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A STUDY ON CARBONATION DEPTH PREDICTION FOR CONCRETE MADE WITH GBFS CEMENT AND FA ADDITION

BADANIE DOTYCZĄCE PROGNOZOWANIA GŁĘBOKOŚCI KARBONATYZACJI BETONU WYKONANEGO Z CEMENTU GBFS Z DODATKIEM FA

Maciej Lech^{1*}, Tomasz Juszczak², Jerzy Wawrzeńczyk¹ ¹Kielce University of Technology, ²Grolman Poland

Abstract

This paper presents the results of the examination of accelerated carbonation of concrete mixes made with CEM III / A blast furnace slag cement and the addition of fly ash. The test program was developed using an experiment design with two factors: a water-binder ratio and a fly-ash / cement ratio. Carbonation depth measurements were carried out according to FprCEN/TS 12390-12 (CO₂ concentration = 4%, T = 20°C, RH = 55%). Associated tests were also carried out, including compressive strength, porosity, depth of absorption, water penetration depth, and capillary suction. Analysis of the test results allowed us to determine the influence of binder composition on concrete carbonization depth

under standard test conditions. The results show that the carbonation depth increases along with the increase in the W/B ratio and as a result of the increase in the fly ash content in the binder.

A mathematical model was developed to describe the carbonation process over time, which can predict the depth and rate of concrete carbonation. Furthermore, it was found that there is no close relationship between other properties tested (e.g. strength) and the depth of the carbonated concrete.

Keywords: concrete carbonation, carbonation model, carbonation accelerated testing, GBFS cement, FA addition

Streszczenie

W pracy przedstawiono wyniki badań przyspieszonej karbonatyzacji mieszanek betonowych wytworzonych cementem żużlowym wielkopiecowym CEM III/A z dodatkiem popiołu lotnego. Program badań został opracowany na podstawie projektu eksperymentu z dwoma czynnikami: stosunkiem wody do spoiwa oraz stosunkiem popiołu lotnego do cementu. Pomiary głębokości karbonatyzacji przeprowadzono zgodnie z FprCEN/TS 12390-12 (stężenie $CO_2 = 4\%$, T = 20°C, RH = 55%). Przeprowadzono również powiązane testy, w tym wytrzymałości na ściskanie, porowatości, głębokości absorpcji, głębokości penetracji wody i ssania kapilarnego. Analiza wyników badań pozwoliła na określenie wpływu składu spoiwa na głębokość karbonatyzacji betonu w standardowych warunkach testowych. Wyniki wskazują, że wraz ze wzrostem stosunku W/B oraz zawartością popiołu lotnego w spoiwie wzrasta głębokość karbonatyzacji.

Opracowano model matematyczny do opisu procesu karbonatyzacji w czasie, który umożliwia przewidywanie głębokości i szybkości karbonatyzacji betonu. Ponadto stwierdzono, że nie ma ścisłego związku między innymi badanymi właściwościami (np. wytrzymałością) a głębokością betonu karbonatyzowanego.

Slowa kluczowe: karbonatyzacja betonu, model karbonatyzacji, przyspieszone badania karbonatyzacji, cement GBFS, dodatek FA

1. INTRODUCTION

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Carbonation depth is a key parameter in the analysis of the service life of reinforced concrete structures and can well characterize the carbonation rate [1-4]. Research on the scope and rate of the carbonation process is of particular interest in the issues of steel reinforcement corrosion and concrete scaling resistance.

The wide range of factors that influence carbonation can be grouped into four categories consisting of mix composition, material properties, environmental factors, and serviceability conditions [5].

Information on the rate and carbonation depth can be obtained in different ways: (a) direct measurement of the carbonation depth on the structure, (b) accelerated carbonation testing with specimens from the structure (e.g. cores), (c) from reference data, if the concrete composition is known (e.g. the type of cement and the water-cement ratio) [6].

Much effort was made to describe the carbonation rate and depth with a variety of models. Czarnecki and Woyciechowski [7] presented a critical review of articles related to mathematical models of carbonation. Ekolu [5] presented a different approach to modeling the carbonation process. Generally, these models may be divided into different categories: empirical models, statistical models, and numerical models, simulation ones. Most of the models in the references are experiential and their mathematical expressions relate the depth of carbonation to the square root of time [1]. Czarnecki and Woyciechowski [7-9] found that in the case of concrete made with the addition of fly ash, the hyperbolic function gives a better description of the carbonation process. Although infinite in time, the carbonation process is limited in the space of concrete.

Under natural conditions, the concrete is alternately dry and wet, and carbonation can continue into the concrete until the rewetting front reaches the current carbonation depth, so any subsequent cycle lasts longer. If concrete damping periods are too short, carbonation will not proceed and as a consequence the front will set at a constant level [7, 8].

With time of exposure, the rate of the carbonation process slows down, as carbon dioxide cannot reach the noncarbonated concrete layer. According to Fagerlund [10], the reason for this may be the diffusion of alkali from the interior of the concrete to the surface, which is opposite to the diffusion of CO_2 .

An important problem for practice is to determine the correlations between accelerated and natural tests, which are needed to predict behavior in a real environment. A detailed discussion of this issue was presented by Lollini and Redaelli [31]. The results of accelerated tests cannot be directly used to design the service life of an RC structure, since they do not take into account the real exposure conditions (such as, for instance, the actual relative humidity, temperature, wetting event) and the curing. The literature provides suggestions for calculation procedures intended for the extrapolation of accelerated test results to natural conditions [21, 22]. A general relationship between them cannot be assessed, since it is strongly affected by exposure conditions [5].

Many researchers have attempted to determine indicators on the basis of which the depth of carbonation could be reliably predicted [11, 12]. However, others believe that general indicators for potential durability, such as water porosity, gas permeability, and chloride diffusion, are not reliable in assessing the resistance of concrete to carbonation [13].

The most common attitude in concrete design and concrete durability control could be named a prescriptive approach. A typical example of this approach is the EN 206 standard [14]. For carbonationinduced corrosion, four classes are defined and described: XC1, XC2, XC3 and XC4. However, this attitude has many disadvantages, as it does not take into account the needs related to the development of up-to-date concrete technologies in terms of sustained development. Harrison [15] analyzed the behavior of hundreds of various concretes from the point of view of the rate and extent of carbonation. He concluded that in many cases the concretes had better parameters than expected, thus demonstrating from a practical and economical point of view the possibility of cheaper concrete production (higher water-cement ratio, less binder, and other cheap components).

In the case of contemporary concretes made with the use of unconventional materials (other binder than those specified in EN-206 [14], there is no information available on what concrete carbonation looks like under natural exposition conditions. Conclusions can be drawn mainly on the basis of the results of accelerated carbonation tests [16-18]. Under laboratory accelerated carbonation tests, testing is usually performed using significantly higher carbon dioxide concentrations to obtain results in possibly the shortest time. Concentrations are usually 3-4% [17, 18] and sometimes very high up to 10-50% [19].

A very important issue, in line with the sustainable development postulate, is the use of various mineral additives and the design of concretes taking into account their durability in a given environment. Therefore, the standard EN-206 introduces three

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concepts for the use of additives: the k-factor concept [20], the equivalent concrete performance concept, the equivalent combination performance concept. The currently common reasoning related to the functioning of these concepts and their application (with examples) is presented in Report CEN/TR 16639: 2014 [23].

It is generally stated that, both technically and economically, the use of BFS or FA in concrete has many advantages. The results of the literature show that concretes with FA or BFS are more resistant to environmental loads such as chloride or sulfate attacks [24, 30]. On the contrary, they are often found to have a lower resistance to carbonation compared to Portland cement concretes [24]. Carbonation is clearly a key point to be analyzed for these kinds of material.

Partial replacement of OPC by BFS or FA alters thus the reaction kinetics and reaction degrees [19]. Previous research has already shown that the microstructure of BFS and FA concrete develops slower and the durability behavior is different from that of OPC concrete.

The calcium hydroxide (CH) content in BFS concrete is known to be drastically lower than that of ordinary Portland cement concrete. In the long term, BFS concrete tends to suffer more from carbonation attack due to its low alkalinity [25]. However, in terms of carbonation resistance, a general decrease in concrete behavior is observed when the cement clinker is replaced by type II additions. A work by Sisomphon and Frank [25] shows that the pozzolanic mixtures studied have a lower carbonation resistance and therefore also have a shorter induction period for carbonation. Rozière et al. [13] point out that from concrete mixtures made with the same water/binder ratio a negative effect of fly-ash can be deduced. Regarding blast furnace slag, Gruyaert et al. [19] conclude that carbonation coefficients increase as the replacement of cement by slag in concrete increases. Younsia et al. [24] also report huge differences in accelerated carbonation kinetics between water-cured and air-cured concretes, especially in the case of concretes with blast furnace slag.

Carbonation coefficients increase as the replacement of cement by slag in concrete increases. The carbonation resistance of BFS concrete is poor and although curing for longer times (up to 3 months) increases the resistance, performance remains low, especially for cement replacement levels of 70% and above [19].

The effect of the slag dosage ratio on the carbonization depth of high-performance concrete (water-binder ratios of 0.25-0.35) is small, and the carbonation depth ratio does not increase significantly with the change

of the mixed quantity significantly; dosage increased from 45% to 60%, the carbonation depth increases slightly, which shows that the influence of changing the slag dosage on the carbonation performance of concrete is very small [11].

Carbonation makes BFS concrete more vulnerable to scaling under the combined load of frost attack and de-icing salts, compared to ordinary Portland cement mixtures [30]. As appears from Deja [26], Giergiczny et al. [27], Wawrzeńczyk [28], the increased content of BFS in the binder results in the deterioration of the structure of the air pores, thus deteriorating the resistance to concrete scaling.

This article presents the results of accelerated carbonation tests of concretes made with CEM III/A blast furnace slag cement and the addition of fly ash. Therefore, the influence of two material factors (GBSF and FA) with a potentially negative impact on the course of the carbonation process was analyzed. The aim was to develop mathematical models to predict the depth of carbonation and the rate of carbonation depending on the binder composition and the water-binder ratio.

2. MATERIALS AND METHODS

2.1. Materials

- The following materials were used in the testing:
- CEM III/A 42.5N blast furnace cement,
- silicone fly-ash,
- crushed limestone grit of 2-8 mm and 8-16 mm,
- plasticizer or superplasticizer.

The characteristics of cement and fly ash are presented in Table 1. Cement contains 50% slag.

