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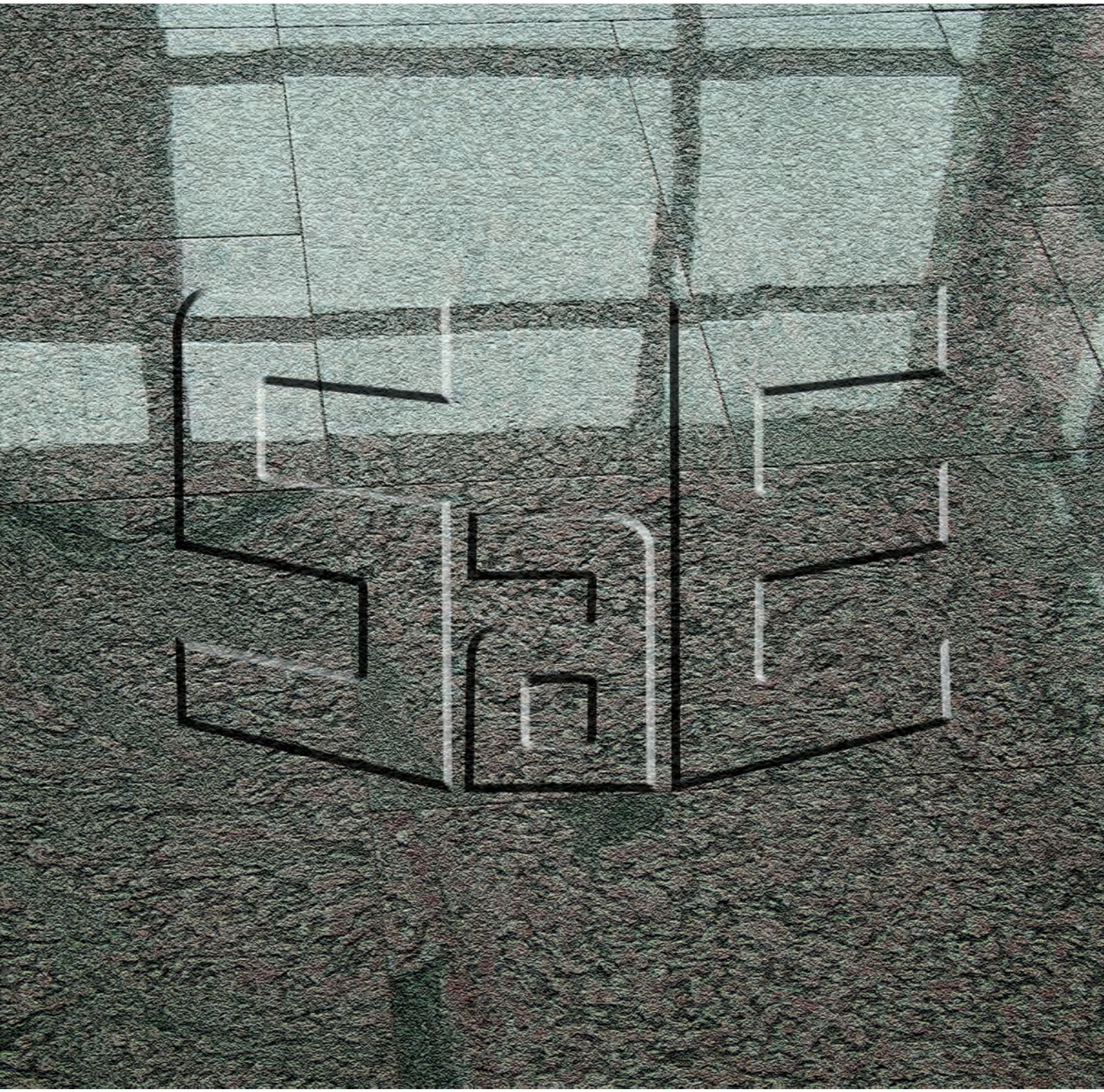

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EFFECT OF MODERN TEACHING METHODS AND NEW EDUCATIONAL TECHNOLOGIES ON THE CREATION OF EDUCATIONAL MATERIALS AND THE FORMATION OF TEACHING AND EDUCATIONAL COMPLEXES "KINDERGARTEN – PRIMARY SCHOOL"

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Abstract

On the basis of use of modern research methods, the requirements for designing new types of teaching and educational complexes "Kindergarten – Primary School" were determined. It was established that the form and methods of kindergarten education have a certain analogy with the education in the first grades of primary school, which is one of the factors of feasibility of blocking and cooperation of the senior kindergarten groups with the elementary grades of general education schools and the formation of teaching and educational complexes on this basis, which enables receptiveness to demographic fluctuations and, if necessary, change of the function of kindergarten to the function of primary school, and vice versa – the flexibility and multivariance of the teaching environment is one of main conceptual provisions in building of network and typology of educational facilities at the present stage, on the basis of which the structural elements of school network in massive restrained urban development are formed.

Keywords: teaching and educational complex, kindergarten, primary school, group center, premises of educational section, cooperation

Streszczenie

Na podstawie zastosowania nowoczesnych metod badawczych określono wymagania dotyczące projektowania nowych typów kompleksów dydaktycznych i edukacyjnych „Przedszkole – szkoła podstawowa". Ustalono, że forma i metody edukacji przedszkolnej mają pewną analogię z edukacją w pierwszych klasach szkoły podstawowej, co jest jednym z czynników umożliwiającym blokowanie i współpracę starszych grup przedszkolnych z pierwszymi klasami szkół podstawowych i tworzenie na tej podstawie kompleksów dydaktycznych i edukacyjnych, i może stanowić odpowiedź na zmiany demograficzne oraz w razie potrzeby, zmianę funkcji przedszkola na funkcję szkoły podstawowej i odwrotnie – elastyczność i wielowariantowość środowiska nauczania jest jeden z głównych pojęć koncepcyjnych w budowaniu sieci i typologii placówek oświatowych na obecnym etapie, na podstawie którego powstają elementy strukturalne sieci szkolnej w masowym rozwoju urbanistycznym.

Słowa kluczowe: kompleks dydaktyczno-edukacyjny, przedszkole, szkoła podstawowa, centrum grupowe, siedziba sekcji edukacyjnej, współpraca

Primary objectives of elementary school are the promotion of child's personality development, cultivation of desire and ability to learn in him/her and self-actualization. Vulnerability, curiosity and thirst for knowledge are typical for preschool and junior school children. At the same time, the younger schoolchildren get tired quickly; they need daytime sleep, reduction of lesson period, increase of breaks between lessons, alteration of classes, wide use of game elements during the educational process [1, 3]. It is recommended that the educational units for children have to be brought closer to nature and to create green recreational areas for them. Duration of primary education is 4 years.

The education of children in the primary segment of school education is traditionally conducted according to the class-lesson system. The premises of this age group include classrooms, rooms for the organization of extended school day, rest, recreation rooms, dressing rooms, toilet rooms. The relatively new and understudied issues in creation of material environment for primary grades include, first of all, the requirements for organization of teaching section for six-year-old children – first-grade students. For the education of young schoolchildren, it is recommended to preserve to a certain extent the kindergarten environment (which is habitual for them) by using predominantly game-based teaching methods and reduced lesson period – to 35 minutes, which will facilitate a consistent transition from the habitual regime of a child's organism [5].

In the class for six-year-old children, besides the desks, the special play space and nature study corners must be present. An important condition for teaching and education of children is their physical training, aesthetic education, music, rhythmic, drawing lessons. For these purposes, it is necessary to create, respectively, schoolwide rooms and special teaching and educational areas that take into account the psychophysiological peculiarities of children of this age.

An important hygienic requirement for the organization of educational and material environment for six-year-old schoolchildren is the provision of daytime sleep. According to sanitary requirements, sleep should last for 1.5–2 hours in a separate well-ventilated room [9] (Table 1).

As evidenced by the analysis below, the additional conditions for education, teaching and recreation are created for children of this age group in accordance with their age characteristics. In practice, teaching classes for six-year-old children are often created at kindergartens located near the school buildings. In terms of functional structure, the sections for children are similar to pre-school institutions.

The premises for second and fourth grades should also be solved universally, by providing various forms of classes during the lesson process.

A compulsory requirement for junior grade sections is the availability of spacious student lounges for organization of a proper rest, during breaks, the recreational areas should provide active games, physical exercising. In such recreations, besides the rest, the schoolwide cultural mass events, rhythmic lessons, gymnastic classes can be held during breaks. The group for junior high school students also includes a singing and music classroom, a choreography studio, a handicraft room, a multifunctional room for extended school day organization.

Medical observations indicate various health-improving aspects of swimming process effect on the organism of schoolchildren. Meanwhile, the level of provision of the school network with swimming pools is significantly lower than in the actual requirements [6].

An important area of school environment improvement is the organic combination of general education with artistic education – improvement of aesthetic education, development of the sense of beauty in children and adolescents, ability to understand and appreciate works of art and architecture.

A new group of premises appears in schools – the club activity rooms. Today, classrooms and laboratories, as before, are widely used not only for lessons but also for the organization of extended school days. In addition to these rooms, there are special club activity rooms: for young naturalists, painting and graphic, sculpture, choreography studios. These premises will further develop in the structure of school buildings. The specific list of club activity premises should be determined in accordance with the local traditions, the folk crafts nature and the level of development of network of children's out-of-school educational facilities.

Studies show that, in modern schools, library becomes the informational and technical center of educational institutions [5]. It is often located in the center of a school building and connects to the surrounding premises through sliding partitions, which allows the lectures to be held simultaneously with several classroom groups. The service premises are also being modernized: dining room, administrative and economic services, medical offices. According to the current regulations, the size of dining halls should provide meals for students in two seats.

Table 1. Characteristics of teaching and educational complex for primary schoolchildren

1.	Daytime sleep	Sleep should last for 1.5–2 hours in a separate well-ventilated room	
2.	Reduction of lesson period	Reduction of lesson period – to 35 min	
3.	Shift increase	Shift period is 10 – 30 min	
4.	Proximity to nature	It is recommended to bring the children educational area closer to nature	
5.	Game elements	Game elements are widely used during the lessons	

Table 2. Social and pedagogical regulations for kindergarten group center premises and primary school educational sections premises

List and Areas of Kindergarten (KG) Group Center Premises				
No.	Name of premises	Measurement unit	Pre-school groups	
1.	Dressing room	sq.m. per one place	0.9	
2.	Game room	sq.m. per one place	3.0	
3.	Bedroom	sq.m. per one place	3.0	
4.	Toilet room	sq.m. per one place	1.0	
5.	Dining room	sq.m.		
List and Areas of Educational Sections for 1st Grades (PS)				
No.	Name of premises	Measurement unit	Educational section for 1st grades for 25-30 students (not less)	
			for 25 students	for 30 students
1.	Game room	sq.m. per one place	2.4	2.0
2.	Bedroom	sq.m. per one place	2.4	2.0
3.	Toilet rooms	sq.m. per one place	1.0	1.0
4.	Recreational room	sq.m. per one place	2.0	2.0
5.	Wardrobe	sq.m. per one place	0.2	0.2
6.	Teacher's room	sq.m.	16	18
List and Areas of Educational Sections for 2nd – 4th Grades (PS)				
No.	Name of premises	Measurement unit	Educational section for 1st grades for 25-30 students (not less)	
			for 25 students	for 30 students
1.	Classrooms	sq.m. per one place	2.4	2.0
2.	Foreign language room	sq.m. per one place	2.4	2.0
3.	Multifunctional room for extended school day groups	sq.m. per one place	2.4	2.0
4.	Handicraft workshop	sq.m. per one place	3.6	3.6
5.	Toilet rooms	sq.m. per one place	0.2	0.2
6.	Recreational room	sq.m. per one place	2.0	2.0
7.	Wardrobe	sq.m. per one place	0.2	0.2
8.	Teacher's room	sq.m.	16	18

The administrative and economic premises are supplemented by a room of teacher's psychological management, a curriculum office and other services.

Thus, as the above analysis shows, the new forms and methods of teaching cause a significant expansion of composition and increase of kindergarten and primary school premises areas (Table 2).

One of the important requirements for the educational and material environment is the creation of conditions for the physical development of a child. Child's body differs from adult's body in that child is in a state of continuous growth and development. Child's body responds to various external factors. At this age, there is the change of the body as a whole. It is to such "hinge" periods that the transition of children from kindergarten to primary school belongs. Therefore, the cooperation of kindergarten and primary school and their combination into an educational and teaching complex contribute to the education of healthy children and, in general, an intact generation.

During the examination of students, the vision disorders and disorders of other body systems are often found. These disorders are most often found in pre-school and primary school-age children. One of the main tasks of education is the proper physical development of a child, which provides the optimal mechanical load on the musculo-skeletal system of growing child's organism. Therefore, it is important to control child's life activity continuously.

Pre-school-age and school-age children have high mobility, but numerous data of studies of dynamic regime for pre-school children and young schoolchildren confirm that children's physical activity decreases when they enter kindergarten and primary school. Restrained physical mobility adversely affects child's growth and mental development. For this reason, neither low physical mobility nor the exercising of sports or works that may adversely affect child's development should be allowed [9].

Properly organized day regime creates cheerful mood, interest in educational and creative activities, games and promotes the normal development of a child.

An important issue of teaching and education of children in a teaching and educational complex is the ensurance of an optimal balance between mental and physical activity in accordance with the anatomical and physiological, psychological characteristics of a child [9].

The hygiene of educational work in the preparatory classes is constantly linked to the students' day regime (Table 3).

