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OF INDUSTRIAL AND MUNICIPAL ECOLOGY

RECENZOVANÝ ČASOPIS PRO VÝSLEDKY VÝZKUMU A VÝVOJE
Z OBLASTI PRŮMYSLOVÉ A KOMUNÁLNÍ EKOLOGIE

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Vážení čtenáři,

máte před sebou letošní čtvrté číslo, jehož patronem je tentokrát WASTen, z.s., centrum transferu špičkových inovativních technologií se zaměřením na materiálové a energetické zpracování průmyslového a komunálního odpadu. Je tomu tak díky jeho dlouhodobé spolupráci s CEMCem, vydavatelem tohoto časopisu, z čehož plyne i jeho patronát nad blížícím se ročníkem symposia ODPADOVÉ FÓRUM 2019 (19. – 21. 3. 2019, Hustopeče). Všichni autoři i čtenáři jsou srdečně zváni (nejen) k aktivní účasti na symposiu.

Příspěvky ze symposia lze následně uveřejnit ve WASTE FORUM. Termín pro přihlášky příspěvků je 15. 1. 2019, pro přihlášky účasti pak 1. 3. 2019. Symposium a souběžně probíhající konference APROCHEM se konají v rámci Týdne výzkumu a inovací pro paraxi a životní prostředí TVIP a veškeré informace k němu najdete spolu s formuláři přihlášek příspěvku i účasti na www.tvip.cz.

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Ondřej Procházka

Editorial

Dear readers,

here you have the fourth number this year, whose patron is WASen, z.s., a center of transfer of top innovative technologies focusing on the material and energy processing of industrial and municipal waste.

I would like to remind you of the coming year of symposium ODPADOVE FORUM 2019 (March 19 – 21, 2019, Hustopeče, Czech Republic). All authors and readers are cordially invited (not only) to participate actively at the symposium. Symposium contributions can then be posted in WASTE FORUM. The symposium is held within the Week of Research and Innovation for the Practice and Environment (TVIP) and all the information you can find on www.tvip.cz.

With the approaching year 2019, I would like to recall the previously announced unification of the publication contributions for articles, regardless of their language. This means that the publishing fee will be CZK 500 per page starting with the next issue.

Ondřej Procházka

Pro autory

WASTE FORUM je časopis určený pro publikování původních vědeckých prací souvisejících s průmyslovou a komunální ekologií. Tj. nejen z výzkumu v oblasti odpadů a recyklace, jak by mohl naznačovat název časopisu, ale i odpadních vod, emisí, sanací ekologických zátěží atd. Vychází pouze v elektronické podobě a čísla jsou zveřejňována na volně přístupných internetových stránkách www.WasteForum.cz.

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Vydávání časopisu není nikým dotované. Proto, abychom příjmově pokryli náklady spojené s vydáváním časopisu, vybíráme publikační poplatek ve výši 200 Kč za každou stránku u příspěvků v anglickém jazyce (platí jen do konce roku 2018), u ostatních je 500 Kč za stránku. Uvedené částky jsou bez DPH. V případě nepublikování příspěvku v důsledku negativního výsledku recenzního řízení je tato částka poloviční.

Uzávěrka nejbližšího čísla časopisu WASTE FORUM je 8. ledna 2019, další pak 8. dubna 2019.

For authors

WASTE FORUM is an electronic peer-reviewed journal that primarily publishes original scientific papers from scientific fields focusing on all forms of solid, liquid and gas waste. Topics include waste prevention, waste management and utilization and waste disposal. Other topics of interest are the ecological remediation of old contaminated sites and topics of industrial and municipal ecology.

WASTE FORUM publishes papers in English, Czech or Slovak. Articles submitted must include a abstract in Czech (Slovak) or English language, respectively.

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All articles submitted for publication in WASTE FORUM undergo assessment by two independent reviewers. The reviews are dispatched to authors anonymously, i.e. the names of the reviewers are not disclosed to the authors.

All papers that was not subjected to a peer-review are labeled in a header of each page by the text ***Not peer-reviewed and commercial papers.***

Revenue to cover at least the costs associated with the issuance of the magazine, we select a publication fee **500 CZK per each new page for articles reviewed part of issue and CZK 1000 for every new page for contributions in the second part of the issue.**

The deadline of the next issue is on January 8, 2019, more on April 8, 2019.

KLASTR
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ODPADY – SUROVINY – ENERGIE NEKONEČNÉ MOŽNOSTI...

WASTen, z.s. je centrem transferu špičkových inovativních technologií se zaměřením na materiálové a energetické zpracování průmyslového a komunálního odpadu v ČR. Poskytuje odborné poradenství a podporu nejen svým členům, ale i široké veřejnosti.

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Multivariate analysis of biomonitoring data on atmospheric deposition: First results

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Summary

The article introduces the possibility of identification of pollution origin using cluster analysis provided by self-organizing (Kohonen) map. The pollution was detected in naturally growing moss to monitor the atmospheric deposition in the Czech-Polish borderlands (Moravian and Silesian regions). The method was applied on the dataset of 44 samples collected from 41 sites where the content of 38 elements was determined using Neutron Activation Analysis. The method was used for the classification without any data transformation necessary and any information loss, so determined clusters hold the information about chemical content needed for the identification of the pollution origin. The method classified biomonitoring data into four clusters with specific chemical composition. Now it is possible to correlate them with emission to determine the origin pollution. The applied method is recommended for the employment after further testing.

Key words: *cluster analysis, atmospheric deposition, biomonitoring, moss*

Introduction

The origin of environmental pollution can be determined by various methods such as modelling or/and special air quality monitoring. Receptor-oriented methods and models define source contributions by characterizing atmospheric aerosol samples, often using chemical elements or compounds (injected or occurring) in samples as tracers for the presence of material from particular kind of sources. Mechanistic source-oriented models conceptually follow pollutant from source to receptor simulating the pollutants' atmospheric transport, dispersion, chemical conversion and deposition [1]. So receptor-oriented methods can define a specific group of chemical elements (“finger print”) in collected environmental samples and associate it to the source. This principle is the basis for using the cluster analysis, which classifies objects with similar characteristics into subsets where an object is as possibly similar to others in the same cluster [2]. Objects in each subset are considered similar when they are closer to other objects in the subset than to objects in other subsets with some selected metric. The article introduces application of self-organizing map (SOM) / Kohonen map representing a type of artificial neural network (ANN) for identification of such clusters [3], [4].

The atmospheric aerosol can be sampled also through the biomonitoring, which is used for the systematic and long-term assessment of the environment comprising the atmospheric deposition [5]. To assess the long-term atmospheric deposition and transfer, bryophytes, in particular, pleurocarpous mosses are commonly used. Mosses are able to concentrate metals and other elements to remarkably high concentrations owing to the high cation exchange capacity of their tissues and lack of root system and protecting cuticle on their leaves [6], [7], [8]. Further, carpet-forming mosses have a large total surface area and other structural properties which promote a mechanical retention of depositing particles. These advantages have facilitated the use of mosses in monitoring heavy metal deposition in many areas of the world [9], [10], [11], [12].

