 0 & 0 \\ 0 & K_{3,2}^1 & K_{3,3}^1 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & K_{n_k-1,n_k-2}^1 & K_{n_k-1,n_k-1}^1 \end{bmatrix} \quad (6.14)$$

$$K_{k,k-1}^0 = -B_k^- \varepsilon_{k-1}(-0); \quad (6.15)$$

$$K_{k,k}^0 = B_k^+ \varepsilon_k(+0); \quad (6.16)$$

$$K_{1,1}^0 = B_1^+ \varepsilon_1(+0); \quad (6.17)$$

$$K_{1,n_k-1}^0 = -B_{n_k}^- \varepsilon_{n_k-1}(-0); \quad (6.18)$$

$$K_{k,k-1}^1 = B_k^- \varepsilon_{k-1}(h_{k-1}^b); \quad (6.19)$$

$$K_{k,k}^1 = -B_k^+ \varepsilon_k(-h_k^b); \quad (6.20)$$

$$K_{1,1}^1 = -B_1^+ \varepsilon_1(-h_1^b); \quad (6.21)$$

$$K_{1,n_k-1}^1 = B_{n_k}^- \varepsilon_{n_k-1}(h_{n_k-1}^b); \quad (6.22)$$

$$\bar{G} = [\bar{G}_1^T \quad \bar{G}_2^T \quad \dots \quad \bar{G}_{n_k-1}^T]^T; \quad (6.23)$$

$$\bar{C} = [\bar{C}_1^T \quad \bar{C}_2^T \quad \dots \quad \bar{C}_{n_k-1}^T]^T; \quad (6.24)$$

$$\begin{aligned} \bar{G}_1 = & \bar{g}_1^+ + \bar{g}_{n_k}^- - B_1^+ \bar{S}_1(x_1^b + 0) - \\ & - B_{n_k}^- \bar{S}_{n_k-1}(x_{n_k}^b - 0); \end{aligned} \quad (6.25)$$

$$\begin{aligned} \bar{G}_k = & \bar{g}_k^- + \bar{g}_k^+ - \\ & - B_k^- \bar{S}_{k-1}(x_k^b - 0) - B_k^+ \bar{S}_k(x_k^b + 0), \end{aligned} \quad (6.26)$$

$k = 2, \dots, n_k - 1$

Symbol $\otimes$ imply direct product of matrices. It is necessary to note that matrices $\varepsilon_k(+0)$ and $\varepsilon_k(-0)$ are independent of x .

We find it vital to note that diagonal blocks of matrix K are practically singular. This fact leads to several problems. Iterative methods of solution can't be applied in particular. Gaussian elimination method with pivoting is required. It is useful to specify ways of disposal of this disadvantage.

Let us transform considering system of equation as follows: each equation of system, since the first (and finishing next to last), we will replace with the sum of this equation with the subsequent (instead of the

initial first equation we take the sum initial the first with initial the second, instead of initial the second – the sum initial the second with initial the third and so on). Instead of initial last equation we take the sum of the initial last with initial the first. Finally we have:

$$K = \begin{bmatrix} \tilde{K}_{1,1} & \tilde{K}_{1,2} & 0 & 0 & \dots & 0 & 0 & \tilde{K}_{1,n_k-1} \\ \tilde{K}_{2,1} & \tilde{K}_{2,2} & \tilde{K}_{2,3} & 0 & \dots & 0 & 0 & 0 \\ 0 & \tilde{K}_{3,2} & \tilde{K}_{3,3} & \tilde{K}_{3,4} & \dots & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \tilde{K}_{n_k-1,1} & 0 & 0 & 0 & \dots & 0 & \tilde{K}_{n_k-1,n_k-2} & \tilde{K}_{n_k-1,n_k-1} \end{bmatrix}. \quad (6.27)$$

Thus we removed the singularity mentioned above.

Acknowledgments

This work was financially supported by the Grant of the President of the Russian Federation for Leading Scientific Schools (SS-8684.2010.8), Grant of Russian Academy of Architecture and Construction Sciences (2.3.9), Analytical Departmental Target Program “Development of Scientific Potential of Higher Education” (Project 2.1.2/12148).

References

- [1] Zolotov A.B., Akimov P.A., Sidorov V.N.: *Correct Discrete-Continual Finite Element Method for Three-Dimensional Problems of Structural Analysis*. Journal of Beijing University of Civil Engineering and Architecture. Vol. 25, No. 2, Jun. 2009.
- [2] Zolotov A.B., Akimov P.A., Sidorov V.N., Mozgaleva M.L.: *Discrete-continual methods of structural analysis*. Moscow, Architecture – S, 2010, 336 pages (in Russian).
- [3] Zolotov A.B., Akimov P.A.: *Semianalytical Finite Element Method for Two-dimensional and Three-dimensional Problems of Structural Analysis*. // Proceedings of the International Symposium LSCE 2002 organized by Polish Chapter of IASS, Warsaw, Poland, 2002, pp. 431-440.
- [4] Horn A.R., Johnson C.R.: *Matrix Analysis*. Cambridge University Press, 1990, 575 pages.

ZDZISŁAWA OWSIAK

Kielce University of Technology
al. Tysiąclecia Państwa Polskiego 7
25-314 Kielce, Poland
e-mail: owsiak@tu.kielce.pl

INVESTIGATION OF ALKALI-AGGREGATE REACTION IN CARBONATE ROCKS

Abstract

Alkali-aggregate reaction (AAR) may occur in concrete through siliceous or carbonate rock and alkaline hydroxides. Depending on the type of minerals present in the rock, it is possible the alkali-silica/silicate (ASR), alkali-carbonate (ACR) or both reactions occurrences. The preliminary study of the rock is an obligatory procedure before the application in a concrete structure.

This paper presents a laboratory study with the main purpose of verifying the potential in causing alkali-silica and alkali-carbonate reactivity of dolomite rock. With this approach, several methodologies in the ASR and ACR investigations and a detailed mineralogical analysis of the mentioned rocks are showed and the tested results discussed.

The results indicate that alkali-silica reaction does not occur in non-siliceous carbonate aggregate even with a very low content of SiO_2 .

Keywords: alkali-aggregate reaction (AAR), ACR

1. Introduction

Alkali-aggregate reaction (AAR) can occur in concrete in some conditions causing damage due to, typically, expansion of aggregate. The alkali-aggregate reaction is a chemical process in which some components of the aggregate react with dissolved alkaline hydroxides in concrete solution. The reaction is divided into three types: alkali-silica reaction (ASR), alkali-silicate reaction and alkali-carbonate reaction (ACR), depending on the mineralogy of the rock. ASR is related mainly to opal, trydimite, cristobalite and volcanic glass [7]; alkali-silicate reaction, which is a specific type of ASR but develops, at a low rate when compared to ASR, involves strained quartz and some phyllosilicate minerals [5]; the third type of AAR that is ACR is attributed to the presence of dolomite from calcitic dolomites and dolomitic limestone [4].

The mechanism of alkali-carbonate reaction is still unclear. It is agreed that there are three key elements causing the alkali-reaction of carbonate aggregate:

- crystal grains of dolomite distributed in the continuous clayish network;
- the dimension of the crystal grains, they are rhombohedron idiomorphic crystal of dolomite, which should be smaller than 50 μm , and the

higher alkali reactivity the less the dimension. If the dimensions of the crystal grains are bigger than 75 μm , then the alkali-reaction of the crystal grains cannot cause the determination of the concrete;

- the content of clay, which made the continuous clayish network, is about 10% ~ 20%.

For the mechanism of alkali-carbonate reaction in carbonate aggregate, three hypotheses have been proposed. The first is dedolomitization hypotheses. In 1960's, D.W. Hadley [6] proposed that the reactive carbonate aggregate reacted with the pore fluid in the concrete. That causes dedolomitization and the formation of brucite, and the expansion. The second hypotheses is that the expansion is caused by the water absorption by dry clay. It was proposed by Swenson and Gillott [8]. They thought that the dry clay exposed, as a result of dedolomitization, and provided the alleyway which the water can pass. Next the surface of the clay absorbs the water and forms the electrical double layer structure. The water absorption by dry clay causes expansion. This is the main reason for the expansion caused by the alkali-carbonate reaction. The third is the synthetical action. This mechanism was proposed by M. Tang in 1989 [9]. He thought that the expansion was caused by topochemical reaction resulting from

the entry of K^+ , Na^+ , and OH^- into the restricted space. That causes considerable expansive pressure. The water absorbed by dry clay cause expansive pressure, the pressure of crystallization of brucite and calcite, and the osmotic pressure caused by difference ion concentration from the liquid after reaction to the pore space in hardened cement. However, these views are contradictory and more research is still necessary.

2. Materials and methods

2.1. Materials

The dolomite aggregate of 2/16 mm fraction and Portland cement CEM I 42.5 were used in the tests. The physico-mechanical properties of the aggregate are presented in Table 1. Table 2 presents the chemical composition of cement.

Table 1. Physico-mechanical properties of the dolomite aggregate

Test	Results	Method
Determination of the resistance to wear – micro – Deval coefficient, M_{DE}	9.70	PN-EN 1097-1: 2000; A1: 2004
Determination of the resistance to fragmentation – Los Angeles coefficient, LA	19	PN-EN 1097-2: 2000; A1: 2008
Loose bulk density, Mg/m^3	1.46	PN-EN 1097-3: 2000
Apparent particle density, Mg/m^3	2.84	PN-EN 1097-6: 2002; A1: 2006
Pre-dried particle density, Mg/m^3	2.77	
Particle density on a saturated and surface dried basis, Mg/m^3	2.80	
Water absorption, %	0.87	
Total sulfur content, %	0.06	PN-EN 1744 – 1: 2000 p. 11

Table 2. The chemical composition of Portland cement CEM I 42.5 (%)

L.O.I.	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Na ₂ O _{eq}
2.45	21.50	4.00	4.25	0.07	63.5	0.60	2.45	0.28	0.55	0.65

2.2. Methods for rock assessment

The investigation methods were selected with the aim to verify the behaviour of carbonate rocks used as aggregate, as well as their reactions with the cement paste. The rocks were assessed in their natural state. They were investigated with several methods, described as follows.

The texture, mineralogical and chemical characterization of the selected carbonate rock were

evaluated through petrographic, mineralogical, diffractometric and chemical analyses.

In addition to the information on the ASTM C-295 [2] standard, the petrographic analysis was conducted in accordance with the conventional techniques of microscopic analysis for determination of texture and composition characteristics of the rock. Microscopic petrographic analyses were performed using the transmitted light optic microscope. The aim was to classify the rock and estimate its mineralogy, mostly in what refers to carbonates and silicates. In this method, the concern was to perform a representative sampling; therefore, three impregnated thin sections were prepared.

Identification of crystalline phase of the carbonate aggregate rock was done through X-ray diffraction (XRD). This analysis was considered very useful as a complementary evaluation to the petrographic classification of the rock. The sample was submitted to a previous grinding (finer than 37 μm) to provide representative fine size material. This material was submitted to powder diffraction x-ray analysis (integral sample).

The chemical analysis was performed according to the complexometric method to obtain Al, Ca, and Mg oxides and gravimetric method to determine siliceous oxide and insoluble residue. The objective of this analysis was to quantify the chemical elements in the aggregate. Also, to correlate them to the potential reactivity of the rock, according to the chemical method [3].

For the investigation of ASR on carbonate rock, the accelerated mortar bar test according to the ASTM C – 1260 standard [6] was used. It was done by casting five mortar bars with selected rock types, as artificial fine aggregate, considering the cement: aggregate proportion of 1: 2.25 and w/c ratio 0.47. The bars were immersed in 1N sodium hydroxide solution at 80°C for 30 days. The cement used contained a low alkaline equivalent (Na_2O_{eq}), representing 0.65% of total (acid soluble) alkalis, respectively.

3. Results

3.1. Rock characterization

The tests involved dolomite aggregate. In macroscopic terms it had non-uniform microstructure. The results from the petrographic analyses are presented in Figure 1 and Figure 2. The microscope analysis show that the aggregate texture is compact with visible pores in the form of druses with sharp edges, the texture sometimes being granular (Fig. 1).

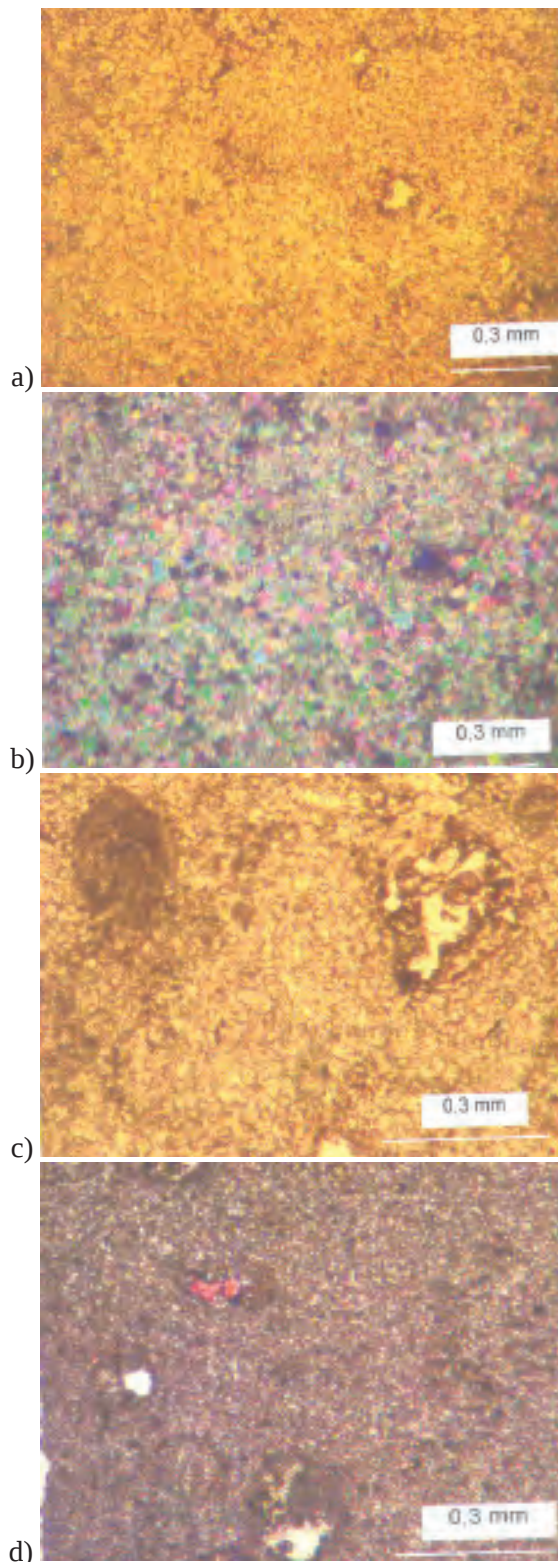


Fig. 1. The microstructure of the grains of compact texture dolomite: a), c), d) parallel polarisers, b) crossed polarisers (colouring with alisarine, calcite grains have a red colour, dolomite grains are colourless)

The content of granular texture dolomite is about 38% and the content of compact texture dolomite is

about 62%. The aggregate has fine grain structure and the colour range from light yellow to pink. The microscopic analysis (Fig. 1) have revealed that it is a compact, random texture dolomite with a fine-grain structure (grains with the mean size from 0.01 to 0.03 mm) mostly the equal-size grain structure, less often the different-size grain structure. At some places one may observe the traces of original structures (oval formations, sometimes with grains smaller than 0.001 mm). Calcite appears sporadically in the form of single automorphic grains with the size of about 0.05 mm. Pores are rare and appear in the form of irregular cracks or druses with the size of about 0.04 mm.

Figure 2 shows examples of microscopic images of dolomite and organogenic limestone grains with calcite as the binder. Grains with weakly marked concentric form have blurred oval outlines, the binder appears in the form of automorphic grains with the size of about 0.1 mm.