Table 3. Approximate organization of the regime for kindergartens and primary school students

No.	Regime elements	Timing
1.	First class	35 min
2.	First break	10 min
3.	Second class	35 min
4.	Second break (breakfast)	20 min
5.	Third class	35 min
6.	Dynamic break (walk)	55 min
7.	Third break	10 min
8.	Fourth class	35 min
9.	Walk	1 h
10.	Dinner	30 min
11.	Sleep	2 h
12.	Supper (snack)	20 min

The second important aspect of the day regime is sleep sufficiency, during which all major metabolic and cellular alterations that determine the formation of child's skeleton take place. The best thing for sleep is the fresh air. It affects the skin, the mucous nose membranes and the upper respiratory tract, causing rapid sleep onset. Sleeping on the open air can replace walking, especially at cold and transitional seasons [9].

At the day regime, 12–12.5 hours of sleep go to junior (3–4 years) and middle (4–5 years) kindergarten groups, 2 hours of which are for a single daytime sleep. For children of senior (5–6 years) and preparatory (6–7 years) groups, 11.5 hours (10 hours at night and 1.5 at day) go to sleep.

A large number of students experience the lack of sleep. It is associated with the early start of classes of the first shift (at 8:30 am and even at 8:00 am) and, correspondingly, the early rising of children, as well as the late bedtime. Late falling asleep is caused by lasting preparation of homework and lasting watching of TV shows and video films. Lack of sleep has a negative effect on the higher nervous activity of children. With lack of sleep, there are mood swings and significantly reduced performance. However, if the correct sleep pattern is set, these disorders tend to disappear.

The day regime in the senior kindergarten groups and first grades of primary school consists of four

lessons daily, three meals, and daytime sleep for 1.5–2 hours. It is very important for children to stay outdoors for 1.5-2 hours. Games and outdoor walks are of particular importance. Open air has a beneficial effect on organism: it activates metabolic processes and has a positive effect on growth and development. Depending on the climatic conditions, the seasons, children have to spend maximum time outdoors. Under any conditions, the daytime walks must take place in the morning and afternoon; the total length of children's staying outdoors should not be less than 4 hours [9].

At pre-school age, the formation of circadian periodicity takes place in the organism activity. The education tasks are significantly larger during this period. Children get accustomed to perform simple duties, simplest working activity, greater self-care. In the middle and senior groups, a lot of work should be done in children's preparation for learning.

The kindergarten day regime must be differentiated according to groups. The junior group consists of 3–4 year-old children, the middle group – of 4–5 year-old children, and the senior group – of 5–6 year-old children.

Kindergarten education and teaching programs provide for the organization of classes according to the morphofunctional characteristics of children:

- for the junior group – 10 classes per week for 10-15 minutes;
- for the middle group – 10 classes per week for 20 minutes;
- for the senior group – 15 classes per week for 20-25 minutes.

The break duration between classes is 10–12 minutes, during which it is advisable to organize mobile games of moderate intensity. In comparison with the senior groups, little children are given more time to have a meal, to cultivate the cultural and hygiene skills that the children begin to master. Staying in the open air during winter should last not less than 3–4 hours, and during summer – all day long [9].

In the regime for middle-group children, the duration of organized classes increases and their nature is somewhat complicated. With senior-group children, 2–3 classes are held daily. All spare time – before breakfast, during walks and especially in the afternoon after daytime sleep – is reserved for games, that is, activities typical for the psychophysiological nature of pre-school child. In this regard, the kindergarten education process is based on children's play activities. For the preparatory group, the compulsory classes are prolonged and complicated.

For the play activities, the time is given in the morning (before breakfast), during the walks in the morning and afternoon, after the daytime sleep and the evening before bedtime. Children's games are diverse in nature and content: peaceful and active, individual and team, everyday and didactic. They help children to perceive the world more deeply, help to form logical thinking, arbitrary attention. Active games affect the development of physical skills, promote the cultivation of activity, ingenuity, courage.

Studies have clearly shown that for six-year children, 45-minutes classes are extremely fatigable, so it is recommended that the classes for first grades of primary school should last 35 minutes, which will facilitate a consistent transition from the usual child's kindergarten routine where the lessons last 30 minutes. It is also advisable to take a physical break every 15-20 minutes so that the children can do some exercises.

In order to organize a proper rest during the breaks, the recreational areas should provide active games, physical exercises.

In developing the regime for students, the peculiarities of nervous system functioning are considered: the high level of the cerebral cortex activity during morning and daytime hours, its decrease after dinner and drop in the evening. The working ability of students during the day has two lifts that coincide in time with periods of high levels of physiological functions: from 8:00 am to 12:00 am and from 16:00 pm to 18:00 pm. In this case, as a rule, the first rise in working capability is higher and longer than the second one.

Outdoor activities are a powerful wellness factor. Children should spend the time outdoors before and after homework preparation. The total length of staying outdoors must be: for junior school age – not less than 3–3.5 hours, for middle age – 2.5–3, and for senior age – 2–2.5 hours. In modern conditions, this day regime element is most often violated due to students' teaching overload: the outdoor time and the physical activity of children are reduced.

Great attention must be paid to the students' visual work conditions. Classroom luminance must be at least 1:5 when orienting toward the southeast side of the horizon. The natural illumination ratio at the distance from window to desks must be 1.5%.

Workplaces for students should provide that the text on the classroom board from the most distant places

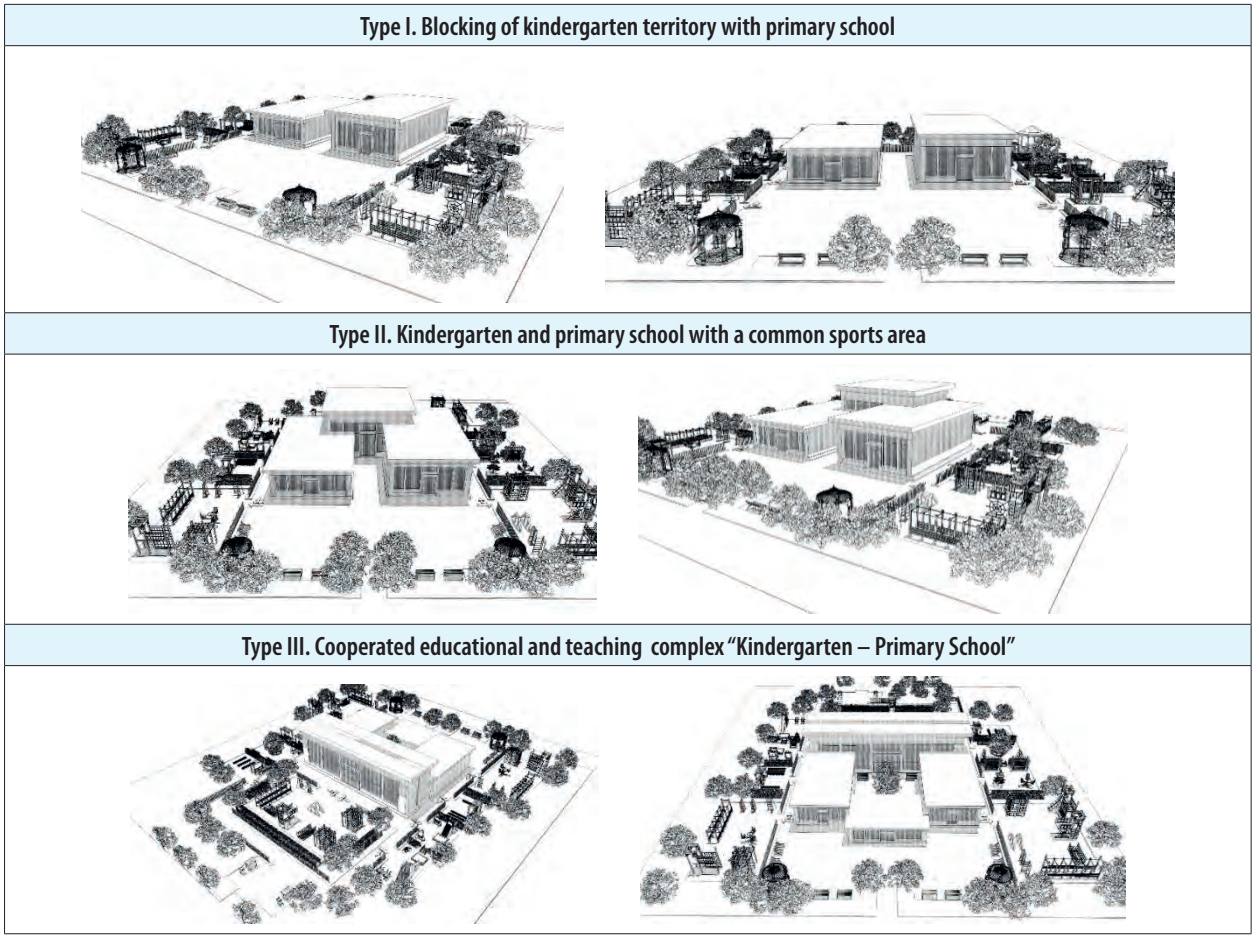

Fig. 1. Methods of formation of educational and teaching complex territory

is normally visible. Therefore, when organizing the educational environment and the placement of classroom tables, it is necessary to ensure the optimal sight angle of the students, which must be more than 30°.

The form and methods of education in kindergarten have a certain analogy with the education in the first grades of primary school, which is one of the factors of feasibility of blocking and cooperation of kindergarten senior groups and first grades of general education schools and formation of educational complexes on this basis (see Fig. 1).

In addition to the pedagogical advantages, the creation of such complexes enables receptiveness to demographic fluctuations and, if necessary, change of the function of kindergarten to the function of primary school and vice versa. Flexibility and multivariance of the teaching environment is one of main conceptual provisions in building of network and typology of educational facilities at the present stage.

The school unit provides the appropriate level of general education for students in accordance with the requirements of the State Standard of General Secondary Education. The school unit can include classes with advanced study of certain subjects, extended school day groups, school residential institution for students living in remote areas, etc.

All this confirms the feasibility of blocking and cooperation of primary schools and kindergartens.

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INFLUENCE OF AGRICULTURAL BIOMASS FLY ASH CEMENT SUBSTITUTION ON THE CARBONATION OF CEMENT AND POLYMER-CEMENT COMPOSITES

WPŁYW POPIOŁU LOTNEGO Z BIOMASY ROLNICZEJ NA KARBONATYZACJĘ KOMPOZYTÓW CEMENTOWYCH I POLIMEROWO-CEMENTOWYCH

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Abstract

Practical use of a new type of combustion waste such as an agricultural biomass fly ash in the building materials requires an assessment of its performance. The paper presents the investigation results on the influence of cement substitution (5% and 30%) by this ash on the cement and polymer-cement composites resistance to carbonation. The composites resistance was assessed on the basis of carbonation process over time (up to 360 days) using the phenolphthalein method. It was found that fly ash from agricultural biomass increases the susceptibility to carbonation of polymer-cement composites to a lesser extent than cement composites compared to composites containing siliceous coal fly ash.

Keywords: carbonation, polymer-cement composites PCC, agricultural biomass fly ash, siliceous coal fly ash

Streszczenie

Praktyczne wykorzystanie w materiałach budowlanych nowego odpadu, jakim jest popiół lotny z biomasy rolniczej, wymaga oceny jego właściwości użytkowych. W pracy zaprezentowano wyniki badań wpływu substytucji cementu (5% i 30%) tym popiołem na odporność kompozytów cementowych i polimerowo-cementowych na karbonatyzację. Odporność kompozytów oceniono na podstawie przebiegu procesu karbonatyzacji w czasie (do 360 dni) za pomocą metody fenoloftaleinowej. Na podstawie wyników stwierdzono, że popiół lotny z biomasy rolniczej powoduje zwiększenie podatności na karbonatyzację kompozytów polimerowo-cementowych w mniejszym stopniu niż kompozytów cementowych w porównaniu do kompozytów zawierających popiół lotny krzemionkowy.