Mosses are resistant against many substances which are highly toxic for other plants. As a consequence of their nutrient cycling and uptake mechanisms, they tend to accumulate pollutants [13], [14]. These moss abilities can be observed even under natural conditions without visible human negative effects. For example, groups of bryophytes specialized on Cu-enriched substrates are known as well as bryophytes which are associated with lead- and zinc-enriched substrates [15] [16] [17].

The main goal of the biomonitoring was to identify the origin of air pollution and study the spatial distribution of trace elements in the region. To meet this goal, different approaches while analysing obtained data are being tested, including the presented method of ANN. The biomonitoring followed the methodology introduced in the Monitoring Manual established by the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation 2015) [22].

Materials and Methods

Biomonitoring

Atmospheric deposition for data analysis was determined by biomonitoring using pleurocarpous mosses. The sampling network covered the area of the Moravian and Silesian region in the Czech-Polish borderland where the concentrations of particulate matter (PM) exceed the annual average limit (for PM_{10} = 40 μg.m^{-3}, for $PM_{2,5}$ = 25 μg.m^{-3}) over long term [20]. Sampling sites were located on a regular 10 x 10 km grid with an extra point in the centre of every cell. The grid numbered 41 points covering area of 1600 km^2 (40 km x 40 km) [21]. See Figure 1.

The moss was sampled within one week in October 2015 to minimalize the intra-annual variability [23]. According to the Manual [22] sampling a single species is preferred because of possibly different accumulation coefficients but the single species hadn’t occurred at all sites so more species were sampled [23]. The most frequently sampled moss species in the area were *Brachythecium rutabulum (Hedw.)* (66% of all samples), then (in descending order of frequency): *Cirriphyllum piliferum (Hedw.)* (12 % of samples), *Hypnum cupressiforme (Hedw.)* (10 %), *Hylocomium splendens (Hedw.)*, *Brachythecium salebrosum Schimp.* and *Eurhynchium hians (Hedw.)*.

The moss samples were transported to the laboratory daily, dried at the constant ambient temperature (20°C) for 24 h and processed immediately. All extraneous material (plant and tree remains, visible particles) was manually removed and using quartation apical segments were separated from the shoots to monitor approx. 3-years deposition. Processed samples were analysed via Epithermal Neutron Activation Analysis (ENAA) at the IBR-2 fast-pulsed reactor in Frank Laboratory of Neutron Physics (FLNP), Joint Institute for Nuclear Research (JINR) in Dubna [24].

Neutron activation analysis (NAA)

NAA is a sensitive analytical technique performing qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples of almost every conceivable field of scientific interests [25]. NAA within the IBR-2 reactor provides activation with epithermal neutrons at low temperatures, convenient for biological samples, and it is equipped with the automatic system for sample transportation and measurement [26]. Neutron flux characteristics and other technical details can be found in Frontasyeva and Pavlov [27]. To determine the element content of mosses, samples were packed in polyethylene and aluminium cups for short-term and long-term irradiation, respectively. The elemental content in moss samples was analysed using the Channel 2 (for short-term irradiation) and the Cd screened irradiation Channel 1 (for long-term irradiation) with neutron flux density φ_{epi}= 3.6×10^{11} n.cm^{-2}.s^{-1} and irradiation time 1 min and 89 h, respectively. After 3 days cooling, the samples were repacked and measured twice on HPGe Radiation Detectors, the first time directly after repacking and the second time 20 days after the irradiation. The measurement time was 0.5 and 1.5 h, respectively. Obtained gamma-spectra was processed using GENIE software [28] and the content of each element in moss was calculated via software developed in the FLNP, JINR [26]. In total 38 elements were determined by NAA: Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Fe, Hf, I, K, La, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, Tm, U, V, W and Zn. For results see Table 1.

Table 1: The minimum, maximum, average and standard deviation (in mg/kg) of the element content

Element	Min.	Max.	Aver.	St. Dev.
Na	117	1150	306.1	176.7
Mg	1450	4790	3001.6	825.9
Al	430	6790	2977.9	1710.5
Cl	102	2240	660.5	454.8
K	1040	20200	11851.8	3289.1
Ca	3600	10600	7690.2	1714.6
Sc	0.076	1.38	0.59	0.34
Ti	59.1	573	236.1	143.5
V	0.781	10.9	4.9	2.7
Cr	2.28	34.1	9.4	6.4
Mn	47	642	187.0	118.4
Fe	690	18700	3106.8	2861.5
Co	0.238	2.13	0.88	0.48
Ni	0.711	6.85	3.15	1.46
Zn	30.6	263	88.5	40.8
As	0.286	2.59	1.0	0.50
Se	0.060	1.48	0.4	0.31
Br	1.65	6.65	3.1	1.08
Rb	6.8	53.2	13.1	7.1
Sr	15.6	54.1	33.0	10.0
Mo	0.172	1.0	0.55	0.21
Cd	0.176	1.78	0.71	0.34
Sb	0.107	1.15	0.40	0.22
I	0.396	4.08	1.51	0.78
Cs	0.148	1.00	0.43	0.23
Ba	15.5	154	63.9	28.0
La	0.260	4.70	1.81	1.06
Ce	1.03	9.79	3.67	2.27
Nd	0.512	5.41	2.49	1.17
Sm	0.039	0.808	0.288	0.171
Tb	0.007	0.116	0.044	0.025
Tm	0.006	0.075	0.026	0.015
Hf	0.048	1.21	0.465	0.309
Ta	0.009	0.153	0.059	0.035
W	0.059	1.38	0.276	0.212
Au	0.0002	0.068	0.003	0.011
Th	0.063	1.75	0.589	0.376
U	0.028	0.562	0.229	0.132

The quality control of ENAA results was ensured by carrying out simultaneous analysis of the reference material. As nuclear reactions and decay processes are virtually unaffected by the chemical and physical structures of the material during and after irradiation, standards with different compositions can be employed [24]. For moss analyses was used standard reference material 2711 Montana II Soil from the National Institute of Standards and Technology (NIST), 1633b Constituent Elements in Coal Fly Ash (NIST) and BCR-667 Estuarine sediment (trace elements) from the Institute for Reference Materials and Measurements (IRMM). The reference materials and 10 – 12 moss samples were packed together at each transport container. Thus four measurements of the reference materials were done for each set of 44 samples.

Self-Organizing Maps (SOM)

Kohonen or Self-Organizing Maps are a kind of neural networks with unsupervised learning. The goal of the unsupervised learning is to set the neural network to provide the same response to similar input vectors, to make a consistent output. This results in data clustering and classification of input objects without the need of knowledge about the desired output.

The Self-Organizing Map defines an ordered mapping, a kind of projection from a set of given data items onto a regular, usually two-dimensional grid [29]. The input data vectors' dimension is reduced to two. Every data item is mapped into the node which has the most similar value to the data item, e.g., has the smallest distance from the data item in some metric.

The visible part of a Kohonen Map is the map space, it consists of components called nodes or neurons. The map space is defined beforehand, usually as a finite two-dimensional region where nodes are arranged in a regular hexagonal or rectangular grid [30].

The node value is then usually a certain weighted local average of the given data items in the data space. But in addition to that, when the models are computed by the SOM algorithm, they are more similar at the nearby nodes than between nodes located farther away from each other on the grid. In this way the set of the models can be regarded to constitute a similarity graph [29].