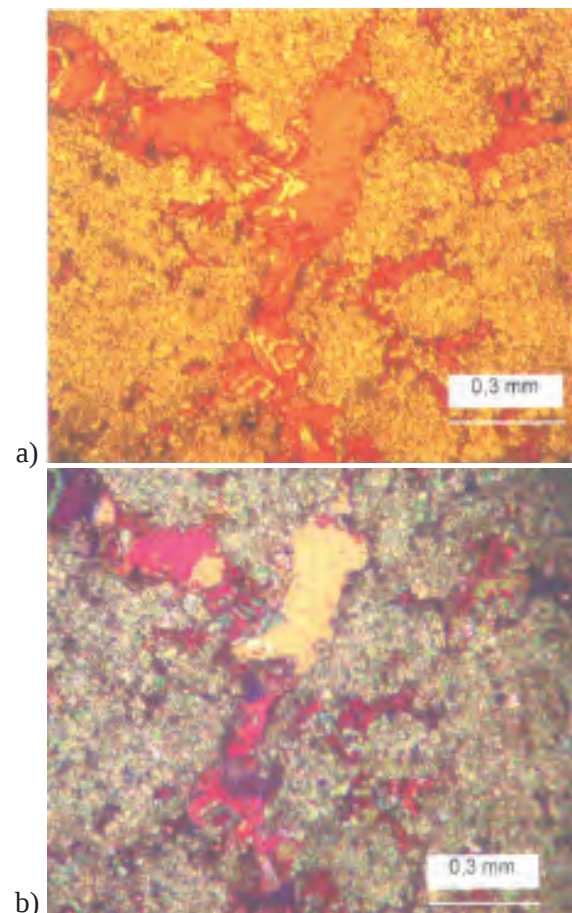


Fig. 2. The microstructure of organogenic dolomite grains with the calcite binder: a) crossed polarisers (colouring with alisarine, calcite grains have a red colour, dolomite grains are colourless)

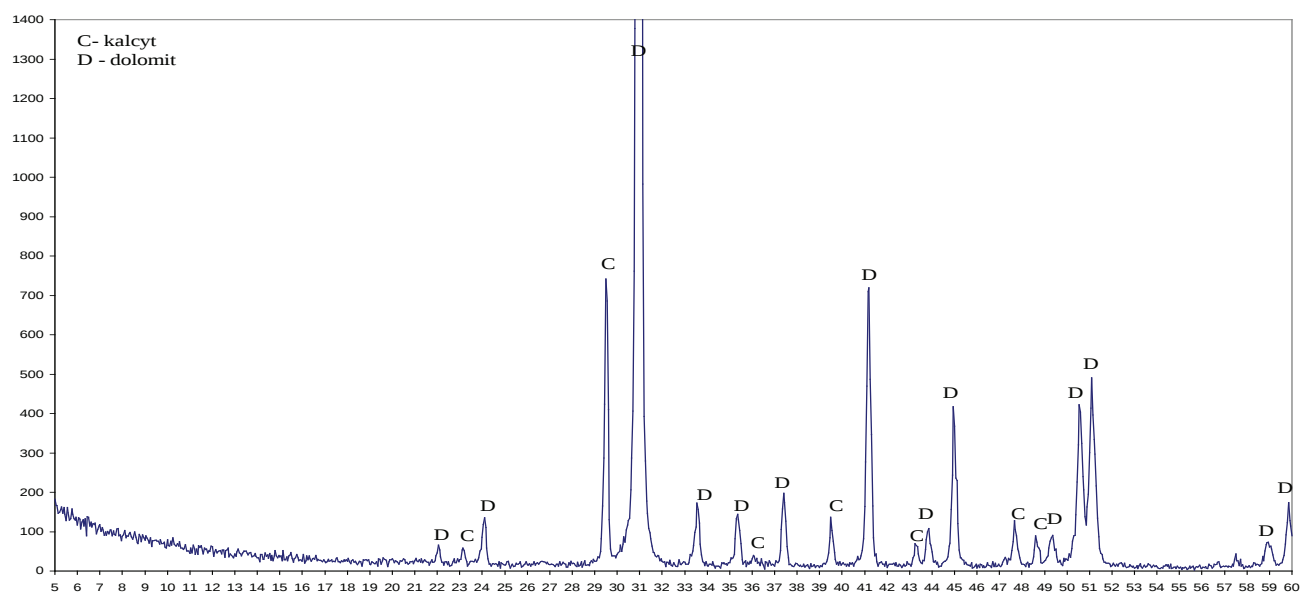


Fig. 3. X-ray diffraction patterns of dolomite rock

The results from the XRD analyses of rock are presented in Figure 3, the SEM micrograph in Figure 4 and the chemical analyses are presented in Table 3.

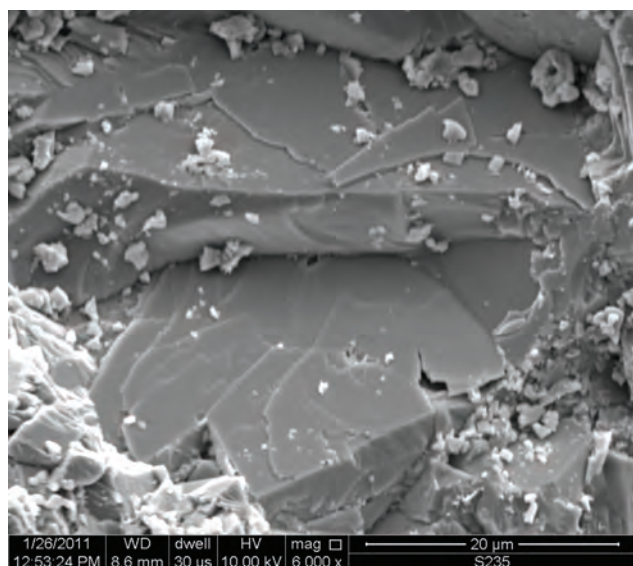


Fig. 4. SEM micrograph of dolomite

Table 3. The composition of the aggregate

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	SO ₃	TiO ₂
Contents, %	6.95	0.65	0.93	29.6	18.5	0.08	0.15	0.02	<0.01	0.02

The dolomite appears as the major component (about 78%), followed by the calcite (about 14%). Silicates occur in all analyzed rock in small (trace) quantities, mainly quartz, illite. Their presence is corroborated by the results from chemical analysis revealing minor contents of SiO₂, Al₂O₃, as well as insoluble residue.

3.2. Expansion test

Figure 5 shows the expansion results by the age of 30 days of the carbonate rock samples.

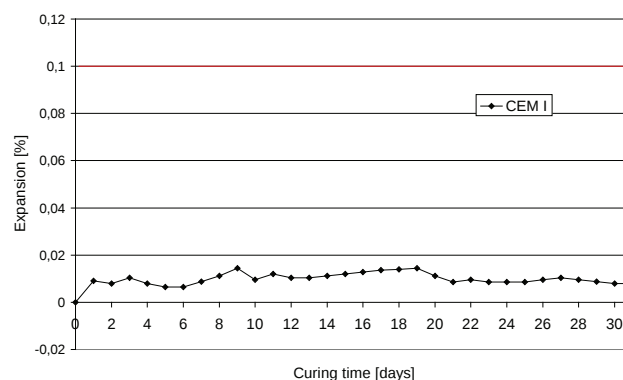


Fig. 5. The expansion results from the period of 30 days of the carbonate rock samples (with ASTM C 1260-04)

The expansion of the aggregate reached 0.008% at 30 days. That was lower than the specified number in ASTM C 1260-04. Thus, non-siliceous carbonate rock, even with a low content of SiO₂, can be nonreactive with alkalis.

4. Discussion

According to ASTM C – 1260 expansion up to 0.20% in 16 days means reactive behaviour of the aggregate. Yet, for expansion below 0.10%, after the same time, the aggregate is considered innocuous. The results reveal that the aggregate showed limited expansion. Thus, the reactivity of the aggregate is low. The expansion is not due to the alkali-aggregate reaction.

The dolomite aggregate has good physical properties and meets the requirements for the concrete aggregates. Dolomite is the main component of the rock, which also includes small quantities of calcite, clay minerals and quartz. The rock has a fine-grain structure and a colour range from light yellow to pink. The content of compact texture dolomite is about 62% and the content of granular texture dolomite is about 32%. Calcite appears randomly in the form of single, automorphic grains with the size of about 0.05 mm. Sometimes iron oxides appear in the rock in the form of oval clusters with the size of about 0.02 to 0.04 mm or as short veins. Pores are rare. They appear in the form of irregular cracks or druses with the size of about 0.04 mm. The investigated grains of the fine-grain micrite dolomite (the size of grains smaller than 0.005 mm) are bonded with coarse-crystalline calcite cement. Calcite with the grain size of about 0.05 mm and bigger appears in the veins and pervades the dolomite in the aggregate-paste interface. There are small quantities of iron oxides and sporadically the grains of corroded quartz and microsilica. There also appear granular pieces of dolomite and organogenic limestone with calcite as a binder and dolomite or calcite grains.

5. Conclusions

Considering its mineral composition, the aggregate applied in this research could have been of the alkali-reactive type. From the analysis it is evident,

however, the aggregate is possibly not reactive with alkali. Neither the alkali-silica reaction nor the alkali-carbonate aggregate reaction were observed.

References

- [1] ASTM C 1260-04, *Standard Test Method for Determining the Potential Alkali Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar Bar Method)*. Annual Book of ASTM Standards 2004.
- [2] ASTM C 295 (2003), *Standard Guide for Petrographic Examination of Aggregate for Concrete*.
- [3] CSA A23.2-26A (2004): *Determination of potential alkali-carbonate reactivity of quarried carbonate rocks by chemical composition*, Canadian Standards Association, CSA International, Canada.
- [4] Gillott, J.E., *Mechanism and Kinetics of Expansion in the Alkali-Carbonate Rock Reaction* Canadian J. of Earth Sciences, 1, 1964, pp. 121-145.
- [5] Grattan-Bellew, P.E., *Microcrystalline Quartz, Undulatory Extinction and Alkali-Silica Reaction* Proc. 9th Intern. Conf. on AAR in Concrete, London 1992, pp. 383-394.
- [6] Hadley, D.W.: *Alkali reactivity of carbonate rocks-expansion and dedolomitization*. Highway Research Board Proceedings (40), 1961, pp. 462-474.
- [7] Owsiak Z., *The Alkali-Silica Reaction in Concrete*, Polish Academy of Science, Polish Ceramics Bulletin vol. 72, Kraków 2002.
- [8] Swenson, E.D., Gillott, J.E.: *Characteristics of Kingston Carbonate Rock Reaction*, Highway Research Board Proceedings (275), 1960, pp. 18-31.
- [9] Tang, M.: *Kinetics of Alkali-Carbonate Reaction*, Proc. of 8th Intern. Conf. on AAR, Ed. by K. Okada, Kyoto, 1989, pp. 147-152.

Zdzisława Owsiak

Badania reakcji alkalia-kruszywo dla skał węglanowych

1. Wstęp

Reakcja alkalia-kruszywo występująca w betonach może powodować w pewnych warunkach uszkodzenia, charakterystyczne dla ekspansji kruszywa. Reakcja alkalia-kruszywo jest procesem chemicznym, w którym niektóre składniki kruszywa reagują z wodorotlenkami sodu i potasu występującymi w fazie ciekłej betonu. Zależnie od składu mineralnego skały, mogą występować trzy rodzaje tej reakcji: reakcja alkalia-krzemionka (ASR), reakcja alkalia-krzemiany i reakcja alkalia-węglany (ACR).

Reakcja alkalia-krzemionka jest spowodowana głównie przez opal, trydymit, krystobalit i szkło wulkaniczne [1]; reakcja alkalia-krzemiany jest wywoływana przez niektóre minerały krzemianowe [2]; trzeci typ reakcji to reakcja alkalia-węglany powodowana obecnością dolomitu węglanowego i kalcytu dolomitycznego [3].

Mechanizm reakcji alkalia-węglany dotychczas nie jest wyjaśniony. Wiadomo jest, że są trzy przyczyny powodujące reakcje alkalia-kruszywo w kruszywach węglanowych:

- 1) ziarna krystaliczne dolomitów z przerostami ilastymi;
- 2) wielkość ziaren krystalicznych dolomitu, romboedryczne, idiomorficzne kryształy dolomitu, są mniejsze niż 50 μm , reaktywność z alkaliami jest tym większa, im ich wielkość jest mniejsza, o ile wielkość ziaren kryształów jest większa niż 75 μm , reakcja z alkaliami tych ziaren nie powoduje uszkodzenia betonu;
- 3) zawartość minerałów ilastych, stanowiących ciągłą sieć, o ile ich zawartość wynosi około 10-20%.

Proponowane są trzy hipotezy opisujące mechanizm reakcji alkalia-węglany w kruszywach węglanowych. Pierwsza jest hipotezą dedolomityzacji. W 1960 roku D.W. Hadley zasugerował, że reaktywne kruszywo węglanowe reaguje z roztworem w porach betonu, natomiast dedolomityzacja i tworzenia brucytu prowadzi do ekspansji.

Druga hipoteza zaproponowana przez Swensona i Gillotta podaje, że ekspansja jest spowodowana absorpcją wody przez suche minerały ilaste. Odsłonięte w wyniku dedolomityzacji minerały ilaste i powstałe rysy, którymi może przepływać woda powodują, że na powierzchni minerałów ilastych absorbuje się woda i tworzy się podwójna warstwa elektryczna. Absorpcja wody przez minerały ilaste powoduje ekspansję i to jest głównym powodem ekspansji spowodowanej reakcją alkalia-węglany.

Trzecia hipoteza dotyczy sztucznego procesu. Mechanizm ten został zaproponowany przez M. Tanga w 1987 r. Według tej hipotezy ekspansja jest spowodowana przez reakcję topochemiczną w wyniku wejścia jonów K^+ , Na^+ i OH^- w ograniczone miejsca, powodując znaczne ciśnienie ekspansji, absorpcja wody przez suche minerały ilaste powoduje ciśnienie ekspansji, ciśnienie krystalizacji brucytu i kalcytu i ciśnienie osmotyczne spowodowane przez różne stężenia jonów w fazie ciekłej po reakcji w porach stwardniałego zaczynu cementowego. Jednak ten pogląd są sprzeczne i dalsze prowadzenie badań jest konieczne.

2. Materiały i metody badawcze

W badaniach zastosowano kruszywo dolomitowe frakcji 2/16 mm oraz cement portlandzki CEM I 42,5. Właściwości fizyko-mechaniczne kruszywa zamieszczono w tabeli 1, a skład chemiczny cementu w tabeli 2.

Metody badawcze zastosowane w doświadczeniu wybrano w celu określenia zachowania się skały węglanowej zastosowanej jako kruszywo w reak-

cji z zaczynem cementowym. Skała była pobrana z naturalnego miejsca jej występowania, a następnie poddana badaniom poniżej opisanymi metodami.

Teksturę, skład mineralny i chemiczny wybranej skały węglanowej badano metodą petrograficzną, analizą dyfrakcji rentgenowskiej i analizy chemicznej. W dodatku do informacji w normie ASTM C-295 [4], analiza petrograficzna była znakomicie połączona z typowymi metodami analiz mikroskopowych dla określenia tekstury i składu charakteryzujących skałę. Mikroskopowa analiza petrograficzna była wykonana przy zastosowaniu mikroskopu optycznego w celu klasyfikacji skały i oceny jej mineralogii, głównie w odniesieniu do węglanów i krzemianów. Identyfikację faz krystalicznych kruszywa ze skały węglanowej przeprowadzono metodą rentgenowskiej analizy dyfrakcyjnej (XRD).

Analizę chemiczną wykonano metodą kompleksometryczną, którą oznaczono zawartość tlenków glinu, wapnia i magnezu, a metodą wagową oznaczono zawartość krzemionki i składników nierozpuszczalnych. Celem tej analizy było określenie składników w kruszywie i ich wpływ na potencjalną reaktywność skały, zgodnie z metodami chemicznymi [5].

Badania reaktywności skały węglanowej (ASR) wykonano metodą przyspieszoną, badając ekspansję beleczek zapraw zgodnie z normą ASTM C – 1260 [6].

3. Wyniki badań

W badaniach zastosowano kruszywo dolomitowe, które pod względem makroskopowym charakteryzowało się niejednorodną mikrostrukturą. Obserwacje mikroskopowe wykazały, że tekstura kruszywa jest zbita z widocznymi porami o charakterze druz o ostrych krawędziach, niekiedy tekstura jest ziarnista. Zawartość dolomitu o teksturze ziarnistej wynosi około 38%, a o teksturze zbitej 62%. Struktura kruszywa drobnoziarnista, barwa od jasnożółtej do różowej. Obserwacje mikroskopowe (rys. 1) wykazały, że jest to dolomit o teksturze zbitej, bezładnej, strukturze drobnoziarnistej, równoziarnistej rzadziej różnoziarnistej, ziarna o średniej wielkości od 0,01 do 0,03 mm. Niekiedy można zaobserwować ślady pierwotnych struktur (twory o kształcie owalnym, czasami o ziarnach poniżej 0,001 mm). Kalcyt występuje sporadycznie, w postaci pojedynczych automorficznych lub hipoautomorficznych ziaren o wielkości rzędu 0,05 mm. Pory występują rzadko, w postaci nieregularnych szczelin lub druz o wielkości rzędu 0,04 mm. Na rysunku 2 pokazano przykładowe obrazy mikrosko-

powe ziaren dolomitu i wapienia organogenicznego, w którym spoiwem jest kalcyt. Ziarna o słabo zaznaczonej budowie koncentrycznej mają mniej lub bardziej wyraźne zarysy owalne, spoiwo występuje w postaci automorficznych lub hipoautomorficznych ziaren o wielkości rzędu 0,1 mm.

Dolomit stanowi główny składnik (około 78%), następnie wapń występuje w ilości około 14%. Krzemiany występują w badanej skale w małych (śladowych) ilościach, głównie kwarc i illit.

4. Dyskusja i wnioski

Ekspansja beleczek zaprawy z kruszywem po 30 dniach osiągnęła 0,008%. Był to wynik niższy niż graniczna ekspansja dla kruszyw reaktywnych badana według ASTM C 1260-04. Zgodnie z tą normą ekspansja powyżej 0,20% po 16 dniach oznacza reaktywne zachowanie kruszywa; jednak przy ekspansji poniżej 0,10% po tym samym czasie kruszywo jest uważane jako niereaktywne.

Wyniki badań wykazały, że kruszywo wykazuje ograniczoną ekspansję. Stąd reaktywność kruszywa

jest niska. Ekspansja występuje nie z powodu reakcji alkalia-kruszywo. Głównie małe ziarna są bardziej skłonne do reakcji alkalia-krzemionka i ekspansja jest większa.

Analizując wyniki badań doświadczalnych wykazano, że ekspansja spowodowana przez reakcję alkalia-węglany i reakcję alkalia-krzemionka jest bardzo mała. Przypuszcza się, że podwójna reakcja nie jest właśnie możliwa teoretycznie, to jednak występuje w niektórych kruszywach. W kruszywach węglanowych możemy badać obydwie reakcje alkalia-krzemionka i alkalia-węglany. Metody badawcze reaktywności alkalicznej kruszywa głównie uwydatniają pojedynczy czynnik. Dla kruszyw, które powodują obydwa typy reakcji konieczne jest rozszerzenie niektórych metod badawczych do oceny ekspansji spowodowanej dwoma rodzajami reakcji. W niektórych niekrzemianowych skałach węglanowych, jednak z małą zawartością krzemionki (około 6%), reakcja alkalia-krzemionka może występować. Reakcje alkalia-krzemionka i alkalia-węglany mogą występować w tym samym czasie, w pewnych kruszywach.



environment
environment

TADEUSZ M. WÓJCIK

AGH University of Science and Technology,
Cracow, Poland
e-mail: tmwojci@agh.edu.pl

ENERGY SAVING USING HEAT EXCHANGERS COVERED WITH POROUS COATINGS

Abstract

Exploitation of technical devices is always related to the energy consumption. Thus, if more efficient heat exchangers are used as part of mechanical systems, it is possible to save energy. The paper presents possible ways of producing more efficient heat transfer surfaces working under the nucleate boiling mode. When porous coverings are used, significant reduction of temperature differences is noticed at the same heat flux. It leads to higher energy efficiency.