Słowa kluczowe: *karbonatyzacja, kompozyty polimerowo-cementowe, popiół lotny z biomasy, popiół lotny krzemionkowy*

1. INTRODUCTION

Atmospheric carbonation of concrete materials is a slow process, but has been receiving increasing research interest in recent years due to the aging of a large number of facilities and the associated risk of degradation. Reduction of calcium hydroxide $Ca(OH)_2$ caused by its reaction with atmospheric carbon dioxide CO_2 lowers pore solution pH, leading to reinforcing steel depassivation and corrosion [1, 2]. Damaged reinforced structures should be repaired in such a way as not only to provide further protection of reinforcing steel but also to protect concrete against harmful conditions that caused the need for repair [3, 4]. Among the materials used in the repair works, polymers are a category of high technological importance. In general, repair mortars consist of portland cement, fine aggregate, plasticizers, mineral admixtures (such as silica fume) and polymers (such as styrene-butadiene copolymer SBR, acrylic polymer or vinyl acetate EVA) [5]. The introduction of polymers significantly improves tensile strength, adhesion, flexural strength, chemical

resistance and durability of mortars and concrete [6-8]. However, the type and amount of polymers used in the mortars is of great importance for the properties of the final product, in particular for its carbonation resistance. For example, the incorporation of 10% of epoxy-based polymer was found to decrease mortar carbonation front by 45% after 14 days' carbonation at 5% CO_2, at 30°C and 60% relative humidity, while for acrylic-based mortars, the carbonation front was only 28% smaller. At 20% epoxy emulsion content, the depth of carbonation has been further reduced by up to about 75% [9]. Research conducted by Nepomuceno A.A. et al. [10] under accelerated carbonation (100% CO_2, 20°C, 60-70% RH) on mortars containing 12% mixture of acrylic-based polymer and silica fume also showed increased resistance to CO_2 due to the reduced number of phases susceptible to carbonation. The same observation was made by Alzahrani M.M et al., who carried out accelerated carbonation (6% CO_2, 55°C, 70% RH) on four types of polymer-cement composites containing polymers with different chemical composition as well as silica fume and/or polymeric fibers. Specimens containing acrylic-based polymer were characterized by complete carbonation after just 2 months. Other types of tested composites were characterized by much better carbonation resistance. The obtained results suggest that the types of polymer used have a significant influence on the carbonation resistance of building materials modified with those polymers. The small depth of carbonation front noted for some of the tested materials may be the result of a more packed microstructure of these materials, due to the use of silica fume, fibers and/or other additives [11]. Silica fume, being a Type I additive, is not reactive with CO_2, but acts as a filler that reduces CO_2 diffusion in concrete. On the other hand, the role of Type II additives characterized by pozzolanic or latent hydraulic properties, such as the fly ash, microsilica or blast furnace slag, is more complicated and should be considered in the interaction system complex. The microstructure of the hardened cement matrix should be taken under consideration when assessment of the carbonation process of concretes containing such additives [12-14]. Research carried out on the polymer-cement composites containing two types of coal fly ash – siliceous and calcareous have shown that the carbonation resistance of those composites is affected by the type and amount of mineral additive as well as the polymer type [15]. Another type of fly ash from biomass combustion process is a relatively new industrial waste, but its utilization is currently difficult due to legal regulations. However, research to date shows that fly ash from biomass combustion process can be an attractive material for the concrete industry. Research conducted by Wang S. et al. [16] showed that fly ash from biomass have at least the same or much better parameters in terms of strength and durability of concrete compared to traditional fly ash. Similar conclusions follow from studies carried out by Teixeira E.R. et al. [17]. They found out that the building materials containing biomass fly ash are characterized by similar carbonation resistance compared to the traditional fly ash materials. Therefore, it seems that the use of biomass fly ash in buildings materials can bring benefits to those materials and additionally indicates a new way of managing this combustion waste. The purpose of the research presented in this paper was to assess the influence of cement substitution by agricultural biomass fly ash on the change in carbonation resistance of cement and polymer-cement composites. For the comparison purpose, an analogous study was conducted on the composites containing siliceous coal fly ash.

2. RESEARCH PROGRAM

Five compositions of cement and polymer-cement composites were designed, differing in type and content of fly ash. Water/binder ratio w/c = 0.5 was adopted for all compositions. In polymer-cement composites an additional constant polymer content (p/c = 15%) was used. As material variables the type of mineral additive and its amount in relation to the cement mass (m/c = 0%, 5% and 30%) were used. As a polymer modifier, an aqueous dispersion of styrene-acrylic copolymer, recommended by the manufacturer for improving concrete properties, in particular in terms of tensile strength under bending and compression, was used. Two types of fly ash: agricultural biomass fly ash (mixture of oat and wheat biomass) – BM and siliceous coal fly ash – PLK were used as a partial cement replacement. The cement binder was CEM I 42.5R portland cement, while as a fine aggregate standard sand in accordance with PN-EN 196-1 [18] was used. Compositions of prepared composites per 1 kg of the mixture are presented in Table 1. Table 2 summarizes used materials while Table 3 summarized basic physical properties of mineral additives used in this research.

Table 1. Material composition of designed composites per 1 kg of mortar

Specimen	Cement, g	Water, g	Fine aggregate, g	Polymer dispersion, g	PLK, g	BM, g
ZN	222.0	111.0	667.0	0.0	0.0	0.0
5BM	211.0	111.0	667.0	0.0	0.0	11.0
5PLK	211.0	111.0	667.0	0.0	11.0	0.0
30BM	156.0	111.0	667.0	0.0	0.0	67.0
30PLK	156.0	111.0	667.0	0.0	67.0	0.0
P	215.0	92.0	645.0	48.0	0.0	0.0
5BMP	204.0	92.0	645.0	48.0	0.0	11.0
5PLKP	204.0	92.0	645.0	48.0	11.0	0.0
30BMP	151.0	92.0	645.0	48.0	0.0	65.0
30PLKP	151.0	92.0	645.0	48.0	65.0	0.0

Table 2. Materials used in mortars preparations

Cement binder	Portland cement CEM I 42.5R (Lafarge)
Fine aggregate	Standard sand
Mineral additive	• Agricultural biomass fly ash (BM) • Siliceous coal fly ash (PLK) cat. B
Polymer	Aqueous dispersion of styrene-acrylic copolymer with 67% solids parts (P)

Table 3. Density, particle diameters and specific surface area of mineral additives

Property	Agricultural biomass fly ash	Siliceous coal fly ash
Density, g/cm^3	2.53	2.04
D_{min}, µm	0.17	0.17
D_{max}, µm	67.52	51.50
Average, µm	16.40	11.20
D_{50}, µm	13.20	11.60
D_{90}, µm	29.90	22.80
S.P., cm^2/cm^3	15528	29198

The dry ingredients were mixed together to form a homogeneous mixture, followed by the addition of the aqueous polymer dispersion and the remaining amount of water that was needed to obtain the w/c ratio. After molding, the specimens were covered with plastic sheet and set for 24 hours. One-day samples were removed from the molds and subjected to further curing. Polymer-cement composites were immersed in water for 5 days and were subsequently dried in the air for 22 days. This treatment allows the formation of a polymer-cement matrix proceeded by cement hydration at the early age. The remaining specimens, without polymer addition, were stored in water throughout the entire curing time. After the age of 28 days, the specimens were moved to a carbonation chamber – in which CO_2 concentration was kept at 1%, with a temperature of 21°C ±1°C and a relative humidity of 60% ±10%. Carbonation resistance was determined in accordance with the European Standard PN-EN 13295: 2005 [19]. The test was carried out on the rectangular specimens with dimension of 40 x 40 x 160 mm.

3. RESULTS

As a preliminary study the properties of fresh mortar mixes were tested. The results of this measurements are presented in Table 4. The plasticity of cement mortars is not affected by presence of fly ashes except for mortars containing 30% of siliceous fly ash. Its plasticity decreased by about 20%, compared to unmodified cement mortar. Both biomass fly ash and siliceous fly ash changed the consistency of cement mortars. For example mortars containing 30% BM were characterized by 34% lower consistency while 30% PLK decreased consistency of about 49%, compared to unmodified cement mortar. Cement replacement by fly ashes did not influence the consistency of polymer – cement mortars. Biomass fly ash slightly increased plasticity of PCC mortars while siliceous fly ash lowered its plasticity, compared to unmodified PCC mortar. Cement replacement by fly ashes did not change air content of tested mortars. Obtained results are differ slightly and in most of the cases is within the error of the measuring instrument.

Table 4. Properties of fresh mortar mixes.

Specimen\Property	Consistency, cm	Plasticity, cm	Air content, %
ZN	5.3	13.5	4.9
5BM	4.9	13.5	5.0
5PLK	6.0	14.1	4.5
30BM	3.5	14.0	4.0
30PLK	2.7	10.9	4.9
P	11.3	26.5	0.8
5BMP	11.5	29.5	1.3
5PLKP	11.5	24.5	0.7
30BMP	11.5	30.0	1.4
30PLKP	11.2	24.5	1.3

The depth of carbonation is presented in Figure 1 as a function of the duration of CO_2 exposure from 14 to 360 days. Phenolphthalein was sprayed on the fractured surface of the specimen and the carbonation

depth was measured on the four edges at an accuracy of 0.1 mm (Fig. 2). The average of the measurements was presented. Because the test was conducted on the rectangular samples with dimension of 40x40x160 mm, the maximum measurable value of the carbonation depth was 20 mm.

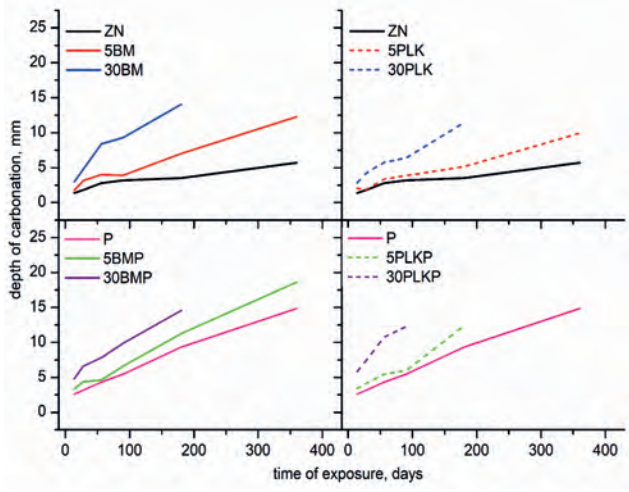

Fig. 1. Carbonation depth of tested specimens

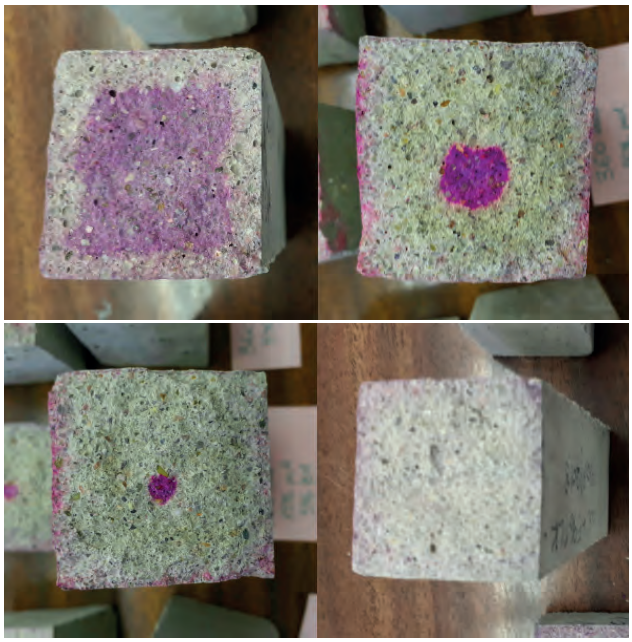

Fig. 2. Specimens after 360 days of CO_2 exposure

Substituting cement with fly ash was found to decrease carbonation resistance of the composite mortars. The reduction in carbonation resistance of composites has been observed with the increased fly ash content, irrespective of the fly ash. The cement substitution with 5% of biomass fly ash doubled the carbonation depth after 360 days of exposure, and 30% addition of biomass fly ash as much as 4 times after 180 days (after 360 days the carbonation depth exceeded 20 mm), compared to standard mortar (ZN). A similar relationship was observed when comparing mortars containing biomass fly ash with mortars with siliceous coal fly ash. For example, carbonation depth after 180 days for composites containing 30% of siliceous coal fly ash was 11.4 mm, while with 30% biomass fly ash it was about 20% higher. PCC composites containing biomass fly ash were characterized by reduced resistance to carbonation compared to unmodified PCC composites.

5% cement substitution by biomass fly ash increased the carbonation front depth by 30%. PCC composites with 30% biomass fly ash were characterized by complete neutralization after 180 days. However, PCC mortars with biomass fly ash were observed with a higher carbonation resistance compared to PCC mortars with siliceous coal fly ash, because in the latter, their complete neutralization took place after 90 and 180 days for 30% and 5% ash, respectively. It should be noted though that polymer modification of cement mortar alone clearly deteriorated its carbonation resistance. Unmodified polymer-cement composites after 360 days were characterized by almost three times higher carbonation depth compared to standard mortar.

Since the cement substitution by fly ash deteriorated the carbonation resistance of polymer-cement composites to a lesser extent than cement mortars, the research was extended with additional compositions of PCC composites with 10% and 25% fly ash content in relation to the cement mass (10BMP, 25BMP, 10PLKP oraz 25PLKP). The carbonation depth was measured after 56 days and the obtained results are shown in Figure 3.

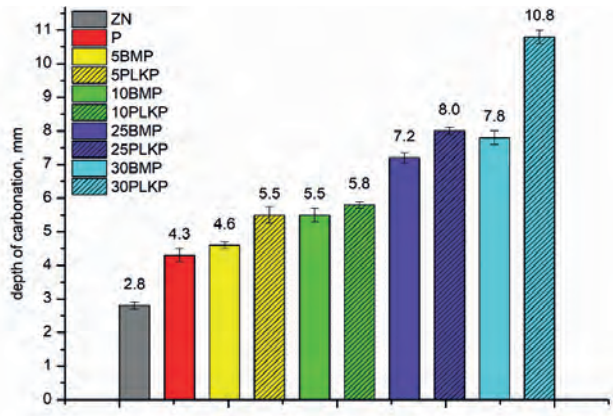

Fig. 3. Carbonation depth after 56 days of CO_2 exposure

The addition of 5% biomass fly ash did not cause a clear change in the carbonation resistance compared

to the unmodified PCC. The PCC composites containing 10% of biomass fly ash were characterized by about 25% higher carbonation depth reaching the same depth as PCC with 5% siliceous fly ash. The greatest impact of the type of mineral additive used on the carbonation of PCC composites can be observed in the case of mortars with 30% fly ash content. PCC composites with 30% biomass fly ash were characterized by a smaller carbonation depth (7.8 mm) compared to mortars containing the same amount of siliceous fly ash (10.8 mm).

4. CONCLUSION

The susceptibility of building materials to carbonation can be assessed on the basis of a carbonation test by the phenolphthalein method. The tested specimens were subjected to accelerated carbonation in a 1% CO_2 chamber, with a temperature 21°C ±1°C and a relative humidity of 60% ±10%. The research shows that the presence of agricultural biomass fly ash (mixture of oat and wheat biomass) in cement mortars increase mortar carbonation to a greater extent than when using siliceous fly ash. The depth of the carbonation front increased with the increase of the mineral additive content in the mortar and also with the duration of carbonation. The presence of agricultural biomass fly ash in polymer-cement composites also increased their susceptibility to carbonation, but to a much lesser extent than siliceous fly ash. After 56 days of exposure to CO_2 biomass fly ash substitution up to 10% of cement mass in PCC mortars does not cause a clear change in the carbonation resistance of those composites compared to the unmodified PCC. However, it should be noted that the mortar modification with aqueous dispersion of styrene-acrylic copolymer alone clearly deteriorated its carbonation resistance. The presented in this paper research clearly shows that the carbonation resistance of cement and polymer-cement composites depends on the type and amount of mineral additives used. When considering carbonation resistance of building materials, agricultural biomass fly ash can be used as mineral additives in polymer-cement composites instead in cement composites but further investigation should be done to determined its compatibility with other types of polymers modifiers.