Table 1. Results of the analysis of cement and fly ash

Parameter	Unit	Cement	FA
Humidity	%		0.3
Loss on ignition	%	2.99	3.54
Insoluble particles	%	0.59	16.6
Silica (SiO ₂)	%	26.67	52.0
Alumina (Al ₂ O ₃)	%	5.6	21.8
Iron oxide (Fe ₂ O ₃)	%	2.28	7.1
Calcium oxide (CaO)	%	53.83	4.32
Magnesium oxide (MgO)	%	3.85	2.48
Sulphur trioxide (SO ₃)	%		0.57
Sodium oxide (Na ₂ 0)	%	0.28	1.15
Potassium oxide (K ₂ 0)	%	0.79	2.70
Sodium oxide (Na ₂ 0) eq	%	0.8	2.93
CI⊤	%	0.064	0.006
Disposable calcium oxide (CaO)	%		0.08
Blaine	cm²/g		2.963
Density	g/cm ³		2.05
x'	μm		66.75

2.2. Testing program

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The testing program was developed using experimental planning theory. In this examination, a bifactor 9-point experimentation plan was applied. This attitude allows us to determine the relationship between the examined characteristic (Y) and the composition factors (X1, X2) as a regression function in the form of a quadratic polynomial:

$$Y = a0 + a1 \cdot X1 + a2 \cdot X2 + a11 \cdot (X1)^{2} + a22 \cdot (X2)^{2} + a12 \cdot X1 \cdot X2$$
(1)

The function could be visualized in the form of a contour or a 3D plot. This provides the possibility of a graphical presentation and identification of the relationship between the feature being examined and composition factors (water-cement ratio and fly-ash percentage).

The following investigated factors were adopted:

- water-to-binder ratio (W/B), code name X1,
- fly-ash additive content in relation to cement (FA% = FA/C), code name X2,

The coded values are to be:

- $X1 = (W/B-0.55)/0.10; X1 \in <-1, +1>,$
- $X2 = (FA/C-0.15)/0.15; X2 \in <-1,+1>,$ respectively.



Fig. 1. Experimental planning scheme

The experimental planning scheme is shown in Figure 1. The coded and natural planning matrix is shown in Table 2.

Ref.	X1	X2	W/B	FA%
1	-1	-1	0.45	0
2	0	-1	0.55	0
3	1	-1	0.65	0
4	1	0	0.65	15
5	1	1	0.65	30
6	0	1	0.55	30
7	-1	1	0.45	30
8	-1	0	0.45	15
9	0	0	0.55	15
10	0	0	0.55	15

The characteristics examined were the following:

- concrete compressive strength, f_c ;
- carbonation depth, d_k ;
- porosity, *p*;
- water absorption, n_w ;
- water penetration depth, D_p ;
- capillary suction, n_{cap} .

2.3. Testing Methods

Concrete mixes were prepared in a laboratory forced mixing device. The sequence of dosing of the components was as follows: dry components, portion of batch water and admixture, and remaining portion of water. The amount of plasticizing admixture was dosed as much to obtain the consistency of S3. The total mixing time was approximately 4 minutes. Once consistency was measured, test samples were prepared as follows:

- 15 cm side cubic samples to test compressive strength and water penetration (9 samples),
- 8×8×35 cm beam samples to test carbonation (3 samples),
- 100 mm side cubic samples to determine water absorption, capillary suction, and porosity (6 samples),

All samples were stored for up to 28 days in water at 20°C. Compressive strength tests were performed after 28 and 90 curing days according to the PN-EN 12390-3 standard.

Porosity characteristics tests were carried out using 100 mm side cubic samples. The samples were soaked with water for 7 days and their weight and volume were determined using the hydrostatic method. The samples were dried to constant weight at 105°C for 48 hours. The samples were placed in an airtight container, air was evacuated by vacuuming and then the sample container was gradually filled with degassed water by heating to 60°C. The samples remained in the container with water for the next 48 hours and then their mass was determined. On the basis of the results obtained, the mass and volume water absorption and the porosity p as volume water absorption under vacuum were calculated.

Capillary suction tests were performed using a single $15 \times 15 \times 5$ cm sample cut from a cubic sample, once the depth of penetration of the water was tested. The samples were stored under laboratory ambient conditions (T = 20°C ±2°C and RH = 65°C ±5%) up to 4 weeks. The side faces of the samples were coated with a resin. The samples were placed on a sponge base in a bath tub filled with water, with the water level 5 cm above the face of the lower sample. Samples were taken from the tub, dried with a rag, and sample weights were determined. These tests were repeated in periods for 8 days.

Capillary suction tests were performed on a $15 \times 15 \times 5$ cm sample cut from a cubic sample after testing the depth of penetration of the water. The samples were stored under laboratory conditions (T = 20°C ± 2°C and RH = 65°C ± 5%) for up to 4 weeks. The side surfaces of the samples were painted with resin. The samples were placed in a bath of water on a sponge cushion so that the water level was 5 mm above the bottom surface of the sample. The samples were taken from the bath, wiped with a cloth, and weighed. These tests were repeated periodically until day 8.

Concrete carbonation tests were carried out using the accelerated method, as prescribed by FprCEN/ TS 12390-12 [17], and applying a special chamber equipped with the following systems:

- temperature control system with the temperature control range of 16÷30°C (±1°C);
- humidity control system with the humidity control range of 30÷90% (±1% RH);
- constant level carbon dioxide concentration control system with the control range of 0÷5%;
- gas transmission system inside the chamber (air circulation);

- recording system of the chamber's inside conditions measurements results.

The testing chamber and control panel views are shown in photo 1.

The test samples were cured for 28 days in water and then for another 14 days in air at a temperature of 18-25°C and a relative humidity of 50-65%. After this period, a petroleum wax coat was applied to the top and lower faces of the sample and two front walls. The two other sample faces were left in a natural condition, and carbonized layer depth measurements were made. Subsequently, the prepared samples were placed in the airtight carbonization chamber equipped with a forced air flow system, with a carbon dioxide concentration of $4.0\% \pm 0.5\%$, temperature of $20^{\circ}C \pm 2^{\circ}C$ and a relative humidity of 55% $\pm 5\%$. Samples were arranged in the chamber to make free air flow around carbon dioxide-saturated faces possible. The carbonation depth examination was carried out five times using three concrete beam samples after 14, 28, 42, 56, and 70 days of storage inside the carbonation chamber. After determined time beam samples were broken to obtain some 50 mm thick pieces (photo 2). The remaining portion of the beam



Photo 1. Views of the chamber (a) and control panel (b)



Photo 2. Method of preparing the samples for examination: (a) block splitter to break a sample,(b) breaking face perpendicular to nonprotected surfaces, (c) broken sample view

was protected as described above and placed in the chamber until the next examination date.

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A phenolphthalein solution was sprayed on the surface of the fresh fracture of the sample, which causes the color of the concrete surface to change to a violet color. After about 60 minutes, the samples were photographed. The carbonation depth was determined by taking measurements on photographs using the NIS-Elements software. First, each photograph was calibrated. The arrangement of the measuring lines on the break surface is shown in Figure 2. Measurements were made at five points on one surface with an accuracy of 0.1 mm, which means a total of 10 measurements on one sample. The carbonation depth for a given sample is the average result. For each series of concrete, the mean value of the carbonation depth and the standard deviation were calculated, taking into account the results obtained on 3 samples. Based on the statistical test, it was checked whether there were outliers (gross errors). Where such occurred, they were ignored in the calculations of the final *dk* value for a given concrete tested.



Fig. 2. Arrangement of the measuring points in the beam break

3. TEST RESULTS ANALYSIS

The results of the carbonation depth and accompanying examinations of the tested concretes are shown in Table 3.

Ref.	Compressiv	ve strength	Carbonation depth				Water penetration	Water absorption	Porosity	Capillary suction	
	<i>fс</i> -28 МРа	<i>fc</i> -90 MPa	d _k -1 mm	d _k -2 mm	d _k -3 mm	d _k -4 mm	d _k -5 mm	D _p mm	n _w %	Р %	n _{cap} g/m²
1	62.0	67.9	2.7	4.0	4.9	6.2	6.0	9	3.3	8.6	1187
2	49.0	55.6	5.0	7.5	8.2	10.3	10.5	14	3.8	10.2	2359
3	41.4	47.2	6.4	9.1	10.3	12.6	12.9	14	4.4	11.7	2531
4	34.6	43.9	8.2	10.4	13.0	15.4	16.3	24	4.5	11.6	2500
5	30.1	38.1	9.7	13.0	16.0	18.4	19.2	20	4.8	12.6	3234
6	40.5	46.1	7.3	9.6	11.3	13.6	14.3	14	4.1	10.5	3078
7	58.5	66.6	5.3	7.5	8.3	9.6	10.8	14	3.2	8.2	1000
8	58.2	65.8	4.7	6.5	7.2	8.7	9.3	10	3.4	8.7	1266
9	47.2	54.8	6.0	8.7	9.6	11.4	12.1	12	3.9	10.0	1734
10	47.9	55.7	6.4	8.3	10.1	11.9	11.9	10	4.0	10,2	1484

Table 3. Average concrete properties results

3.1. Carbonation depth and concrete composition relations

The influence of concrete composition on the depth of carbonation was analyzed by determining the relationships in the regression function form of the $d_{ki} = f$ (X1, X2). Regression functions in the form of incomplete quadratic polynomials (higher-

order components turned out to be irrelevant) were determined using the *Design Expert 8* software. The a_i regression and the *R* correlation coefficients for specific examination dates (measurements 1 through 5) are shown in Table 4.



Table 4. The regression coefficients at and R for the function $d_{ki} = f(X1, X2)$

Regression	Examination ref.						
coefficients	<i>d</i> _{<i>k</i>} – 1	$d_k - 2$	<i>d</i> _{<i>k</i>} -3	$d_k - 4$	<i>d</i> _{<i>k</i>} - 5		
a0	6.17	8.46	9.89	11.81	12.31		
a1	1.93	2.42	3.15	3.64	3.72		
a2	1.37	1.58	2.03	2.10	2.46		
a12	0.17	0.10	0.57	0.62	0.36		
R	0.98	0.97	0.99	0.99	0.99		

The contour plots 3 and 4 show examples of dependencies. As appears from the comparative analysis of those plots, the carbonation depth depends on both the water-to-binder ratio (W/B) and the fly-ash (FA) content in the binder. The lower the W/B ratio, the concrete is more watertight, and thus the carbonation depth is lower. Increased fly-ash content at a given W/B ratio results in higher porosity and larger carbonation extend.



Fig. 3. Influence of concrete composition on the depth of carbonation d_k -1 after 14 days of exposure in the CO₂ chamber



Fig. 4. Influence of concrete composition on the depth of carbonation of d_k - 5 after 70 days of exposure in the CO₂ chamber

3.2. Relation between carbonation and hardened concrete properties

The interactions found between the specific properties determined for the tested concretes are illustrated in Figure 5 as a matrix chart. Relations shown on the graph indicate the presence of quite good correlations; however, these are not sufficiently close correlations that could be a basis for determining the carbonation depth. Neither the 'volume-related' characteristics, such as water absorption n_w and porosity p, nor the 'surface-related' characteristics, such as D_p water pressure penetration depths and capillary suction n_{cap} , create sufficiently good indicators of carbonation ratios.



Fig. 5. Matrix diagram illustrating relations between concrete properties

The relationship between the depth of carbonation dk and the strength of the concrete fc-28 and various percentages of *FA* ash are presented in Figure 6.



Fig. 6. Relation between the depth of carbonation of d_k and the concrete strength of fc-28 and the different percentages of FA ash content

It could be seen that the higher the strength, the lower the depth of carbonation. However, no simple linear relationship is clear. A trend line shift related to the fly ash content is visible: a higher fly ash content with the same concrete strength results in an increased carbonation depth, which could be explained by modifications in the concrete porosity structure.