Keywords: boiling, porous coatings

1. Introduction

In thermodynamic cycle the temperature differences between the evaporator section and the heat source, and between the condenser and the heat sink, are sources of irreversibility. To obtain high coefficients of performance, the temperature differences need to be as small as possible. For example, in a refrigeration system the reduction in temperature difference from 15°C to 5°C results in the reduction of required work by about 42% [13]. That leads to energy saving. Such a reduction in temperature differences in heat exchangers can be achieved due to introduction of porous coverings on the surfaces. In boiling, they might dissipate the same heat flux as smooth surfaces, but at significantly lowered temperature differences. Such microstructures might be used in many industrial applications – in refrigeration, chemical engineering. Orman discussed their possible application in automotive heat exchangers [7] or in heating and ventilation systems [8].

2. Boiling heat transfer augmentation

The heater surface can be modified with roughness or the application of microstructures of different geometry. Mechanical mixing of the fluid or inducing vibrations is also possible [1, 2]. Microstructures can be produced on the heater surface by deposition or by mechanical means. There are many kinds of such structures [9, 14]. Their application might lead to a significant enhancement of heat transfer.

Zhang and Zhao [23] discovered that boiling heat transfer coefficients for the surfaces with porous coatings produced with the thermal spraying

technique were 2 – 5 times higher than for the smooth surface – the coverings of 0.3 mm, 0.9 mm and 1.14 mm height were used. Zhang and Chen [22] investigated water and ethanol boiling on a horizontal surface covered with porous layer of sintered bronze powder. Microstructure height was 0.5 – 4 mm, while the grain diameter ranged from 100 – 400 μm . Heat transfer coefficient of such a surface was 3 to 10 times higher than of the smooth surface. For the same heat flux the temperature difference with the use of porous layers was much lower. For example water test results indicated, that for heat flux of 10 W/cm^2 the required temperature difference for the smooth surface was about 10 K; while for the porous covering of 0.5 mm height – about 4 K. For ethanol and the same heat flux the temperature difference for the smooth surface amounted to about 16 K while for the microstructure – only some 1.8 K. Cieřliński [3] analysed water boiling on horizontal surfaces coated electrochemically with a 0.3 – 1.1 mm porous layer of copper, aluminum and silver. The heat transfer coefficient for the porous coating turned out to be even 4 times higher than for the smooth surface. Rainey and You [16] experimentally analysed FC-72 (fluorinert – a dielectric fluid) boiling on the copper 10x10 mm surface covered with 1 mm wide square pin – fins. There were 5x5 pins on the surface located 1 mm apart from each other. The height of the pins was 0.25, 0.5, 1, 2, 4 and 8 mm. For the same heat flux of 1 W/cm^2 the temperature difference required for the smooth surface was about 15 K, while for the micro – finned surface about 8 K.

Another type of microstructural coatings are metal, fibrous porous structures. The considerable increase in heat transfer coefficient due to attachment to the surface of the heat exchanger metal, fibrous porous structures was reported by Wójcik in [19]. He presented that the heat transfer coefficient amounted to $8 \cdot 10^4 \text{ W/m}^2\text{K}$ for the heat flux of 105 W/m^2 (water, porosity 85%, thickness 0.8 mm). In the boiling process there is a strong dependence of boiling heat transfer coefficient from the structural parameters (porosity, thickness). The maximum value of the heat transfer coefficient was recorded when the covering was 0.6 – 0.8 mm thick. The heat transfer augmentation for such structures was confirmed by Orzechowski and Orman [10]. Moreover, for the same heat flux of about 200 kW/m^2 the temperature difference for the smooth surface was 12 K, while for the porous layers 9 K (for water). In the case of the same heat flux for ethanol boiling the smooth surface temperature difference amounted to about 17.5 K and about 14 K for the porous structures.

Quite common are also wire mesh microstructures [14]. The data presented in [11] proves that heat transfer augmentation is possible with the application of such structures. A coating consisting of three copper mesh layers of wire diameter 0.18 mm and mesh aperture 0.55 mm was used. Heat flux for the mesh structure was even a few times higher than for the smooth surface. For the heat flux of 200 kW/m^2 the required temperature difference for water boiling heat transfer on the smooth surface was about 12.5 K, while for the mesh covering 6 K; while for ethanol: about 18 K and 8.5 K for smooth and porous surfaces, respectively. Orzechowski and Orman [12] also experimentally analysed boiling heat transfer from mesh structures consisting of two mesh layers – each from a different material: copper and stainless steel – sintered together on a copper heater surface.

Many techniques can be used to enhance heat transfer. Xiuling et al. [21] studied boiling of nitrogen on a copper finned tube. The fins' height was 1.5 mm and an additional porous coating was sintered onto the finned tube. This covering was 0.5 mm high and had porosity of 50%. For the same heat flux the heat transfer coefficient of the finned surface with the coating was 6 – 8 times higher than of the smooth tube. It was also higher than of the tube without the fins and only with the porous layer.

New methods of heat transfer augmentation are developed. Radek and Orman [15] experimentally analysed electro – spark deposition as a means of

boiling heat transfer enhancement. Significant values of the heat transfer coefficient provide new generation coverings investigated by Wójcik et al. [20]. These structures are sintered from copper powder with the addition of copper oxide powder.

3. Modelling boiling heat transfer for porous coatings

Modelling of boiling heat transfer is of practical value – for example in the design of heat exchangers. One of the models has been proposed by Nishikawa et al. [4]. Heat is assumed to be transferred through conduction from the heater surface to liquid according to the equation for the heat flux:

$$q = \frac{\lambda_m}{\delta} \Delta T \quad (1)$$

where: δ is the height of the porous layer, ΔT is the difference between the temperature of the heater surface and the saturation temperature of the liquid (often referred to as wall superheat), λ_m describes effective thermal conductivity.

λ_m is calculated as:

$$\lambda_m = \varepsilon \lambda_l + (1 - \varepsilon) \lambda_s \quad (2)$$

where: ε is porosity of the microstructure, λ_l and λ_s conductivity values of liquid (l) and structure material (s), respectively.

The value of λ_m is crucial for the model calculations. It usually leads to elevated heat fluxes using equation (1) in comparison to the experimental data. According to [17] formula (2) describes the effective conductivity of the liquid – solid system if the solid elements are parallel to the heater. In the case of the perpendicular direction the following equation has been proposed in [17]:

$$\lambda_n = \frac{\lambda_l \lambda_s}{(1 - \varepsilon) \lambda_l + \varepsilon \lambda_s} \quad (3)$$

Most coverings – for example metal fiber structures have a complex geometry and do not satisfy assumption of the parallel solid heat flow. In the case of these microstructures another method of thermal conductivity calculation needs to be adopted according to the equation given in [17] as:

$$\lambda_{\text{eff}} = \lambda_m^F \lambda_n^{1-F} \quad (4)$$

This concept has been used by Orman [5] to determine with the fitting procedure the coefficient F for copper metal, fibrous structures, which for water equalled 0.5852. Figure 1 presents comparison of

the experimental results of water boiling on a copper fiber porous structure of 40% and 2 mm thickness according to data by Wójcik [18] with the calculations performed using the Nishikawa model – original and with a modified conductivity value according to equation (4) and $F = 0.5852$. The results are graphically presented as so called “boiling curves” – dependences of heat flux vs. wall superheat.

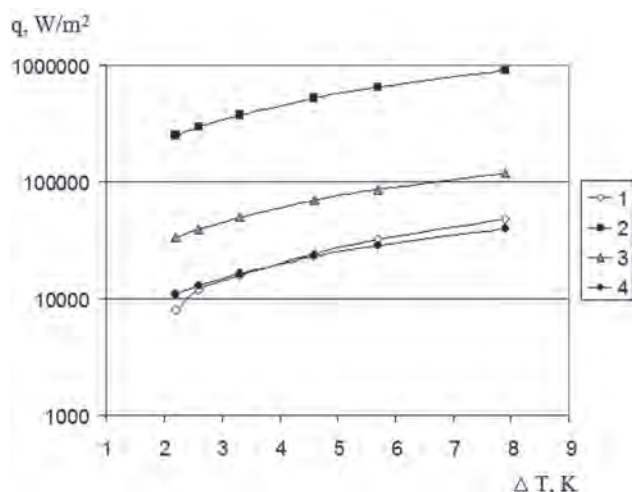


Fig. 1. Boiling curves for water for the copper fibrous structure: 1 – experimental data [18], 2 – calculations with the original Nishikawa model, 3 – calculations with the modified Nishikawa model with $F = 0.5852$, 4 – calculations with the new F value of 0.3612.

The calculated heat flux values based on the original Nishikawa model and the model modified by Orman [5] with a different effective thermal conductivity value (curves 2 and 3, respectively) overpredict the experimental data. In [5] the coefficient value of 0.5852 was determined for a porous structure of porosity 50% and thickness 1 mm. In [18] the geometrical parameters of the coating are different. Consequently, a different value of F should be expected. Having considered this, calculations have been performed to determine a new value of F for the analysed microstructure. It has been calculated as 0.3612. The results are presented as the curve No 4 and are almost identical with the experimental data.

4. Discussion

Although porous coatings offer significant possibilities in heat transfer enhancement and reduce the temperature difference for the same heat flux, the knowledge of the physical processes inside porous structures is still insufficient. Consequently, there are considerable difficulties in creating a model to predict

heat flux or heat transfer coefficient based on physical and chemical properties of the microstructure. In the case of smooth surfaces more is known. In [6] the discussion of this issue is presented.

For porous layers due to the complexity of the structures and different production methods, it is very difficult to propose a satisfactory correlation or a model. However, the concept presented here (based on modified Nishikawa model) might be interesting to consider. A method of calculating the F value, which seems to be related to the structural properties of the porous covering, could be a new approach. That might be further developed both: experimentally and theoretically.

References

- [1] Bergles A.E., (1997): *Enhancement of pool boiling*, Int. J. Refrigeration, Vol. 20, 8, pp. 545-551.
- [2] Bergles A.E., (1998): *Techniques to Enhance Heat Transfer*, in Handbook of Heat Transfer, ed. Rohsenow W.M., Hartnett, J.P., and Cho, Y.I., McGraw-Hill, New York.
- [3] Cieśliński J.T., (1991): *An experimental study of nucleate pool boiling heat transfer from a flat horizontal plate covered with porous coatings*, Archive of Thermodynamics, Vol. 12, No 1-4, pp. 69-76.
- [4] Nishikawa K., Ito T., Tanaka K., (1979): *Augmented heat transfer by nucleate boiling on a sintered metal layer*. Heat Transfer – Japanese Research, Vol. 8, pp. 65-81.
- [5] Orman Ł.J., (2008): *Analiza efektywnej przewodności cieplnej mikropokryć porowatych (Analysis of effective thermal conductivity of porous microcoatings)*, Proc. of Conf. „Terotechnologia 2008”, Zeszyty Naukowe nr 11, Nauki Techniczne: Budowa i Eksploatacja Maszyn, pp. 215-220.
- [6] Orman Ł. J., (2008): *Nucleate boiling heat transfer on a smooth surface of a fin*, Proc. of XII Int. Symposium on „Heat Transfer and Renewable Sources of Energy” HTRSE – 2008, pp. 363-369.
- [7] Orman Ł.J., (2009): *Possibilities of heat transfer enhancement in automotive heat exchangers*, Proc. of 13th Int. Conf. „Transport Means 2009”, Kaunas University of Technology, Lithuania, pp. 116-119.
- [8] Orman Ł.J., (2010): *Possibility of the application of microstructures in heating and ventilation systems*, Structure and Environment, Kielce University of Technology, 1, Vol. 2, pp. 41-45.
- [9] Orman Ł.J., Orzechowski T., (2004): *Analysis of the influence of the surface roughness on the heat transfer from extended surfaces*, Science Report, CEEPUS Project PL-127: Measurement Technology in Advanced Machine Manufacturing Systems.

- General Editors: S. Adamczak, P.H. Osanna, Kielce University of Technology, pp. 115-123.
- [10] Orzechowski T., Orman Ł.J., (2006): *Boiling heat transfer on surfaces covered with copper fibrous microstructures*, Proc. of XI Int. Symposium on „Heat Transfer and Renewable Sources of Energy” HTRSE – 2006, Szczecin, pp. 613-619.
- [11] Orzechowski T., Orman Ł.J., (2006): *Mikropowierzchnie strukturalne w wymianie ciepła (Microstructures in heat transfer engineering)*, Proc of Conf. „Terotechnologia 2006”, Zeszyty Naukowe nr 1, Nauki Techniczne: Budowa i Eksploatacja Maszyn, Kielce, s. 171-177.
- [12] Orzechowski T., Orman Ł.J., (2007): *Wymiana ciepła przy wrzeniu pęcherzykowym na żebrze z dwuwarstwową strukturą siatkową (Nucleate boiling heat transfer on the fin with a two – layer wire mesh structure)*, Proc of „XIII Sympozjum Wymiany Ciepła i Masy”, Koszalin – Darłówek, s. 763-768.
- [13] Palm B., (1991): *Enhancement of boiling heat transfer by aid of perforated metal foils*, Ph.D. Thesis, The Royal Institute of Technology, Stockholm.
- [14] Poniewski M.E., (2001): *Wrzenie pęcherzykowe na rozwiniętych mikropowierzchniach*, Wydawnictwo PŚk, Kielce.
- [15] Radek N., Orman Ł.J. (2008): *Water boiling on electro-spark deposited copper coating*, ВІСНИК, 6, pp. 233-236.
- [16] Rainey K.N., You S.M. (2000): *Pool boiling heat transfer from plain and microporous, square pin-finned surfaces in saturated FC-72*, Journal of Heat Transfer, Vol. 122, pp. 509-516.
- [17] Ramvir S., Kasana H.S. (2004): *Computational aspects of effective thermal conductivity of highly porous metal foams*, Applied Thermal Engineering, 24, pp. 1841-1849.
- [18] Wójcik T.M. (2004): *Boiling on cylindrical surfaces with thick – layered porous covering*, Proc. of X Int. Symposium on „Heat Transfer and Renewable Sources of Energy”, HTRSE – 2004, pp. 653-660.
- [19] Wójcik T.M. (2006): *Intensyfikacja wymiany ciepła dla wrzenia (Boiling heat transfer enhancement)*, Inżynieria i Aparatura Chemiczna, No 3, 45 (37), (in Polish), pp. 3-9.
- [20] Wójcik T.M., Poniewski M., Dziadoń A., Depczyński W. (2008): *Experimental investigation of boiling heat transfer on new porous coverings*, Proc. of XII Int. Symposium on “Heat Transfer and Renewable Sources of Energy” HTRSE – 2008, pp. 403-411.
- [21] Xiuling Y., Hongji X., Yaozhen S., Dongji C., Yuweng Z., Hongzhang Q. (1990): *Experimental research of nucleate pool boiling heat transfer from compound enhanced porous surface in liquid nitrogen*, Cryogenics, vol. 30, Supplement, pp. 297-302.
- [22] Zhang H.J., Chen L. (1988): *Pool boiling heat transfer on the sintered porous surfaces*, T. Nejat Verizoglu (ed), Particulate Phenomena and Multiphase Transport, Hemisphere, Vol. 1, pp. 529-538.
- [23] Zhang H.J., Zhao X.B. (1990): *Experimental research on pool boiling heat transfer from a spraying porous surface*, Preprints of 7th Int. Heat Pipe Conf., Minsk, pp. 187-194.

Tadeusz M. Wójcik

Oszczędność energii przez zastosowanie wymienników ciepła z pokryciem porowatym

1. Wstęp

Wymagane różnice temperatury w wymiennikach ciepła mają wpływ na wydajność takich układów. Wykazano, że w przypadku systemu chłodniczego zredukowanie różnicy temperatury z 15°C do 5°C prowadziło do zmniejszenia wymaganej pracy o około 42% [13]. W konsekwencji prowadzi to do oszczędności energii. Takie obniżenie wymaganej różnicy temperatur w wymiennikach można zrealizować poprzez zastosowanie pokryć porowatych do konstrukcji powierzchni wy-

mieniających ciepło. W przypadku wrzenia mogą one odprowadzać takie same gęstości strumienia ciepła co powierzchnie gładkie, ale przy znacznie mniejszych różnicach temperatur. Tego typu pokrycia znajdują szerokie zastosowanie przemysłowe.

2. Intensyfikacja wymiany ciepła przy wrzeniu

Powierzchnię grzejną można modyfikować poprzez jej chropowacenie lub zastosowanie mikrostruktur. Zhang and Chen [22] badali wrzenie wody i etanolu

na powierzchni pokrytej warstwą porowatą z proszków spiekanych. Dla takiego układu współczynnik przejmowania ciepła był od 3 do 10 razy wyższy niż dla powierzchni gładkiej. Dla takiej samej gęstości strumienia ciepła wymagana różnica temperatur przy zastosowaniu pokrycia porowatego była dużo niższa. Na przykład wyniki dla wody wskazują, że przy gęstości strumienia ciepła 10 W/cm^2 wymagana różnica temperatur dla powierzchni gładkiej sięgała ok. 10 K, natomiast dla mikrostruktury o wysokości 0,5 mm – ok. 4 K. W przypadku etanolu i tej gęstości strumienia ciepła różnica temperatur dla powierzchni gładkiej wynosiła ok. 16 K, a dla mikrostruktury – tylko ok. 1,8 K. Rainey and You [16] badali wrzenie FC – 72 na powierzchni miedzianej o wielkości $10 \times 10 \text{ mm}$ pokrytej mikrożebami o szerokości 1 mm. Wyniki wskazywały, że przy gęstości strumienia ciepła 1 W/cm^2 wymagana różnica temperatur dla powierzchni gładkiej wynosiła ok. 15 K, a dla mikrożebów ok. 8 K.