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ASSESSMENT OF THE CURRENT STATE OF THE CONCRETE STRUCTURE OF THE TRIBUNE

OCENA BIEŻĄCEGO STANU KONSTRUKCJI BETONOWEJ TRYBUNY

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Abstract

The paper is focused on diagnostics of reinforced concrete structure of the tribune of Závodisko Bratislava. The structure was realized by a combination of monolithic and prefabricated concrete elements as well as steel load-bearing elements. The complex state of the rough construction was evaluated, including the verification survey of the foundation of the construction. Non-destructive and destructive methods were used. Based on the results of the diagnostics and recalculation, it was decided to further progress the finish of the tribune.

Keywords: reinforced concrete, tribune, diagnostics, non-destructive testing, destructive testing

Streszczenie

Artykuł koncentruje się na diagnostyce konstrukcji żelbetowej trybuny zlokalizowanej na „Závodisko Bratysława". Konstrukcja została zrealizowana przez połączenie monolitycznych i prefabrykowanych elementów betonowych oraz stalowych elementów nośnych. Oceniono złożony stan konstrukcji, w tym badanie weryfikacyjne fundamentu konstrukcji. Zastosowano metody nieniszczące i niszczące. Na podstawie wyników diagnostyki i ponownych obliczeń zdecydowano o dalszych działaniach, aby ukończyć trybunę.

Słowa kluczowe: żelbet, trybuna, diagnostyka, badania nieniszczące, badania niszczące

1. INTRODUCTION

Závodisko Bratislava (state-owned enterprise) in 2010 announced a public tender for the construction of the tribune of Závodisko located in the cadastral area Petržalka in the estimated value of 2.8 mil. Euro without VAT. The multifunctional tribune (SO-01 Tribune B), with dimensions 73.6 m by 22.5 m, should have four floors and covered by a trapezoidal sheeting (Fig. 1). Part of the tender was also to build a paddock, paved areas and related landscaping.

After the evaluation of the tender and the start of realization, the construction of the tribune stopped in 2012. In 2017, the University of Žilina was asked with a request to assess the current state of the unfinished tribune. After realization of diagnostics in 2018 and after recalculation of the structure, steps were proposed in terms of possible completion of the tribune (detailed results with a design of actual solutions will be published in the near future).

The paper presents the results of the realized survey and the description of the diagnostics. A detailed evaluation is given in the Inspection and Diagnostics Report [1].

2. DESCRIPTION OF THE TRIBUNE

The tribune was designed as a reinforced concrete skeleton with a combined steel-reinforced concrete roofing. The skeleton is reinforced concrete, partly monolithic and partly prefabricated. The object should have four floors and was designed as a

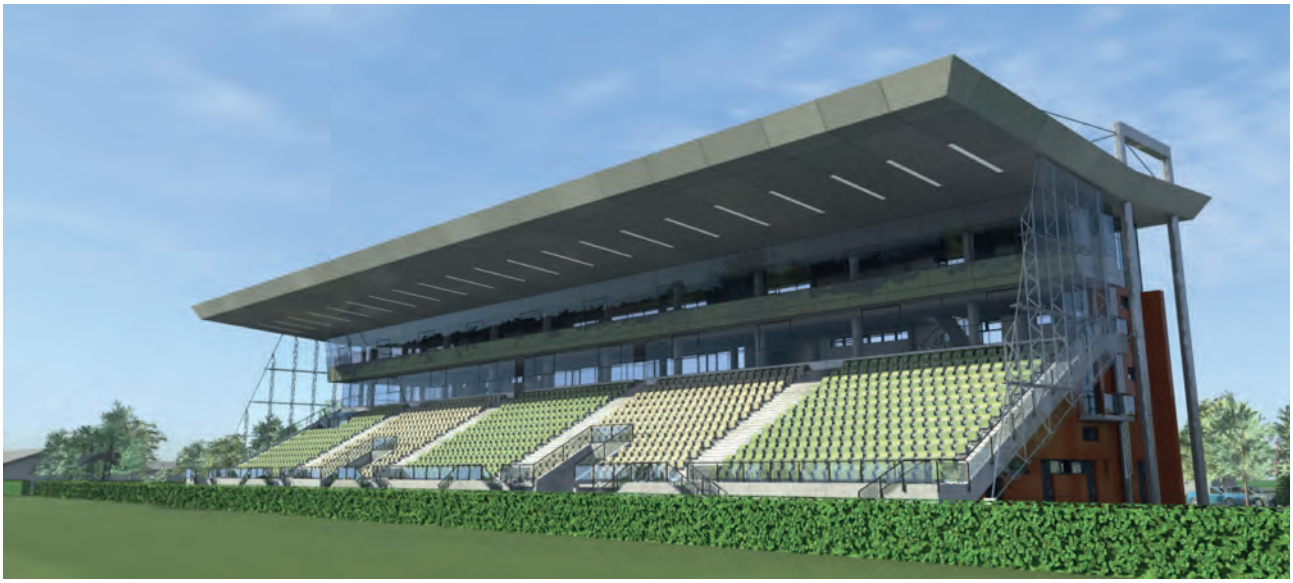

Fig. 1. Original visualization of the planned tribune

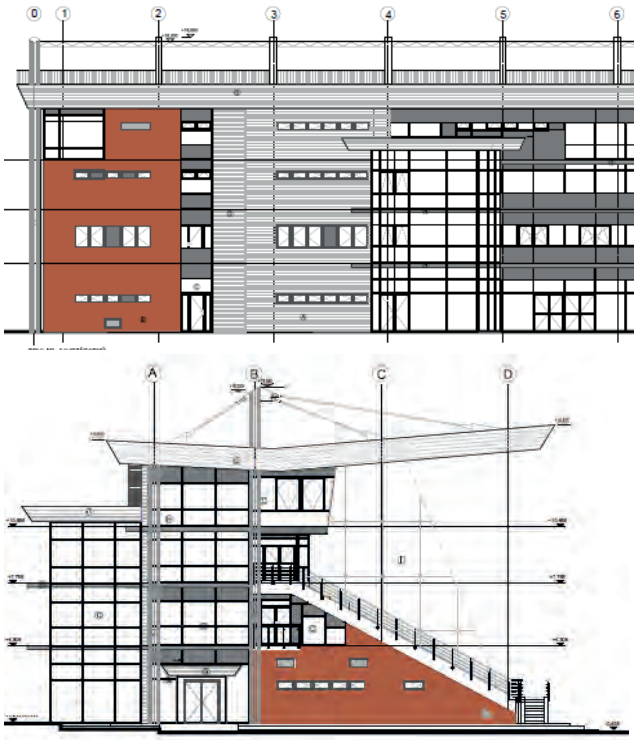

Fig. 2. Division of tribunes into sections

multifunctional building. The object is divided in the longitudinal direction by the axes "0" – "12" and in the transverse direction "A" - "D" (Fig. 2).

The object of tribune is based on deep foundations. The deep foundations consist of piles of diameter 600 mm, 800 mm and 1 200 mm, at depths of 4 m – 16 m. They are reinforced with reinforcement B 500B and used concrete class is C 25/30 XA2. The piles are around the perimeter in the points of columns, load-bearing perimeter walls, stiffening walls within the elevator shafts and at the points of stairs connected foundation strips. The foundation strip concrete is designed from class C 25/30 XC2. The foundation strips have the thickness of: 300 mm, 400 mm, 450 mm, 500 mm, 750 mm, 800 mm and 875 mm. The height of the foundation strips is 700 mm. The strips are connected by a base slab. The base slab of 100 mm thickness is made of C 25/30 concrete and leveling screed of concrete class C 12/15 with thickness 50 mm – 100 mm.

The prefabricated and monolithic reinforced concrete columns, tribune prefabricates, rungs and prefabricated L-shaped benches are designed within the skeleton. The axial distance of the transverse bonds between axes '2' to '10' is 7.2 m, and a span of 6.0 m is proposed at the edges between the axes '0' – '1' and '11' – '12'. The transverse bond on the storey of the first and second floors consists of monolithic and prefabricated columns, reinforced concrete slabs with a thickness of 200 mm, and inclined prefabricated tribune beams. On the axes "0" to "12" leeward steel walls are designed.

3. DIAGNOSTICS OF THE TRIBUNE

The subject of diagnostics was the object under construction of the Závodisko tribune. At the time of assessment, only two overground floors of the load-bearing structure of the tribune were built (Fig. 3).

Fig. 3. View of part of the tribune under construction (January 2018)

After the building was preserved in February 2012, the object partially under construction dilapidated and until today the building is not completed.

As a part of the comprehensive diagnostics [2-8] the following was carried out:

- visual inspection of the whole object,
- checking the dimensions of some load-bearing elements,
- checking the construction of reinforced concrete monolithic and prefabricated structures, steel structures, column anchors and some details,
- indicative measurement of deflections of ceiling slabs,
- measurement of the inclination of some columns,
- passport of defects and deficiencies in terms of construction realization,
- determination of concrete strength in a non-destructive and destructive way,
- scanning of reinforcement in reinforced concrete elements - slabs, walls, columns (prefabricated and monolithic), floor beams,
- uncovering of reinforcement in some load-bearing reinforced concrete elements,
- evaluation of status of uncovered reinforcement and check of cross-sectional characteristics of reinforcement,
- carbonation of concrete (using phenolphthalein),
- checking the bulk density of lightweight concrete,
- verification survey of the foundation of the building.

Construction diagnostics showed some differences between the actual realization and the original project documentation. As part of the diagnostics, several control core boreholes were carried out on the slabs and walls (Fig. 4).

Fig. 4. Core borehole in the slab (2nd floor)

One sample was also taken from the base slab, whose thickness was approximately 100 mm. One layer of reinforcement with 8 mm diameter, at distance 100 mm (in both directions) was directly at the bottom edge of the base slab. The second layer of reinforcement was just below the base slab, i.e. the reinforcement in the base slab was almost without cover. Cracks on the base slab were recorded in the range of 0.5 mm to 2.0 mm.

Scanning of the slab reinforcement was carried out linear and areal in several places. Each scan position showed the actual reinforcement placement and the cover that matched the original project. The originally

designed profile and the type of reinforcement were also confirmed by destructive probes. By the reinforced concrete walls were found to be denser reinforcement but a smaller reinforcement profile compared to the original project. The difference in cross-sectional area between these different reinforcement is approximately 4.0%. The reinforcement of the monolithic and prefabricated columns was checked in a non-destructive way – by scanning the reinforcement with a scanner and destructively by exposing the reinforcement directly. Both for the slabs and for the verified columns, in reinforcement the conformity was confirmed with the original project.

Detailed chemical analysis (e.g. profiles of the pH distribution of concrete pore liquid on the thickness of the cover) was not carried out.

4. THE CURRENT STATE OF THE TRIBUNE AND CONCEPT PROPOSALS FOR COMPLETION

During the inspection, a statically unsuitable solution of openings in the perimeter walls was found (Fig. 5). In this part of the wall there is a ceiling slab and the load-bearing wall is insufficiently supported at one end. It was recommended to statically strengthen this wall.

Fig. 5. Incorrectly static distribution of holes in the load-bearing wall

At the same time, it was recommended to concreting the doorway at the "C" axis, by adding the steel inter-window pillars to hold this wall at the place of window and between the existing doorways. Another possibility was to demolish the wall, whereby the existing ceiling slab has to be sufficiently temporarily supported and a new one have to be concreted with another statically suitable arrangement of the openings.

The realized load-bearing walls are in contradiction with the original project documentation. It was recommended to demolish the lintel (Fig. 6) and to concrete a new one, or to use another suitable method of repair.

Fig. 6. Part of monolithic lintel with missing cover

In Figure 6 is showed the removed side cover layer of monolithic lintel. Probably the layer was removed due to inaccurate realization and the original cover interfered with the prefabricated elements that were to be placed at this location.

Cracks in the width of 0.1 mm to 0.2 mm were present on the tribune beams (Fig. 7). Cracks occurred on the beams on both floors.

Fig. 7. Cracks on the tribune beam on the 2nd floor

The anchoring (Fig. 8) of reinforced concrete prefabricated columns with dimensions of 300 mm by 500 mm had to be checked on all columns. It was recommended to dismantle the steel frame along the perimeter and to properly inspect, clean and repair

the frame. During the diagnostics, an interruption of the anchorage reinforcement was detected in some places.

Fig. 8. Detail of incorrect anchoring of columns

5. CONCLUSIONS

The results of the diagnostics show that the unfinished load-bearing structure of the tribune is poorly realized in some parts. Insufficient quality of realization was visible on some of the load-bearings elements and it leads to the following conclusions: In several places of the load-bearings elements of the structure (walls, staircases, floor beams and columns) the concrete was not sufficiently compacted. In some places the reinforcement was uncovered or the reinforcement cover was not observed. At the joints of the load-bearing elements, whether prefabricated - monolith or monolith - monolith, the filling of the joints with PUR foam was seen. Poorly concreted inter-window pillars in several places had to be repaired. Since their dimension in terms of bearing capacity is insufficient, they cannot be considered as load-bearing elements. Poor arrangement of load-bearing elements due to window and door openings. The anchoring of the rectangular columns to the foundation structures was incorrectly realized. At the time of diagnostics, the steel anchor parts were affected by surface corrosion. In some places, the cavities were under the steel anchoring elements, which is unacceptable for column anchorage. The inner circular reinforced concrete columns were not concreted exactly in the vertical position. For this reason, it was recommended to repair them, respectively strengthen them [9, 10]. Repair of columns is necessary not only because of geometric inaccuracy due to faulty realization, but also because of static resistance of these columns.