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3.3. Carbonation depth and exposure time relations

The relationship between carbonation depth d_k and exposure time to carbon dioxide in the carbonation chamber is shown in Figure 7. In standard time, the depth of the d_k ranged from 6.0 mm to 12.8 mm for the CEM III concrete, from 9.3 mm to 16.3 mm with a 15% fly ash content and from 10.8 mm to 19.2 mm with a 30% ash content.



Fig. 7. Relation between the depth of carbonation of d_k and the exposure time in the CO₂ chamber

3.4. General carbonation model

The following results from the graph shown in Figure 7:

- The deeper the carbonation depth after 14 days, the higher the depth in the later period.
- The depth of carbonation after 14 days depends on the concrete composition (W/B, F/A%) that was manifested in the contour plot no. 8.
- The growth rate of the carbonation depth *dk* depends not only on the exposure time *t* but also on the concrete composition.
- Analysis of the relation d_k and the exposure time relation indicated the function $d_k(t) = a + K \cdot \sqrt{t}$ describes this relation in the best for a specific concrete.

The generalized function describing the relation of the depth of dk() and the factors examined shall be composed of two sections:

$$d_{k}\left(\frac{W}{B}, FA\%, t\right) = f\left(\frac{W}{B}, FA\%\right) + g\left(\frac{W}{B}, FA\%\right) \cdot \sqrt{t}$$

$$(2)$$

The functions f() and g() in the form of polynomials were adopted. The calculations of the regression coefficients were carried out using the *Statistica* software, and the following relations were obtained for natural values.

$$d_{k}\left(\frac{W}{B}, FA\%, t\right) = 0.709 - 0.126 \cdot \frac{W}{B} - 8.02 \cdot FA\% + 22.417 \cdot \frac{W}{B} \cdot FA\% + (3) + \left(-1.71 + 4.203 \cdot \frac{W}{B} + 1.258 \cdot FA\%\right) \cdot \sqrt{t}$$

The comparison of the measured dk with calculated values of the d_k () function is shown in Figure 8.



Fig. 8. Relation between measured d_k and calculated values $d_k()$ function

3.5. Carbonation rate

The k carbonation rate was determined graphically by transforming Figure 7. The average carbonation depth at each exposure time was plotted against the square root of the exposure time in days, and linear regression was performed through the points according to the classical formula:

$$d_k = a + K \cdot \sqrt{t} \tag{4}$$





Fig. 9. The relationship between the carbonation rate index K and factors X1, X2 examined

The slope of the linear function illustrates the *K* carbonation rate index. Carbonation rates varied from 0.8 to 2.0 mm/day^{0.5} for the tested concretes. The relationship between the carbonation rate *K* and the factors examined X1, X2 is shown in Figure 9. The contour line arrangement shows that the carbonation rate depends on both the *W/B* ratio and the amount of *FA*% fly-ash additive. Therefore, it is

similar to the contour line arrangement illustrated in Figures 3 and 4.

4. CONCLUSIONS

This article presents the results of accelerated carbonation tests of concretes made with CEM III / A blast furnace slag cement and the addition of fly ash. Therefore, the influence of two material factors (GBSF and FA) with a potentially negative impact on the course of the carbonation process was analyzed.

The results of the test are as follows:

- 1. The carbonation depth increases with increasing the water-binder W/B ratio and as a result of increasing the fly-ash content in the binder.
- 2. It was found that there is no close relationship between other properties tested (for example, strength) and the depth of carbonated concrete.
- 3. The mathematical model of carbonation over time that can predict the depth of carbonation. Analysis of the relation d_k and exposure time relation indicated the function $d_k(t) = a + K \cdot \sqrt{t}$ describes this relation in the best for a specific concrete.
- 4. It was found that the concrete carbonation rate *K* is not a constant value as it depends on both the *W*/*B* ratio and the fly-ash content in the binder.

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MANAGEMENT OF SALT HYDRATES IN PHOTOVOLTAIC INSTALLATIONS IN LIGHT OF EXISTING ENVIRONMENTAL LEGISLATION

ZARZĄDZANIE HYDRATAMI SOLI WYKORZYSTANYMI W INSTALACJACH FOTOWOLTAICZNYCH W ŚWIETLE OBOWIĄZUJĄCYCH PRZEPISÓW DOTYCZĄCYCH OCHRONY ŚRODOWISKA

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Abstract

This paper discusses an environmental criterion rarely addressed in the literature for the selection of salt hydrates for use in photovoltaic installations as Phase change materials. The aim of the paper is to assess the possibility of utilization of used salt hydrates from photovoltaic installations according to current Polish legal requirements concerning the environment. The properties of the composition components of hydrated salts were discussed in terms of their safety for the environment before and after the period of exploitation in photovoltaic panels. A method of dealing with used salt hydrates was proposed and a waste code was assigned. It has been established that spent salt hydrates will be allowed to be collected in no-outflow tanks and accepted at liquid waste collection points, which operate at water supply and sewerage companies, and the load of permissible pollutants should not exceed the value for industrial sewage.

Keywords: photovoltaic, environmental, PCM, utilization, salt hydrates

Streszczenie

W artykule omówiono rzadko poruszane w literaturze kryterium środowiskowe wyboru hydratów solnych do zastosowania w instalacjach fotowoltaicznych jako materiałów zmiennofazowych (PCM). Celem pracy jest ocena możliwości utylizacji zużytych hydratów soli z instalacji fotowoltaicznych zgodnie z aktualnymi polskimi wymaganiami prawnymi dotyczącymi środowiska. Omówiono właściwości składników kompozycyjnych soli uwodnionych pod kątem ich bezpieczeństwa dla środowiska przed i po okresie eksploatacji w panelach fotowoltaicznych. Zaproponowano sposób postępowania ze zużytymi hydratami solnymi i nadano im kod odpadu. Ustalono, że zużyte hydraty solne będą mogły być gromadzone w zbiornikach bezodpływowych i przyjmowane w punktach gromadzenia nieczystości ciekłych, działających przy przedsiębiorstwach wodociągowo-kanalizacyjnych, a ładunek dopuszczalnych zanieczyszczeń nie powinien przekraczać wartości dla ścieków przemysłowych.

Słowa kluczowe: fotowoltaika, środowisko, PCM, utylizacja, hydraty solne

1. INTRODUCTION

Solar energy is one of the most promising renewable energy sources because it is free, available in all locations and non-polluting [1]. There are many types of technologies used to produce electricity based on the principle of photovoltaics. The main technology is crystalline silicon used commercially. The efficiency of silicon solar cells is in the range of 18-22% with an upward theoretical limit of 33% [2]. Other technologies are still being explored to produce more efficient solar cells [3]. Of particular interest in the scientific world is the use of salt hydrates as phase change materials (PCM) for thermal energy storage in photovoltaic systems [4-7]. The performance of classical systems depends on: load resistance, sunlight intensity, temperature cell, shading and crystal structure [8]. When the cell temperature rises above its standard operating temperature (25°C), the panel operates less efficiently and efficiency losses can range from 0.3-0.4% per degree [8]. It is possible to improve the efficiency of the panels by using specially dedicated storage with low-temperature phase-change material in PV modules. For this purpose, hydrated salts are placed in carbon nanotubes, for example [9]. The PV module generates heat through dedicated storage, thus it is possible to convert more of the stored heat into electricity using the Seebeck effect [10].

Salt hydrates, which make up a large portion of inorganic PCM, have a number of beneficial properties that predispose them to applications in solar heating systems [4, 11]. These include: low price, large-scale availability non-toxicity, good compatibility with materials thermoplastic, high latent heat of phase change per unit volume, high thermal conductivity, low volume change with dehydration and thermal hydration [11-15]. For photovoltaic panel systems, salt hydrates are used with well-defined phase transition temperature ranges that must meet practical applications. If these cannot be met, the salt hydrates can be mixed to adjust their melting point (MLT). The most common salt hydrates used in photovoltaic installations are sodium sulfate decahydrate (MLT = 32.4°C) [16], calcium chloride hexahydrate (MLT = $24^{\circ}C$; $30^{\circ}C$) [17] and magnesium chloride hexahydrate (MLT = 58° C) [16]. The most commonly cited problems with the use of salt hydrates include: incongruent and semi-congruent melting resulting in irreversible dehydration and loss of efficiency and difficulty in crystal nucleation, overcooling and corrosive properties [15]. These properties can be continuously improved, e.g. by combining PCM with porous materials the problems of phase separation and leakage during phase transformation are solved. The use of nanoparticle additives improves the thermal conductivity and reduces the subcooling of most hydrates [18].

On the one hand, salt hydrates are considered to be non-toxic substances [15] on the other hand, it seems obvious that the toxicity of a substance is determined by its dose [19]. It is also an indisputable fact that after use, salt hydrates will constitute waste that requires disposal. In literature, the authors [19, 20] indicate that environmental safety is one of the most important criteria for selecting hydrates salts. Donkers et al. [19] emphasize that the safety assessment of hydrates should be evaluated on a case-by-case basis. The authors write that there are salt hydrates that are clearly listed as toxic in the Material Safety Data Sheets (MSDS) [19, 20]. In addition, some of them can react to form by-products such as acids HCl, H₂S [20] whether oxidizing substances $(Ca(ClO_4)_2)$, CrCl₂ and FeCl₂[19, 20]. In addition, the authors [9, 19] indicate that for all hydrates, the stability of the material should be considered in terms of service life. This is because it cannot be ruled out that the properties of salt hydrates and their reaction with the material will not change after years of use. Zbair and Bennici [20] write that most salts are compatible for long-term exposure with stainless steel. However, contact of some salt hydrates with carbon steel and aluminum can lead to modification of the carrier material.

In spite of the fact that salt hydrates are still one of the top topics in the field of renewable energy sources, only in a publications authors pay attention to the importance of the environmental criterion of their selection [19, 20]. There is a lack of information in the literature regarding guidelines for handling hydrates at the selection stage and before and after their operational life. The authors also did not reach a paper that evaluated the disposal options for spent hydrated salts. This seems to be a key element of the environmental criterion, especially in countries where environmental policy is very restrictive. The problem is also becoming relevant in Poland, where fossil fuels are being abandoned and renewable energy sources are gaining in importance.

In view of the above, the authors analyse in the publication how to deal with salt hydrates from photovoltaic installations in accordance with Polish environmental legislation at the stage of their selection, before and after operation. Then they present the concept of disposal of used salt hydrates.

2. ENVIRONMENTAL CRITERION FOR SELECTION OF HYDRATED SALTS

One of the most important criteria for the selection of hydrated salts as Thermochemical Storage Materials (TCMs) in PV plants is the evaluation of their environmental safety. The selection of suitable substances should take into account their properties both before and after the operation period. Hydrated salt compositions should be selected in such a way that they do not constitute hazardous waste after use and have as many characteristics as possible of inert waste in the meaning of the Act on Waste [21]. It is important that these substances have a stable chemical composition, do not undergo biodegradation processes, do not adversely affect the matter they come into contact with, do not pollute the environment and the negative impact of the leachate on the environment is insignificant, do not pose a threat to the quality of surface water, groundwater, soil and ground. In case of mixtures of substances, all environmentally hazardous properties should be assessed using the concentration limits of the components of the mixture classified as environmentally hazardous substances [22]. The characteristics of a substance can be assessed on the basis of Safety Data Sheets, which are the basic document defining the properties of a chemical and its scope is determined by the European Parliament Regulation No. 1907/2006 on the Registration, Evaluation, Authorization and Restriction of Chemical Sales. According to the regulation 1907/2006/WE The Safety Data Sheet of a chemical substance is the main tool for the flow of information on hazards and risk management in the marketing of these substances. On its basis we can assess: what environmental legislation the substance is subject to, procedures in case of accidental release into the environment, handling and storage of the substance, chemical stability, reactivity and possibility of hazardous reactions, hazardous properties of salts, toxicity of the substance for organisms including bioaccumulation and susceptibility to degradation in the aquatic environment, mobility in soil, waste management.