Innym typem pokryć są struktury metalowo-włókniste. Wójcik [19] obserwował znaczący wzrost współczynnika przejmowania ciepła w przypadku zastosowania pokryć miedzianych włóknistych. Potwierdzenie znacznej intensyfikacji wrzenia dla tego typu układów można znaleźć w pracy Orzechowskiego i Ormana [10]. Podano tam, że przy tej samej gęstości strumienia ciepła 200 kW/m^2 różnica temperatur dla powierzchni gładkiej wynosiła 12 K, a dla porowatej włóknistej 9 K (dla wody). W przypadku etanolu i tej samej gęstości strumienia ciepła różnica temperatur dla powierzchni gładkiej sięgała ok. 17,5 K, a dla porowatej ok. 14 K.

Dość powszechne są też struktury siatkowe. Wyniki w pracy [11] wskazują, że ich zastosowanie prowadzi do znacznej intensyfikacji wrzenia. Dla gęstości strumienia ciepła 200 kW/m^2 wymagana różnica temperatur przy wrzeniu wody na powierzchni gładkiej była ok. 12,5 K, a dla powierzchni siatkowej 6 K. Dla etanolu było to odpowiednio ok. 18 K i 8,5 K. Orzechowski i Orman [12] badali także wrzenie na powierzchniach siatkowych, złożonych z dwóch różnych materiałów – pokrycia ze spieczonych siatek: miedzianej i stalowej. Trwają prace nad nowymi metodami intensyfikacji wrzenia. Np. w [15] analizowano powierzchnie po obróbce elektro-iskrowej, zaś w [20] spiekane z mieszaniny proszków miedzi i tlenku miedzi.

3. Modelowanie wrzenia na powierzchniach z pokryciem porowatym

Prawidłowe modelowanie wymiany ciepła ma duże znaczenie praktyczne – np. w projektowaniu wymienników ciepła. Jednym z przykładów jest model Nishikawy i innych [4], w którym zakłada się, że ciepło jest przewodzone z powierzchni grzejnej do cieczy. Model zawiera zastępczą przewodność cieplną, której wartość zmodyfikowano w pracy [5] dla powierzchni metalowo-włóknistych o porowatości 50% i grubości 1 mm. Na podstawie rysunku 1 można stwierdzić, że model Nishikawy prowadzi do zawyżonych wartości gęstości strumienia ciepła w odniesieniu do danych eksperymentalnych z [18]. Podobnie model Nishikawy o zmodyfikowanej wartości przewodności zgodnie z równaniem (4) i wielkości $F = 0,5852$. Dane eksperymentalne [18] dotyczą jednak struktury o innych parametrach geometrycznych i modyfikacja wartości F jako 0,3612 spowodowała bardzo dobre dopasowanie wyników obliczeń i danych pomiarowych (krzywa nr 4, rys. 1).

4. Dyskusja

Chociaż pokrycia porowate oferują znaczące możliwości intensyfikacji wymiany ciepła i obniżenia wymaganej różnicy temperatur dla danej gęstości strumienia ciepła, to wiedza na temat procesów fizycznych wewnątrz struktur jest wciąż niewystarczająca. W związku z tym pojawiają się trudności w stworzeniu modelu, mogącego przewidywać gęstość strumienia ciepła w oparciu o parametry mikrostruktury. W przypadku powierzchni gładkich wiedza jest szersza. W pracy [6] zaprezentowano dyskusję na ten temat.

W przypadku pokryć porowatych, w związku z ich złożoną budową i różnymi metodami produkcji, bardzo trudno jest zaproponować uniwersalny model lub korelację. Jednak koncepcja wykorzystana w niniejszej pracy, bazująca na modyfikacji modelu Nishikawy może być interesująca, szczególnie jeśli ustalona zostanie zależność wartości parametru F od parametrów pokrycia porowatego.

MARIA ŻYGADŁO¹
AGNIESZKA SEWERYN²
MAGDALENA WOŹNIAK³

Kielce University of Technology
al. Tysiąclecia Państwa Polskiego 7
25-314 Kielce, Poland

¹ e-mail: zygadlo@tu.kielce.pl

² e-mail: aseweryn@anr.rz.pl

³ e-mail: maka@tu.kielce.pl

EVALUATION OF THE USE OF COAL FLY ASH FROM MUNICIPAL HEAT – POWER PLANT WITH REGARD TO FOREIGN EXPERIENCES

Abstract

The residues from coal combustion are classified as a byproduct harmful to the environment, difficult for transportation and use. These are mainly fly and bottom ashes and slag. Although some of them find practical application, mainly in the construction industry, the majority is still stored. This is particularly true for ashes from power plants. Understandably, the disposal of ashes is of great ecological and economic importance. Recycling and recovery are the best available options here. Foreign experiences have shown that fly ashes can be a valuable resource for production of synthetic zeolites.

Natural zeolites are used in numerous economic and industrial sectors. Their limited resources raise the need to look for and apply synthetic products. Since fly ashes obtained from coal are similar to natural zeolites in terms of structure and chemical composition, it is possible to use them as a raw material for the synthesis of zeolites. The aim of the research was to assess the possibility of zeolite synthesis from fly ash - obtained from the municipal power plant – by means of chemical conversion method. In the experiment, the coal ash collected from under electrostatic precipitators in Kielce Power Plant was used. The effect of chemical activation on the sorption properties of coal ash was examined. The chemical conversion consisted in fly ash – NaOH solution interaction under specified temperature and pressure. The influence of changes in the structure of individual grains of fly ash (SEM studies) on their sorption properties was estimated. The level of adsorption on the model stand was tested by means of spectrophotometric method using methylene blue. The modification results and sorption properties of ashes for the set parameters (NaOH concentration, temperature, reaction time) were assessed. The microscopic and X-ray observations as well as specific surface changes indicate that after modification new crystal structures improving sorption capacity were obtained.

The aim of the paper is to assess the possibility of utilizing the furnace waste from Kielce Power Plant. A necessary condition for the recovery and utilization of the waste is to identify their characteristics and properties.

Keywords: coal fly ash, fly ash recycling, zeolites

1. Introduction

According to the Polish standard PE-EN-450 the criteria limiting the use of ash in concrete production is a high content of chlorides, sulfates and loss on ignition. The high ignition loss is usually typical of ashes from power plants and makes them unsuitable for use in construction engineering. Therefore, they are deposited in landfills. This, however, generates costs connected with securing and monitoring the landfills and poses a threat to the environment. Thus, the need arises for finding ways and means for secure application of the fly ashes.

A relatively new direction discussed in the literature is the use of sorption capacity of ash (Woolard et al., 2002). Ashes collected directly from under the electrostatic precipitators have high sorption capacity for pollutants in wastewater so they are applied in the production of sorbents used in the treatment of wastewater and waste gases (Cheerarot and Jaturapitakkul, 2004; Iyer, 2002).

Chemically modified ashes show even higher sorption capacity. Fly ashes, especially those with significant content of aluminum and silicon, can be used to manufacture zeolites by means of chemical

conversion. The impact of alkalis (NaOH, KOH) on the coal ashes at specified temperature and pressure conditions leads to the creation of zeolite-structure bodies. [Zones and Davis, 1996, Woolard et al., 2002; Hollman et al., 1999].

Fly ash is collected by electrostatic or mechanical precipitation (Łączny, 2002). It is a fine-grained powder, a heterogeneous mixture of particles of different shapes and sizes, composed of spherical glass particles, a large number of irregular aggregates and balls of colorless slag glaze with an empty interior. Fly ash contains also a small amount of elongated slivers of unburned carbon.

Grain size of furnace waste is closely related to the specific surface area of ash, as measured by both Blaine and BET method (Blanco et al., 2005). The specific surface area of ash determined by Blaine's method for silicate ash is above 250 m²/kg, for aluminum ash above 300 m²/kg, and for calcium ash ranges from 300 to 500 m²/kg (Łączny, 2002).

The density of the furnace waste depends on the type of coal burned. The density of fly ash is affected by: the composition of mineral matter, the amount of unburned carbon and the shape and structure of individual grains of ash (Bastian, 1980). The density of furnace waste is 1.9 ÷ 2.4 g/cm³, and is smaller than the density of sandy and silty soil, which is 2.6 ÷ 2.75 g/cm³ (Kucowski, 1997).

The degree of development of fly-ash grain surface and the size of the specific surface area to a large extent determine their usefulness (Łączny, 2002). In the basic phase composition of fly ash the following phases are distinguished (Łączny and Adamski, 2002; Ilic et al. 2003):

- glassy phase (with a large number of irregular aggregates) and considerable number of spherical grains,
- crystalline phase which consists of mullite, quartz, hematite, magnesium oxide, gypsum, magnetite, calcite, calcium oxide,
- clay phase (amorphous).

The following mineral composition of furnace ash was found: (Skalmowski, 2002; Scheetz and Earle, 1998):

- oxide minerals – Al₂O₃, Fe₂O₃, MgO, CaO;
- metallic grains – mainly Fe (having a spherical form);
- silicates and aluminosilicates – of the insular, ring, chain, layered and spatial structure. The morphological diversity of ash particles is shown in Figure 1.

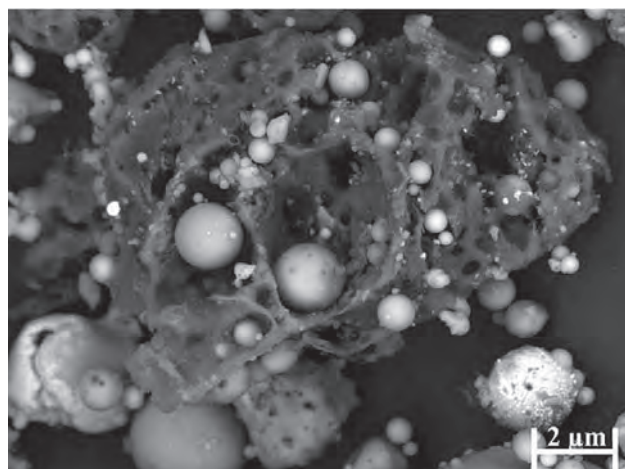


Fig. 1. A porous char residue (unburnt carbon) showing capture (trapping) of fine particles of fly ash (microspheres). SEM carbon natural surface on the ESP fly ash sample (Goodarzi i Sanei, 2009)

The chemical composition of the furnace waste varies in broad ranges – which is one of the reasons hindering their full utilization. The properties of fly ash are determined by a number of factors, of which the most important are: the type of coal burned and the type of installation in which the coal is burned (a type of boiler and technological conditions of coal burning) (Giergiczny, 2005).

Figure 2 illustrates the areas of coal ash utilization limited by the following criteria: pozzolanic properties, particle size and chemical composition. Pozzolanic properties of coal ash enable obtaining materials of low mechanical strength that can be used to stabilize the waste and as an ingredient in cement production.

Due to high splitting ash can be used as filler for asphalt, plastics, paper and its coarser fractions for grinding and polishing powders. In addition, ash is used for the production of ceramic products such as brick, glass and refractory materials.

With the right chemical composition fly ash can be a valuable source for the recovery of magnetite microspheres (a very good filler for rubber and plastics), coal, silica, alumina, iron. It is also used as a raw material in cement production if the quality condition is fulfilled. In addition, it can be a beneficial additive to agricultural soils.

The construction and road industries are the areas where fly ash is most widely applied. It is utilized in: land reclamation, fillings in underground mining, land fillings, fortifications of embankments, highway engineering and construction of dams.

Figure 3 illustrates utilization of coal ash in the construction industry.

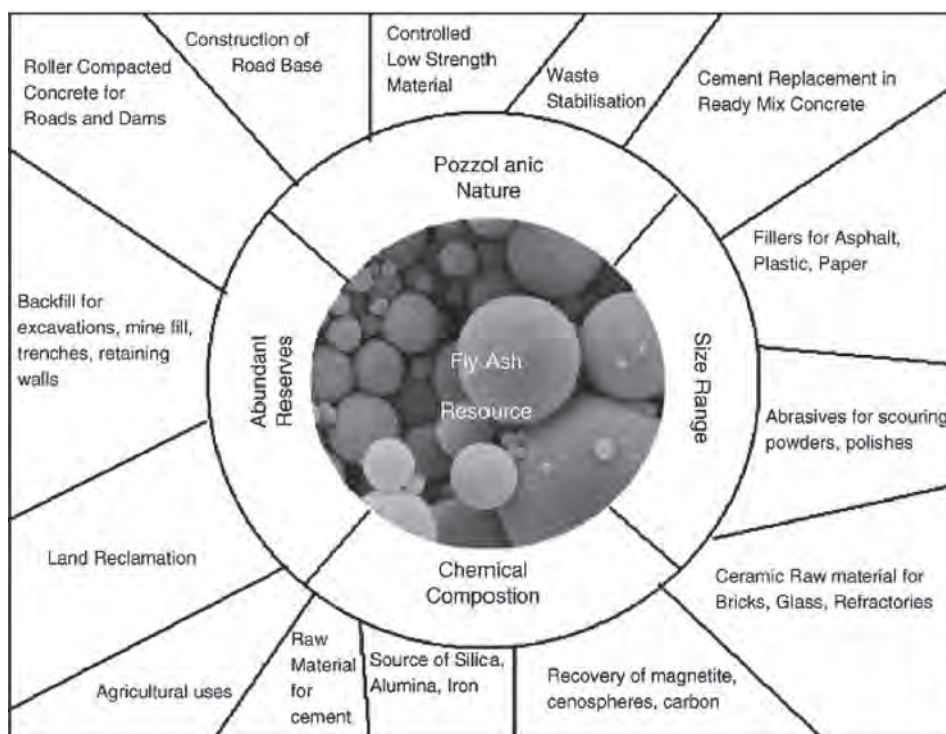


Fig. 2. Possible uses of coal fly ash (Shaobin i Hongwei, 2006)

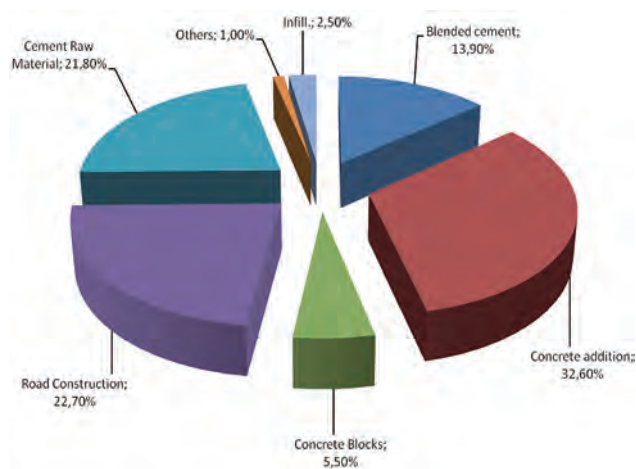


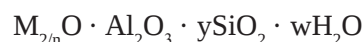
Fig. 3. Utilization of Fly Ash In the Construction Industry and Underground Mining In Europe (EU15) in 2008 total utilization: 17.7 million tonnes. (European Coal Combustion Product Association, <http://www.ecoba.org>)

2. The use of fly ash in the environmental protection

Several studies have shown that adsorptive capacity of fly ash is used for waste gas treatment, namely: removal of sulfur compounds, the adsorption of NO_x (Shaobin and Hongwei, 2006), removing heavy metals from wastewater (Wang et al., 2006, Wang et al., 2007, Hui et al., 2005), removal of mercury and the adsorption of organic gases (Majchrzak-Kucęba and Nowak, 2005).

A separate research direction developed recently is the modification of fly ash structure to zeolite by chemical conversion. A considerable diversity of methods for obtaining zeolites with fly ash used as a raw material is observed. Different ranges of heat treatment, proportions of components (ash: NaOH) and procedures are applied. It should be stressed that numerous zeolite structures can be synthesized in different process conditions (Querol et al., 2002; Tanaka, 2002 Tanaka, 2003; Tanaka, 2004; Hollman et al., 1999).

Zeolites are crystalline aluminosilicate metals of IA and IIA groups, such as Na, K, Mg, Ca. The general formula is as follows: (Ziolek and Smith, 1999, Paderewski, 1999):



where:

$y \geq 2$,

n – cation valence,

w – water content,

M – extra lattice cation.

The basic unit of three-dimensional crystal structure of zeolite are tetraedrits (Si,Al)O₄, characterized by varying ratio of silicon to aluminum and creating different multi-walled configurations – octahedral units.

Free spaces in the zeolite structure are so well developed that the cations and water molecules are

able not only stay in them but also roam freely under the influence of physical and chemical factors (Fig. 4).

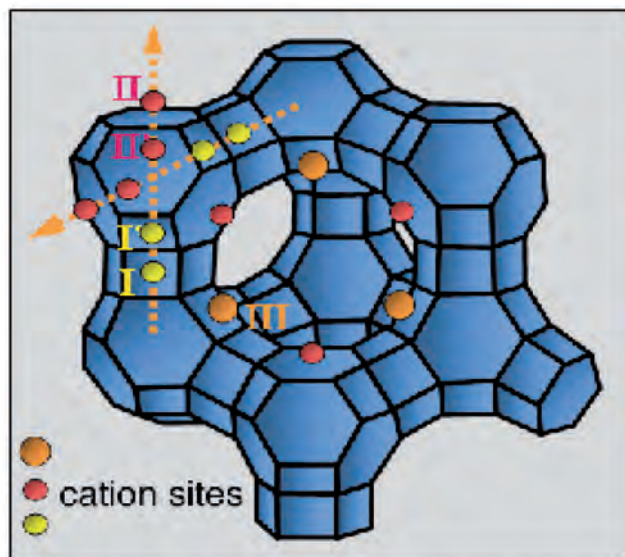


Fig. 4. The X zeolite structure – the main cationic sites in the unit cell (Resonant Contrast Diffraction for Direct Localisation of Atoms in Mixed Occupancy Powders <http://www.esrf.eu/UsersAndScience/Publications/Highlights/2005/Materials/MAT13>)

The extra lattice cations undergo ion exchange easily as they are mobile. Zeolites in the dry state show the sorption, catalytic and molecular-sieve properties.