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PHARMACEUTICALS IN WATER AND WASTEWATER – OVERVIEW

FARMACEUTYKI W WODACH I ŚCIEKACH

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Abstract

The paper presents concentrations of pharmaceuticals in surface water and sewage. Special attention was paid to the content of estrogens in municipal sewage and the method of their disposal. Concentrations of various pharmaceuticals in raw and treated wastewater were compared and the pharmaceuticals in different countries and waters were presented in tables. The most frequently identified drugs in sewage are sex hormones (etradiol, ester, ethinylestradiol, 17 β-estradiol) and the antiepileptic drug Carbamazepine. These drugs are difficult to remove from water and therefore appropriate treatment processes are used, such as: adsorption on active carbon, UV irradiation, etc. Contamination of water with pharmaceuticals has a negative impact on the development of aquatic organisms and can lead to serious human health problems.

Keywords: surface waters, pharmaceuticals, estrogens, wastewater, pollution

Streszczenie

W pracy przedstawiono stężenia farmaceutyków w wodach powierzchniowych oraz ściekach. Szczególną uwagę skupiono na zawartości estrogenów w ściekach komunalnych oraz na sposobie ich usuwania. Porównano stężenia różnych farmaceutyków w ściekach surowych oraz ściekach oczyszczonych, a także zostały przedstawione tabelarycznie farmaceutyki występujące w różnych państwach oraz wodach. Najczęściej identyfikowanymi lekami w ściekach są: hormony płciowe (etradiol, estron, etinyloestradiol, 17 β-estradiol) oraz lek przeciwpadaczkowy – Karbamazepina. Leki te są ciężko usuwalne z wód, dlatego też stosuje się odpowiednie procesy ich oczyszczania, takie jak: adsorpcje na węglu aktywnym, naświetlanie promieniami UV itp. Zanieczyszczenia wód farmaceutykami wpływa negatywnie na rozwój organizmów wodnych, a także może prowadzić do poważnych problemów zdrowia ludzkiego.

Słowa kluczowe: wody powierzchniowe, farmaceutyki, estrogeny, ścieki, zanieczyszczenia

1. INTRODUCTION

The pharmaceutical industry is an ever-growing economic sector worldwide. Due to the spread of various diseases, infections and infections both in humans and animals, the most commonly prescribed pharmaceuticals are antibiotics, anti-inflammatory and antiepileptic drugs as well as hormonal agents, which have a huge impact on the quality of drinking water, human health but also the development of aquatic organisms [1]. The antibiotics prescribed worldwide every year exceed 12.000 Mg, of which 65% are used in the treatment, 29% in veterinary medicine and 6% are used in veterinary medicine as growth inhibitors [2]. The consumed drugs undergo the metabolic process in the body. The metabolism of drugs, however, never occurs in 100%, thus the free and metabolized form is expelled from the body and then seeped into sewage. Moreover, a big problem is the introduction of overdue, poorly disposed drugs into sewage, which are simply thrown into the sewage system [2]. At present, sewage treatment plants are not obliged to check the effectiveness of treatment for pharmaceuticals. Through studies carried out over the last few years in various countries over 80 different pharmaceuticals present in the aquatic environment were found. The exposure of organisms even to low concentrations of

drugs may cause endocrine disorders, resistance to pathogens and toxic effects [3].

This article presents the role of pharmaceuticals in the aquatic environment and the detailed influence of estrogens on water quality and human health.

2. SOURCE OF ESTROGEN IN MUNICIPAL WASTEWATER

Oestrogen is an important problem of water environment pollution. They deserve special attention, as only a small number of people are aware of the huge impact they have on human health and functioning. Estrogens are steroid female sex hormones. For a long time this aspect has been ignored because estrogens are natural substances formed in the human body, however they are divided into natural and synthetic. The first group includes progesterone, testosterone, ester, oestradiol, phytoestrogens; synthetic hormones are components of pharmaceutical preparations and may include gestagens, ethinylestradiol, diethylstylbestrol [4]. In recent years, estrogens are more and more often used in veterinary animal treatment and hormone replacement therapy, and most of all estrogens can be found in contraception, which is very popular nowadays [5]. The hormones taken by humans are excreted from the body through urine, then they are introduced into the aquatic environment by discharging raw and treated sewage [6]. Estrogens are divided into three types: ester (E1), estradiol (E2), estriol (E3) and the natural hormone produced during pregnancy, estrol (E4) [4]. The content of this hormone in wastewater depends on the population of people living in a given area as well as the number of women in the reproductive and menopausal period and pregnant women. A pregnant woman's organism produces even 120 times more hormone 17-estradiol than a woman's organism during the menopause [3]. Table 1 presents the mean daily production of estrogens by humans.

The most hormones are produced by pregnant women, where the level of ester during the day is 787 µg/day and estriol is almost 10 thousand. Considering that the pregnancy lasts 9 months it is a lot and even though these are natural hormones they can adversely affect water quality. In contrast, women in the menopausal period are in second place but produce much lower hormone values, however, it should be noted that estriol, which is 90.70 µg/day and 59.20 µg/day 17 β-estradiol prevails. Subsequent groups produce hormones in the range 0 to 10 µg/day except for women in menstruation where they produce 17.40 µg/day oestriol.

Table 1. Average steroid estrogen excretion by humans (per person) µg/day [7]

	Estrone, µg/day	17 β-estradiol, µg/day	Estriol, µg/day
Pregnant women	787	277	9850
Menopausal, with HRT	31.50	59.20	90.70
Menstruating woman	9.32	6.14	17.40
Women	7.00	2.40	4.40
Menstruating females	3.50	8.00	4.80
Adult male	3.50	1.83	3.21
Menopausal, no HRT	2.93	1.49	3.90
Menopausal females	2.30	4.00	1.00
Males	1.60	3.90	1.50
Female child	0.60	2.50	0.918

Oestrogens in water are usually detected in low concentrations, but they can nevertheless affect the proper functioning of organisms, causing quite serious disturbances in the development of organisms and reproductive processes such as, for example, reduced fertility in animals or development of testicular cancer [6].

Steroid sex hormones can be eliminated from sewage by adsorption on the activated sludge, ozonization, ozonization/H_2O_2 and by using biological filters [8]. The method of elimination is chosen according to what hormone and to what extent we want to remove it from the sewage. For example, using the adsorption method on activated sludge, about 70-90% of ester can be removed from sewage [1].

Table 2 presents the hormone content in Polish rivers. The analysis of water samples taken from these rivers shows that ester is present in two rivers with concentrations of 1.3 µg/dm^3 and 1.1 µg/dm^3, whereas in the Vistula River estradiol with concentration of 1.3 µg/dm^3 was detected. The remaining oestrogens entered the amount below 1 ng/l, i.e. at the method determination limit in the range of 0.5÷1 µg/dm^3 [3].

Table 2. Hormone content in Polish rivers [9]

Polish rivers	Hormone content, μg/dm³		
	estron	estradiol	etinyloestradiol
Odra	1.3	gom.	gom.
Kanał Gliwicki	1.1	gom.	gom.
Wisła	gom.	1.3	gom.

gom. – limit of determination of the method

Concentrations of these hormones in Polish rivers are relatively low compared to other countries such as Germany, Italy, the Czech Republic or Japan, where hormone concentrations in surface waters are several times higher than in Poland, as shown in Table 3.

Table 3. Occurrence and concentration of hormones in water [10]

Hormone	Occurrence	Concentration, μg/dm³	Country
Estradiol	surface waters	0.0006	Germany
	drinking water	0.0003	Germany
	surface waters	0.0021	Japan
Estron	surface waters	0.0007	Germany
	drinking water	0.0004	Germany
	surface waters	0.0015	Italy
Etinyloestradiol	surface waters	0.0001÷0.0051	Germany
	surface waters	0.00004	Italy
	surface waters	0.0046	Czech Republic
17 β-estradiol	drinking water	0.0003÷0.0021	Germany

Oestrogen concentrations in water reach values below 1 μg/dm³, but are nevertheless of great concern. Low estrogen content in water is caused by accumulation of compounds in bottom sediments, which may cause a secondary source of water supply with steroid hormones. The following oestrogen values at levels have been recorded in bottom sediments: E1-1.5÷33.0 (11.43) μg/kg and E2-0.71÷16.0 (5.43) μg/kg, while as far as ethinylestradiol EE2-8.43 μg/kg is concerned. The accumulation of estrogenic compounds in bottom sediments may be caused by their physicochemical composition and specific local conditions [11]. Identification of the decomposition of these compounds in water is not easy as their half-life in bottom sediments and water is about 2÷6 days with simultaneous observation of changes in the water environment under the influence of microorganisms [12]. In adipose tissues of aquatic organisms, overestimation of estrogen levels is observed. This level is expressed on the basis of the logarithm of the so-called bioaccumulation factor as the ratio of compounds in aquatic organisms to their content in water. An example is fish, where their level ranges from 2.22 (E1) to 2.83 (EE2). In this case, we can say that this is a growing threat to the aquatic environment [13].

After the analysis of samples in water in Poland, the presence of hormonal compounds was detected, which may contribute to the degradation of the aquatic environment. Moreover, it was shown that they may have a negative impact on the development of animal organisms as well as on human reproductive processes, especially on the foetus, which can be observed at a later stage of human maturation. Therefore, the level of estrogens in water should be constantly controlled and the purification process should ensure complete removal of these compounds [5].

3. OESTROGEN REMOVAL FROM WASTE WATER

According to various sources of hormonal pollution can be removed from the wastewater by accumulation on suspended solids, however, the degree of treatment is not very effective and therefore ancillary processes are used. These include: active carbon adsorption, UV irradiation, advanced catalytic oxidation and the use of membrane reactors. The Table 4 presents data from the course of wastewater treatment in terms of estrogen presence [3].

Table 4. Concentration of hormones at the input and output of the plant and the degree of purification [3]

Hormone	Concentration in raw sewage, μg/dm³	Concentration in treated wastewater, μg/dm³	Degree of purification, %
Estradiol	0.003	0.0004	85
Estron	0.0024	0.0044	0

Aerobic microorganisms can convert one estrogen into another as shown in Figure 1. For example, some microorganisms (e.g. nitrifying bacteria) can convert E1 to E3 and others decompose E1, E2 and EE2 (e.g. Novosphingobium sp. in active sediment). Moreover, synthetic EE2 can be converted to E1 by Sphingobacterium sp [14]. There are also many strains of anaerobic bacteria, which can convert one estrogen into another. For example, in lake water and sediments under anaerobic conditions, E2 was chemically converted to E1 under methanogenic,

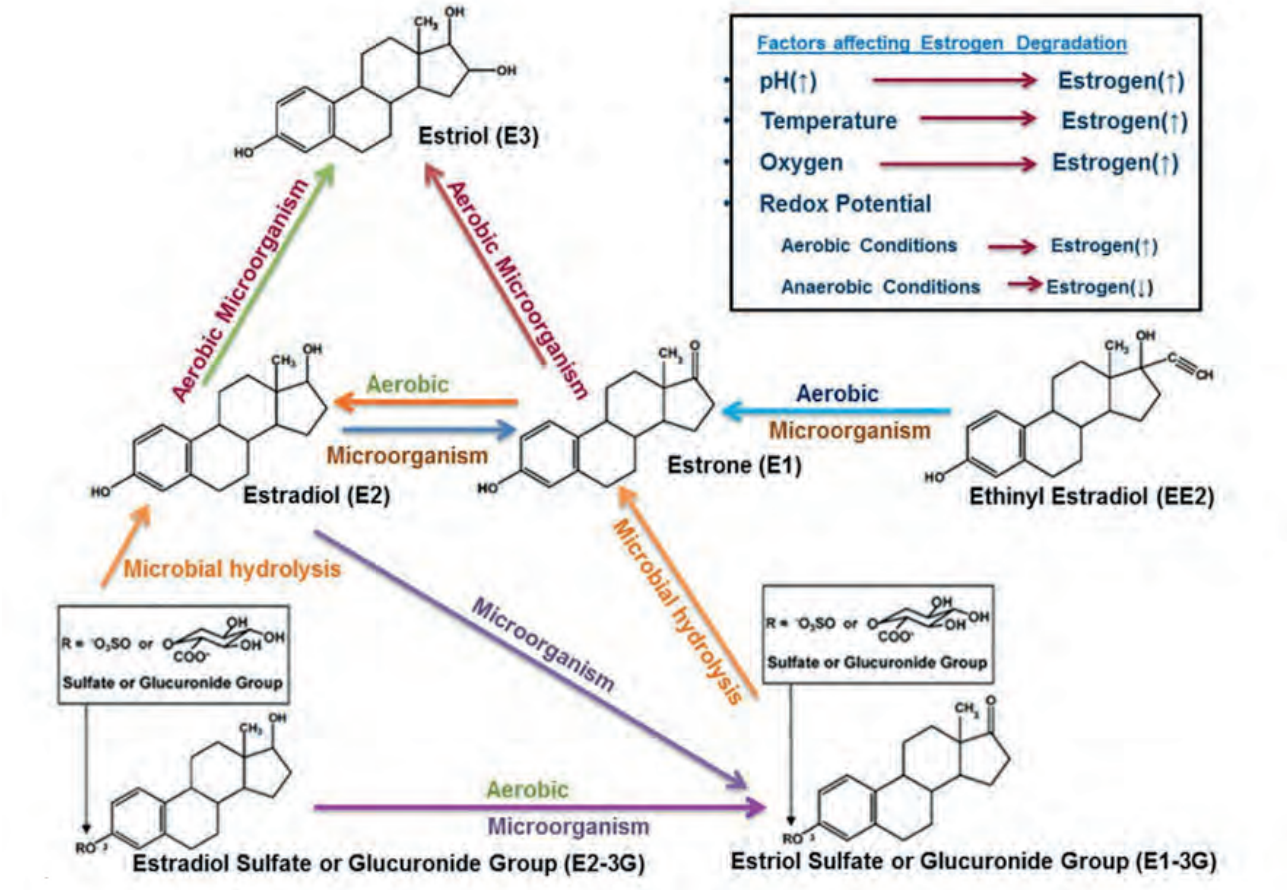

Fig. 1. Interconversion pathways of natural and synthetic estrogens [7]

sulphate, ferric and nitrate reducing conditions; however, no degradation of EE2 was observed [15].