3. DEALING WITH SALT HYDRATES USED IN PHOTOVOLTAIC INSTALLATIONS BEFORE AND AFTER THEIR EXPLOITATION IN THE LIGHT OF LEGAL ACTS 3.1. Before the period of operation

In addition to the selection of environmentally safe components of hydrated salts according to the criteria discussed in section 2, the appropriate way of handling such substances when designing photovoltaic installations is important. Investors should make sure that the designed installation will not be included in the Regulation of the Minister of Environment of 27 August 2014 on types of installations that may cause significant pollution of particular natural elements or the environment as a whole [23]. Next, they should set waste prevention as a goal. According to the Waste Act: means the measures taken in respect of a product, material or substance, before it becomes waste, that reduce (a) the quantity of waste, including through reuse or prolongation of the continued use of the product, (b) the negative environmental and human health impacts of the waste generated, (c) the content of harmful substances in the product and material. Therefore, at each stage of plant design, environmental aspects should be taken into account with the intention of improving the characteristics of the impact that a given product has on the environment throughout its entire life cycle, the so-called 'eco-design'. The realization of this goal could be introduced by selecting as components of the salt composition hydrated substances that do not have a negative impact on the environment and have as many characteristics of inert waste in the meaning of the Act on Waste [21] and by constant control of changes in the properties of hydrated salt compositions supported by laboratory tests.

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Particular attention should be paid to the fact that the hydrated salt compositions and their degradation products do not pose chronic or delayed potential hazard for the aquatic environment in accordance with the Regulation of the Minister of Health of 10 August 2012 on the criteria and method of classification of chemical substances and their mixtures. Hydrated salt compositions created should be susceptible to rapid degradation in the aquatic environment (when the ratio of BOD_5 (Biochemical oxygen demand)/ *COD*(*Chemical oxygen demand*) is ≥ 0.5), should not bioaccumulate (log P < 1 - n-octanol-water partition coefficient for organic matter) and shall not be toxic to fish or Daphnia on a chronic basis at a concentration 1 mg/dm³, at prolonged exposure > 1 mg/dm³. It is useful to create salt compositions from inorganic substances, which in turn can be transformed by normal environmental processes to either increase or decrease the bioavailability of toxic species. Additionally, substances should not be placed on the list of Substances of Very High Concern (SVHCs) [30]. Substances fulfilling one or more of the criteria defined in Article 57 of the REACH standards for

the Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (*REACH*) can be identified as *SVHC*. Substances on *REACH SVHC* list are substances meeting the criteria for classification as carcinogenic, mutagenic or reprotoxic (*CMR*) category 1 or 2; persistent, bio-accumulative and toxic (*PBT*) substances; or very persistent and very bio-accumulative (*vPvB*) substances; substances for which there is evidence for similar concern, such as endocrine disruptors.

Another important criterion is that the hydrated salt compositions created should not interact with the material they contact. The *TCM* material should have a specified lifetime of 15-20 years, during which the applied substance must retain its properties, and the rate of its decomposition should be as long as possible [4]. Undesirable reactions include: susceptibility to oxidation in humid environments ($CrCl_2$, $FeCl_2$) (risk of explosion during fire); decomposition of substance by degassing (MgCl₂) separated HCl at high temperatures (*TCM* weight reduction, possible corrosion and increase in pressure); (Na₂S) with the release of highly corrosive H₂S [11].

The following is a summary of environmental requirements that should guide investors in the selection of components of salt hydrate compositions for photovoltaic installations:

- should not be classified as hazardous substances
 "N" in the Regulation of the Minister of Health of 10
 August 2012 [29] on the criteria and classification of chemical substances and their mixtures.
- Substances should not be placed on the list of Substances of Very High Concern (SVHCs).
- Published by *ECHA* and updated every six month [30].
- Substances should not have hazardous properties (substance after use should not meet the definition of hazardous waste according to the Law on Waste [21], moreover they should not be classified in the *MSDS* as explosive, reactive under normal environmental conditions.
- The substance should be presented in the safety data sheet as chemically stable under normal environmental conditions.
- Substance in the safety data sheet should be classified as not hazardous to the aquatic environment $LC_{50} > 100 \text{ mg/l}$ (The value of LC_{50} for a substance is the concentration required to kill half the members of a tested population after

a specified test duration) according to 1272/2008/EC, substance is not bioaccumulative logP < 1, substance should be susceptible to degradation in the aquatic environment $BOD_{s}/COD \ge 0.5$.

3.2. After the operation period

Spent salts hydrated after a period of operation will meet the definition of waste under the Waste Act [21]. Waste according to Art. 3 is defined as "substance that the holder disposes of or intends or is obliged to dispose of". It should not contain substances particularly harmful to the aquatic environment, causing water pollution that should be eliminated (List I), and substances particularly harmful to the aquatic environment, causing water pollution that should be reduced (List II). The cited lists are included in the Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 [27] on substances particularly harmful to the aquatic environment and conditions to be met when discharging waste water into waters or onto the ground, and when discharging rainwater or snowmelt into waters or into water facilities. Used salt compositions should not constitute hazardous waste within the meaning of Commission Regulation (EU) No 1357/2014 of 18 December 2014 [28]. As hydrated salt compositions are often mixtures of substances and their effects in duet are not always known it is worthwhile to perform additional laboratory analyses such as: stability of the chemical composition and thermal stability in order to exclude unfavorable reactions and to assess the impact on the lifetime of the installation, evaluation of pH and specific electrical conductivity in the converter operating temperature range in order to assess possible concentration of the substance under certain pH conditions and unfavorable corrosive effects or substance leaks, evaluation of particle size changes to exclude dehydration, determination of organic matter content and analysis of possible transformations, determination of inorganic carbon content (as a background for testing to exclude release of carbon compounds from the casing to the hydrated salts under operating conditions of the converter), evaluation of the effects of salt compositions on plant growth (new knowledge regarding assessment of the impact on the environment and in the direction of searching for potential methods of disposal).

The following is a summary of the requirements that hydrated salt compositions should meet when they become waste so that they do not have a potentially harmful effect on the environment or on the carrier:

- pH (6.5-9);
- chlorides < 1000 mg/l, sulfates < 500 mg SO₄/l, sodium < 800 mg/l, potassium < 80 mg/l;
- salt compositions are thermally stable at temperatures in the range of 0-70°C;
- salt compositions have a stable chemical composition, which will not change the classification of the chemical substance (permissible deviations are given in Table 1). The table is derived from the Regulation of the Minister of Health of 10 August 2012 on the criteria and classification method of chemical substances and their mixtures;
- hydrated salt compositions should not show any carrier material in their composition;
- hydrated salt compositions should not show significant compositional changes particle size under converter operating conditions. According to ISO 13320:2009, the precision should be less than 3% for grains D_{v50} and less than 5% for grains D_{v10} i D_{v90} .

Table 1. Permissible deviations from the initial component of the substance depending on concentration of the initial component in the mixture

Range of starting concentrations of the component in the mixture	Permissible deviation from initial component concentration
concentration < 2.5%	±30%
2.5% < concentration < 10%	±20%
10% < concentration < 25%	±10%
25% < concentration < 100%	±5%

4. WASTE CODING AND TREATMENT

According to the Regulation of the Minister of Environment of 9 December 2014 on the catalog of waste [24]. The entity generating waste is obliged to assign a waste code. In turn, according to the Act of 14 December 2012 on waste [21]. The waste should be handed over to an entrepreneur, who has a permit from the competent authority for waste management or the method of waste disposal should be agreed with the competent local Department of Environmental Protection. The authors proposed a waste code for the used hydrated salt compositions from photovoltaic installations according to Table 2. At present, the Waste Law [21] art. 122 prohibits landfilling 1) occurring in liquid form, including waste containing water in an amount exceeding 95% of the total mass, excluding sludges. Therefore, the waste generated cannot be disposed of in liquid waste dumpsters. The waste with the assumed waste code 161002 can be

collected in non-drainage tanks and accepted at the liquid waste disposal points, which operate at the water and sewerage companies.

Table 2. Proposed waste codes for used hydrated salts from photovoltaic installations

1610	Hydrated liquid wastes for off-site recovery or disposal
161001*	Hydrated liquid wastes containing hazardous wastes
161002	Hydrated liquid wastes other than those mentioned in 161001

Municipalities are managed in this respect under the Act of 13 September 1996 on Maintaining Cleanliness and Order in Municipalities [25]. In accordance with the Regulation of the Minister of Infrastructure of 17 October 2002 on the conditions for introduction of liquid waste to septic tanks [26], the permissible load of pollutants in liquid sewage, which is discharged to a sewage lifting station, is agreed between the owner of the sewage lifting station and the owner of the sewage treatment plant where the sewage will be treated and results from the balance of quantity and quality of sewage and the treatment processes applied in the sewage treatment plant. Therefore, it is not possible to give specific pollution loads that hydrated salt compositions should meet in order to be accepted at such a station. However, it is advisable that the compositions meet the more restrictive standards that are given for industrial wastewater. Within the meaning of the Water Law and Environmental Protection Law, waste water, when introduced to water or to the ground becomes sewage. According to the Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 [27] on substances particularly harmful to the following daily average limits for expected pollutants are given for the water environment and the conditions to be met when discharging waste water into waters or onto the ground, as well as when discharging rainwater or snowmelt into waters or into water facilities: temperature < 35°C, pH 6.5-9, chlorides 1000 mg/l, sulphates 500 mg SO₄/l, sodium 800 mg/l, potassium 80 mg/l.

5. CONCLUSIONS

In this publication, the authors discuss which properties of chemical substances, that are components of compositions of hydrated salts in photovoltaic installations, should be taken into account to make them safe for the environment. Properties for the substance before and after the period of operation

are presented. The directions of proceeding with salt hydrates at each stage of designing photovoltaic installations were discussed. A method of dealing with used salt hydrates was proposed and a waste code was assigned. It has been established that spent salt hydrates (waste code 161002) will be allowed to be collected in no-outflow tanks and accepted at liquid waste collection points, which operate at water supply and sewerage companies. The load of permitted

pollutants should not exceed the values for industrial wastewater in accordance with the Ordinance of the Minister of Maritime Affairs and Inland Navigation of 12 July 2019 on substances that are particularly harmful to the aquatic environment and the conditions to be met when introducing wastewater into waters or into the ground, and when discharging rainwater or snowmelt into waters or into water facilities.