The SOM was originally developed for the visualization of distributions of metric vectors, such as ordered sets of measurement values or statistical attributes, but it can be shown that a SOM-type mapping can be defined for any data items, the mutual pairwise distances of which can be defined [29].

The element composition data from moss samples were clustered by a Kohonen map with 2x2 rectangular map space grid. So, data were clustered into 4 separate clusters. The analysis was performed in the R statistical software via the *'kohonen'* package [31]. The output of the analysis in R can be found in Table 2.

Table 2: Determined clusters via the '**kohonen*****' package: Output of the R software***

No	Sample ID	Latitude	Longitude	Cluster
1	PLS15-05-01	50.00012	18.72923	3
2	CZT15-01-01	49.96902	18.17001	3
3	PLS15-02-01	49.97675	18.30889	1
4	PLS15-03-01	49.98432	18.44780	2
5	PLS15-04-01	49.99173	18.58676	3
6	PLS15-29-01	49.82392	18.74425	4
7	CZT15-26-01	49.92812	18.24544	3
8	PLS15-27-01	49.93577	18.38241	4
9	PLS15-28-01	49.94325	18.52302	4
10	CZT15-08-01	49.89566	18.45821	3
11	PLS15-10-01	49.91283	18.74737	4
12	CZT15-06-01	49.87495	18.18211	3
13	CZT15-07-01	49.88738	18.32156	3
14	PLS15-09-01	49.95356	18.65898	4
15	CZT15-30-01	49.84154	18.25709	3
16	CZT15-31-01	49.84659	18.39420	4
17	PLS15-33-01	49.81147	18.62174	3
18	PLS15-33-02	49.81147	18.62174	3
19	CZT15-32-01	49.85179	18.53764	3
20	CZT15-13-01	49.80514	18.47095	3
21	PLS15-15-01	49.82363	18.74420	3
22	CZT15-12-01	49.79597	18.34116	3
23	PLS15-14-01	49.81147	18.62168	3
24	CZT15-11-01	49.78381	18.19548	2
25	PLS15-37-01	49.77478	18.63198	3
26	CZT15-34-01	49.75054	18.26842	4
27	CZT15-35-01	49.75775	18.40639	4
28	CZT15-36-01	49.76405	18.54587	4
29	CZT15-17-01	49.70903	18.34840	2
30	CZT15-18-01	49.71640	18.48285	3
31	PLS15-20-01	49.73192	18.76080	4
32	CZT15-16-01	49.69894	18.21002	2
33	CZT15-19-01	49.72291	18.62060	4
34	CZT15-40-01	49.67743	18.56031	3
35	CZT15-39-01	49.66703	18.41824	3
36	CZT15-41-02	49.68173	18.69553	3
37	CZT15-41-01	49.68173	18.69553	4
38	CZT15-38-01	49.65716	18.28579	2
39	CZT15-38-02	49.65837	18.28730	2
40	CZT15-21-01	49.61475	18.21676	3
41	CZT15-22-01	49.61842	18.35601	3
42	CZT15-23-01	49.62594	18.49393	4
43	CZT15-24-01	49.63330	18.63188	4
44	CZT15-25-01	49.64049	18.76988	3

Result and discussion

The element composition data from moss samples were clustered by a Kohonen map with 2x2 rectangular map space grid. So, data were clustered into 4 separate clusters. The analysis was performed in the R statistical software via the *'kohonen'* package [29]. The result was visualized as the map in the ArcGIS [32] with the OpenStreetMap as a base map. (Figure 1)

There were three sites - PLS15-33, CZT15-38, CZT15-41, where two samples with different species of moss were collected. All sample couples were put into same clusters by the computation algorithm.

The elemental content was classified into the clusters by significance using box-plots as illustrated on the diagram in Figure 2:

- Cluster 1 – no element
- Cluster 2 – Al, Br, Ca, Fe, K, La, Nd, Sm, Sr, Ti, Tm, Zn
- Cluster 3 – As, Ce, Co, Hf, Mn, Ni
- Cluster 4 – Ba, Cd, Cl, I, Mo, Rb, Sc, Ta, Tb, Th, U, V

Au, Cr, Cs, Mg, Na, Sb, Se, W were not included in any cluster as no significance was found.