4. CONTENT OF OTHER PHARMACEUTICALS IN AN AQUATIC ENVIRONMENT

Estrogens are not the only pharmaceuticals that pollute the water environment. Carbamazepine should be mentioned here, it is the most commonly used antiepileptic drug, which is absorbed very slowly from the gastrointestinal tract, while the maximum concentration is observed from 4÷6 days. This drug is excreted in urine, earlier metabolism takes place in the liver. Carbamazepine is usually detected in surface water, although it is also found in drinking water. This drug is difficult to remove from waste water during treatment processes and is resistant to biodegradation processes. To remove this drug from the waste water, ozone treatment can be used, which treats the waste water from carbamazepine up to 90%, another process is adsorption on active carbon, where the effectiveness of removing this drug is up to 90%, and phytolysis is an equally effective process. The Table 5 presents the occurrence and concentration of carbamazepine in comparison to other compact pharmaceuticals in waters of different countries [3].

Table 5. Presence and concentration of pharmaceuticals in water [3]

Substance	Presence	Concentration, µg/dm³	Country
Carbamazepine	surface waters	0.025÷1.07	Germany
	drinking water	0.258	USA
	surface waters	0.001÷0.009	United Kingdom
Diazepam	surface waters	0.88	Germany
Clofiberic acid	surface waters	below 0.45	Germany
	drinking water	0.07÷0.27	Italy
Bezafibrat	drinking water	0.0027	Germany
Metoprolol	surface waters	0.05÷0.15	Poland
Propanolol	surface waters	0.005÷0.007	United Kingdom
	surface waters	0.015÷0.178	Spain
Athensolol	surface waters	0.318÷6.167	Spain

Compared to other pharmaceuticals, carbamazepine has a fairly high concentration, but not the highest. In Germany, the concentration of this drug in water can reach up to 1.07 μg/dm^3 in surface water, while in drinking water in the USA the concentration is much lower at 0.258 μg/dm^3. Nevertheless, this drug has an adverse effect on the aquatic environment and the organisms living in it.

Table 6 shows the concentration at the exit and entry of the pharmaceuticals in question. Carbamazepine is removed from wastewater only 8%, a very small percentage compared to Bezafibrate, which has a treatment rate of 91%, while clofiberic acid is not removed at all in wastewater treatment processes.

Table 6. Concentrations at the input and output of the plant and the degree of purification [3]

Medicine	Concentration in raw sewage, μg/dm^3	Concentration in treated wastewater, μg/dm^3	Degree of purification, %
Carbamazepine	1.78	1.63	8
Bezafibrat	2.6	0.24	91
Clofiberic acid	0.15÷0.25	0.15÷0.25	0

Carbamazepine contributes to the growth inhibition of green algae of the species S. capricornutum in concentrations from 2.1 to 20 000 mg/dm^3, whereas for D. magna EC50 = 157 000 mg/dm^3 and for D. subspicatus EC50 = 85 000 mg/dm^3 [9].

In addition to the above mentioned in the table of pharmaceuticals, surface waters have high levels of caffeine, which is found in coffee, energy drinks, medicines and supplements. However, it was found that this substance does not pose a risk to the human body. In contrast, the concentrations of drugs such as cocaine and matamfetamine iecstasy detected in water have very strong pharmacological effects and may be toxic to aquatic organisms [3].

There are many ways to remove or minimize pharmaceuticals in water and wastewater. These include biological methods, membrane processes using bioreactors, the use of active carbon, UV radiation, chlorination and ozone. According to research on the effectiveness of pharmaceutical removal, only about one fifth of the compounds are removed in a classic two-stage treatment plant. The removal of carbamazapine and diazepam in 85% can be achieved by using powdered activated carbon in a membrane bioreactor to absorb pharmaceuticals from urban wastewater.

5. SUMMARY AND CONCLUSIONS

Pollution of water and wastewater with various types of pharmaceuticals creates quite serious problems in the aquatic environment, however, Polish and European law has so far not set a limit for water pollution with drugs and hormones. In Europe, on 31 January 2012, the European Commission established the addition of 15 chemical compounds to the list of 33 polluting compounds whose concentration should be monitored in EU waters. The added compounds include diclofenac, ethinylestradiol, 17 β-estradiol [16].

Pharmaceuticals contained in water adversely affect aquatic organisms, and the presence of drugs in drinking water can lead to serious problems for human health, infants and young children. Also, great attention should be paid to the content of estrogens in water, as they may contribute to the incidence of pedestrian and testicular cancer [1].

However, there are serious gaps in our knowledge of estrogen levels in the environment, and there is a need to call for more data on many other sampling sites worldwide. Among the available data, synthetic oestrogen, ethinylestradiol, is more persistent in the environment than natural oestrogens and may be of greater concern for the environment. Oestrogens should be listed as a toxic organic pollutant, which is confirmed by several studies.

Oestrogen contamination is becoming a significant environmental problem and has harmful effects on the growth and development of humans, animals and plants at significant levels. Attention to this issue is essential and requires further in-depth research. The issue of estrogen in waste water will continue in subsequent publications, after appropriate research by the authors.

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ANALYSIS OF THE MOBILITY OF HEAVY METALS IN SLUDGE FOR THE SEWAGE TREATMENT PLANT IN DALESZYCE

ANALIZA MOBILNOŚCI METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH DLA OCZYSZCZALNI ŚCIEKÓW W DALESZYCACH

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Abstract

Sewage sludge is a by-product of wastewater treatment processes. However, it has high fertilising and soil-forming properties, but it cannot always be used for this purpose. The two main criteria limiting their natural use are heavy metals and parasite eggs. Sewage sludge taken from the Daleszyce wastewater treatment plant has been analysed for heavy metals. For this purpose a space analysis was performed to divide the total metal content into four mobility fractions. The mobility issue determines the ability of an element, or one of its forms, to move in the environment. The studies were performed using a four-stage BCR procedure. The results were analyzed and compared to the limits applicable in Poland for sewage sludge intended for environmental use.

Keywords: sewage sludge, speciation analysis, BCR, environmental use of sewage sludge, mobility of heavy metals

Streszczenie

Osady ściekowe są produktem ubocznym procesów oczyszczania ścieków. Wykazują jednak wysokie właściwości nawozowe oraz glebotwórcze, jednak nie zawsze mogą być one wykorzystane w tym celu. Dwa główne kryteria ograniczające ich przyrodnicze wykorzystanie to zawartość metali ciężkich oraz jaj pasożytów. Osady ściekowe pobrane z oczyszczalni ścieków w Daleszycach zostały poddane analizie zawartości metali ciężkich. W tym celu wykonano analizę specjacyjną, pozwalającą podzielić całkowitą zawartość metali na cztery frakcje mobilności. Mobilność określa zdolność pierwiastka, lub któregoś z jego form, do przemieszczania się w środowisku. Badania wykonano, stosując czteroetapową procedurę BCR. Wyniki poddano analizie i porównano do limitów obowiązujących w Polsce dla osadów przeznaczonych do wykorzystania przyrodniczego.

Słowa kluczowe: osady ściekowe, analiza specjacyjna, BCR, przyrodnicze wykorzystanie osadów, mobilność metali ciężkich

1. INTRODUCTION

Sewage sludge generated in sewage treatment plants has high soil-forming and fertilizing properties. They can be used in agriculture as a valuable organic fertilizer provided that they are hygienised and the content of organic and inorganic micro-pollutants (heavy metals) does not cause negative effects in the soil environment [1]. Limits of heavy metals in the aspect of sewage sludge utilisation in Poland and worldwide are presented in Table 1.

Table 1. Normative limit values for heavy metals in sewage sludge for agricultural use

Region	Poland Regulation [2]	EU Directive 86/278/ EEC [3]	Chinese Regulation GB 18918-2002 [4]		USA Regulation 40 CFR Part 503, 503.13 [5]	South African Guideline (Pollutant Class a) [6]
			pH < 6.5	pH > 6.5		
Cd	20	20-40	5	20	39	40
Ni	300	300-400	100	200	420	420
Zn	2500	2500-4000	500	1000	2800	2800
Cu	1000	1000-1750	250	500	1500	1500
Cr	500	–	600	1000	–	1200
Pb	750	750-1200	300	1000	300	300

Heavy metals in sewage are in suspension and dissolved form. Sewage treatment processes, including the process of simultaneous precipitation of phosphorus and chemical precipitation with lime, cause adsorption and co-precipitation of heavy metals in the separated sludge, which results in their removal from sewage [7]. Moreover, the processes of mass bioaccumulation by microorganisms in the activated sludge chambers and methane fermentation process (formation of immobile heavy metal sulphides) promote the transfer of heavy metals from sewage to sludge [8]. The above transformations affect the differentiation of chemical forms of heavy metals accumulated in the sewage sludge, only some of which (mobile forms) can penetrate from the sludge to the ground environment [9]. The term „mobility of elements" describes the ability of an element, or one of its chemical forms, to move in the environment [10]. The determination of mobility is decisive in the assessment of the risk associated with the introduction into the environment of substances containing hazardous components, e.g. heavy metals. The metals present in water-soluble compounds and those associated with carbonates are considered to be the most mobile (Table 2). Metals bound to iron and manganese oxides are released to the environment much more slowly. The metals which are temporarily immobile are those which form permanent links with organic matter or occur in the form of sulphides [11]. The unavailable metals are those associated with aluminosilicates. The specialist literature contains numerous studies on the sequential extraction of heavy metals from soils, sewage and river (marine) sludge and compost [12]. The most important factors influencing the assimilability of heavy metals by plants include: total metal content in soil, metal type, soil reaction, organic matter content and clay fraction [13]. Bioaccumulation of heavy metals in plants growing on soils contaminated with metals depends on the plant species and the content of mobile metal fractions in the soil. In soil analysis, multistage extraction of heavy metals should be used [14].

As a result of laboratory tests to compare different sequential extraction procedures, it was found that the optimal way to identify the bioavailable metal fractions for certified soil samples is to use EDTA or acetic acid [15].

Table 2. Mobility of heavy metals depending on the form of occurrence [1]

Type of connection	Degree of extraction	Form of metal presence in the ground
Mobility	0	Remaining in pore water
	1	Occurring in ion exchange complexes which are retained or eluted depending on the ionic composition of the pore water
	2	Carbonate related
Permanently	3	Related to manganese oxides and amorphous iron oxides
	4	Related to amorphous and weakly crystalline iron oxides
	5	Sulphides and organometallic compounds
	6	Bound to silicates and forming part of crystalline structures

2. THE USE OF SPECULATIVE ANALYSIS METHODS TO ASSESS THE MOBILITY OF HEAVY METALS

In the case of sewage sludge samples, the best results were obtained using a four-stage procedure developed by the European Community Bureau of Refe-rence, abbreviated to BCR [1]:

Stage I: extraction of CH_3COOH – to determine the content of assimilable and carbonate-bound metals (FI fraction – interchangeable).

Stage II: extraction of $NH_2OH{\cdot}HCl$ – for the determination of the content of metals associated with amorphous iron and manganese oxides (FII fraction – reductive).

Stage III: H_2O_2/CH_3COONH_4 extraction – for the determination of the content of the organometallic and sulphide fractions (FIII fraction – oxidation).

Stage IV: mineralization of the residual fraction with a mixture of concentrated acids (HCl, HF, HNO_3) – for the determination of the content of metals bound to silicates (fraction FIV – residual).

By means of X-ray microanalysis the validity of sequential BCR extraction can be confirmed. Adsorbents are present in the matrix, which allow to bind metals in FI to FIV fractions. In the sample sewage sludge from the sewage treatment plant in Daleszyce, heavy metals are combined with organic matter, iron oxides, sulphides and aluminosilicates (Fig. 1).

The results of the study indicate that the migration of heavy metals delivered to the soil with sewage sludge is small, however, it may increase in sandy soils with low pH [16]. Zinc is the most susceptible to metal migration [17]. The profiles obtained from unused limestone soils under study contained trace contents of heavy metals. For this purpose, the columns were filled with the sludge from the local sewage treatment plant mixed with the top 15-centimeter layer of limestone soil [16]. During the study, natural weather conditions were simulated on the columns: constant air temperature and humidity were maintained and samples were irrigated with water in an amount corresponding to the local precipitation. A trace amount of metals which moved from the layer of sediments into the studied profiles was shown. The highest migration capacity was found in the sample with the highest addition of sediments. Nickel proved to be the most mobile metal. Nickel was also the best assimilable to plants and its concentration was highest in leachate from columns. The study clearly shows that the mobility of metals contained in sewage sludge is so low that it does not significantly affect the groundwater quality [16].