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THERMOVISION IN MEDICAL AND ENVIRONMENTAL APPLICATIONS

TERMOWIZJA W ZASTOSOWANIACH MEDYCZNYCH I INŻYNIERII ŚRODOWISKA

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Abstract

Thermovision offers a wide range of possible use in many areas of science. The paper presents applications of the thermovision technology with regard to healthcare and environmental issues. Apart from the literature review it also provides experimental results of the thermal image of the foot and surface temperature distributions as well as their analyses. The article lists common errors and limitations that need to be considered during infrared measurements to avoid significant mistakes at the stage of image analysis. The issue presented in the article is especially important because of reduced costs of the thermovision systems and their widespread availability to both private and institutional users.

Keywords: thermovision, IR applications, experimental uncertainties

Streszczenie

Termowizja oferuje szeroki zakres możliwych zastosowań w wielu dziedzinach nauki. W artykule przedstawiono zastosowania techniki termowizyjnej w aspekcie ochrony zdrowia i ochrony środowiska. Oprócz przeglądu literatury artykuł zawiera również wyniki badań eksperymentalnych rozkładów temperatury oraz ich analizę. W artykule wymieniono typowe blędy i ograniczenia, które należy wziąć pod uwagę podczas pomiarów w podczerwieni, aby uniknąć znaczących blędów na etapie analizy obrazu. Zagadnienie przedstawione w artykule jest szczególnie istotne ze względu na obniżone koszty systemów termowizyjnych oraz ich powszechną dostępność zarówno dla użytkowników prywatnych, jak i instytucjonalnych.

Slowa kluczowe: termowizja, pomiary w podczerwieni, niepewności pomiarowe

1. INTRODUCTION

Thermovision is one of the most rapidly developing measuring methods today. It is commonly applied in chemical industry, energy related applications, environmental engineering, medicine and machinery diagnostics [1]. It has been made possible mostly due to the reduced costs of production and improved design. Infrared cameras and other IR devices (such as pyrometers) are more and more available. This technology has become cheaper which, together with growing opportunities of its use in clinical applications, should lead to a more common use of thermovision in hospitals (while pyrometers have been used for many years for temperature measurements) and well as monitoring the environment. There is

already a significant number of applications in which this technique has proven itself to be a useful and powerful tool. However, attention has to be paid to measurements both at the stage of performing tests and also during result analyses. It stems from the fact that experimental errors might have an impact on forming diagnosis or conslusions basing on infrared test results.

It also needs to be noted that temperature measurement with infrared methods is easy, precise and fast – the results are actually available in real time if a camera if equipped with a display screen (which do not happen only for some stationary systems). Moreover, it is a safe diagnostics method. Computer software (often with enhanced graphical presentation possibilities) that enables the processing of the images generated by the cameras is an additional advantage of the system. It enables to connect thermographic devices to PC computes and analyze data, perform visualizations on the screen, which are useful for preparing reports.

2. MEDICAL AND ENVIRONMENTAL APPLICATIONS OF THERMOVISION

The infrared technology can be effectively used in medicine. It has been successfully applied in tests for breast cancer and cancers of other organs. This technique enables to detect warmer spots and abnormalities which could then be analysed in detail with other techniques.

The measurements using infrared cameras can be applied in surgery and orthopaedics in order to test osteomyelitis, posttraumatic, degeneration as well as cancerous states. It can also be applied to assist in wound and fracture healing [1]. Dental applications can cover, among others, investigations of temperature changes during polymerization of composites thorough measuring infrared emissions from surfaces of resin composite restoration during photocuring [2]. Thermovision method can also be used in skin diseases to detect abnormalities. It has been successfully applied, for example, in the infection caused by Clostridium perfringens in order to observe the complete extent of the viability of tissues [3]. Recently, Mačianskytė and Adaškevičius [4] experimentally analysed the use of infrared technique to discern the presence or absence of tumors located on orofacial and maxillofacial area in patients. The authors assessed the application of a special feature vector taken from face and mouth cavity thermograms and used it for classifying the images against the possible presence of tumors. While Baic et al. [5] performed tests on women

after mastectomy to verify the changes regarding temperature distribution at 12 months after the end of radiotherapy. The described technique is regarded as a tool that can replace cranial computed tomography (CCT) for screening in testing of shunt function in hydrocephalic patients. The advantage here is the fact that infrared technique a safe tool, while CCT requires radiation [6].

Badža et al. [7] focused on the detection of the injury of muscle as well as changes of the temperature of the runner's feet exposed to low temperature. Considerable hypothermia of the feet was observed. Maksymowicz [8] discussed the use of thermovision in forensic medicine and medical-legal post-mortem diagnostics. Cholewka [9] compared the infrared temperature readings with experimental data from the equipment. It was proven that infrared technique can be applied in sports medicine with the view to be used in efficiency evaluation. In [10] sixty patients were invuestigated in order to determine the usefullness of infrared technology in assessing the effects of hyperbaric O_2 therapy to wounds healing. Ivanitsky [11] discussed the mechanisms of heat generation within a body, control methods as well as the impact of the surrounding environment. Gizińska et al. [12] analysed eighty one patients ill with rheumatoid arthritis and thirty nine healthy ones. Thermovision was used to determine the surface temperature of the dorsal side of the foot. The authors reported large differences in average temperatures between the healthy and unhealthy volunteers.

Environmental applications of thermography are also quite broad. Stokowiec et al. [13] analysed temperature distribution on the surfaces of chimneys of the heat and power plant in Kielce. A similar study, but focused on the determination of the impact of the physical condition of thermal insulation of the chimney on the spread of air pollutants from it has been done by Orzechowski and Orman [14]. The tests were done on the chimney of the cement plant, which is a significant source of environmental contamination. The results indicate that the heat losses as a result of poor thermal insulation (as evidenced by thermal images) leads to the reduction in the temperature of the exhaust gases and, consequently, the solid particles in the gases fall down closer to the chimney as opposed to the situation when they travel further if the insulation is in a better state. Żygadło et al. [15] conducted research focused on the landfill site in Ostrowiec Świętokrzyski. Due to the fact that at landfills biochemical processes occur at elevated

temperatures, it is possible to use thermovision for monitoring activities. The tests in the paper indicate that there is a temperature difference between the freshly supplied household waste (which proved to be warmer) and the older one (reported to be cooler). Thermal imaging proved to be a useful tool, especially that the vast areas of landfills can be covered quickly. The concept of airborne measurements has also been used in [16], where the earth's temperature was recorded over a large area. These data can be useful for environmental assessments such as plant vegetation, evaporation rates, soil humidity determination as well as energy balances of the ecosystems. Similar studies can be made over the sea surface, as presented in [17]. It can be applied to the detection of anomalies in the marine environment and climate change issues. It has been shown that waters which are isolated and shallow undergo more extreme variations in temperature than those located deeper or the coastal ocean. An important area of thermovision use is the building industry. This technique can be applied to detect areas of intense heat losses (thermal bridges) and well as humid surfaces on the outside or the inside of buildings. Antczak et al. [18] analysed two buildings located in Leszczyny near Kielce. The measurements enabled to determine the areas of heat losses to the environments – typically windows and a balcony. In the case of the latter, significant heat fluxes were observed to be exchanged with the outside air, probably due to insufficient insulation. A thorough review of the application of the infrared technique in the studies of plant - environment interactions has been presented in [19]. The authors mentioned, among others, crop protection issues as well as stress detection and its management.

3. SELECTED MEASUREMENT LIMITATIONS AND UNCERTAINTIES – EXPERIMENTAL DATA

Determination of temperature of a given object with infrared methods is based on the radiation intensity measurement, which according to the Stefan-Boltzmann law is emitted by any body whose temperature exceeds 0 K. The radiation heat flux is proportional to temperature to the forth power, emissivity (a property of a surface from 0 to 1) and the Stefan-Boltzmann's constant. Because the thermovision camera detects and processes infrared radiation energy emitted from a body, its main element is a detector. The signal from the detector is magnified and transformed into a digital signal, which can then be used to calculate temperature of individual pixels of the image.

The measurement with infrared devices is not difficult in itself, however, proper analysis of the obtain thermal map is not easy and a lot of experience is needed to correctly determine temperature of the points in the thermograph. A good insight into measurement limitations for non – destructive testing is given in [20].

The interpretation of the thermal images can be challenging and the knowledge of the physics of thermal radiation phenomenon is necessary in order to properly conclude about the thermal state of the object. Thermal radiation is a wave and it is subject to the same laws as other waves. In analyzing thermographs it is especially vital to detect if a reflection of radiation has not occurred, which impact the readings. Figure 1 presents a bottle with a hot liquid located on the reflective floor. The phenomenon of reflection of radiation (generated by the hot liquid) can be easily seen. The floor and the reflective surface behind the bottle seems to be warm, but in fact they are not. The illusion is produced because radiation is reflected from the smooth surfaces and reaches the camera. Thus, creating the wrong illusion of the elevated temperature on the surfaces behind and below the hot object.



Fig. 1. Phenomenon of thermal radiation reflection – bottle filled with hot water and its reflections behind and below

Besides, it needs to be mentioned that thermal radiation travels through the medium (in our case: air) and some of it might be absorbed by carbon dioxide and water vapour which are present in the atmosphere. Thus, a reduction in the heat flux might occur (the temperature of the observed object might be lower).

One of the most important element in ensuring correct temperature testing is a precise determination

of emissivity. If the incorrect value is input, then the obtained results might have a larger or smaller error. In order to deal with this problem, the contact methods of temperature measurement might be applied to calibrate the device and set the actual value of emissivity (although they might be find in literature, but those might also generate errors). However, in many applications it is usually not important to determine the temperature itself, but rather temperature differences between – for example parts of the body or cells. As an example a foot's thermal map presented (Fig. 2) with the background erased for clarity.



Fig. 2. Thermovision image of the foot (background was removed)

The example given above will serve as an illustration of most typical mistakes that can be made when analyzing medical infrared images. An operator who conducts thermovision tests should have in mind that the measurement of temperature on curved surfaces is governed by the Lambert law and the temperature reading might not be correct on curved surfaces, which has been shown in Figure 3 for line L1 (indicated on Fig. 2).

Analyzing Figure 3 it can be proven that temperature on the curved part just at the edge of the foot is much lower. It could be attributed to the fact that the camera can only receive part of the intensity of thermal radiation, which according to the Lambert law, changes with the angle of observation and is highest in the normal direction. Consequently, care is needed in such cases to prevent erroneous conclusions about the temperature values on the curvatures. The accuracy (errors) of the thermovision measurements are usually below 2% of the measuring range. In this case it would be maximally about 2°C, however, the proper calibration of the device enables to significantly reduce these errors.



Fig. 3. Temperature distribution along line L1

Another very important limitation to be considered (partly mentioned before) is the reflection of radiation from heat sources located in the vicinity (e.g. central heating radiators). In such cases the thermovision camera receives more radiation for example from the patient's body than the body emits due to its temperature, because additional radiation is present in the signal. An example is line L2 (indicated in Fig. 2), since the radiation from the edge of the foot in this area is magnified by radiation from a nearby very hot element located about 50 cm away. Consequently, temperature distribution presented in Figure 4 has a peak, which seems much hotter than the rest of the foot. Naturally, real temperature of this area is lower.