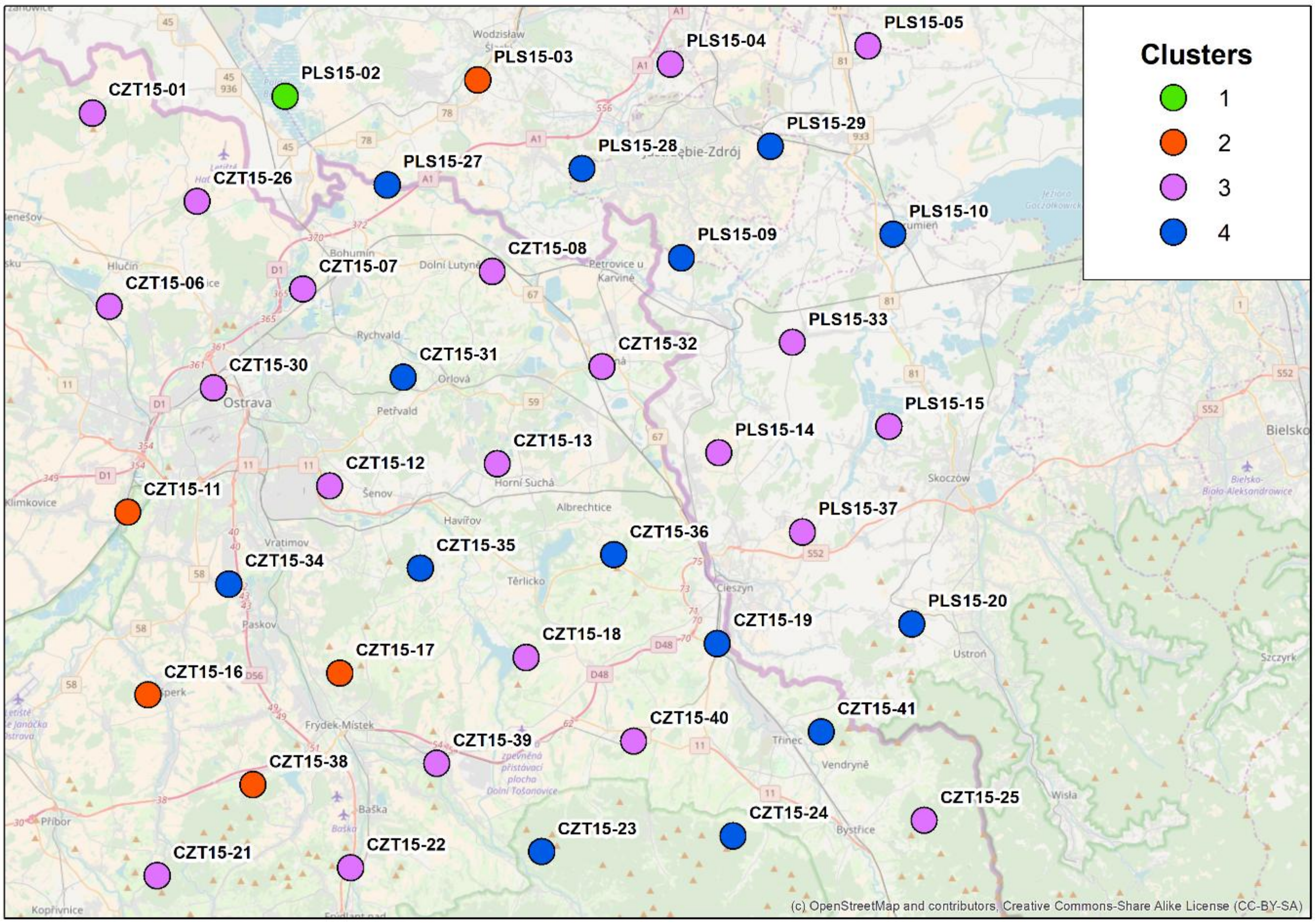

Figure 1: Moss sample clusters determined by Kohonen maps

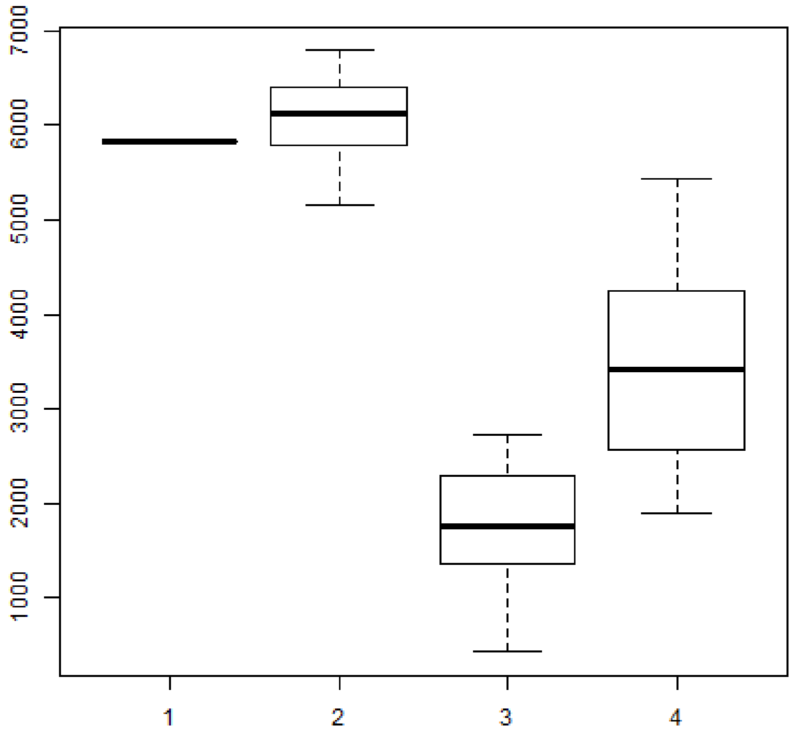

Figure 2: Box plot showing the significance of Al in respective clusters (Al content in [mg/kg] / cluster)

Standard statistical algorithms used for the cluster analysis [33] of biomonitoring data work with the assumption that input data are unconstrained and independent, the input data vectors are therefore vectors of an Euclidian space. This is not the case of moss sample data which are compositional. The data are constrained in two ways. The composition of each element is a number greater or equal to zero and the total sum of all compositions has to be less or equal than some ceiling value (f.e. 100%, 1 000 000 ppm, etc.). Existence of such constraints prevents usage of standard multivariate statistical methods, such as PCA or k-means clustering with standard L^p metrics because those methods can be applied only on unconstrained data.

When standard statistical algorithms are used, these constraints are either omitted which is mathematically wrong or the data needs to be transformed into the new set of unconstrained variables. In that case, the analyst losses the key analytical information about elemental compositions in each cluster.

Artificial neural network algorithms, including Kohonen maps, do not assume calculation with unconstrained, Euclidian data. The cluster analysis may be performed on original data without any necessary transformation which allows further analyses based on the presence of a specific element or elements and in this case identify the origin of the pollution.

Conclusion

Taking into consideration the specifics of biomonitoring data, this article presents the application of ANN for the cluster analysis and recommends this method for further testing as promising supposed results for the identification of pollution origin which will be published later on. Although this algorithm needs greater computing time, it is much universal, robust, user friendly (not as demanding on mathematical skill of the analyst) and easily automated.

The next step for the full employment of the method is to (1) test the other computing ANN algorithm (*K-means* [34]) and its combination with Kohonen maps; (2) compare the ANN clustering with standard statistical methods [33]; (3) apply the method on the bigger dataset (biomonitoring within the project AIR TRITIA numbering 299 moss samples) - the publication is being prepared

As presumed, the application of this method allows to classify biomonitoring data to clusters which are supposed to have the same origin of the pollution with maintaining the information about the chemical composition of each element in the respective cluster. This is one of the key information when determining the origin of pollution.

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Shluková analýza dat o atmosférické depozici zjištěné pomocí biomonitoringu

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Souhrn

Článek uvádí možnost identifikace původu znečištění pomocí shlukové analýzy prostřednictvím samoorganizující (Kohenenovy) mapy. Za účelem stanovení atmosférické depozice bylo na česko-polském pohraničí (region Moravy a Slezska) monitorováno znečištění v přirozeně rostoucím mechu. Metoda byla aplikována na datové sadě čítající 44 vzorků shromážděných ze 41 míst, ve kterých byl určen obsah 38 prvků za použití neutronové aktivační analýzy. Metoda byla využita ke klasifikaci bez nutnosti jakékoliv transformace dat a bez jakékoli ztráty informací, takže takto určené klastry obsahují informace o chemickém obsahu prvků potřebném pro identifikaci původu znečištění. Aplikovaná metoda se doporučuje po dalším testování použít.

***Klíčová slova**: shluková analýza, atmosférická depozice, biomonitoring, mechy*

Selective non catalytic reduction of NO_X by ammonia – Effect of iron additives

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Summary

Selective non catalytic reduction of NO_x by ammonia (SNCR) represents relatively easy process for NO_x emissions decrease. However, regarding to its relatively low efficiency, there is an effort to find the way, how to increase it. Accessible and cheap Fe additives (gray cast-iron and siderite) were tested for understanding their catalytic effect on the SNCR process at laboratory conditions, where no radicals formed during fuel combustion are present. The catalytic effect of iron additives was tested in the fix bed reactor with feed containing NO, NH_3, O_2 and water vapor. It was found out that Fe additives have inhibitory effect on the SNCR process, which can be explained by the ability of the formed Fe oxides to oxidize ammonia non-selectively into nitrogen and/or NO_x. However, this negative effect of Fe additives on SNCR can be minimized by adjusting the temperature, oxygen amount in the feed gas, NH_3/NO_x ratio or ensuring pre-oxidation of the Fe materials by oxygen by their dosing into oxygen rich area or ensuring appropriate time delay between contact of additive with oxygen and NO_x and ammonia.