Sieve effect means that only the particles below a certain critical size (window size) pass to the interior channels while larger ones remain outside the sieve. The sorption properties of zeolites are determined by their internal structure. Thanks to it they are used for drying, cleaning and separating of gases. The zeolites show selectivity and significant sorption capacity in relation to water (due to its dipole properties) which makes them useful in drying inert gases and atmospheric air.

A characteristic feature of zeolites is the surface area of the order of $300 - 1000 \text{ m}^2 \cdot \text{g}^{-1}$. (Payra i Dutta, 2003; Ziółek i Nowak, 1999).

The process of zeolite synthesis from the coal ash can be single or multistage. Four methods of obtaining zeolites from fly ash can be distinguished (Sucheck, 2005):

- classic alkaline conversion of fly ash,
- alkaline fusion + classic alkaline conversion of fly ash,
- conversion of dry or molten salt,
- two-stage synthesis.

The concept of chemical conversion of ash into the zeolite consists in treating the grains rich in alumina and silica (amorphous forms) with alkali. In the first stage the aluminosilicate gel is formed which then crystallizes to zeolite (Elliot and Dong-ke Zhang, 2005; Murayama et al., 2002).

The zeolitization mechanism according to Murayama is shown in Figure 5.

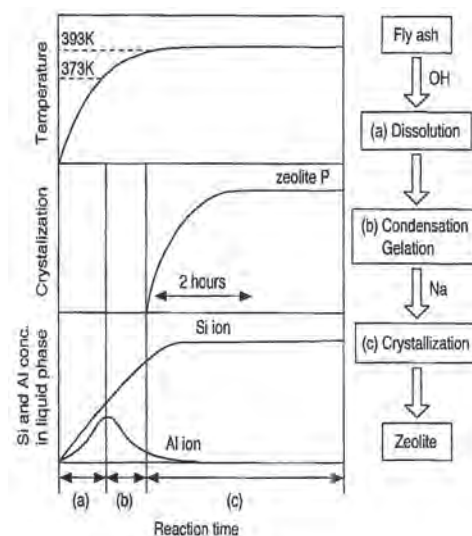


Fig. 5. Proposed reaction mechanism for zeolite synthesis from coal fly ash (Murayama i in., 2002)

The mechanism for zeolite synthesis from fly ash in a batch hydrothermal synthesis process includes three stages:

- 1) the dissolution of aluminium and silicon from fly ash,
- 2) the deposition of aluminosilicate gel on ash surface,
- 3) the crystallization of zeolite from aluminosilicate gel (Murayama i in., 2002).

Three phases in fly ash from which the aluminium and silicon come are observed:

- 1) amorphous aluminosilicate glass,
- 2) quartz, and
- 3) mullite.

The aluminosilicate glass phase is the largest and most unstable of the phases in the hydrothermal environment, and therefore has the highest rate of dissolution, and is the largest contributor to the zeolites produced. Quartz is less stable than mullite, although quartz and mullite phases are significantly more stable than the glass phase to the extent that some authors report little to no reactivity for quartz and for mullite (Elliot i Dong-ke Zhang, 2005; Murayama i in., 2002).

Different pore sizes and the presence of exchangeable cations in the structure of zeolites make them applicable in the selective adsorption of gaseous mixture components. The research on application of zeolites in removal of CO_2 , SO_2 or NO_x from gaseous mixtures resulted in a positive outcome also for zeolites synthesized from fly ash (Ahmaruzzaman, 2010; Cheerarot and Jaturapitakkul, 2004; Iyer, 2002).

The development of methods for the synthesis of zeolites from coal fly ash caused considerable interest in the possibility of their utilization in industry and environmental protection.

3. Materials and research methods

Characteristics of fly ash used in the research

The ash used in the research was collected in the years 2007, 2008, and 2009 from the heat recovery installation of Kielce Power Plant. The criterion of ash selection was its chemical composition making it suitable for use in the construction engineering (limiting criteria PE-EN 450-1:2005). The ash was collected directly from under the electrical precipitator in accordance with the standard POBOR PROB BS EN 450-1. The selected ash shows a high content of unburned carbon and high content of silicon and aluminum oxides (Table 1).

Table 1. Physical and chemical characteristics of fly ash used in the research

Chemical properties			
Oxide composition	Percentage[%]	Mineral composition	Percentage [%]
SiO_2	45.67	Quarto	12.4
SiO_2 reactive	33.17	Mullite	13.3
Fe_2O_3	8.01	CaO	0.7
Al_2O_3	23.47	periclase	2.4
CaO	5.09	hematite	1.8
MgO	3.69	maghemite	1.1
SO_3	0.61	anhydrite	2.4
wCaO	0.064	amorphous f.	66.0
Na_2O	0.83		
K_2O	1.40		
Physical properties			
Loss on ignition	7.52		
Fineness	28.9%		
Specific density	2.13 g/cm ³		
Specific surface area	6170 cm ² /g		

To estimate the repeatability of burned coal quality and hence ash quality the basic parameters of the coal burned in Kielce Power Plant are presented in Table 2.

Table 2. Parameters of coal burned in Heat and Power Station in Kielce

	2007	2008	2009
Calorific value [kJ/kg]	22614	23010	23565
Ash content [%]	17.3	16.8	14.5
Sulphur content [%]	0.57	0.49	0.39

Size distribution of fly ash were measured with laser diffractometer Malvern Mastersizer Microplus which allows measurement in the range from 0.05 to 500 μm . The measurements were conducted in 0.1% sodium pyrophosphate solution in recirculation conditions. During the measurement process ultrasounds were used to break up agglomerates – the time of ultrasound application was dependent upon the moment of re-agglomeration. The results are presented on a graph showing sample grain-size distribution.

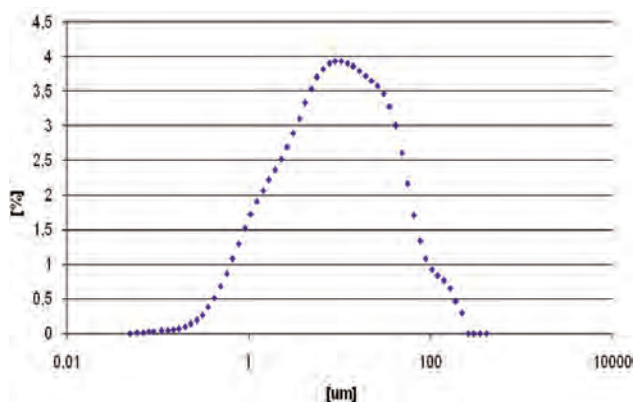


Fig. 6. Size distribution of fly ash sample taken from electrical precipitator at power plant in Kielce

The analysis of qualitative and quantitative phase composition was performed by X-ray diffraction using D8 Discover X-ray diffractometer produced by Bruker AXS. Data recording was carried out in the angular range $2 - 90^\circ 2\theta\text{CuK}\alpha$, for a step of 0.02° and counting time: 1.5 seconds per step. The content of crystalline phases was determined quantitatively with internal parameters computed on the basis of the standard NIST SRM 660a – LaB6. In order to quantify crystalline phases and determine the total content of amorphous phase the X-ray method with the inserted internal formula was used. Due to chemical stability

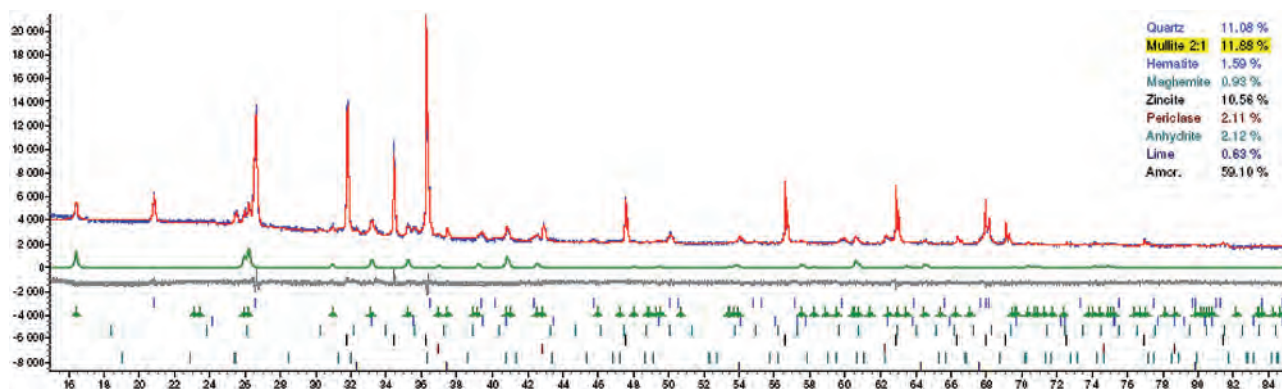


Fig. 7. X-ray determination of fly ash sample taken from power plant in Kielce

and incompatibility with important reflections of the phases zinc oxide (ZnO) was selected. (ŚRODON et al., 2001).

Procedure of chemical modification for ash

In order to assess the usefulness of ashes as sorbents, chemical modification was carried out in NaOH. The effectiveness of chemical conversion of ash into a hypothetical form of zeolite was evaluated by comparing ash sorption for methylene blue after conversion with ash sorption before chemical conversion. In addition, sorption isotherms, chemisorption, and BET were examined.

Chemical treatment consisted in treating ash with NaOH solution at room temperature $180^{\circ}\text{C} \pm 10^{\circ}\text{C}$ and at atmospheric pressure. For this purpose, 1g of ash was placed in a solution of 7M NaOH. The contact time of ash with NaOH was 21 hours. Then the precipitate was drained, washed with hot distilled water and ethanol, filtered and dried at 105°C . In order to determine the differences in sorption capacity of fly ash before and after chemical modification the sorption intensity of organic compounds using methylene blue as a model organic compound was examined. Consequently the loss of color substance in the solution was analyzed by spectrophotometry.

Sorption tests consisted in mixing 1 g of ash with 0.1 dm^3 of a suitably prepared dye solution (methylene blue). The concentration of dye was determined experimentally at the optimum level in order to measure the color intensity by spectrophotometry. The suspension was shaken for 4 hours and then filtered. The concentration of the dye was determined in a filtered solution using the spectrophotometer Thermo Scientific AQUAMAT.

The sorption capacity of the modified ash was calculated from the difference of dye concentrations

before and after the sorption process. This result was compared to the one obtained for sorption of ash not undergoing chemical conversion. Grain morphology before and after modification was examined by SEM Neophot 2.

4. Results and discussion

It should be noted that ash collected directly from under the electrical precipitator shows high sorption capacity towards dye and can serve as a good sorbent before chemical modification. As a result of chemical reaction the material of significantly increased sorption capacity towards methylene blue was obtained, as shown in Figure 8.

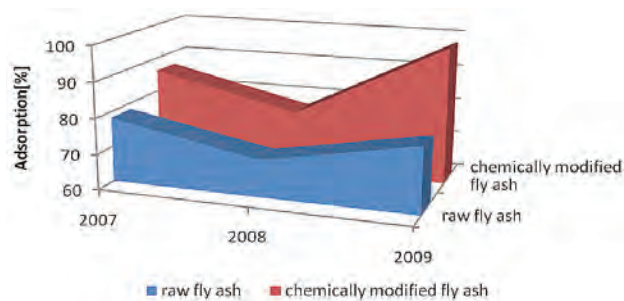


Fig. 8. Sorption capacity of raw and modified fly ash collected from power plant in Kielce in the period 2007-2009

The process is caused by changes of ash surface character as shown in Figure 9. and Figure 10. Unmodified ash grains have almost smooth surfaces (Fig. 9A). However, as a result of chemical treatment new structures are formed on the surface of ash particles highly increasing their porosity (Fig. 9B and 10). The observation is confirmed by the results obtained for the specific surface area (Table 3). The change of ash surface character determines the increase of their sorption properties towards methylene blue.

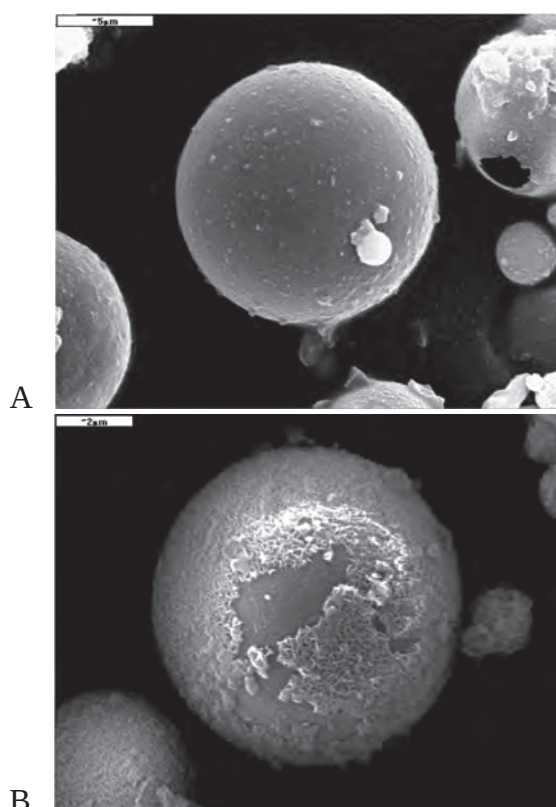


Fig. 9. SEM. Microscopic structure of individual grains of fly ash before modification - (A), and after chemical modification - (B). (Power Plant in Kielce), 5000 x magnification

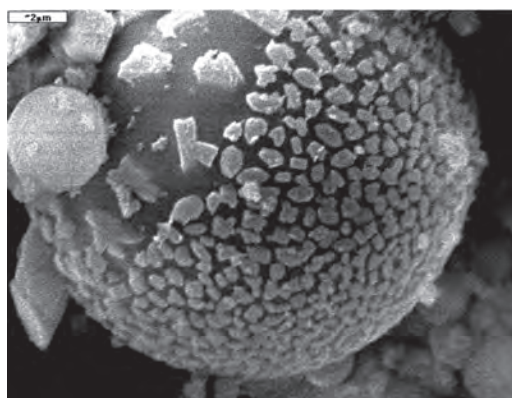


Fig. 10. SEM. Microscopic structure of individual grain of fly ash after modification (Heat and Power Station in Kielce), 7500x magnification

The amorphous phase with the aluminium and silicon compounds is particularly susceptible to chemical conversion (Table 1). During chemical treatment Si / Al glass on the grain surface turns into gel and then crystallization of a zeolite structure takes place. (Elliot and Dong-ke Zhang, 2005; Murayama et al., 2002). The more of amorphous phase in the ash sample the more effective the process. As shown by

X-ray examination the ashes contain about 66% of amorphous phase, which facilitates the formation of zeolite structures.

Table 3. Comparison of changes in the specific surface area of fly ash before and after modification

Test method	Raw fly ash [m ² /g]	Fly ash after modification NaOH [m ² /g]
Specific surface area measured by BET method	3.8719	104.8395
Specific surface area measured by Langmuir method	4.9153	132.1400

In order to estimate the impact of time when the samples were collected (the ashes collected in three different years were tested) upon repeatability of results the statistical test was conducted on the basis of monoagent analysis of variance of sorption results. At the beginning the assumption was made that sampling time affects the adsorption capacity of fly ash. In the case of raw fly ash collected in the years 2007-2009 the border level of significance was 0.53 which proves that the test samples of fly ash are relatively homogeneous and the sampling time has no significant effect on the sorption capacity.

5. Summary

Although fly ash is well-recognized and widely used it seems reasonable to look for its new applications, especially as far as ash from power plants is concerned.

Our research confirms that ashes which due to their chemical properties are not utilized in construction engineering can be used in raw state as sorbents. Sorption capacity of ash was improved by chemical conversion in NaOH solution. The chemical conversion was confirmed by the examination of ash specific surface area and morphology picture of ash grains. The results of obtained by electron microscopy confirmed both the formation of new crystalline structures on the surface of ash particles and the increase of roughness. The BET results showed that specific surface area of samples increases radically after chemical modification. The observation is consistent with the results obtained for the sorption of methylene blue in which the chemical activation of fly ash caused the increase of the specific surface area.

Basing on our research it seems justified to further explore the sorption capacity of the ashes towards

pollutants in municipal or landfill wastewater. The application of fly ash to produce sorbents allows to make use of furnace waste which has not been used but stored so far. Currently, depositing waste on landfills in power plants requires both large areas and constant monitoring, thereby generating significant costs.