Fig. 4. Temperature distribution along line L2



Fig. 5. Temperature distribution along line L3

It needs to be observed that Figure 2 also reveals that temperature of different parts of the body is not uniform. As can be seen below in Figure 5 toes are colder, which is undoubtedly related to the blood circulation in the body and good cooling conditions related to a high surface area subject to the colder environment of indoor air.

4. SUMMARY AND CONCLUSIONS

Precise infrared measurements require knowledge and experience. An operator needs to be aware of the reflection phenomenon, which might be a source of significant errors. Similarly an improper determination of emissivity might be a problem. Its value is always input into an infrared camera either before tests or during image analyses. An incorrect value will result in errors of temperature measurements. Thus, this value should be individually determined using contact temperature measuring methods, however, in medical and environmental applications it might be often neglected since it is the temperature difference rather than temperature value itself that is of interest during the testing.

Thermovision has many advantages over traditional methods of temperature measurement. It is non – invasive and tests results are available in real time. Its medical and environmental applications offer interesting opportunities and its use will undoubtedly increase, however, care and knowledge of experimental limitations and uncertainties are needed at the stage of analyzing thermographs in order to draw correct conclusions about the real surface temperature. Moreover, contact methods of temperature measurements might sometimes be necessary to verify the data obtained with the infrared technique.

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Kielce University of Technology

ANALYSIS OF AIR QUALITY ASSESSMENT IN KIELCE IN RELATION TO THE COVID-19 PANDEMIC

ANALIZA OCENY JAKOŚCI POWIETRZA W KIELCACH W ZWIĄZKU Z PANDEMIĄ COVID-19

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Abstract

Air pollution has a significant impact on citizens' well-being and overall life quality. In this regard, regular air quality monitoring aims to keep pollution levels within prescribed limits and to identify the factors (winds, traffic, seasons, ambient temperature, air humidity, and so on) that influence pollution levels. To carry out a preliminary analysis of the air quality in Kielce, a specialist detector of PM2.5 and PM10 particles Steinberg 10030389 SBS-PM2.5 was used. Besides, the analysis referred to pollutants such as SO₂; NO₂; C_6H_6 , which were provided from the Chief Inspectorate of Environmental Protection. Controlling the above mentioned pollutants for monthly and hourly averages of the selected time period in 2020 and 2021, taking into account the epidemiological situation (lockdown), graphs with the results were prepared. Then the analysis was carried out, with the preliminary assumption that the air quality is worse when the population functions normally than when it remains indoors, and that air quality is usually better at night than during the day.

Keywords: air quality, particulate matter, pollution monitoring

Streszczenie

Zanieczyszczenie powietrza ma znaczący wpływ na samopoczucie obywateli i ogólną jakość życia. W związku z tym regularne monitorowanie jakości powietrza ma na celu utrzymanie poziomu zanieczyszczeń w wyznaczonych granicach oraz identyfikację czynników (wiatry, ruch uliczny, pory roku, temperatura otoczenia, wilgotność powietrza itp.), które wpływają na poziom zanieczyszczeń. Do przeprowadzenia wstępnej analizy jakości powietrza w Kielcach wykorzystano specjalistyczny detektor cząstek stałych PM2,5 i PM10 Steinberg 10030389 SBS-PM2,5. Ponadto w analizie uwzględniono takie zanieczyszczenia jak SO₂; NO₂; C_6H_6 , które zostały udostępnione przez Główny Inspektorat Ochrony Środowiska. Kontrolując ww. zanieczyszczenia dla średnich miesięcznych i godzinowych z wybranego okresu w latach 2020 i 2021, z uwzględnieniem sytuacji epidemiologicznej (blokada), sporządzono wykresy z wynikami. Następnie przeprowadzono analizę, przyjmując wstępne założenie, że jakość powietrza jest gorsza, gdy ludność funkcjonuje normalnie, niż gdy pozostaje w pomieszczeniach zamkniętych, oraz że jakość powietrza jest zwykle lepsza w nocy niż w ciągu dnia.

Słowa kluczowe: jakość powietrza, pył zawieszony, monitoring zanieczyszczeń

1. INTRODUCTION

In modern day world, air quality monitoring is essential in the continuous efforts to reduce smog and enhance overall air quality. Every year, the intensity of traffic increases, as do the exhaust fumes emitted into the environment. This is frequently compounded by factory chimney smoke, which can also be harmful in composition. Because of that, relatively large cities, made continuous efforts to keep the rising dense fog, colloquially known as smog, at bay [1]. On the other hand, in relatively small towns where rural areas prevail, the air should seemingly be cleaner than in urban agglomerations. During the heating season, however, this is not a strict rule.

Technology is evolving rapidly in the twentyfirst century. As a consequence, there are numerous outdoor and indoor sensors on the market, as well as numerous mobile applications that allow anyone to monitor air pollution. This gives citizens the ability to control whether the air quality parameters are within proscribed limits throughout the day, and thus whether it is safe to be outside or open a window at home without fear of harmful substances entering our bodies from outside. Due to the fact that the most common sensors on the market are PM10 and PM2.5 particulate matter detectors, the PM2.5 and PM10 SBS-PM2.5 particle detector, which is also a professional air quality meter, was used to measure these particles in Kielce during the total shutdown caused by the outbreak of the pandemic and a year later in the same period of time when the society was functioning normally. Using publicly available measurements from the Chief Inspectorate of Environmental Protection in order to read the measurements related to the levels of CO, $NO_2, C_6H_6.$

2. MATERIALS AND METHODS

In order to make a preliminary analysis of air quality in Kielce, this study utilized a specialist detector of PM2.5 and PM10 particles shown in Figure 1, and used data obtained from the Chief Inspectorate for Environmental Protection in the period from 15 March 21 to 15 April 21. That after, the study calculated daily and monthly averages and did a detailed comparison for one selected week in March of the year 2020 when coronavirus and the first lockdown occurred and for the same time period in the previous year were no restrictions.



Fig. 1. SBS-PM2.5 and PM10 particle detector Source: personal photo

This detector is a practical air quality meter by Steinberg Systems, which detects harmful airborne dust with its sensitive sensors. It is relatively easy to use and can be easily moved, which makes it possible to measure practically in any place. The measurement takes place in real time, hence the measurement is very up-to-date. The detection ranges for PM10 and PM2.5 is from 0 to 999.9 μ g/m³ [3].

3. IMPACT OF PM10, PM2.5, CO, NO₂, SO₂ AND C₆H₆ ON THE HEALTH OF SOCIETY

Studies show that concentrations of PM10 and PM2.5 particulate matter usually exceed their norms in winter due to the fact that it is the heating season and smog phenomenon, dangerous to health, is often observed [4]. Pollutants from road traffic weigh on air quality assessment especially in larger towns, while those from residential heating in suburban and rural agglomerations, where the air should generally be cleaner. WHO has shown that NO₂, PM10 and benzoapirene that enter the environment through traffic and from biomass burning were often unacceptably high compared to urban agglomerations. Hence, toxicity tests of PM extracts with lung epithelial cells showed higher toxicity for stations from smaller towns [5, 6]. In order to reduce air pollution and what effects it has on the health of the community, it is necessary to have a good understanding of its source [7]. Studies show that ambient air pollution contributes to millions of deaths worldwide (up to 4.2 million). This is because when inhaled, pollutant particles can penetrate deep into the lungs [8]. A potential measure of the health effects associated with a particular exposure in ecological studies is the relative risk of

Air Quality Index	PM10 [μg/m³]	PM2.5 [μg/m³]	NO ₂ [μg/m³]	SO ₂ [μg/m³]	С ₆ Н ₆ [µg/m³]	CO [µg/m³]	
very good	0-20	0-13	0-40	0-50	0-6	0-3	
good	20.1-50	13.1-35	40.1-100	50.1-100	6.1-11	3.1-7	
moderate	50.1-80	35.1-55	100.1-150	100.1-200	11.1-16	7.1-11	
sufficient	80.1-110	55.1-75	150.1-200	200.1-350	16.1-21	11.1-15	
bad	110.1-150	75.1-110	200.1-400	350.1-500	21.1-51	15.1-21	
very bad	>150	>110	>400	>500	>51	>21	
no index	an air quality index is not determined due to the lack of measurement of the dominant pollutant in the province						

Table 1. Assessment of air quality in relation to acceptable standards of pollution

Source: Chief Inspectorate of Environmental Protection. Air quality portal. Available online: http://powietrze.gios.gov.pl/pjp/archives.

increased illness or death in response to an increase in the concentration of a particular pollutant. Table 1 shows the WHO recommended concentration limits for each pollutant in the air.

3.1. PM10 and PM2.5 - harmful to health

Considering total suspended particulate matter (TSP), one can distinguish fractions with grain sizes above 10 μ m and those with grain diameters below 10 μ m. Regarding, PM10 fraction there is a fraction with the diameter of grains below 2.5 μ m (PM2.5 particulate matter, whose particles are very hazardous to health) [9, 10].

According to the World Health Organization (WHO), as well as independent studies, there is a huge impact of particulate matter on human health with a special emphasis on PM2.5 [11]. Having a longer contact with this dust such as this, especially its finer fractions, one can shorten the life length by a year [12]. These dusts have particularly harmful effects on the respiratory system [13]. They may contribute to bronchial asthma, chronic obstructive pulmonary disease or common respiratory infections, including pneumonia. Exposure especially to PM2.5 in pregnant women may translate into poor respiratory function in the child later in life [14]. Lung cancer is an increasingly common effect of particulate air pollution, the risk of cancer can be 20-40% higher for areas with elevated dust concentrations compared to those places where these concentrations are low [15, 16]. Another negative effect of dust exposure is the dangerous effects on the cardiovascular system. PM2.5 and even smaller dust particles get from the alveoli to the circulatory system and subsequently to the internal organs causing undesirable health conditions from inflammation, oxidative stress and secondary activation of the sympathetic nervous system may result in damage to the vascular endothelium, destabilization or formation of new atherosclerotic plaques [17]. The occurrence of strokes, hypercoagulability of blood, formation of venous and arterial thrombosis are other possible consequences of the effects of particulate matter on the human body [18]. The nervous system is also exposed to dust penetration. Neurodegenerative diseases may occur leading to more frequent depressive states and acceleration of the aging process for the nervous system [19].

3.2. Carbon monoxide - harmful to health

Carbon monoxide (CO) is a highly toxic and odorless gas. Hence, it is often referred to as the silent killer. Apart from the fact that it can escape in a poorly ventilated apartment as a result of heating we also have to deal with it on a daily basis as it is one of the components of smog. However, it is not as dangerous to health in this form as the one we come into contact with in a closed room. Carbon monoxide very easily combines with red blood pigment, which means that it impedes the delivery of oxide molecules to tissues. Depending on the force with which it acts on the body it results in more or less hypoxia. If the volumetric concentration of carbon monoxide in the air is 100-200 ppm (0.01-0.02%) after the contact with it the symptoms for the human body are insignificant (headache, burning on the face), but if the concentration is 400 ppm (0.04%)it causes a strong headache already after about an hour of breathing the contaminated air. If the concentration is about 800 ppm (0.08%) it will cause dizziness or vomiting in a similar time. The higher the concentration the more severe the symptoms. A concentration of more than 1% will cause unconsciousness after just a few breaths, and may lead to death after a few minutes of breathing such polluted air [20].