***Keywords**: SNCR, additive, Fe oxides, NO_x reduction*

Introduction

Air pollution by nitrogen oxides is one of the current problems of the industrial society. More strict emission limits for NO_x are planed according to BAT Reference Document[1], which point out the need to find new technologies for NO_x removal. Selective non catalytic reduction of NO_x by ammonia (SNCR) represents relatively easy process for NO_x emissions decrease and is worldwide commercially used (equation 1-3). However, high efficiency, which can be achieved in the laboratory conditions is not easy to reach at real industrial conditions, because there are a lot of factors influencing SNCR process (temperature, mixing degree, gas composition, residence time, etc.), which are difficult to be maintained constant. Ammonia can be non-selectively oxidized in the presence of oxygen according to undesirable reactions to N_2, N_2O and NO (equations 4-6) and each of the above mentioned parameters can influence if these reactions take place and thus decrease overall efficiency.

$$4\,NH_3 + 6\,NO \rightarrow 5\,N_2 + 6\,H_2O \qquad (1)$$
$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (2)$$
$$8\,NH_3 + 6\,NO_2 \rightarrow 7\,N_2 + 12\,H_2O \qquad (3)$$
$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \qquad (4)$$
$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 3\,H_2O \qquad (5)$$
$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \qquad (6)$$

The detailed overview of the SNCR process was published by Tayyeb Javed[2]. Reaction mechanism is of radical type with key role of $OH^\cdot$ radicals. NO reduction is initiated by the reaction of NH_3 with hydroxyl radicals giving amidogen ($–NH_2$). In the absence of water vapor, amidogen can be also formed by the reaction of NH_3 with oxygen atom (O). The SNCR mechanism can be explained in terms of $OH^\cdot$ radicals concentration or the dominance of the chain branching or chain terminating sequence. $NH_2^\cdot$ radical is very selective towards NO at optimum temperature even in oxidizing atmosphere. NO is primarily decomposed by reactions with $NH_2^\cdot$, but besides reactions with species of NH_i type NO can be decomposed by reaction with CH_i species from the fuel. The presence of oxygen in waste gas is prerequisite for successful SNCR. However, the influence of oxygen is described by various authors differently. Liang[3] introduced a more comprehensive description - at lower temperatures, the NO reduction efficiency increases with increasing O_2 concentration and at the same time with higher NH_3 consumption. Conversely, at higher temperatures, an increasing amount of O_2 inhibits NO reduction, but suppresses the formation of unwanted N_2O. Another important SNCR parameter is the NH_3/NO_x molar ratio. It has been found that the optimum reduction temperature increases with an increasing molar ratio of NH_3/NO_x, with the highest NO_x conversion being achieved at NH_3/NO_x value of about 1.6. Some work reports that the increasing NH_3/NO_x molar ratio does not shift the optimum reduction temperature but extend the temperature window and increase NO_x conversion[2]. The NH_3/NO_x ratio is closely related to residual ammonia emissions – ammonia slip. The ammonia slip starts to appear at NH_3/NO_x molar ratio higher than 1.3 and is dependent on the specific conditions of the SNCR technology (gas composition, reaction time, NH_3 blending efficiency with exhaust gas, temperature etc.)[2].

SNCR is widely used but this technology will not ensure the fulfilling of planned new strict emission limits for NO_x. Therefore, there is an effort to increase the SNCR process efficiency. Most commonly it is tried to change or fix the above mentioned parameters in order to increase the efficiency. Also the addition of some additive was tested, since it was supposed, that additives can intensify NO_x reduction process. The most commonly mentioned SNCR additives are: H_2, CO, CH_4, various alcohols, phenols and toluene[2, 4]. Li[5] studied the effect of Na_2CO_3, C_2H_5OH and $FeCl_3$ on SNCR efficiency, but in the presence of excess of NO and NH_3 over O_2. The addition of these additives extended the temperature window and moved conversion maximum to lower temperatures, resulting in an optimal temperature drop and an increase in NO_x destruction. The observed effect was explained by the positive influence on formation of $OH^\cdot$ radicals at lower temperatures.

The use of iron-based additives to reduce NO_x emissions from stationary combustion processes was published by V. Lissianski[6,7]. The tests were carried out on real combustion facility (300 kW).The patent of the same authors[8] stated that the additive can be added to the main combustion chamber as well as to the reburning chamber and that the addition of the metal-based additive to the reburning chamber is effective in the presence of a reducing agent (N-reagent) and surprisingly even in its absence. In the case of additive dosing with overfire air (OFA), very low NO_x reduction efficiency was achieved, indicating that a fuel-rich atmosphere containing CH_i or NH_2 and/or CO radicals is required for the proper operation of the iron additive. The authors state that by adding additive to the main combustion chamber together with fuel and into reburning zone, a 30% reduction of NO_x and a 20% reduction of NO_x can be achieved, respectively. The possible mechanism of heterogeneous NO_x reduction includes direct catalytic reduction of adsorbed NO and indirect effects of radical loss. Radical loss means that in the presence of iron containing additives, the concertation of non-carbon radicals is smaller and more carbon-containing radicals can participate in reaction with NO. The recommended way of dosing the additive is to mix them with fuel, separate dosing or dosing together with a reducing agent, in one or even in more locations.

Iron oxides were also tested within existing research on selective catalytic reduction of NO_x by ammonia (SCR), but this is commonly done on the temperature range below 500 °C, under conditions where SCR by NH_3 is normally used. The influence of Fe and its oxides on NO_x reduction by NH_3 above 500 °C and thus applicable for modification of SNCR process was published only minimally[9]. However, the understanding of the effect of iron-based additive at conditions suitable for SNCR can be helpful for the improved application of the SNCR process.

The aim of our work was to use commonly accessible and cheap Fe materials, namely gray cast-iron (Fe) and siderite ($FeCO_3$), and test them as SNCR additives at conditions suitable for SNCR to study their catalytic effect on the SNCR process at laboratory conditions. The laboratory conditions allow studying the effect of additives on the SNCR without presence of CH_i radicals formed from the combustion of fuels. The results obtained in laboratory conditions should be helpful for planning/operation of real combustion test, since the additive can be dosed in many different locations (which are suitable for SNCR), in different ways (eg. stable load of “catalyst”, powder which fly together with off gas, fluidized bed, mixed or dosed with fuel etc.) and in different oxidation states.

Experimental

The surface areas of Fe-additives were determined by N_2 adsorption/desorption at -196 °C using 3Flex instrument (Micromeritics, USA) and evaluated by BET method. Prior to the measurement, the samples were dried at 150 °C for 72 hours.

For phase composition of additives, the powder X-ray diffraction (XRD) patterns were recorded using a Rigaku SmartLab instrument with the Bragg-Brentano geometry and D/teX Ultra 250 detector, Co radiation source (λ_1 = 1.78892 nm, λ_2 = 1.79278 nm), 40 kV, 40mA, 2θ measured range from 5 to 90°, step size 0.02° and rate 1.5 $°.min^{-1}$. The phase composition was evaluated according to the database issued by ICDD (PDF-2).

Thermogravimetric and differential thermal analysis of siderite were performed on a SETARAM TG/DTA SETSYS Evolution-1750 at 950 °C in an air atmosphere (20 ml/min) at a heating rate of 10 °C/min with a sample loading of 70 mg.