References

- [1] Ahmaruzzaman M., 2010, *A review on the utilization of fly ash.*, in: *Progress in Energy and Combustion Science.*, No 36, pp. 327-363.
- [2] Bastian S., 1980, *Construction concrete with fly ash* Arkady, Warsaw (in Polish).
- [3] Blanco F., Garcia M.P., Atala J., 2005, *Variation in fly ash properties with milling and acid leaching*, Fuel, vol. 84, pp. 89-96.
- [4] Cheerarot R., Jaturapitakkul Ch., 2004, *A study of disposed fly ash from landfill to replace Portland cement*, in: *Waste Management* 24, pp. 701-709.
- [5] Elliot A.D., Dong-ke Zhang, 2005, *Controlled Release Zeolite Fertilisers: A Value Added Product Produced from Fly Ash*, *International Ash Utilization Symposium (IAUS) and World of Coal Ash (WOCA)*.
- [6] European Coal Combustion Product Association, <http://www.ecoba.org>
- [7] Giergiczny Z. 2005, *Fly ash with high lime content: Cement Wapno Beton* nr 5, 271-282 in Polish.
- [8] Goodarzi F., Saneii H., 2009, *Plerosphere and its role in reduction of emitted fine fly ash particles from pulverized coal-fired power plants*, in: *Fuel* 88, pp. 382-386.
- [9] Hollman G.G., Steenbruggen G., Jansses-Jurkovičová M., 1999, *A two-step process for the synthesis of zeolites from coal fly ash*, in: *Fuel* 78, pp. 1225-1230.
- [10] Hui K.S., Chao C.Y.H., Kot S.C., 2005, *Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash*, in: *Journal of Hazardous materials*, B127, pp.89-101.
- [11] Ilic M., Cheeseman Ch., Sollars Ch., Knight J., 2003, *Mineralogy and microstructure of sintered lignite coal fly ash*, in: *Fuel*, 82, pp. 331-336.
- [12] Iyer R., 2002, *The surface chemistry of leaching coal fly ash*, in: *Journal of Hazardous Materials*, B93, pp. 321-329.
- [13] Łączny J., Adamski M., *The Mathematical Model of the Impact of Landfills Storing Waste Energy Products upon Environment*, Zakład Narodowy im. Ossolińskich, Wydawnictwo Polskiej Akademii Nauk, Wrocław-Warszawa-Kraków 2002 (in Polish).
- [14] Łączny M.J., 2002, *Unvonventional Methods of Fly Ash Utilization*, Główny Instytut Górnictwa, Katowice (in Polish).
- [15] Kucowski J., Laudyn D., Przekwas M., *Power Engineering and Environmental Protection*, Wydawnictwo Naukowo-Techniczne, Warszawa 1997 (in Polish).
- [16] Majchrzak-Kucęba I., Nowak W., 2005, *A thermogravimetric study of the adsorption of CO₂ on zeolites synthesized from fly ash*, in: *Science Direct, Thermochimica Acta* 437, pp. 67-74.
- [17] Murayama N., Yamamoto H., Shibata J., 2002, *Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction*, in: *International Journal of Mineral Processing*, 64, pp. 1-17.
- [18] Standard PN-EN 450 (U). *Fly ash for concrete production. Part 1.: Definitions, requirements and compatibility criteria* (in Polish).
- [19] Paderewski M.L., *Adsorption processes in chemical engineering*, Wydawnictwo Naukowo-Techniczne, Warszawa 1999 (in Polish).
- [20] Payra P., Dutta P.K., 2003, *Zeolites: A Primer*, in: *Handbook of zeolite science and technology*, ed. Auerbach S.M., Carrado K.A., Dutta P.K., Marcel Dekker, New York-Basel, p. II.
- [21] Querol X., Moreno N., Umaña J.C., Alastuey A., Hernández E., López-Soler A., 2002: Plana F.: *Synthesis zeolites from coal fly ash: an overview*, *International Journal of Coal Geology* 50, pp. 413-423.
- [22] A Statistical Yearbook, Environmental Protection, 2008 (in Polish).
- [23] Resonant Contrast Diffraction for Direct Localisation of Atoms in Mixed Occupancy Powders <http://www.esrf.eu/UsersAndScience/Publications/Highlights/2005/Materials/MAT13>.
- [24] Shaobin W., Hongwei W., 2006, *Environmental-benign utilization of fly ash as low-cost adsorbents*, in: *Journal of Hazardous Materials*, B136, pp. 482-501.
- [25] Scheetz B.E., Earle R., 1998, *Utilization of fly ash*, in: *Current Opinion in Solid State and Materials Science*, no3, pp. 510-520.
- [26] Skalmowski K., *Manual of waste management: guide for professionals and clerks dealing with environmental issues*. Verlag Dashofer, Warsaw 2002 (in Polish).
- [27] Suchecki T.T., *Zeolites from fly ash. Synthesis and applications in environmental engineering*. Zakład Narodowy im. Ossolińskich- Wydawnictwo, Wrocław 2005 (in Polish).
- [28] Środoń J., Drits V.A., McCarty D.K. Hsieh J.C.C., Eberl D.D., 2001, *Quantitative SRD analysis of clay – rich rocks from random preparations*. *Clays&Clay Minarals* 49, pp. 514-528.
- [29] Tanaka H., Furusawa S., Hino R.: *Synthesis, 2002, Characterization, and formation Process of Na-X Zeolite from Coal Fly Ash*, in: *Journal of Materials Synthesis and Processing*, 10, pp. 143-148.
- [30] Tanaka H., Matsumura S., Furusawa S., Hino R., 2003, *Conversion of coal fly ash to Na-X zeolites*, in: *Journal of Materials Science Letters* 22, pp. 323-325.
- [31] Tanaka H., Matsumura S., Hino R., 2004: *Formation process of Na-X zeolites from coal fly ash*, *Journal of Materiale Science* 39, pp. 1677-1682.

- [32] Wang S., Soudi M., Li L., Zhu Z.H., 2006, *Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater*, in: *Journal of Hazardous Materials B* 133, pp. 243-251.
- [33] Wang S., Soudi M., Li L., Zhu Z.H., 2007, *Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater*, in: *Journal of Hazardous Materials B* 139, pp. 254-259.
- [34] Woolard C.D., Strong J., Erasmus C.R., 2002: *Evaluation of the use of modified coal ash as a potential sorbent for organic wastes streams*. in. *Applied Geochemistry*, No. 17, pp. 1159-1164.
- [35] Ziółek M., Nowak I., *Heterogeneous catalysis. Selected issues*, Wydawnictwo Naukowe UAM, Poznań 1999 (in Polish).
- [36] Zones S.I., Davis M.E., 1996, *Zeolite materials: recent discovers and future prospects*, in: *Current Opinion In Solid State & Materials Science*, 1, pp. 107-117.

Maria Żygadło
Agnieszka Seweryn
Magdalena Woźniak

Rozpoznanie możliwości użytkowych popiołów z elektrociepłowni miejskiej na tle doświadczeń zagranicznych

1. Wstęp

Według polskiej normy PE-EN-450 kryteriami ograniczającymi wykorzystanie popiołu do betonu jest wysoka zawartość chlorków, siarczanów i straty prażenia. Wysoka strata prażenia zazwyczaj charakteryzuje popioły pochodzące z elektrociepłowni i jednoznacznie dyskwalifikuje je do wykorzystania w budownictwie. Wobec tego deponuje się je na składowiskach. Generuje to koszty związane z zabezpieczeniem i monitoringiem, stanowi zagrożenie dla środowiska naturalnego. Zachodzi zatem potrzeba znalezienia sposobów i środków bezpiecznego wykorzystywania popiołów, które dotąd nie znalazły zastosowania.

Stosunkowo nowym kierunkiem zastosowań omawianym w literaturze jest wykorzystanie zdolności sorpcyjnych popiołów (Woolard i in., 2002). Popioły bezpośrednio pobrane spod elektrofiltrów posiadają wysokie zdolności sorpcyjne wobec zanieczyszczeń w wodach zużytych. Znalazły dzięki temu zastosowanie do produkcji sorbentów wykorzystywanych w oczyszczaniu ścieków i gazów odlotowych (Cheer-arot i Jaturapitakkul, 2004; Iyer, 2002). Jeszcze wyższe zdolności sorpcyjne posiadają popioły poddane modyfikacji chemicznej.

Popioły lotne, zwłaszcza te ze znaczną zawartością glinu i krzemu, można w drodze konwersji chemicznej wykorzystać do produkcji zeolitów. Oddziaływanie na popioły powęglowe alkali (NaOH, KOH) w okre-

ślonych warunkach temperatury i ciśnienia prowadzi do utworzenia struktur o budowie zeolitów [Zones i Davis, 1996; Woolard i in., 2002; Hollman i in., 1999].

Prezentowany artykuł ma na celu oszacowanie możliwości zagospodarowania odpadów paleniskowych z elektrociepłowni kieleckiej. Niezbędnym warunkiem odzysku i zagospodarowania tych odpadów jest rozpoznanie ich charakterystyki i właściwości.

2. Ogólna charakterystyka popiołów lotnych ze spalania węgla kamiennego

Popiół lotny gromadzony jest przez elektrostatyczne lub mechaniczne strącanie (Łączny, 2002). Jest to drobnoziarnisty proszek, heterogeniczna mieszanina cząstek o różnych kształtach i rozmiarach, złożony ze sferycznych cząstek szkła, dużej ilości nieregularnych agregatów, kulek bezbarwnego szkliwa żużlowego o pustym wnętrzu. Popioły lotne zawierają także nieznaczную ilość wydłużonych okruchów niespalonego węgla.

Stopień rozwinięcia powierzchni ziaren i wielkość powierzchni właściwej w dużym stopniu decydują o ich przydatności (Łączny, 2002). W podstawowym składzie fazowym popiołów lotnych można wyróżnić (Łączny i Adamski, 2002; Ilic i in. 2003):

- fazę szklistą (o dużej ilości nieregularnych agregatów, a także znacznej liczbie ziaren kulistych),

- fazę krystaliczną, w składzie której występuje: mullit, kwarc, hematyt, tlenek magnezu, gips, magnetyt, kalcyt, tlenek wapnia,
- fazę ilastą (bezpostaciową).

W składzie mineralnym popiołów paleniskowych ustalono występowanie (Skalmowski, 2002; Scheetz i Earle, 1998):

- a) minerałów tlenkowych – Al_2O_3 , Fe_2O_3 , MgO , CaO ;
- b) ziaren metalicznych – głównie Fe (w postaci form kulistych);
- c) krzemianów i glinokrzemianów – o budowie wypowej, pierścieniowej, łańcuchowej, warstwowej i przestrzennej. Obraz zróżnicowania charakteru morfologicznego, cząstek popiołowych zilustrowano na fot. 1.

Skład chemiczny odpadów paleniskowych zmienia się w szerokich przedziałach, co jest jednym z powodów utrudniających ich pełne wykorzystanie. O właściwościach popiołów lotnych decyduje szereg czynników, z których najistotniejsze są: rodzaj spalanego węgla i rodzaj instalacji, w której odbywa się spalanie węgla (typ kotła, technologiczne warunki spalania) (Giergiczny, 2005).

3. Zakres wykorzystania popiołów lotnych z węgla

Na rysunku 2 zilustrowano obszary wykorzystania popiołów lotnych z węgla kamiennego limitowane kryteriami, takimi jak: właściwości pucolanowe, wielkość cząstek, czy skład chemiczny. Właściwości pucolanowe popiołów umożliwiają pozyskanie materiałów o niewysokiej wytrzymałości mechanicznej: mogą służyć do stabilizacji odpadów, mogą być stosowane także jako składnik do produkcji cementu. Dzięki dużemu rozdrobnieniu popioły mogą być wykorzystane jako wypełniacze do asfaltów, plastików, papieru, grubsze frakcje wykorzystywane są do proszków ściernych i polerskich. Popioły znalazły zastosowanie w produkcji wyrobów ceramicznych, tj. cegły, szkła, materiałów ogniotrwałych. Przy odpowiednim składzie chemicznym popioły mogą stanowić cenne źródło surowcowe do odzysku magnetytu, mikrosfer jako (cenny wypełniacz gumy, plastików), węgla, krzemionki, glinu, żelaza. Są wreszcie wykorzystywane jako surowiec do produkcji cementów, przy spełnieniu kryteriów jakościowych. Mogą być także korzystnym dodatkiem do gleb w rolnictwie.

Przemysł budowlany i drogownictwo stanowią najbardziej chłonny obszar wykorzystania popiołów z węgla. Tu bowiem popioły znalazły zastosowanie jako materiał do rekultywacji gruntów, do podsadzek w wyrobiskach kopalnianych, wypełnień gruntów,

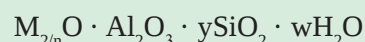
umocnień wałów, budowy nawierzchni i podbudowy dróg, budowy zapór wodnych.

4. Wykorzystanie popiołów w ochronie środowiska

W wielu badaniach wykazano zdolności adsorpcyjne popiołów lotnych, zastosowanych do oczyszczania gazów odlotowych: usuwanie związków siarki, adsorpcja NO_x (Shaobin i Hongwei, 2006), usuwanie metali ciężkich ze ścieków (Wang i in., 2006, Wang i in., 2007, Hui i in., 2005), usuwanie rtęci, adsorpcja gazów organicznych (Majchrzak-Kucęba i Nowak, 2005).

Odrębnym kierunkiem badań rozwijanym w ostatnich latach jest modyfikacja struktury popiołów lotnych w drodze konwersji chemicznej do postaci zeolitów. Obserwuje się znaczne zróżnicowanie metod uzyskiwania struktur zeolitów z wykorzystaniem popiołów jako surowca wyjściowego. Stosowane są różne zakresy obróbki termicznej, proporcje składników (popiół: NaOH), procedury postępowania. Należy także zwrócić uwagę na mnogość struktur zeolitycznych możliwych do zsyntezowania w zróżnicowanych warunkach procesu (Querol i in., 2002; Tanaka, 2002; Tanaka, 2003; Tanaka, 2004; Hollman i in., 1999).

Zeolity są krystalicznymi glinokrzemianami metali grup IA i IIA, takich jak Na, K, Mg, Ca. Ogólny wzór przedstawia się następująco (Ziółek i Nowak, 1999; Paderewski, 1999):



gdzie: $y \geq 2$,

n – wartościowość kationu,

w – zawartość wody,

M – kation pozasieciowy.

Podstawową jednostką trójwymiarowej krystalicznej struktury zeolitu są tetraedry $(\text{Si}, \text{Al})\text{O}_4$, charakteryzujące się zmiennym stosunkiem krzemu do glinu i tworzące różne konfiguracje wielościenne – jednostki oktaedryczne (tzw. kubooktaedry).

Wymianie jonowej podlegają bardzo łatwo kationy pozasieciowe, jako mobilne. Zeolity w stanie wysuszonym wykazują właściwości sorpcyjne, katalityczne i molekularno-sitowe.

Efekt sita polega na tym, że do wnętrza kanałów przechodzą tylko te cząsteczki, które mają rozmiary poniżej pewnej wielkości krytycznej (rozmiar okna), natomiast cząsteczki o większych rozmiarach pozostają na zewnątrz sita. Budowa wewnętrzna warunkuje właściwości sorpcyjne zeolitów. Dzięki niej są one wykorzystywane do osuszania i oczyszczania gazów, a także do rozdzielania gazów. Materiały te cechuje selektywność oraz znaczna pojemność sorpcyjna

względem wody z uwagi na jej właściwości dipolowe, dlatego zeolity stosuje się przykładowo do osuszania gazów obojętnych oraz do osuszania powietrza atmosferycznego.

Charakterystyczną cechą zeolitów jest powierzchnia właściwa, rzędu $300 - 1000 \text{ m}^2 \cdot \text{g}^{-1}$ (Payra i Dutta, 2003; Ziółek i Nowak, 1999).

Proces syntezy zeolitu z popiołu powęglowego realizowany może być jako jedno- lub wielostopniowy. Wyróżnić można cztery metody otrzymywania zeolitów z popiołów lotnych. Są to (Suchecki, 2005):

- klasyczna alkaliczna konwersja popiołu lotnego,
- alkaliczna fuzja + klasyczna alkaliczna konwersja popiołu lotnego,
- konwersja sucha lub stopionych soli,
- dwustopniowa synteza.

Idea konwersji chemicznej popiołu do zeolitu polega na traktowaniu alkalią ziarna bogatego w glin i krzemionkę (w postaci amorficznej). W pierwszym etapie powstaje żel glinokrzemianowy, który następnie krystalizuje do postaci zeolitu (Elliot i Dong-ke Zhang, 2005; Murayama i in., 2002).

Zróżnicowanie wielkości porów oraz obecność kationów wymiennych w strukturze zeolitów sprawiają, że są one stosowane do selektywnej adsorpcji składników mieszanin gazowych. Prowadzone badania nad zastosowaniem ich w usuwaniu z mieszanin gazowych CO_2 , SO_2 bądź NO_x zakończyły się pozytywnym rezultatem, także w odniesieniu do zeolitów syntezowanych z popiołów lotnych (Ahmaruzzaman, 2010; Cheerarot i Jaturapitakkul, 2004; Iyer, 2002).

Opracowanie metod syntezy zeolitów z popiołów lotnych powęglowych wywołało duże zainteresowanie możliwościami ich zastosowania w przemyśle oraz w ochronie środowiska.

5. Materiały i metody badań

Charakterystyka popiołu wykorzystanego w badaniach

Do badań wykorzystano popiół pochodzący z instalacji odzysku ciepła z elektrociepłowni Kielce, pobrany w latach 2007, 2008, 2009. Popiół ten został wytypowany do badań, ponieważ jego skład chemiczny nie pozwala wykorzystać go w budownictwie (kryteria ograniczające wg PE-EN 450-1:2005). Popiół pobierano bezpośrednio spod elektrofiltra zgodnie z normą: PN- EN 450-1.

Wybrany popiół charakteryzuje się dużą zawartością niespalonego węgla i wysoką zawartością tlenków krzemu i glinu (tabela 1)

W celu oszacowania powtarzalności jakości spalanego węgla, a co za tym idzie – popiołu, w tabeli 2 przedstawiono podstawowe parametry charakteryzujące węgiel spalany w EC Kielce.

Wykorzystano dyfraktometr laserowy, Mastersizer Microplus firmy Malvern. Przy pomocy tego urządzenia wykonywany jest pomiar w zakresie 0,05 do 500 μm . Pomiary wykonano w 0,1% roztworze pirofosforanu sodowego w warunkach recyrkulacji. W trakcie pomiarów stosowano ultradźwięki do rozbicia aglomeratów – czas stosowania dobierano do momentu ponownej aglomeracji. Otrzymano wyniki w postaci wykresu rozkładu ziarnowego próbkii.

Analizę składu fazowego jakościowego i ilościowego wykonano metodą dyfrakcji promieni rentgenowskich za pomocą dyfraktometru rentgenowskiego D8 Discover firmy Bruker AXS. Rejestrację danych przeprowadzono w zakresie kątowym $2 - 90^\circ 2\theta\text{CuK}\alpha$, stosując krok $0,02^\circ$, czas zliczeń: 1,5 sekundy na krok. Zawartość faz krystalicznych oznaczono ilościowo z uwzględnieniem parametrów wewnętrznych obliczonych na podstawie wzorca NIST SRM 660a – LaB_6 . Do oznaczenia ilościowego faz krystalicznych i określenia sumarycznej zawartości faz amorficznych wykorzystano metodę pomiaru rentgenowskiego z wprowadzonym wzorcem wewnętrznym. Ze względu na stabilność chemiczną i niepokrywanie się z ważnymi refleksami oznaczanych faz, wybrano do tego celu tlenek cynku (ZnO) (Środoń i in., 2001).