A simplified BCR sequential extraction method was used to plan a soil phytemediation treatment in one of the Spanish mining regions: Cartagena - La

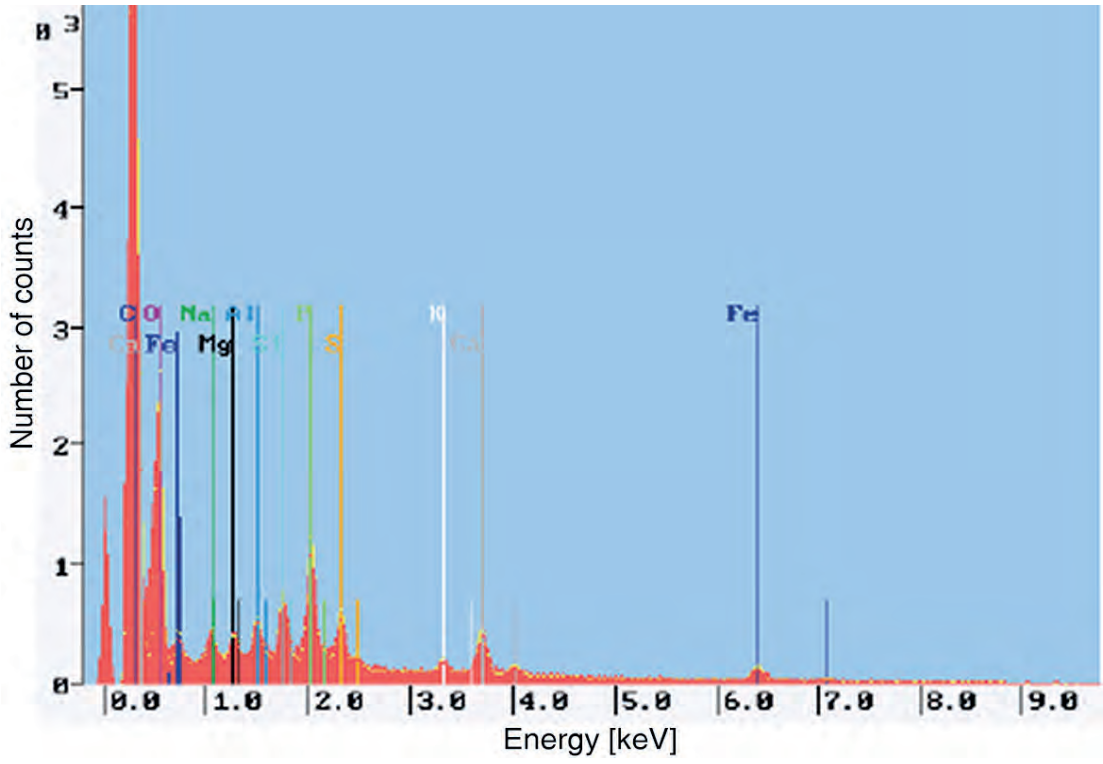

Fig. 1. XRF spectrum of sewage sludge sample from sewage treatment plant O7 [1]

Union [159]. This method was used to assess the degree of bioavailability of heavy metals to plants during the phytremediation process. One of the first observations made was that only a small amount of heavy metals contained in the soil occurred in mobile forms, easily assimilated by plants. However, after extraction, some heavy metals changed their forms to more mobile ones. This indicates the possibility of increased mobility of heavy metals. The conducted studies have shown that some lead, cadmium and zinc have changed into easily assimilable forms, thus posing a potential threat to the environment [18]. However, in the soil, the process of strong binding of these metals in the crystalline mineral networks took place. The formation of such complexes practically limits further migration of heavy metals to zero. Some of the metals were bound in oxidized forms, which due to low solubility also became immobile. However, a change in soil reaction and its oxidative potential may cause the mobilization of oxidized forms. It can therefore be concluded that the release of heavy metals and their possible assimilation by plants is a long-term process that requires appropriate conditions, but is highly likely to occur.

Studies on the mobility of heavy metals were also conducted for samples taken from marshy areas [16]. The conditions in the marshy environment are considered conducive to the immobilization of metals, which has been applied, e.g. in the treatment of contaminated waters. The situation is complicated by the presence of plants in the system. The greatest differences were observed in the rhizosphere. An increase in the amount of oxygen supplied through the root system can be observed here. However, the uptake of nutrients by plants leads to changes in the amount and structure of organic matter. These changes are encouraged by the appearance of new species of microorganisms accompanying the plants. Fungi and bacteria are mainly able to bind heavy metals. During the immobilization of metals, various mechanisms are used, such as precipitation, complexation, sorption or transport to the cell [19]. Moreover, the presence of plants affects the redox potential and soil pH [20].

Under these conditions, processes that immobilise and mobilise heavy metals may occur at the same time. For example, the release of metals may be facilitated by an additional amount of oxygen causing the oxidation of structures that have hitherto been „traps" for heavy metals, such as iron sulphides (FeS). At the same time – the same forms of metals – can be bound into structures of newly formed organic compounds due to plant metabolism. An additional difficulty in the analysis of this phenomenon is the seasonality of processes. It looks different in the phase of intensive plant growth, and different in the time of their dying. The features of the native soil cannot be omitted, which may significantly affect the course of the processes [16].

Despite many factors that can show that the presence of plants can increase the mobility of metals, the presence of swamp vegetation does not cause their mass mobilization. Therefore, it is clear that the use of plants for immobilization of heavy metals or for purification of contaminated areas is most advisable provided that the existing conditions are recognized [16].

A group of Australian researchers proved that the addition of comminuted clay or bauxite clay to the sediment limits the mobility of heavy metals [21]. This clay is an effective sorption „trap" for metals released due to oxidation of organic compounds washed out by water, activated by the metabolism of plants and microorganisms and by the processes of sediment processing (e.g. drying). The effectiveness of this treatment depends to a large extent on the form in which the element occurs in the sediment. In general, however, it is an excellent solution for limiting the mobility of heavy metals. The majority of metals, after the addition of clay, move from organic forms into the residual phase - i.e. the residue in which the metals are immobilized [21]. Even in laboratory conditions, the separation of metals from the residual phase requires the use of strongly oxidizing mixtures, e.g. royal water. Among the elements studied: chromium, lead, zinc, cadmium, nickel and copper, only copper, which occurs mainly in stable organic forms in the sediment, did not show a tendency to move to the residual phase [21].

An effective method of temporary immobilization of heavy metals is liming of sewage sludge. Although the liming process favours lowering the fertilising value of sludge, it is still used as the best form of prevention of heavy metals uptake by plants [22].

3. STUDY METHODOLOGY

A two-kilogram sample of sewage sludge taken before the hygienization process from all objects was used to study metal mobility. Determinations were performed using Perkin-Elmer 3100 F-AAS atomic absorption spectrometer with ball valve option. The

tests were carried out by BCR sequential extraction. Mineralization of the residual fraction was carried out with royal water. The sample taken was reduced to 8 g and dried (air-dry conditions) at 20ºC for 48 hours. Next, 0.5 g of sewage sludge with 80% hydration was weighed and transferred to a 100 cm^3 centrifuge tube. After addition of 40 cm^3 of 0.11 mol acetic acid solution, the test was shaken for 16 hours at room temperature. The extract obtained was separated from the sediment by centrifugation (4000 rpm). The content of water soluble metals in the obtained liquid was determined. The sewage sludge was washed 20 cm^3 of distilled water by shaking and centrifugation. Then 40 cm^3 of 0.1 mol hydroxylamine hydrochloride solution of pH = 2 was added to the sewage sludge. Nitric acid was used for pH correction. It was proceeded as in the previous stage (shaking and centrifuging). In the liquid the metals of fraction II were determined and the sewage sludge was rinsed. The sewage sludge was quantitatively transferred to quartz steamers and 10 cm^3 30% hydrogen peroxide was added. The content of the evaporator was heated in a water bath at 85ºC for one hour. The operation was repeated by adding to the sewage sludge 10 cm^3 of 8.8 mol hydrogen peroxide solution. After cooling to room temperature the sewage sludge samples were transferred to rotor tubes and 50 cm^3 of ammonium acetate solution was added (1 mol/dm^3, pH = 2 after HNO_3 correction). The sample was shaken for 16 hours and then the sludge was separated from the extract. In the solution the metals of fraction III were determined. Sewage sludge was washed and dried to constant mass. Mineralization of the residual fraction was carried out with royal water. To a 300 cm^3 conical flask containing 0.5 g of sewage sludge, 30 cm^3 HCl concentration and 10 cm^3 HNO_3 concentration were added. The content of the flask was heated for 30 minutes, then evaporated to dry. After cooling down, 25 cm^3 HCl (1+5) was added to dissolve the sewage sludge and transferred to a volumetric flask and supplemented with distilled water to 50 cm^3, then the contents of the flask were stirred and seeped into a dry container. In the filtrate, fraction IV metals were determined. The content of heavy metals in the extracts obtained was determined according to ISO 9001:2000 on Perkin-Elmer 3100 F-AAS atomic absorption spectrophotometer, in four independent samples of sewage sludge. A recovery check was carried out based on certified reference material BCR CRM 143R. The results were statistically analysed to exclude coarse errors. Dixon and Grubbs tests were used for this purpose.

4. STUDY RESULTS

Table 3 shows the average heavy metal content in sludge dry matter in the four mobility fractions. The content of the mobile fraction (FI, FII) and the conditionally immobile fraction (FIII) compared to the residual fraction (FIV) was very low (Fig. 2). In the case of heavy metals obtained from FI fractions, water-soluble and carbonate-bound, a significant, 18.4% share was recorded for zinc. No copper was detected in this fraction and lead content was trace (0.6%). In the fraction bound with amorphous iron oxides (FII) zinc and cadmium dominate. The share of both these heavy metals exceeds 16%. A significant percentage of heavy metals was determined in the form of sulfides and in organometallic bonds (FIII). The highest percentage was found in copper (69.2%). The remaining metals also show significant content in FIII: Zn – 40.4%, Cd – 39.4% and Ni – 36.5%. The exception is lead, whose content in the FIII fraction is only 3.8%. Almost all lead content equal to 408,4 mg/kg d.m. is concentrated in the immobile FIV fraction. The relative lead content in the residual FIV fraction is 95.6%. Chromium – 55.9%, nickel – 46.1% and cadmium – 31.9%, respectively, occurred in the lower percentage share. The content of the residual FIV fraction for copper is 30.8%, but for zinc this value drops already to 25.0%.

Table 3. Average content of heavy metals in dry mass of sludge from the sewage treatment plant in Daleszyce in four stability fractions obtained by BCR sequential extraction method

Speciacion	Cu, mg d.m./kg	Cr, mg d.m./kg	Cd, mg d.m./kg	Ni, mg d.m./kg	Pb, mg d.m./kg	Zn, mg d.m./kg
Fraction I	0	13	1.2	2	2.5	509.9
Fraction II	0	4.2	1.5	0.9	0	447.3
Fraction III	14.6	29.4	3.7	6.1	16.2	1119
Fraction IV	6.5	59.1	3	7.7	408.4	693.2

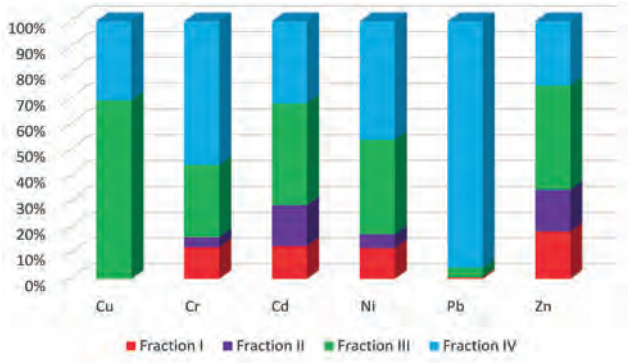

Fig. 2. Average percentage of heavy metals in sludge from the Daleszyce wastewater treatment plant depending on the fraction

The average percentage of heavy metals in the separated fractions in the analysed sewage sludge from the treatment plant in Daleszyce was presented in the following decreasing series of contents:

– for Cu: FIII(69.2%) > FIV(30.8%) > FII(0.0%) > FI(0.0%) (Fig. 3)

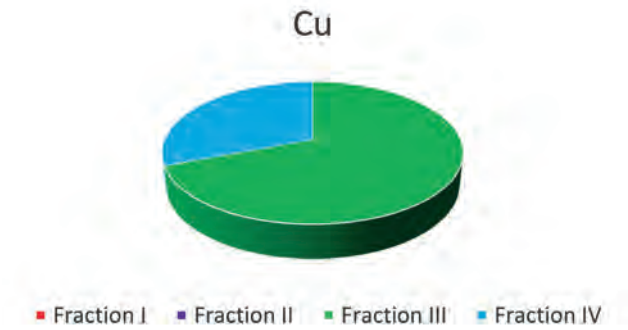

Fig. 3. Average percentage of copper in sewage sludge from the Daleszyce sewage treatment plant depending on the fraction

– for Cr: FIV(55.9%) > FIII(27.8%) > FI(12.3%) > FII(4.0%) (Fig. 4)

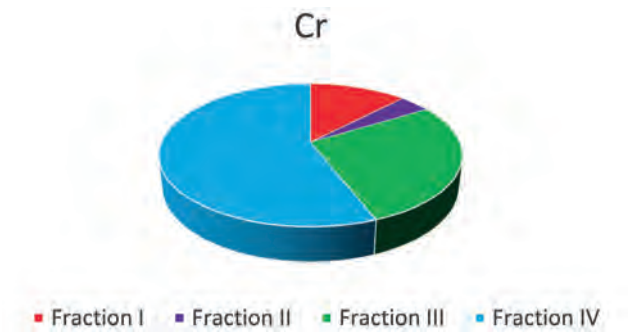

Fig. 4. Average percentage of chromium in sewage sludge from the Daleszyce sewage treatment plant, depending on the fraction