The catalytic effect of iron-based additives (additive in powder form diluted with inert glass sand) on the SNCR was tested in the fix bed ceramic reactor (internal diameter of 8 mm). Feed to the reactor contained 0.05 mol. % NH_3, 0 (NH_3 oxidation) or 0.05 mol. % NO, 0 - 10 mol. % oxygen and 2 mol. % water vapor in N_2 at 700 and 900 °C; total flow rate was 700 ml/min (21 °C, 101325 Pa). For each test and each temperature, the fresh sample was used. The sample was heated in N_2 to the appropriate temperature and then it was switched to the inlet mixture. The outlet concentrations were measured for two hours in order to monitor the changes of the additive oxidation state caused by the reaction and its consequent catalytic effects. The effect of additive was evaluated on the basis of comparison with the test without additive, which reflects response of the catalytic setup system (blank test). Blank test was realized as a step response of inlet mixture and included effect of NH_3 adsorption on the walls of the system and homogeneous SNCR NO_x by ammonia. Fourier transform infrared analyzer FTIR (Antaris IGS, Nicolet) was used for analysis of NO, N_2O, NO_2 and NH_3. In the real combustion process, it is supposed that additive would be dosed also as the powder of the same grain size.

Results and Discussion

Physico-chemical properties of additives are shown in Table I. Both additives could be regarded as macroporous material with low specific surface area of 1 $m^2.g^{-1}$ and 3 $m^2.g^{-1}$ for grey cast-iron and siderite, respectively.

$FeCO_3$ additive is a subject to thermal decomposition at higher temperatures; therefore, thermogravimetric and differential thermal analysis was also conducted. During heating, siderite decomposes to CO_2 and iron oxides depending on the decomposition conditions. Ferric oxide or ferrous oxide can be formed. The latter is stable only above 575 °C and decomposes to iron and ferric-ferrous oxide below this temperature. From the thermoanalytic curves (Figure 1), it can be seen that thermal decomposition occurs between 400-600 °C followed by a smaller weight loss of about 700 °C. The whole process is completely terminated at 760 °C. Due to the fact that the catalytic tests were carried out at 700 and 900 °C, $FeCO_3$ was decomposed before the tests started with formation of FeO, which were further oxidized in the tests. Since our FTIR analysis allowed semiquantitative monitoring of CO_2, it was found that massive CO_2 formation occurred during heating in the above-mentioned temperature interval but also to a lesser extent at the start of the reaction (independently of temperature).

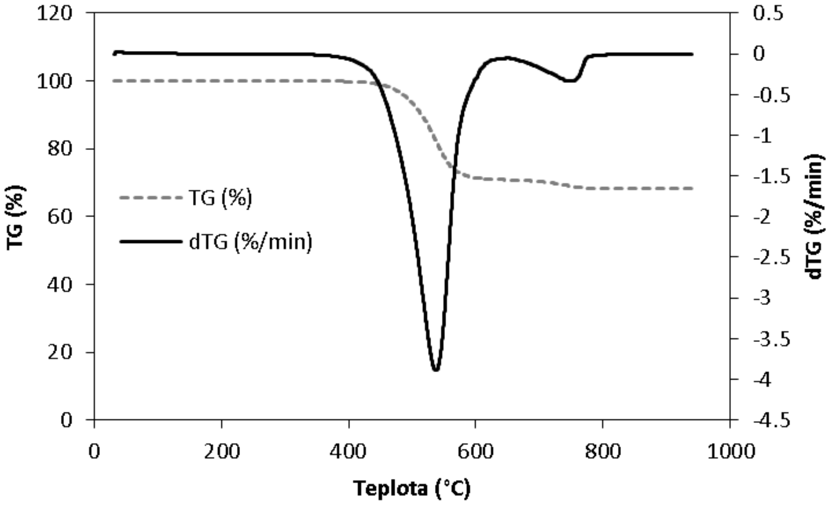

Figure 1: Thermoanalytic curve of siderite.

For this reason, it can be concluded that the decomposition of siderite could proceed according to equations (7) and (8).

$$FeCO_3 \rightarrow FeO + CO_2 \qquad (7)$$

$$4\ FeCO_3 + O_2 \rightarrow 2\ Fe_2O_3 + 4\ CO_2 \qquad (8)$$

The additives in the fresh state and also after the reaction were measured by XRD to determine the phase composition (Table I). It is clear that during SNCR and NH_3 oxidation tests (test where NO was not present), the partial oxidation of grey cast iron to Fe_2O_3 and the decomposition of $FeCO_3$ into iron oxides followed by gradual oxidation to Fe_2O_3 and Fe_3O_4 occurred. It is also possible that under the reaction conditions, a part of iron may also be present in the form of FeO, which is not stable at lower temperatures and after cooling of the additive after the reaction in the air, it is oxidized to Fe_3O_4.

Table I: Physico-chemical properties of fresh and spent Fe-additives

Additive	**Additive state**	**Majority phases (XRD)**	**Minority Phases (XRD)**	**S_{BET} (m^2/g)**
$FeCO_3$	fresh	Siderite $FeCO_3$	Dolomite $CaMg(CO_3)_2$	3
Fe		Iron Fe	Graphite C	1
Fe	after SNCR 900 °C	Iron Fe	Hematite Fe_2O_3	n.d.
$FeCO_3$		Hematite Fe_2O_3 Magnetite Fe_3O_4	-	n.d.
Fe	after NH_3 oxidation 900 °C	Iron Fe Hematite Fe_2O_3	Magnetite Fe_3O_4 Graphite C	n.d.
$FeCO_3$		Hematite Fe_2O_3 Magnetite Fe_3O_4	-	n.d.
$FeCO_3$	after SNCR 700 °C	Hematit Fe_2O_3 Magnetite Fe_3O_4	-	n.d.
Fe	after NH_3 oxidation 700 °C	Iron Fe Hematite Fe_2O_3	Magnetite Fe_3O_4	n.d.
$FeCO_3$		Hematite Fe_2O_3 Magnetite Fe_3O_4	-	n.d.

The laboratory experiments were focused on studying of various parameters affecting the SNCR efficiency: temperature, additive composition, oxygen amount in the feed gas and NO_x/NH_3 molar ratio in the feed mixture. For comparison, NH_3 oxidation tests (without NO_x) were also performed. The results are shown in Figures 2 – 6. For each measurement, graphs showing conversion of NH_3 and NO_x at selected reaction times from zero to 120 minutes are given. Values reported at 120 minutes in many cases cannot be considered as steady state value, indicating the slow progress of occurring processes. When discussing the results, it is always necessary to keep in mind that after the placing the additive into the laboratory reactor, several different processes can now take place. These are (i) homogeneous SNCR NO_x by ammonia, (ii) homogeneous non-selective oxidation of NH_3 to NO, N_2O or N_2, (iii) heterogeneous non-selective oxidation of NH_3 to NO, N_2O or N_2 (heterogeneous catalytic effect of additive), (iv) catalytic decomposition of NH_3 to N_2 and H_2 on Fe[9], (v) oxidation/reduction of additive – the rate can be controlled by diffusion of reactants and products and Fe ions[10-12], (vi) adsorption of NH_3 on the additive.