3.3. Nitrogen dioxide - harmful to health

Nitrogen dioxide NO₂ is a highly reactive variety of nitric oxide. The source of its origin is mainly the fuel combustion of cars or heavy machinery. Only 5-10% of NO₂ is that emitted directly from nitrogen oxides. NO_x are directly involved in chemical transformations resulting in formation of particulate matter which is very harmful to health [21]. If we are briefly exposed to with exceeded permissible concentrations of NO₂ in the air can result in respiratory irritation, chemical inflammation, and pulmonary edema because NO₂ reacts with body fluids to form nitric acid and nitrous. If the exposure to high concentrations of NO₂ is prolonged, it may lead to the development of asthma, decrease the immunity of the respiratory system, and thus cause its more frequent viral and bacterial infections; in the case of people already suffering from asthma, it may contribute to increased mortality [22].

3.4. Sulfur dioxide - harmful to health

Sulfur dioxide in the air comes mainly from the commercial power and heating industry, as well as various technological processes. Its level in the air is also significantly influenced by what we heat our homes with. To the smallest extent, SO₂ enters the air from exhaust of car engines [23, 24]. If its permissible concentration is exceeded, it shows toxic effects [25]. According to the results of environmental epidemiology studies, such pollutants as particulate matter and sulfur dioxide suggest that they may affect the occurrence of cardiovascular diseases and increase mortality especially in people over 65 years old [26, 27]. Further ailments associated with prolonged exposure to particulate matter with NO₂ may be increased permeability in lung tissue and with it the appearance of pulmonary edema especially in people with damaged heart muscle [28]; increased left atrial pressure may occur [29]; pneumonia or bronchiolitis [30]; congestive heart failure (with comorbidities [31]. If there is a reduction in nitrogen dioxide in the air we breathe it may contribute to a decrease in cardiovascular problems among the public [32].

3.5. Benzene – harmful to health

Benzene C_6H_6 like other air pollutants may have a natural origin, e.g. as a result of forest fires or anthropogenic origin, i.e. tobacco smoke, burning of fuels and processing of petroleum products, industry or building materials. Benzene C_6H_6 like other air pollutants may have natural origin, e.g. as a result of forest fires, or anthropogenic origin, i.e. tobacco smoke, burning of fuels and processing of products of petroleum origin, from industry or building materials. Long-term contact with benzene of higher than permissible concentration may cause mutagenic changes and even lead to leukemia [33]. Benzene is characterized by the fact that it is a colorless liquid, flammable with a sweet smell (it can be smelled at the gas station) [34]. It is said that "the only absolutely safe concentration of benzene is zero", which means that even small amounts of C_6H_6 can be harmful for our body. Unfortunately, due to the fact that benzene is one of the fuel components, its presence in the air we breathe is almost unavoidable [35]. It attacks mainly the liver, lungs, heart, kidneys and even the brain so abnormalities in the nervous system may also occur. Symptoms after prolonged exposure to benzene may be narcotic in nature, the person may behave as after alcohol intoxication, they are visible, characteristic and may signal that something wrong is happening in the body. And the most dangerous are the ones we don't notice. They can lead to chronic bone marrow damage [36].

4. RESULTS

Figures 2-3 show the average daily concentrations of PM10 and PM2.5 in the air in Kielce for 32 days from 15.03-15.04 for 2020 and 2021. In the studied period in 2020, the highest concentrations were: PM10 – 90 μ g/m³; PM2.5 about 65 μ g/m³, which as shown in Table 1 are at sufficient level. Mostly on those days it did not exceed 50 μ g/m³ for PM10, and 30 μ g/m³ so the air quality was generally good. As for 2021, the highest recorded value of PM10 is 140 μ g/m³, PM2.5 is 60 μ g/m³. For the most part of the study period PM10 level was moderate.

4.1. Average results of PM10, PM2.5 measured in the period 15.03-15.04.2020 and 15.03-15.04.2021





In terms of the remaining pollutants, SO₂ concentrations were at a maximum of approximately 20 μ g/m³ for both of the study periods in 2020 and 2021, that is relatively acceptable concentration. In 2020 the average value for NO₂ was 38 μ g/m³; for C₆H₆ 2.5 μ g/m³ and for CO no values were recorded. In 2021 NO₂ averaged around 22 μ g/m³; C₆H₆ – 2 μ g/m³ and carbon monoxide was not detectable in the air and remained at the level equal to 0 μ g/m³. For these pollutants, the concentration values remained at a very good level for the whole study period. Hence, they had no excessive harmful effects on citizens' health.

for 2020 and 2021 during the period from March 16 to 22. The highest values during the study period for 2020 were: PM10 - 150 µg/m³; PM2.5 - 120 µg/m³; $SO_2 - 25 \ \mu g/m^3$; $NO_2 - 55 \ \mu g/m^3$; $C_6H_6 - 12 \ \mu g/m^3$ and CO $- 2.1 \,\mu\text{g/m}^3$. These values, as can be seen from Table 1, varies the levels of air quality - from very good to very bad, which results in moderate air quality. It is worth mentioning that concentrations of pollutants were the highest on 18th and 19th of March. The values on the graphs increase up to those days, and then they start decreasing. Before and after reaching the maximum value they remain at good and very good level. Analyzing 2021 we can see that the highest values are: PM10 - 60 μ g/m³; PM2.5 - 58 μ g/m³; $SO_2 - 16 \ \mu g/m^3$; $NO_2 - 30 \ \mu g/m^3$; $C_6H_6 - 8.5 \ \mu g/m^3$ and CO $- 0 \mu g/m^3$. Unlike in 2020, in Figures 10, 12, 14, 16 and 18 we can see that the line does not form a "parabola" but the values on it increase and decrease alternately, not giving worse air quality as good. Assuming a pandemic broke out in 2020, one would expect the pollutant values to be lower as for 2021, but for most pollutants they are higher.

4.2. Results of PM10, PM2.5, NO_2 , SO_2 , C_6H_6 , CO. Measurement at 04:00 a.m. in the period 16.03-22.03.2020 and 16.03-22.03.2021





Figures 4 and 5 show the results of measurements for all sampled pollutants in the air measured at 4:00 a.m.

4.3. Results of PM10, PM2.5, NO₂, SO₂, C₆H₆, CO. Measurement at 10:00 a.m. during the period 16.03-22.03.2020 and 16.03-22.03.2021



Fig. 6. Results of PM10, PM2.5, SO₂, NO₂. Measurement at 10:00 a.m. Kielce 2020



Fig. 7. Results of PM10, PM2.5, SO₂, NO₂. Measurement at 10:00 a.m. Kielce 2021

Figures 6 and 7 show the results of measurements for all tested pollutants in the air measured at 10:00 a.m. for 2020 and 2021 during the period from March 16 to 22. The highest values during the study period for 2020 were: PM10 – 65 μ g/m³; PM2.5 – 45 μ g/m³; SO₂ – 20 μ g/m³; NO₂ – 30 μ g/m³; C₆H₆ – 5.5 μ g/m³ and CO – 0.9 μ g/m³. These values, as can be seen from Table 1, are at different levels of air quality from very good to moderate which results in good air quality.

4.4. Results of PM10, PM2.5, NO₂, SO₂, C₆H₆, CO. Measurement at 4:00 p.m. in the period 16.03-22.03.2020 and 16.03-22.03.2021



Fig. 8. Results of PM10, PM2.5, SO₂, NO₂. Measurement at 4:00 p.m. Kielce 2020



Measurement at 4:00 p.m. Kielce 2021

Figures 8 and 9 show the measurement results for all tested pollutants in the air measured at 4:00 p.m. for 2020 and 2021, during the period from March 16 to 22. The highest values during the study period for 2020 were: $PM10 - 28 \ \mu\text{g/m}^3$; $PM2.5 - 45.18 \ \mu\text{g/m}^3$; $SO_2 - 18 \ \mu\text{g/m}^3$; $NO_2 - 22 \ \mu\text{g/m}^3$; $C_6H_6 - 0.6 \ \mu\text{g/m}^3$, which remained at this level for 3 days and $CO - 0.7 \ \mu\text{g/m}^3$. These values, as it results from table 1 are on two levels of air quality – very good to good which as a result it

gives us very good air quality. It is worth mentioning that the highest concentrations of pollutants do not exceed values below those indicating good air quality. The values on the graphs are distributed ascending to the highest concentration, then descending. Analyzing 2021, it can be seen that the highest values are: PM10 - 18 μ g/m³; PM2.5 - 18 μ g/m³; $SO_2 - 18 \ \mu g/m^3$; $NO_2 - 5.5 \ \mu g/m^3$; $C_6H_6 - 1.5 \ \mu g/m^3$ and CO – 0 μ g/m³. These values as for 2020 are on a scale from good to very good air quality. In Figure 8 one can notice how until 20th of March comparable values from two different time periods were nearly equal however on 20th of March for most of the pollutants the highest concentrations were recorded then a decrease is seen. Overall the results show very good air quality in the discussed hour.

4.5. Results of PM10, PM2.5, NO₂, SO₂, C₆H₆, CO. Measurement at 10:00 p.m. in the period 16.03-22.03.2020 and 16.03-22.03.2021



Fig. 10. Results of PM10, PM2.5, SO₂, NO₂. Measurement at 10:00 p.m. Kielce 2020



Fig. 11. Results of PM10, PM2.5, SO₂, NO₂. Measurement at 10:00 p.m. Kielce 2021

Figures 10 and 11 show the results of measurements for all tested pollutants in the air measured at 10:00 p.m. for 2020 and 2021 during the period from March 16 to 22. The highest values during the study period for 2020 were: $PM10 - 130 \mu g/m^3$; $PM2.5 - 70 \mu g/m^3$;

 $SO_2 - 15 \ \mu g/m^3$; $NO_2 - 30 \ \mu g/m^3$; $C_6H_6 - 5 \ \mu g/m^3$ and $CO - 1.9 \ \mu g/m^3$. These values, as can be seen from Table 1, fall within the levels of air quality – very good to poor which results in good air quality. In other cases, the results are mixed especially for PM10 where the discrepancy is from 10 to 120 \ \mu g/m^3 in the examined period. Analyzing 2021 it can be seen that the highest values are: PM10 - 50 \ \mu g/m^3; PM2.5 - 90 \ \mu g/m^3; SO_2 - 18 \ \mu g/m^3; NO_2 - 70 \ \mu g/m^3; C_6H_6 - 12 \ \mu g/m^3 and CO - 0 \ \mu g/m^3. These values are on a scale from very good to poor in terms of air quality, which results in the worst rating on 7 of the surveyed days at moderate level, while on the remaining days the quality is better.

5. CONCLUSIONS

The findings of the analyses dealing with major air pollutants for two selected periods in 2020, from the first days of the COVID-19 pandemic to the same period in 2021 when there was no lockdown, are quite surprising.

The average daily concentrations of the pollutants (PM10 and PM2.5) that determined air quality from 15.03 to 15.04.2020 remained good, while they were moderate in 2021. The improvement in air quality due to reduction of floating particulate matter in the year 2020, could be caused by forced isolation of residents in their homes, which resulted, among other things, in a significant reduction of motorized transport in the study area.