6. Procedura modyfikacji chemicznej popiołu

W celu oszacowania użyteczności badanych popiołów w charakterze sorbentów przeprowadzono procedurę modyfikacji chemicznej w środowisku NaOH . Efektywność konwersji chemicznej popiołów do hipotetycznej postaci zeolitów oceniono porównując sorpcję popiołów względem błękitu metylenowego po konwersji do sorpcji popiołów przed konwersją chemiczną. Ponadto wykonano badanie izoterm sorpcji, chemisorpcji i BET.

Obróbka chemiczna popiołów polegała na oddziaływaniu na popiół roztworu NaOH w warunkach temperatury pokojowej $18^\circ\text{C} \pm 1^\circ\text{C}$ i pod ciśnieniem atmosferycznym. W tym celu reakcji poddano nawagę 1 g popiołu, którą umieszczono w roztworze 7 M NaOH . Czas kontaktu popiołu z NaOH wynosił 21 godzin. Następnie osad odsączono, przemyto ciepłą wodą destylowaną i etanolem, odfiltrowano i wysuszono w temperaturze 105°C .

W celu określenia różnic w zdolności sorpcyjnej popiołów przed i po modyfikacji chemicznej badano intensywność sorbowania związków organicznych,

wykorzystując jako model związku organicznego błękit metylenowy. Tym samym możliwa była analiza ubytku substancji barwnej w roztworze metodą spektrofotometryczną.

Badania sorpcji polegały na wymieszaniu naważki popiołu (1 g) z odpowiednio przygotowanym roztworem barwnika (błękit metylenowy) w ilości 0,1 dm³. Dobór stężenia barwnika ustalono eksperymentalnie na poziomie optimum ze względu na możliwości pomiaru intensywności barwy metodą spektrofotometryczną. Zawiesinę wytrząsano przez cztery godziny, a następnie przesączano. W przefiltrowanym roztworze określono stężenie barwnika. Oznaczenia prowadzono na spektrofotometrze AQUAMATE Thermo Scientific.

Zdolność sorpcyjną zmodyfikowanego popiołu obliczono z różnicy stężeń barwnika w roztworze przed i po procesie sorpcji. Wynik ten porównano do wyniku sorpcji popiołu niepoddanego konwersji chemicznej. Badania SEM, morfologii ziaren przed i po modyfikacji przeprowadzono na mikroskopie skaningowym typ Neophot 2.

7. Wyniki badań i dyskusja

Zwraca uwagę, że popiół lotny, pobrany bezpośrednio spod elektrofiltrowa, wykazuje dużą zdolność sorpcyjną względem barwnika, a więc jeszcze przed modyfikacją chemiczną może pełnić rolę dobrego sorbentu. W wyniku przeprowadzonej reakcji chemicznej uzyskano materiał o znacznie podwyższonej zdolności sorpcji wobec błękitu metylenowego, co zilustrowano na rysunku 8. Jest to spowodowane zmianami charakteru powierzchni ziaren popiołów, co zilustrowano na rysunkach 9 i 10. Ziarna popiołu niemodyfikowanego posiadają prawie gładkie powierzchnie (rys. 9A). Natomiast w wyniku obróbki chemicznej następuje utworzenie nowych struktur na powierzchni ziaren popiołów, w wyniku czego cechują się one wysoką porowatością (rys. 9B i 10). Znajduje to potwierdzenie w wynikach badań powierzchni właściwej (tabela 3). Zmiana charakteru powierzchni badanych popiołów decyduje o wzroście ich właściwości sorpcyjnych wobec błękitu metylenowego.

Szczególnie podatna na konwersję chemiczną jest faza amorficzna z obecnością tych związków glinu i krzemu (tabela 1). Podczas obróbki chemicznej następuje reakcja szkła Si/Al na powierzchni ziaren do formy żelu, a następnie krystalizacja struktur o charakterze zeolitów (Elliot i Dong-ke Zhang, 2005; Murayama i in., 2002). Proces ten jest tym bardziej efektywny im więcej fazy amorficznej występuje w próbce popiołu.

Jak wykazały badania rentgenowskie, badane popioły zawierają około 66% fazy amorficznej, co sprzyja tworzeniu tych struktur.

W celu oszacowania wpływu czasu poboru prób (badano popioły pobrane w trzech różnych latach) na powtarzalność wyniku wykonano badanie statystyczne oparte na jednoczynnikowej analizie wariancji uzyskanych wyników sorpcji. Przyjęto na wstępie hipotezę że czas poboru próby ma wpływ na zdolności sorpcyjne popiołów lotnych.

W przypadku popiołów surowych pobranych w latach 2007-2009 wykazano graniczny poziom istotności na poziomie 0,53, co pozwala stwierdzić, że badane próby popiołów lotnych są stosunkowo jednorodne i czas poboru próby nie ma istotnego wpływu na zdolności sorpcyjne.

Podsumowanie

Mimo że popioły lotne są materiałem dobrze rozpoznanym i wykorzystywanym w świetle, uzasadnione jest dalsze poszukiwanie ich nowych zastosowań, zwłaszcza dla popiołów z elektrociepłowni.

W prezentowanych badaniach własnych potwierdzono, że popioły, których właściwości chemiczne dyskwalifikują ich wykorzystanie w budownictwie, mogą być stosowane w charakterze sorbentów w stanie surowym. Zdolności sorpcyjne tych popiołów uległy poprawie w wyniku konwersji chemicznej w środowisku NaOH. Konwersję chemiczną potwierdzono w badaniach powierzchni właściwej i struktury popiołów. Wyniki badań przeprowadzonych w mikroskopie elektronowym potwierdziły tworzenie się nowych struktur krystalicznych, na powierzchni ziaren popiołów i wzrost chropowatości. Wyniki badań BET wykazały radykalny wzrost powierzchni właściwej prób po modyfikacji chemicznej. Pozostaje to w zgodzie z wynikami badań sorpcji błękitu metylenowego, w których aktywacja chemiczna popiołów przyczyniła się do poprawy tej zdolności.

W świetle przeprowadzonych badań wydaje się uzasadnione dalsze rozpoznanie zdolności sorpcyjnych popiołów względem zanieczyszczeń obecnych np. w ściekach komunalnych lub odciekach składowiskowych.

Wykorzystanie popiołów lotnych do produkcji sorbentów pozwala zagospodarować odpad paleniskowy, dotąd składowany. W obecnym stanie deponowanie odpadów na składowisku odpadów elektrociepłowni wymaga dużych powierzchni; obiekt ten wymaga ciągłego monitoringu, co generuje znaczne koszty.

THE APPLICATION OF SELECTED ACTIVATED CARBONS TO DYE WASTEWATER TREATMENT

Abstract

In the presented study I have undertaken the research concerning the efficiency of dye removal which is crystal violet (the dye used for fabric dyeing and production of printing paste) from water solution with the use of activated carbons. In the research I have used fresh commercial active carbons WDex and WG-12. These carbons differ in their porous structure parameters (S , V , iodine, methylene and detergent values) as well as chemical properties of the surface (surface acidity, ability to dechlorine). It has been found that having the initial dye concentration 20 mg/L in the presence of activated carbons, the process of solution decolourisation takes place. Sorption capacity of activated carbon WDex equals 35 mg/g and in case of WG-12 – 12 mg/g. The sorption process of examined activated carbons is better described by Langmuir isotherm.

Keywords: activated carbon, dye wastewater, sorption, crystal violet

1. Introduction

Activated carbon is obtained by carbonization and activation of raw materials such as charcoal, lignite, semi-coke, coke, peat, wood, lignin, fruit seeds, nuts shells, organic polymers, industrial waste (rubber, rubber Bakelite or overburden).

The materials named above are subjected to carbonization i.e. pyrolysis of source material. As a result a carbonized product with a disordered structure is obtained. This disordered structure leads to formation of slots, which transform into pores. These pores are filled with the tarry matter or the products of decomposition (or at least blocked partially by disorganized carbon). The obtained product has a low absorption activity, with the surface area of several m^2/g . In the next stage, the carbonized product is further developed and enhanced during the activation process. It converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended surface area of the product. The activation process is usually carried out in an air, CO_2 , or water vapour in the temperature ranges from 800° to 900°C . Finally, the activated carbon with specific physicochemical properties is obtained [1].

Activated carbons have a developed porous structure and the resulting high area surface with

specific chemical properties. That makes it suitable for purification purposes. They are used for purification of gas (purification of tail gases, removal of volatile organic compounds, Hg , SO_2 , NO_x , polychlorinated biphenyl dioxin, separation of gas mixtures), water and sewage (drinking water treatment, preparation of process water, preparation of medicated baths, purification of groundwater, industrial waste water, landfills leachate) and other (purification of substrates and products in the sugar industry, food industry, pharmaceutical industry, cosmetic industry, chemical industry and acquisition of high grade purity substances). Activated carbons are also used as catalyst carriers in heterogeneous reactions in gas and liquid phases [2, 3].

As mentioned above, one of the important applications of activated carbons is water waste treatment, particularly industrial waste treatment. Due to diversified, industry type-dependent sewage composition and different technologies used, industrial wastewater treatment is a complex process. As such it has been a subject of numerous research projects [1, 5, 6, 7]. An example of industrial wastewater is that of textile and paint and dye industries. It contains dyes (more than 100 000 industrial dyes with an estimated output of 7×10^5 – 1×10^6 ton a year [8]), mineral and silicon oils, polycyclic aromatic

hydrocarbons, pesticides, detergents, inorganic acids, strong oxidants used as bleaching substances, glues and alkalis. Their characteristic feature is toxicity to water organisms; they also delay self-purification processes by decreasing the light permeability in the water environment. Typical feature of such wastewater is the presence of hard-biodegradable compounds and their high loading. Depending on the dye class, COD (Chemical Oxygen Demand) of exhausted dyes baths reaches the value between 1000 and 15 000 mg O₂/dm³ [9]. High requirements related to wastewater discharge into the municipal sewer facilities [9], groundwater and ground [10] reveal inefficiency of traditional purification methods. Therefore it seems necessary to search for more effective solutions, for instance the sorption process [1, 4]. Well developed porous structure and large number of pores (micro, mezo- and macro pores) of activated carbons, as well as chemical properties of surface facilitate the dyes retention on the surface of activated carbons. The combination of sorption and traditional processes of waste water treatment makes it possible to remove diluted organic impurities. That produces colour and smell, contribute to reducing the concentration of by-products of oxidation and disinfection, and to removing substances which pose direct threat to human health [11].

This paper presents the investigation in efficiency of eliminating crystal violet from a water solution by means of activated carbons. Crystal violet, i.e., hexamethyl-p-rosaniline hydro-chlorine belongs to triphenylmethane dyes called aniline dyes. It is used for fabric dyeing and production of paper products and printing paste. The dye is listed as harmful and dangerous to the environment. For that reason it has to be removed from the wastewater.

Assessment of sorption capacity is one of the stages of research on wastewater treatment in the presence of activated carbons and use of advanced oxidation processes (AOP).

2. Experimental part

The research was focused on WD_{ex} and WG-12 activated carbons, commercially used as sorbents.

2.1. Characteristics of investigated activated carbons

The porous structure was determined on basis of low temperature absorption of nitrogen (77 K). Absorption and desorption isotherm was determined by the volumetric method with Sorptomatic 1900

and ASAP 2010 Micromeritics apparatus. Moreover, for the investigated carbons the following factors, qualities and properties were determined: the porous structure, the dechlorination capacity (determined according to DIN 19603), iodine adsorption number (determined according to PN-83/C-97555.04), the ash content (determined according to PN-82/C-97555.08), the methylene number (determined according to PN-82/C97555.03), and detergent number (according to PN-84/C-97555.07).

Acidic-basic character of surface (the total content of acidic groups was determined by titration with 0.01M solution of HCl against the unreacted 0.01 M NaOH, which had been used for flooding the tested samples of carbons. The total content of basic groups was determined by titration with 0.01 M solution of NaOH against the unreacted 0.01 M HCl, which had been used for flooding the tested samples of carbons) and the content of soluble substances (according to PN-88/C-97555.11) were determined. The results are presented in Table 1.

Table 1. Physicochemical characteristics of investigated activated carbons

Activated carbon	Parameter							S [m ² /g]	Vp [cm ³ /g]
	Dechlorination capacity [cm]	Ferrum content [mg/g]	Methylene numbers [cm ³]	Iodine adsorption numbers [mg/g]	Detergent number [mg/g]	Ash content [%]	Water-soluble substances [%]		
WD _{ex}	5	0.5	36	990	20.62	20.64	1.07	1050	0.95
WG-12	6	0.44	32	1230	32	8.85	2.48	980	0.89

2.2. Crystal violet sorption on investigated activated carbons

a) Sorption kinetics.

In 500 cm³ conical flasks 0.5 g of each of the activated carbons WD_{ex} and WG-12 were weighed out. The weighed samples were flooded with 400 cm³ of crystal violet solution of concentration of about 20 g/dm³ and shook for 12 hours. In solutions from above the activated carbons, the concentration of crystal violet was determined at hourly intervals.

b) Sorption isotherms

0.1; 0.2; 0.5; 1.0; and 1.5 g of each of tested

activated carbons, WD_{ex} and WG-12 were weighed out in 500 cm³ conical flasks and flooded with crystal violet solution of concentration of about 20 mg/dm³ and shook for 12 hours.

The concentration of crystal violet was determined by the use of UV/VIS Marcel Media spectrophotometer at the wave length $\lambda = 590$ nm.

3. Analysis of the results

The assessment of physicochemical properties of chosen activated carbons determined by FIBDM (F – phenol, I – iodine, B – methylene blue, D – sodium lauryl sulphate, M – molasses) indicator was done in the first stage. This indicator expresses the relative adsorption capacity of investigated activated carbons in terms to five index substances. Those substances represent different groups of impurities occurring in waters, which vary in terms of chemical character, structure, and molecule size. The following substances are used as indicators: F – phenol (a simple ring, dimension 0.5 nm), J – iodine (a spherical molecule, diameter 1 nm), B – methylene blue (complex ring, length 1.5 nm), D – sodium lauryl sulphate (length chain 1.9 nm) and M – molasses (mixture of chain and ring molecules, about 2.8 nm average size) are used as indicators. The FIBDM indicator has a form of five-digit number, each of them in a conventional scale from 0 to 9, (the higher number, the better carbon), indicates the activated carbon class in terms of its adsorption capacity in relation to the standard substance [11].

Data presented in Table 1 show that among the investigated activated carbons: WD_{ex} and WG-12, WD_{ex} is characterized by the bigger area surface and higher total volume of pores. The parameters for WD_{ex} are 1050 m²/g and 0.95 cm³/g respectively. This carbon has also the higher value of methylene number (36 cm³). This clearly confirms its good sorption capacity. WG-12 carbon has lower area surface, 980 cm³/g and the volume of pores, 0.89 cm³/g, which together with other parameters, indicates its weaker sorption capacity.

The established sorption kinetics shows that contact-time of activated carbon-crystal violet lasts 12 hours. The investigated carbons were used as sorbents of crystal violet from water solution. The sorption isotherms presented in Figure 1 prove that WD_{ex} has a better sorption capacity (35 mg/g) and the highest surface acidity of 0.98 mval/g. This means that factors which foster crystal violet sorption include not only the surface area and availability of

pores (which is indicated by the methylene number (36 cm³) and the detergent number (21 mg/g), but also negative charge of activated carbon surface resulting from the effect of ionization of superficial acidic groups and from the interaction between positive charge of resonant structure of crystal violet and delocalized π electrons of activated carbon graphite structure. This explains lower sorption capacity of the second carbon, WG-12, which is 12 mg/g. It is despite the extended surface area and availability of pores, which is showed by the methylene number (32 cm³) and the detergent number (32 mg/g).

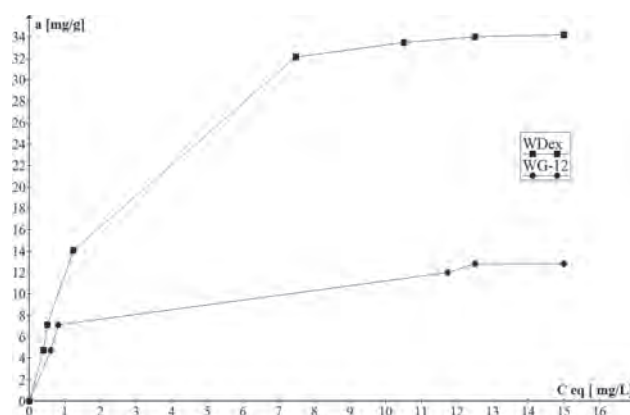


Fig. 1. Sorption isotherms of crystal violet on investigated activated carbons

The sorption process from the water solution can be described

– by the Langmuir equation:

$$\frac{y}{m} = \frac{a \cdot b \cdot C}{1 + b \cdot C} \quad (1)$$

where: y – the amount adsorbed, m – sorbent mass, C – concentration, a – experimentally calculated constant, b – experimentally calculated constant

– and the Freundlich equation:

$$\frac{y}{m} = K \cdot C^{\frac{1}{n}} \quad (2)$$

where: K – experimentally determined value of the coefficient, n – experimentally determined value of the coefficient.

Calculated parameters presented in Table 2 indicate better matching of the results of crystal violet sorption on the investigated carbons to the Langmuir isotherm, which means that the saturation rate of carbon with the dye was achieved.

Table 2. Coefficients of the Freundlich and Langmuir equation for crystal violet adsorption on investigated activated carbons.