At first, influence of additive was studied at 700 °C. The results are shown in Figure 2. The additive did not affect the NH_3 conversion in first three minutes compared to the homogeneous SNCR, but from the fifth minute of measurement, the NH_3 conversion increased significantly compared to the SNCR. The difference between the individual additives was not visible. In terms of NO_x conversion, the difference was evident already in the first minute of the reaction. In both cases, significant amount of NO_x was produced (NO_x conversion was negative) by heterogeneous non-selective oxidation of ammonia catalyzed by additives or by their decomposition/oxidation products. The amount of formed NO_x is depended on the reaction time. At the beginning of the reaction, more NO_x evolved on grey cast iron; it can be assumed that iron in a zero oxidation state catalyzes the non-selective oxidation of NH_3 to NO_x more significantly.

The non-selective oxidation of NH_3 to NO_x was confirmed by a separate NH_3 oxidation test at 700 °C (Figure 3a). In line with additive assisted SNCR results at the beginning of the reaction, more NO_x were produced on gray cast iron. In the presence of $FeCO_3$, slightly less NO_x was produced but significantly more than in homogeneous SNCR. It can be concluded that at the beginning of the reaction, iron contained in the grey cast iron was present as Fe^0, which efficiently oxidized NH_3 to NO_x. Fe^0 was slowly oxidized into Fe_2O_3 and Fe_3O_4 during reaction. The slightly different catalytic activity of additives at 120 minutes from the start of the reaction can be explained by the different ratio of individual phases (Fe_2O_3, Fe_3O_4 or FeO) in each sample. A long-term NH_3 oxidation test showed that under steady state conditions, all ammonia was oxidized in the presence of additives mainly to NO_x (70-80 %) and N_2 without N_2O formation (not shown).

The influence of the additive on SNCR efficiency at 900 °C is shown in Figure 4. Unlike the situation at 700 °C, the addition of the additive at 900 °C did not almost affect the NH_3 conversion. The amount of NO_x produced is much lower than that at 700 °C and the amount of NO_x produced over time varies with each additive. In the beginning of the reaction, similarly to situation at 700 °C, more NO_x was produced on grey cast iron. However, from the fifth minute, the negative effect of additives changed and lower NO_x conversion was achieved on $FeCO_3$ additive. The grey cast iron effect was constant from the tenth minute while the effect of $FeCO_3$ changed during whole period of 120 minutes.

The observed trends can be again explained by the different efficiency of various iron oxides (different oxidation state) to catalyze the non-selective oxidation of NH_3. Also at 900 °C, the fastest process was recognized on Fe^0. From phase analysis it was observed that at the beginning of the reaction, the Fe^0 present in the grey cast iron was partially oxidized to Fe_2O_3. In the case of $FeCO_3$, a mixture of Fe_2O_3 and Fe_3O_4 was found after the reaction at 900 °C, which explains the further catalytic activity of this sample 120 minutes from the start of the reaction. However, the effect of other elements such as Mn, Ca or Mg contained as impurities in $FeCO_3$ cannot also be excluded.

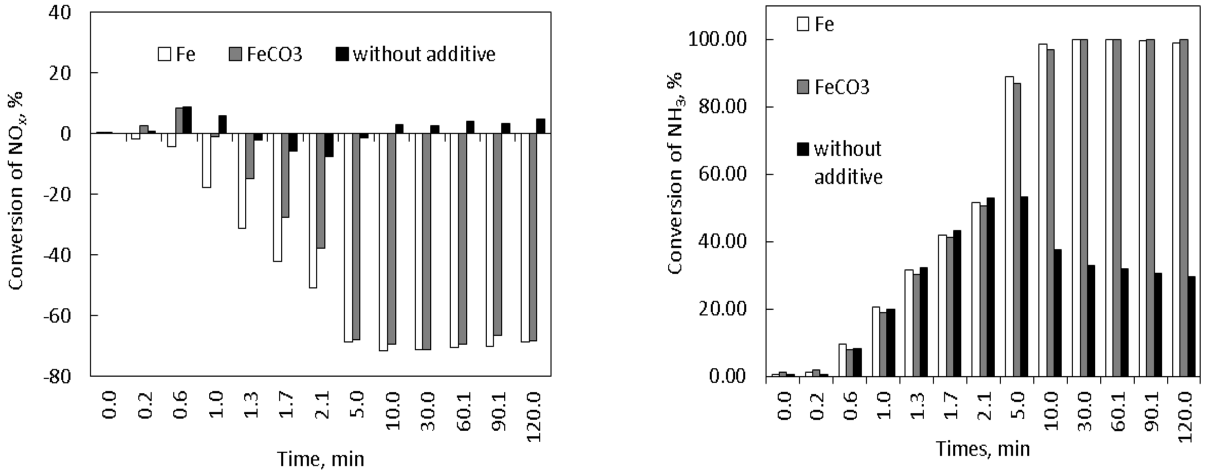

Figure 2: SNCR at 700 °C. ***Conditions: 0.05 mol. % NH_3, 0.05 mol. % NO, 10 mol. % oxygen and 2 mol. % water vapor in N_2, total flow rate was 700 ml/min (21 °C, 101325 Pa), additive amount: 0.1 g.***

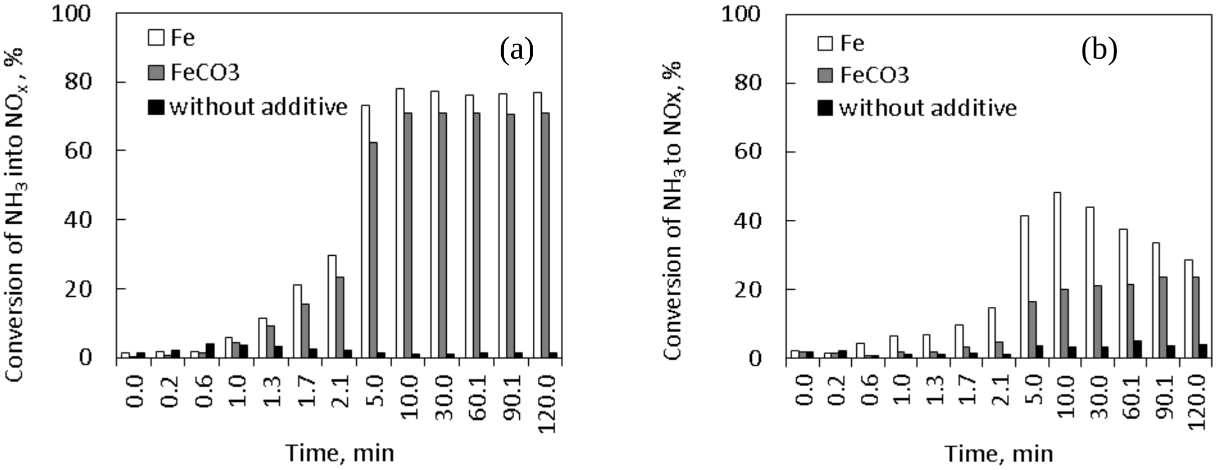

Figure 3: Ammonia oxidation (without NO) at (a) 700 °C (b) 900°C. ***Conditions: 0.05 mol. % NH_3, 10 mol. % oxygen and 2 mol. % water vapor in N_2, total flow rate was 700 ml/min (21 °C, 101 325 Pa), additive amount: 0.1 g.***

The effect of the Fe-additives on the oxidation of NH_3 (without NO_x in the feed mixture) at 900 °C is shown in Figure 3b, where conversion of NH_3 into NO_x is shown. Total NH_3 conversion (the sum of conversions into NO_x, N_2 and N_2O) did not changed in comparison with situation at 700 °C (not shown). Conversion of NH_3 into NO_x was higher during all studied time period in the presence of both additives at 900 °C, similarly to 700°C, than during homogeneous SNCR, however significantly less NO_X originated at 900 °C. The selectivity of the reaction changed during studied time and differed markedly from the situation at 700 °C. After two hours of reaction, conversion of NH_3 to NO_x on grey cast iron and $FeCO_3$ were comparable (around 30 %), while after one hour of measurement, the conversion obtained over $FeCO_3$ was twice lower than that of grey cast iron.