For the remaining pollutants NO_2 , C_6H_6 and CO the results remained at least at moderate level and SO_2 was usually at very good level.

Subsequent measurements were made 4 times per day (4:00 a.m., 10:00 a.m., 4:00 p.m., and 10:00 p.m.) for a selected week from March 16 to 22 for 2020 and 2021. The first measurement at 4:00 a.m. for the period March 16 to 22 recorded higher concentrations

for 2020. For 10:00 a.m., higher pollutants were already recorded for 2021 compared to 2020, due to work and remote education, which significantly reduced motorized transport between 6:00 a.m. and 8:00 p.m., which was already significantly noticeable for 2021, worsening air quality.

The 4:00 p.m. surveys for 2020 and 2021 showed values that were at least good. In 2020. PM10; PM2.5; NO₂ and C_6H_6 at 4:00 have the highest values and there is a decreasing trend in the following hours, but during the fourth hour at 10:00 p.m. they increase again. SO₂ concentration decreases until 4:00 p.m. then remains constant until 10:00 p.m. Analyzing 2021 we can see a little bit opposite situation as in 2020. PM10 and PM2.5 are higher with each measurement and at 10:00 p.m. it decreases and at 10:00 p.m. it is the same index, SO₂ decreases until 4:00 p.m. it is higher. C_6H_6 initially increases, at 4:00 p.m. it has a low value, and at 10:00 p.m. it is high again.

6. DISCUSSION

The values of PM2.5 and PM10 pollutants are strongly correlated. In most cases PM10 slightly exceeds PM2.5. It is interesting to note that air concentrations of pollutants PM10 and PM2.5 did not turn out to be lower at all during the period, the first isolation in March 2020 compared to March 2021. NO₂ SO₂ CO and C₆H₆ concentrations also did not turn out to be lower during the pandemic period, but tests performed at 10:00 a.m. and 10:00 p.m. showed that concentrations were higher in March 2020. The degree of pollution at 4:00 a.m. was at a similar level. The initial assumption of the measurements was that air quality improved during social isolation; however, the study found that air quality was of similar or worse quality during quarantine.

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A STUDY ON CARBONATION DEPTH PREDICTION FOR CONCRETE MADE WITH GBFS CEMENT AND FA ADDITION

BADANIE DOTYCZĄCE PROGNOZOWANIA GŁĘBOKOŚCI Karbonatyzacji betonu wykonanego z cementu GBFS z dodatkiem fa

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Abstract

This paper presents the results of the examination of accelerated carbonation of concrete mixes made with CEM III / A blast furnace slag cement and the addition of fly ash. The test program was developed using an experiment design with two factors: a water-binder ratio and a fly-ash / cement ratio. Carbonation depth measurements were carried out according to FprCEN/TS 12390-12 (CO₂ concentration = 4%, T = 20°C, RH = 55%). Associated tests were also carried out, including compressive strength, porosity, depth of absorption, water penetration depth, and capillary suction.

Analysis of the test results allowed us to determine the influence of binder composition on concrete carbonization depth under standard test conditions. The results show that the carbonation depth increases along with the increase in the W/B ratio and as a result of the increase in the fly ash content in the binder.

A mathematical model was developed to describe the carbonation process over time, which can predict the depth and rate of concrete carbonation. Furthermore, it was found that there is no close relationship between other properties tested (e.g. strength) and the depth of the carbonated concrete.

Streszczenie

W pracy przedstawiono wyniki badań przyspieszonej karbonatyzacji mieszanek betonowych wytworzonych cementem żużlowym wielkopiecowym CEM III/A z dodatkiem popiołu lotnego. Program badań został opracowany na podstawie projektu eksperymentu z dwoma czynnikami: stosunkiem wody do spoiwa oraz stosunkiem popiołu lotnego do cementu. Pomiarv glebokości karbonatvzacji przeprowadzono zgodnie z FprCEN/TS 12390-12 (stężenie $CO_2 = 4\%$, T = 20°C, RH = 55%). Przeprowadzono również powiązane testy, w tym wytrzymałości na ściskanie, porowatości, głębokości absorpcji, głębokości penetracji wody i ssania kapilarnego. Analiza wyników badań pozwoliła na określenie wpływu składu spoiwa na głębokość karbonatyzacji betonu w standardowych warunkach testowych. Wyniki wskazują, że wraz ze wzrostem stosunku W/B oraz zawartością popiołu lotnego w spoiwie wzrasta głębokość karbonatyzacji. Opracowano model matematyczny do opisu procesu karbonatyzacji w czasie, który umożliwia przewidywanie głębokości i szybkości karbonatyzacji betonu. Ponadto stwierdzono, że nie ma ścisłego związku między innymi badanymi właściwościami (np. wytrzymałością) a głębokością betonu karbonatyzowanego.



MANAGEMENT OF SALT HYDRATES IN PHOTOVOLTAIC INSTALLATIONS IN LIGHT OF EXISTING ENVIRONMENTAL LEGISLATION

ZARZĄDZANIE HYDRATAMI SOLI WYKORZYSTANYMI W INSTALACJACH FOTOWOLTAICZNYCH W ŚWIETLE OBOWIĄZUJĄCYCH PRZEPISÓW DOTYCZĄCYCH OCHRONY ŚRODOWISKA

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Abstract

This paper discusses an environmental criterion rarely addressed in the literature for the selection of salt hydrates for use in photovoltaic installations as Phase change materials. The aim of the paper is to assess the possibility of utilization of used salt hydrates from photovoltaic installations according to current Polish legal requirements concerning the environment. The properties of the composition components of hydrated salts were discussed in terms of their safety for the environment before and after the period of exploitation in photovoltaic panels. A method of dealing with used salt hydrates was proposed and a waste code was assigned. It has been established that spent salt hydrates will be allowed to be collected in no-outflow tanks and accepted at liquid waste collection points, which operate at water supply and sewerage companies, and the load of permissible pollutants should not exceed the value for industrial sewage.

Streszczenie

W artykule omówiono rzadko poruszane w literaturze kryterium środowiskowe wyboru hydratów solnych do zastosowania w instalacjach fotowoltaicznych jako materiałów zmiennofazowych (PCM). Celem pracy jest ocena możliwości utylizacji zużytych hydratów soli z instalacji fotowoltaicznych zgodnie z aktualnymi polskimi wymaganiami prawnymi dotyczącymi środowiska. Omówiono właściwości składników kompozycyjnych soli uwodnionych pod kątem ich bezpieczeństwa dla środowiska przed i po okresie eksploatacji w panelach fotowoltaicznych. Zaproponowano sposób postępowania ze zużytymi hydratami solnymi i nadano im kod odpadu. Ustalono, że zużyte hydraty solne będą mogły być gromadzone w zbiornikach bezodpływowych i przyjmowane w punktach gromadzenia nieczystości ciekłych, działających przy przedsiębiorstwach wodociągowo-kanalizacyjnych, a ładunek dopuszczalnych zanieczyszczeń nie powinien przekraczać wartości dla ścieków przemysłowych.



THERMOVISION IN MEDICAL AND ENVIRONMENTAL APPLICATIONS

TERMOWIZJA W ZASTOSOWANIACH MEDYCZNYCH I INŻYNIERII ŚRODOWISKA

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Structure and Environment vol. 14, No. 1/2022, p. 18

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Abstract

Thermovision offers a wide range of possible use in many areas of science. The paper presents applications of the thermovision technology with regard to healthcare and environmental issues. Apart from the literature review it also provides experimental results of the thermal image of the foot and surface temperature distributions as well as their analyses. The article lists common errors and limitations that need to be considered during infrared measurements to avoid significant mistakes at the stage of image analysis. The issue presented in the article is especially important because of reduced costs of the thermovision systems and their widespread availability to both private and institutional users.

Streszczenie

Termowizja oferuje szeroki zakres możliwych zastosowań w wielu dziedzinach nauki. W artykule przedstawiono zastosowania techniki termowizyjnej w aspekcie ochrony zdrowia i ochrony środowiska. Oprócz przeglądu literatury artykuł zawiera również wyniki badań eksperymentalnych rozkładów temperatury oraz ich analizę. W artykule wymieniono typowe błędy i ograniczenia, które należy wziąć pod uwagę podczas pomiarów w podczerwieni, aby uniknąć znaczących błędów na etapie analizy obrazu. Zagadnienie przedstawione w artykule jest szczególnie istotne ze względu na obniżone koszty systemów termowizyjnych oraz ich powszechną dostępność zarówno dla użytkowników prywatnych, jak i instytucjonalnych.



ANALYSIS OF AIR QUALITY ASSESSMENT IN KIELCE IN RELATION TO THE COVID-19 PANDEMIC

ANALIZA OCENY JAKOŚCI POWIETRZA W KIELCACH W ZWIĄZKU Z PANDEMIĄ COVID-19

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Abstract

Air pollution has a significant impact on citizens' wellbeing and overall life quality. In this regard, regular air quality monitoring aims to keep pollution levels within prescribed limits and to identify the factors (winds, traffic, seasons, ambient temperature, air humidity, and so on) that influence pollution levels. To carry out a preliminary analysis of the air quality in Kielce, a specialist detector of PM2.5 and PM10 particles Steinberg 10030389 SBS-PM2.5 was used. Besides, the analysis referred to pollutants such as SO_2 ; NO_2 ; C_6H_6 , which were provided from the Chief Inspectorate of Environmental Protection. Controlling the above mentioned pollutants for monthly and hourly averages of the selected time period in 2020 and 2021, taking into account the epidemiological situation (lockdown), graphs with the results were prepared. Then the analysis was carried out, with the preliminary assumption that the air quality is worse when the population functions normally than when it remains indoors, and that air quality is usually better at night than during the day.

Streszczenie

Zanieczyszczenie powietrza ma znaczacy wpływ na samopoczucie obywateli i ogólną jakość życia. W związku z tym regularne monitorowanie jakości powietrza ma na celu utrzymanie poziomu zanieczyszczeń w wyznaczonych granicach oraz identyfikację czynników (wiatry, ruch uliczny, pory roku, temperatura otoczenia, wilgotność powietrza itp.), które wpływają na poziom zanieczyszczeń. Do przeprowadzenia wstępnej analizy jakości powietrza w Kielcach wykorzystano specjalistyczny detektor cząstek stałych PM2,5 i PM10 Steinberg 10030389 SBS-PM2,5. Ponadto w analizie uwzględniono takie zanieczyszczenia jak SO₂; NO₂; $C_{\alpha}H_{\alpha}$, które zostały udostępnione przez Główny Inspektorat Ochrony Środowiska. Kontrolując ww. zanieczyszczenia dla średnich miesięcznych i godzinowych z wybranego okresu w latach 2020 i 2021, z uwzględnieniem sytuacji epidemiologicznej (blokada), sporządzono wykresy z wynikami. Następnie przeprowadzono analizę, przyjmując wstępne założenie, że jakość powietrza jest gorsza, gdy ludność funkcjonuje normalnie, niż gdy pozostaje w pomieszczeniach zamkniętych, oraz że jakość powietrza jest zwykle lepsza w nocy niż w ciągu dnia.

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