Activated carbon	Freundlich isotherm			Langmuir isotherm		
	K	n	R ²	a	b	R ²
WD _{ex}	9.73	1.92	0.956	50	0.33	0.997
WG-12	6.30	3.70	0.933	14.29	1.00	0.996

4. Summary

Activated carbons are commonly used as sorbents. Fresh, commercial active carbons and a crystal violet (as a dye) were used for the investigation. When removing crystal violet for the water solution with the use of the given activated carbon, the sorption capacity decides on the removal efficiency. The sorption capacity depends on porous surface parameters, chemical properties of the surface, and the conditions of reaction. WD_{ex} activated carbon shows better sorption capacity (35 mg/g) than the other activated carbon, WG-12, which is characterized by both higher surface area (1050 m²/g), the total volume of pores (0.95 cm³/g) and the high value of the methylene number (36 cm³).

The presented results of the study related to the removal of the dye from the water solution with the use of the sorption process show the efficiency of the process. Long contact-time, however, causes a necessity to search for even better solutions, for instance, the advanced oxidation.

Anna Picheta-Oleś, a PhD student, receives a scholarship funded from the Kielce University of Technology Didactic Potential Development Programme: Education for Success, under the agreement No. UDA-POKL.04.01.01-00-175/08-02, co-funded from the European Social Fund within the framework of PO KL, Priority IV, Measure 4.1, Sub-measure 4.1.1.

The study employed Statistica software, the purchase of which was financed from the funds of the project mentioned above.

References

- [1] Bansal R. Ch., Goyal M., *Activated Carbon Adsorption*, CRC Press 2005.
- [2] Jankowska H., Świątkowski A., Choma J., *Węgiel aktywny, (Activated Carbon)*, Warszawa, WNT, 1985 [in Polish].
- [3] Buczek B., Czepirski L., *Adsorbenty węglowe – surowce, otrzymywanie, zastosowanie. (Carbon adsorbents- raw materials, obtaining, application)* Gospodarka Surowcami Mineralnymi/Mineral Resources Management, 2001 [in Polish].
- [4] Christie R.M., *Environmental Aspect of Textile Dyeing*, Woodhead, Boca Raton, Cambridge, 2007.
- [5] Santos V.P., Pereira M.F.R., Faria P.C.C., Orfão J.J.M., *Decolourisation of dye solutions by oxidation with H₂O₂ in the presence of modified activated carbons*, Journal of Hazardous Materials, 2009.
- [6] Majewska-Nowak K., *Usuwanie barwników ze ścieków przemysłowych, (Dyes removal from industrial wastewater)*, Ochrona Środowiska/Environmental Protection, 433/4, 17-22, 1986 [in Polish].
- [7] Jamroz T., Ledakowicz S., Żyła R., Sencio B., *Biologiczna ocena skuteczności odbarwiania roztworów w procesie pogłębionego utleniania, (Biological testing of effectiveness of solutions decolourisation by advanced oxidation)*, Ochrona Środowiska/Environmental Protection, 2001.
- [8] Gupta V.K., Suhas, *Application of low-cost adsorbents for dye removal – A review*, Journal of Environmental Management, 2009.
- [9] Mikulka M., (pod red.), (ed.), *Charakterystyka technologiczna przemysłu włókienniczego w Unii Europejskiej, (Technological characteristics of the textile industry)*, Ministerstwo Środowiska/Ministry for Environment, Warszawa, September 2003 [in Polish].
- [10] Regulation of the Minister for Construction of 14/07/2006 on the obligations waste generators and on standards of wastewater discharge into the sewer system (Dz.U.06.136.964).
- [11] Regulation of the Minister for Environment of 24/07/2006 on requirements relating to wastewater discharge into the water or the ground and a list of substances particularly hazardous to water environment (Dz.U. No.137, item 984) [in Polish].
- [12] Nawrocki J., Biłozora S., red., *Uzdatnianie wody. Procesy chemiczne i biologiczne, (Water treatment, Chemical and biological processes)*, Warszawa-Poznań, PWN, 2000 [in Polish].
- [13] Council Directive 67/548/EEC of 27/06/1967 on the classification of dangerous substances (as amended).

Wykorzystanie wybranych węgli aktywnych do oczyszczania ścieków farbiarskich

1. Wstęp

Węgiel aktywny jest najstarszym ze stosowanych sorbentów. Otrzymywany jest na skalę przemysłową na drodze karbonizacji i aktywacji takich surowców jak: węgla kamiennego i brunatnego, półkoks, koks, torfu, drzewa, ligniny, pestek owoców, skorup orzechów, polimerów organicznych, odpadów przemysłowych (gumy, bakelitu, skał płonnych). Wymienione materiały poddaje się w pierwszym etapie karbonizacji, czyli pirolizie wyjściowego materiału, w efekcie czego uzyskuje się karbonizat będący nieuporządkowaną strukturą, co prowadzi do powstawania szczelin, które przekształcając się tworzą pory. Następnie wypełniają się substancją smolistą, produktami rozkładu lub częściowo są blokowane przez nieuporządkowany węgiel. Powstały produkt jest mało aktywny adsorpcyjnie, o powierzchni właściwej kilku m^2/g . W następnym etapie karbonizat poddawany jest procesowi aktywacji, gdzie ma miejsce przekształcanie karbonizatu surowego materiału w postać o największej ilości dowolnie rozłożonych porów w różnych rozmiarach i kształtach, tworząc produkt o dużym polu powierzchni. Proces aktywacji karbonizatu prowadzi się w atmosferze powietrza, CO_2 lub pary wodnej w temperaturze w zakresie $800 - 900^\circ\text{C}$. W efekcie uzyskuje się węgiel aktywny o określonych cechach fizykochemicznych [1].

Węgla aktywne charakteryzujące się rozwiniętą strukturą porowatą i wynikającą z tego dużą powierzchnią właściwą o specyficznych właściwościach chemicznych, wykorzystuje się do usuwania zanieczyszczeń. Węgla aktywne powszechnie wykorzystywane są w oczyszczaniu gazów (oczyszczanie gazów odlotowych, usuwanie lotnych związków organicznych, Hg , SO_2 , NO_x , odorów, polichlorowanych bifenyli dioksyn, rozdzielanie mieszanin gazów), wody i ścieków (uzdatnianie wody pitnej, przygotowanie wody procesowej, przygotowanie wody do kąpeli leczniczych, oczyszczanie wód gruntowych, ścieków przemysłowych i odcieków ze składowisk odpadów),

a także innych substancji (oczyszczanie substratów i produktów w przemyśle cukrowniczym, spożywczym, farmaceutycznym, kosmetycznym, chemicznym, oraz pozyskiwanie substancji o wysokiej klasie czystości). Węgla aktywne znajdują również zastosowanie jako nośniki katalizatorów w reakcjach heterogenicznych zachodzących w fazie gazowej, a także w reakcjach w fazie ciekłej [2, 3].

Jak przedstawiono powyżej jednym z obszarów wykorzystania węgli aktywnych jest oczyszczanie ścieków, a w szczególności ścieków przemysłowych. Jest to złożony proces będący tematem licznych badań [1, 5, 6, 7]. Wynika to z faktu zróżnicowanego składu ścieków zależnego od rodzaju przemysłu i zastosowanej technologii. Przykładem ścieków przemysłowych są ścieki z przemysłu farbiarskiego i włókienniczego. Ścieki te zawierają w swoim składzie barwniki (obecnie jest ponad 100 000 barwników przemysłowych o szacunkowo obliczonej produkcji $7 \times 10^5 - 1 \times 10^6$ ton rocznie [8]), oleje mineralne i silikonowe, wielopierścieniowe węglowodory aromatyczne, pestycydy, detergenty, kwasy nieorganiczne, silne utleniacze stosowane jako środki wybielające, kleje oraz alkalia. Charakteryzują się toksycznością w stosunku do organizmów wodnych, a także opóźniają procesy samooczyszczania się poprzez ograniczanie przenikania światła w głąb zbiornika. Cechą charakterystyczną tych ścieków (obok obecności związków trudno biodegradowalnych) jest również ich wysokie obciążenie. Zależnie od klasy barwników ChZT wyczerpanych kąpeli barwiarskich osiąga wartość od 1000 do 15 000 mgO_2/dm^3 [9]. Wysokie wymagania stawiane ściekom odprowadzanym do miejskich urządzeń kanalizacyjnych [9] oraz do wód i ziemi [10] sprawiają, że w wielu przypadkach oczyszczania ścieków (zawierających związki trudno rozkładalne) tradycyjne metody oczyszczania są nieskuteczne i dlatego konieczne jest poszukiwanie bardziej efektywnych rozwiązań, czego przykładem może być właśnie proces sorpcji [1, 4]. Dobrze

rozwinięta struktura porowata, a tym samym duża ilość porów (mikro-, mezo- i makroporów) węgla aktywnych, jak i chemiczne właściwości powierzchni sprzyjają zatrzymywaniu barwników na powierzchni węgla aktywnych. Równoczesne wykorzystanie tradycyjnych procesów oczyszczania ścieków i sorpcji, pozwala na usuwanie z wody rozpuszczonych zanieczyszczeń organicznych, które powodują barwę i zapach, przyczyniając się do zmniejszenia stężenia ubocznych produktów utleniania i dezynfekcji, a także usunięcia z wody substancji stanowiących bezpośrednie zagrożenie dla zdrowia [11].

W prezentowanej pracy podjęto badania nad skutecznością usuwania barwnika jakim był fiolet krystaliczny z roztworu wodnego z wykorzystaniem wybranych węgla aktywnych. Fiolet krystaliczny czyli chlorowodorek heksametylo-p-rozaniliny, zaliczany jest do barwników trifenylometanowych, zwanych także barwnikami anilinowymi. Stosowany jest do barwienia tkanin, wyrobów papierniczych oraz farb drukarskich. Barwnik ten jest zaliczany do substancji szkodliwych i niebezpiecznych dla środowiska, dlatego musi być usuwany ze ścieków [12].

Ocena zdolności sorpcyjnych jest jednym z etapów badań nad oczyszczaniem ścieków z wykorzystaniem węgla aktywnych i utleniania, czyli zastosowaniem metod pogłębionego utleniania (*Advanced Oxidation Process* – AOP).

2. Część doświadczalna

Przedmiotem badań były węgle aktywne świeże handlowe o symbolu WD_{ex} i WG-12, powszechnie wykorzystywane jako sorbenty.

2.1. Charakterystyka badanych węgla aktywnych

Strukturę porowatą określono na podstawie badań niskotemperaturowej adsorpcji azotu (77 K). Izotermę adsorpcji i desorpcji wyznaczono metodą objętościową przy użyciu aparatu Sorptomatic 1900 oraz ASAP 2010 Micromeritics. Ponadto dla badanych węgla aktywnych oznaczono strukturę porowatą, zdolność do dechloracji (oznaczaną wg DIN 19603), liczbę adsorpcji jodu (oznaczaną wg PN-83/C-97555.04), zawartość popiołu (oznaczaną wg PN-84/C-97555.08), liczbę metylenową (oznaczaną wg PN-82/C-97555.03), liczbę detergentową (oznaczaną wg PN-84/C-97555.07), a także oznaczono kwasowo-zasadowy charakter powierzchni (sumaryczną zawartość grup o charakterze kwasowym oznaczono na podstawie miareczkowania roztworem 0,01 M HCl nadmiaru nieprzereagowane-

go 0,01M NaOH, którym uprzednio zalano próbki badanych węgla. Natomiast sumaryczną zawartość grup o charakterze zasadowym oznaczano na podstawie miareczkowania roztworem 0,01 M NaOH nadmiaru nieprzereagowanego 0,01 M HCl, którym uprzednio zalano próbki badanych węgla) oraz zawartość substancji rozpuszczalnych (oznaczaną wg PN-88/C-97555.11). Wyniki badań przedstawiono w tabeli 1.

2.2. Sorpcja fioletu krystalicznego na badanych węglach aktywnych

a) Kinetyka sorpcji.

W kolbach stożkowych o pojemności 500 cm³ odważono kolejno po 0,5g węgla aktywnych: WD_{ex} i WG-12. Naważki zadawano roztworem fioletu krystalicznego o objętości 400 cm³ i stężeniu ok. 20 mg/g. Całość wytrząsano przez 12 godzin. W roztworach znad węgla aktywnych oznaczono stężenie fioletu krystalicznego w godzinnych odstępach czasowych.

b) Izotermy sorpcji.

W kolbach stożkowych o pojemności 500 cm³ odważono kolejno po 0,1; 0,2; 0,5; 1,0 i 1,5g każdego z węgla aktywnych: WD_{ex} i WG-12, a następnie zadawano roztworem fioletu krystalicznego o stężeniu ok. 20 mg/dm³ i wytrząsano w czasie 12 godzin.

Stężenie fioletu krystalicznego było wyznaczane przy użyciu spektrofotometru UV/VIS Marcel Media przy długości fali $\lambda = 590$ nm.

3. Omówienie wyników badań

W pierwszym etapie badań dokonano oceny właściwości fizykochemicznych wybranych węgla aktywnych, określonych przez wskaźnik FIBDM. Ten wskaźnik wyraża względną zdolność adsorpcyjną badanych węgla aktywnych wobec pięciu substancji wskaźnikowych reprezentujących różne grupy zanieczyszczeń występujących w wodach, różniących się charakterem chemicznym, strukturą i wielkością cząsteczek. Jako substancje wskaźnikowe stosuje się: F – fenol (pierścień prosty o wymiarze 0,5 nm), I – jod (cząsteczka kulista o średnicy 1 nm), B – błękit metylenowy (pierścień złożony o długości 1,5 nm), D – laurylosiarczan sodowy (łańcuch o długości 1,9 nm) i M – melas (mieszanina cząsteczek łańcuchowych i pierścieniowych średniej wielkości około 2,8 nm). Wskaźnik FIBDM ma postać liczby pięciocyfrowej, z których każda w umownej skali od 0 do 9 (im wyższa tym dany węgiel lepszy) wskazuje na

„klasę” danego węgla pod względem jego zdolności adsorpcyjnej wobec substancji wzorcowej [11].

Z przedstawionych w tabeli 1 danych wynika, że spośród badanych węgli aktywnych WD_{ex} i WG-12 większą powierzchnią właściwą oraz całkowitą objętością porów charakteryzuje się węgiel aktywny WD_{ex} dla którego parametry te wynoszą odpowiednio $1050 \text{ m}^2/\text{g}$ i $0,95 \text{ cm}^3/\text{g}$. Węgiel ten charakteryzuje się jednocześnie wyższą wartością liczby metylenowej (36 cm^3). To jednoznacznie potwierdza dobre zdolności sorpcyjne tego węgla, natomiast mniejszą powierzchnię właściwą $980 \text{ m}^2/\text{g}$ i objętość porów $0,89 \text{ cm}^3/\text{g}$, jak i wartości pozostałych parametrów posiada węgiel WG-12, co wskazuje na jego nieco słabsze zdolności sorpcyjne.

Ustalona została kinetyka sorpcji, z której wynika, że czas kontaktu węgiel aktywny – roztwór fioletu krystalicznego wynosi 12 godzin. Badane węgle aktywne wykorzystano jako sorbenty fioletu krystalicznego z roztworu wodnego. Z przedstawionych na rysunku 1 izoterm sorpcji, zgodnie z oczekiwaniem, wynika, że lepszymi zdolnościami sorpcyjnymi (35 mg/g) charakteryzuje się węgiel aktywny WD_{ex} , który równocześnie posiada najwyższą wartość kwasowości powierzchni wynoszącą $0,98 \text{ mval/g}$, oznacza to, że sorpcji fioletu krystalicznego sprzyja nie tylko wielkość powierzchni i dostępność porów na co wskazuje wielkość liczby metylenowej (36 cm^3) i detergentowej (21 mg/g), ale również ujemny ładunek powierzchni węglu będący wynikiem jonizacji powierzchniowych grup kwasowych jak i oddziaływania dodatniego ładunku struktur rezonansowych fioletu krystalicznego ze zdelokalizowanymi elektronami π struktur grafitowych węgla aktywnego. To też tłumaczy zdecydowanie niższą zdolność sorpcyjną drugiego węgla – WG-12 wynoszącą 12 mg/g , który

pomimo rozwiniętej powierzchni właściwej i dostępności porów, co wynika z wartości liczby metylenowej (32 cm^3) i detergentowej (32 mg/g).

Proces sorpcji z roztworu wodnego można opisać odpowiednio równaniem Langmuira (1) i Freundlicha (2).

Wyliczone parametry przedstawione w tabeli 2 wskazują na lepsze dopasowanie wyników sorpcji fioletu krystalicznego na badanych węglach aktywnych do izoterm Langmuira, co oznacza, że został osiągnięty stopień nasycenia badanych węgli barwnikiem.

4. Podsumowanie

Węgłe aktywne są powszechnie wykorzystywane jako sorbenty. Do badań zostały wykorzystane dwa świeże handlowe węgle aktywne oraz fiolet krystaliczny jako barwnik. W przypadku usuwania fioletu krystalicznego z roztworu wodnego przy wykorzystaniu danego węgla aktywnego o skuteczności usuwania decydują zdolności sorpcyjne, które są zależne od parametrów struktury porowatej i chemicznych właściwości powierzchni, a także od warunków prowadzenia reakcji. Węgiel aktywny WD_{ex} wykazuje lepsze zdolności sorpcyjne (35 mg/g) niż węgiel aktywny WG-12 (12 mg/g) na co wskazuje zarówno większa powierzchnia właściwa ($1050 \text{ m}^2/\text{g}$), całkowita objętość porów ($0,95 \text{ cm}^3/\text{g}$), a także wysoka wartość liczby metylenowej (36 cm^3).

Przedstawione wyniki usuwania barwnika z roztworu wodnego z wykorzystaniem procesu sorpcji wskazują, że jest to proces skuteczny. Długi czas kontaktu wskazuje jednakże na poszukiwanie lepszych rozwiązań czego przykładem jest zastosowanie metod pogłębionego utleniania z wykorzystaniem węgli aktywnych, co będzie tematem dalszych badań.