– for Cd: FIII(39.4%) > FIV(31.9%) > FII(16.0%) > FI(12.8%) (Fig. 5)

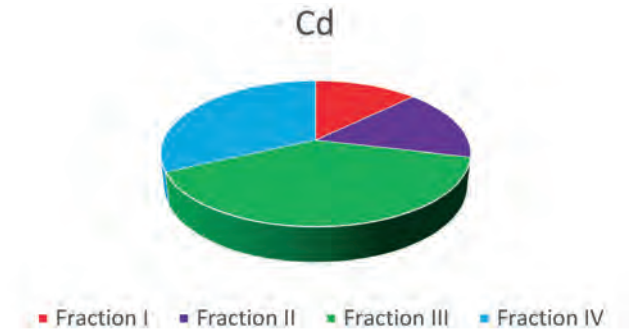

Fig. 5. Average percentage of cadmium in sewage sludge from the Daleszyce WWTP depending on the fraction

– for Ni: FIV(46.1%) > FIII(36.5%) > FII(12.0%) > FII(5.4%) (Fig. 6)

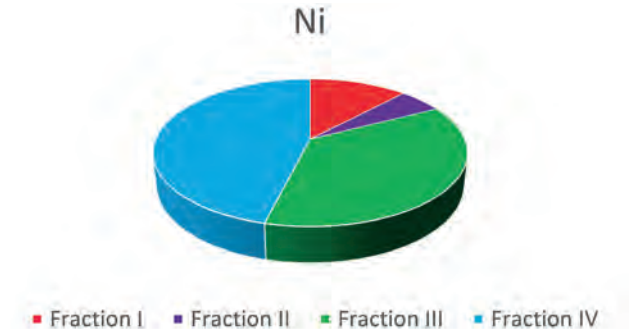

Fig. 6. Average percentage of nickel in sludge from the Daleszyce WWTP depending on the fraction

– for Pb: FIV(95.6%) > FIII(3.8%) > FI(0.6%) > FII(0.0%) (Fig. 7)

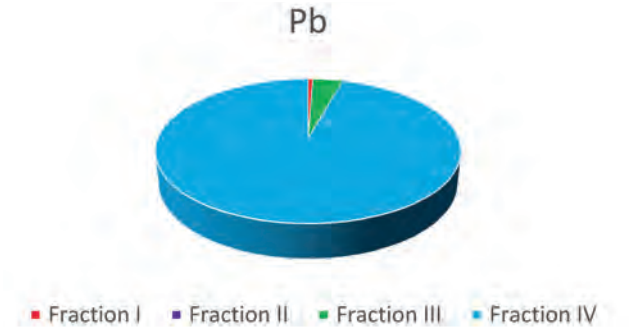

Fig. 7. Average percentage of lead in sewage sludge from the Daleszyce WWTP depending on the fraction

– for Zn: FIII(40.4%) > FIV(25.0%) > FI(18.4%) > FII(16.1%) (Fig. 8)

Fig. 8. Average percentage share of zinc in sludge from the Daleszyce sewage treatment plant depending on the fraction

5. RESULTS

The results obtained allow us to conclude that the content of heavy metals in the tested sediments did not exceed the permissible limits applicable in Poland for sediments intended for natural use, with the exception of zinc, whose maximum permissible content is 2500 mg/kg d.m. In most cases, heavy metals were found in non-mobile fractions, from which they will not get into the soil. The analysis of the mobility of heavy metals is of great importance in assessing the environmental risk of heavy metals. Therefore, it can be concluded that, in terms of the content of heavy metal mobility fractions, sediments are eligible for their natural use. This is one of the three basic criteria to be met by sediments for natural use, in addition to the content of Salmonella bacteria and zero parasite eggs per kg of dry matter. However, it should be considered whether the immobilisation of heavy metals is sufficient and guarantees that there will be no later transfer of metals to mobile forms under the influence of physico-chemical factors such as temperature or electromagnetic radiation. The problem seems to be important, and research on the mobility of heavy metals will continue in further publications.

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OLHA HOMON

EFFECT OF MODERN TEACHING METHODS AND NEW EDUCATIONAL TECHNOLOGIES ON THE CREATION OF EDUCATIONAL MATERIALS AND THE FORMATION OF TEACHING AND EDUCATIONAL COMPLEXES

"KINDERGARTEN – PRIMARY SCHOOL"

WPŁYW NOWOCZESNYCH METOD NAUCZANIA I NOWYCH TECHNOLOGII EDUKACYJNYCH NA TWORZENIE MATERIAŁÓW EDUKACYJNYCH I TWORZENIE KOMPLEKSÓW NAUCZANIA I EDUKACJI

„PRZEDSZKOLE – SZKOŁA PODSTAWOWA"

Structure and Environment No. 2/2020, vol. 12, p. 59 DOI: 10.30540/sae-2020-006

Abstract

On the basis of use of modern research methods, the requirements for designing new types of teaching and educational complexes "Kindergarten – Primary School" were determined. It was established that the form and methods of kindergarten education have a certain analogy with the education in the first grades of primary school, which is one of the factors of feasibility of blocking and cooperation of the senior kindergarten groups with the elementary grades of general education schools and the formation of teaching and educational complexes on this basis, which enables receptiveness to demographic fluctuations and, if necessary, change of the function of kindergarten to the function of primary school, and vice versa – the flexibility and multivariance of the teaching environment is one of main conceptual provisions in building of network and typology of educational facilities at the present stage, on the basis of which the structural elements of school network in massive restrained urban development are formed.

Streszczenie

Na podstawie zastosowania nowoczesnych metod badawczych określono wymagania dotyczące projektowania nowych typów kompleksów dydaktycznych i edukacyjnych „Przedszkole – szkoła podstawowa". Ustalono, że forma i metody edukacji przedszkolnej mają pewną analogię z edukacją w pierwszych klasach szkoły podstawowej, co jest jednym z czynników umożliwiającym blokowanie i współpracę starszych grup przedszkolnych z pierwszymi klasami szkól podstawowych i tworzenie na tej podstawie kompleksów dydaktycznych i edukacyjnych, i może stanowić odpowiedź na zmiany demograficzne oraz w razie potrzeby, zmianę funkcji przedszkola na funkcję szkoły podstawowej i odwrotnie –elastyczność i wielowariantowość środowiska nauczania jest jeden z głównych pojęć koncepcyjnych w budowaniu sieci i typologii placówek oświatowych na obecnym etapie, na podstawie którego powstają elementy strukturalne sieci szkolnej w masowym rozwoju urbanistycznym.

DOMINIKA STAŃCZAK
BEATA JAWORSKA

INFLUENCE OF AGRICULTURAL BIOMASS FLY ASH CEMENT SUBSTITUTION ON THE CARBONATION OF CEMENT AND POLYMER-CEMENT COMPOSITES

WPŁYW POPIOŁU LOTNEGO Z BIOMASY ROLNICZEJ NA KARBONATYZACJĘ KOMPOZYTÓW CEMENTOWYCH I POLIMEROWO-CEMENTOWYCH

Structure and Environment No. 2/2020, vol. 12, p. 66 DOI: 10.30540/sae-2020-007

Abstract

Practical use of a new type of combustion waste such as an agricultural biomass fly ash in the building materials requires an assessment of its performance. The paper presents the investigation results on the influence of cement substitution (5% and 30%) by this ash on the cement and polymer-cement composites resistance to carbonation. The composites resistance was assessed on the basis of carbonation process over time (up to 360 days) using the phenolphthalein method. It was found that fly ash from agricultural biomass increases the susceptibility to carbonation of polymer-cement composites to a lesser extent than cement composites compared to composites containing siliceous coal fly ash.

Streszczenie

Praktyczne wykorzystanie w materiałach budowlanych nowego odpadu, jakim jest popiół lotny z biomasy rolniczej, wymaga oceny jego właściwości użytkowych. W pracy zaprezentowano wyniki badań wpływu substytucji cementu (5% i 30%) tym popiołem na odporność kompozytów cementowych i polimerowo-cementowych na karbonatyzację. Odporność kompozytów oceniono na podstawie przebiegu procesu karbonatyzacji w czasie (do 360 dni) za pomocą metody fenoloftaleinowej. Na podstawie wyników stwierdzono, że popiół lotny z biomasy rolniczej powoduje zwiększenie podatności na karbonatyzację kompozytów polimerowo-cementowych w mniejszym stopniu niż kompozytów cementowych w porównaniu do kompozytów zawierających popiół lotny krzemionkowy.

MIROSLAV BRODŇAN
PETER KOTEŠ

ASSESSMENT OF THE CURRENT STATE OF THE CONCRETE STRUCTURE OF THE TRIBUNE

OCENA BIEŻĄCEGO STANU KONSTRUKCJI BETONOWEJ TRYBUNY

Structure and Environment No. 2/2020, vol. 12, p. 72 DOI: 10.30540/sae-2020-008

Abstract

The paper is focused on diagnostics of reinforced concrete structure of the tribune of Závodisko Bratislava. The structure was realized by a combination of monolithic and prefabricated concrete elements as well as steel load-bearing elements. The complex state of the rough construction was evaluated, including the verification survey of the foundation of the construction. Non-destructive and destructive methods were used. Based on the results of the diagnostics and recalculation, it was decided to further progress the finish of the tribune.

Streszczenie

Artykuł koncentruje się na diagnostyce konstrukcji żelbetowej trybuny zlokalizowanej na „Závodisko Bratysława". Konstrukcja została zrealizowana przez połączenie monolitycznych i prefabrykowanych elementów betonowych oraz stalowych elementów nośnych. Oceniono złożony stan konstrukcji, w tym badanie weryfikacyjne fundamentu konstrukcji. Zastosowano metody nieniszczące i niszczące. Na podstawie wyników diagnostyki i ponownych obliczeń zdecydowano o dalszych działaniach, aby ukończyć trybunę.

AGNIESZKA GRDULSKA
ROBERT KOWALIK

PHARMACEUTICALS IN WATER AND WASTEWATER – OVERVIEW

FARMACEUTYKI W WODACH I ŚCIEKACH

Structure and Environment No. 2/2020, vol. 12, p. 79 DOI: 10.30540/sae-2020-009

Abstract

The paper presents concentrations of pharmaceuticals in surface water and sewage. Special attention was paid to the content of estrogens in municipal sewage and the method of their disposal. Concentrations of various pharmaceuticals in raw and treated wastewater were compared and the pharmaceuticals in different countries and waters were presented in tables. The most frequently identified drugs in sewage are sex hormones (etradiol, ester, ethinylestradiol, 17 β-estradiol) and the antiepileptic drug Carbamazepine. These drugs are difficult to remove from water and therefore appropriate treatment processes are used, such as: adsorption on active carbon, UV irradiation, etc. Contamination of water with pharmaceuticals has a negative impact on the development of aquatic organisms and can lead to serious human health problems.

Streszczenie

W pracy przedstawiono stężenia farmaceutyków w wodach powierzchniowych oraz ściekach. Szczególną uwagę skupiono na zawartości estrogenów w ściekach komunalnych oraz na sposobie ich usuwania. Porównano stężenia różnych farmaceutyków w ściekach surowych oraz ściekach oczyszczonych, a także zostały przedstawione tabelarycznie farmaceutyki występujące w różnych państwach oraz wodach. Najczęściej identyfikowanymi lekami w ściekach są: hormony płciowe (etradiol, estron, etinyloestradiol, 17 β-estradiol) oraz lek przeciwpadaczkowy – Karbamazepina. Leki te są ciężko usuwalne z wód, dlatego też stosuje się odpowiednie procesy ich oczyszczania, takie jak: adsorpcje na węglu aktywnym, naświetlanie promieniami UV itp. Zanieczyszczenia wód farmaceutykami wpływa negatywnie na rozwój organizmów wodnych, a także może prowadzić do poważnych problemów zdrowia ludzkiego.

ROBERT KOWALIK
JAROSŁAW GAWDZIK
BARBARA GAWDZIK
ALICJA GAWDZIK

ANALYSIS OF THE MOBILITY OF HEAVY METALS IN SLUDGE FOR THE SEWAGE TREATMENT PLANT IN DALESZYCE

ANALIZA MOBILNOŚCI METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH DLA OCZYSZCZALNI ŚCIEKÓW W DALESZYCACH

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Abstract

Sewage sludge is a by-product of wastewater treatment processes. However, it has high fertilising and soil-forming properties, but it cannot always be used for this purpose. The two main criteria limiting their natural use are heavy metals and parasite eggs. Sewage sludge taken from the Daleszyce wastewater treatment plant has been analysed for heavy metals. For this purpose a space analysis was performed to divide the total metal content into four mobility fractions. The mobility issue determines the ability of an element, or one of its forms, to move in the environment. The studies were performed using a four-stage BCR procedure. The results were analyzed and compared to the limits applicable in Poland for sewage sludge intended for environmental use.

Streszczenie

Osady ściekowe są produktem ubocznym procesów oczyszczania ścieków. Wykazują jednak wysokie właściwości nawozowe oraz glebotwórcze, jednak nie zawsze mogą być one wykorzystane w tym celu. Dwa główne kryteria ograniczające ich przyrodnicze wykorzystanie to zawartość metali ciężkich oraz jaj pasożytów. Osady ściekowe pobrane z oczyszczalni ścieków w Daleszycach zostały poddane analizie zawartości metali ciężkich. W tym celu wykonano analizę specjacyjną, pozwalającą podzielić całkowitą zawartość metali na cztery frakcje mobilności. Mobilność określa zdolność pierwiastka, lub któregoś z jego form, do przemieszczania się w środowisku. Badania wykonano, stosując czteroetapową procedurę BCR. Wyniki poddano analizie i porównano do limitów obowiązujących w Polsce dla osadów przeznaczonych do wykorzystania przyrodniczego.

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