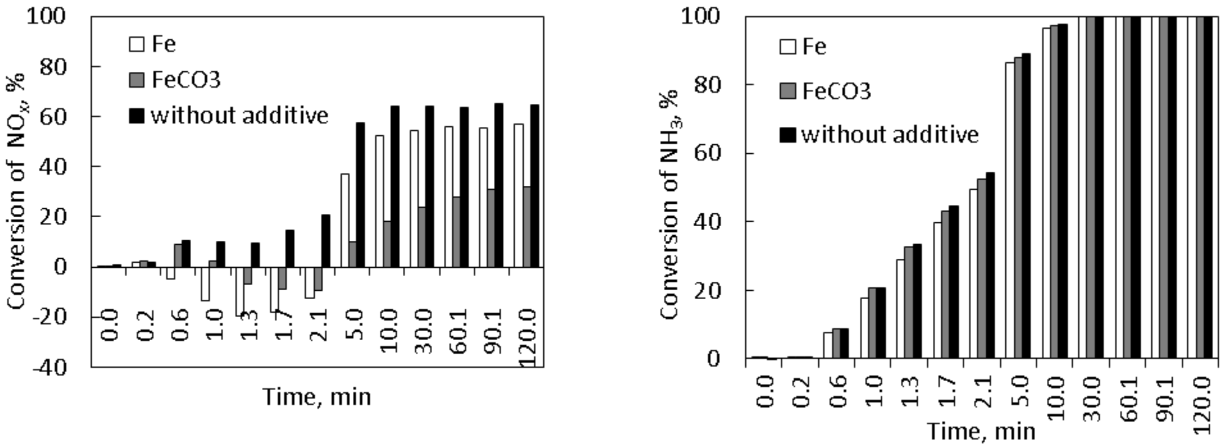

Figure 4: SNCR at 900 °C. Conditions: 0.05 mol. % NH_3, 0.05 mol. % NO, 10 mol. % oxygen and 2 mol. % water vapor in N_2, total flow rate was 700 ml/min (21 °C, 101 325 Pa), additive amount: 0.1 g.

Due to the different effects of additives on SNCR and NH_3 oxidation at 900 °C, it is supposed that different atmosphere (presence of NO_x) cause changes of additive oxidation states, affected the porosity of the formed oxides[13] and thus influences the achieved NO_x conversion. NO_x conversion is closely connected with the amount of accessible ammonia and the tests showed that additives and their decomposition/oxidation products catalyze ammonia oxidation differently.

Since the amount of oxygen in feed gas is detrimental for SNCR, the influence of O_2 was also studied for both additives at 900 °C. Two concentrations of O_2 (5 and 10 mol. %) were used. Test without oxygen was also performed on gray cast iron. The results are shown in Figure 4a for gray cast iron and in Figure 5b for siderite. When no oxygen was present in the feed gas, the NO_x conversion passed through the maximum and then declined to zero (time dependency), probably after complete oxidation of the Fe additive. As in the case of homogeneous SNCR, it is evident that oxygen is essential for NO_x reduction, however the nonselective ammonia oxidation seems to be dependent on the oxygen amount and thus increasing amount of oxygen in the feed gas decreased NO_x conversion for both tested additives. The time dependence was similar for both additives, at first local minimum of NO_x conversion was visible, which can be explained by the non-selective ammonia oxidation on the additives with low oxidation states with subsequent NO_x conversion increase and slow stabilization of catalytic performance, when the additive was oxidized into its stable form.

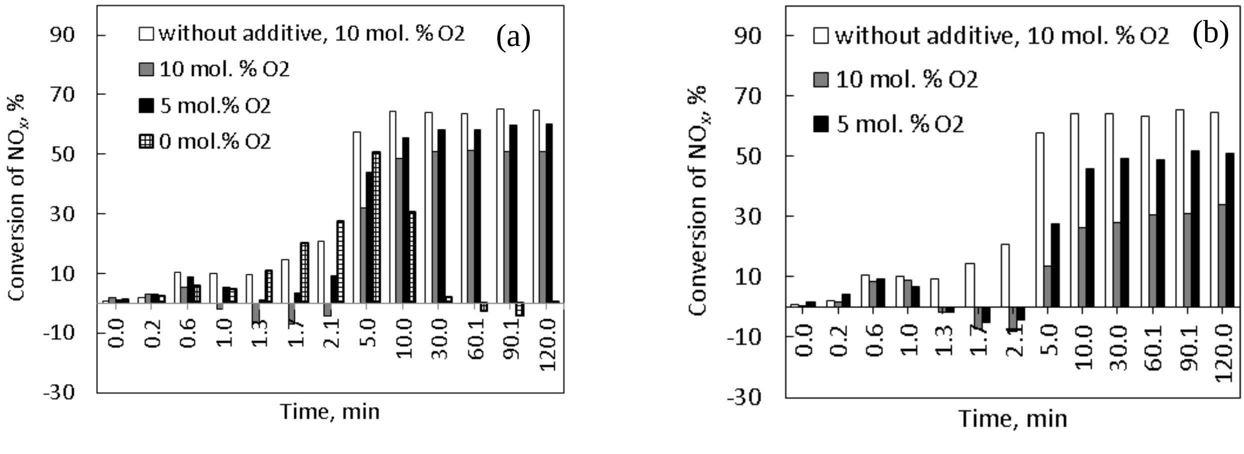

Figure 5: Effect of O_2 on SNCR at 900 °C, a) Fe, b) $FeCO_3$. Conditions: 0.05 mol. % NH_3, 0.05 mol. % NO, 0 – 10 mol. % oxygen and 2 mol. % water vapor in N_2, total flow rate was 700 ml/min (21 °C, 101 325 Pa), additive amount: 0.073 g Fe, 0.1451 g $FeCO_3$.

For both additives another important parameter, which can be easily adjusted in real process, was also studied - the NH_3/NO_x molar ratio. The effect of NH_3/NO_x molar ratio at 900 °C is shown in Figure 6. In both cases, a slight excess of the reducing agent to NO_x (molar ratio of 1.4) is desirable, which is consistent with the finding for homogeneous SNCR.

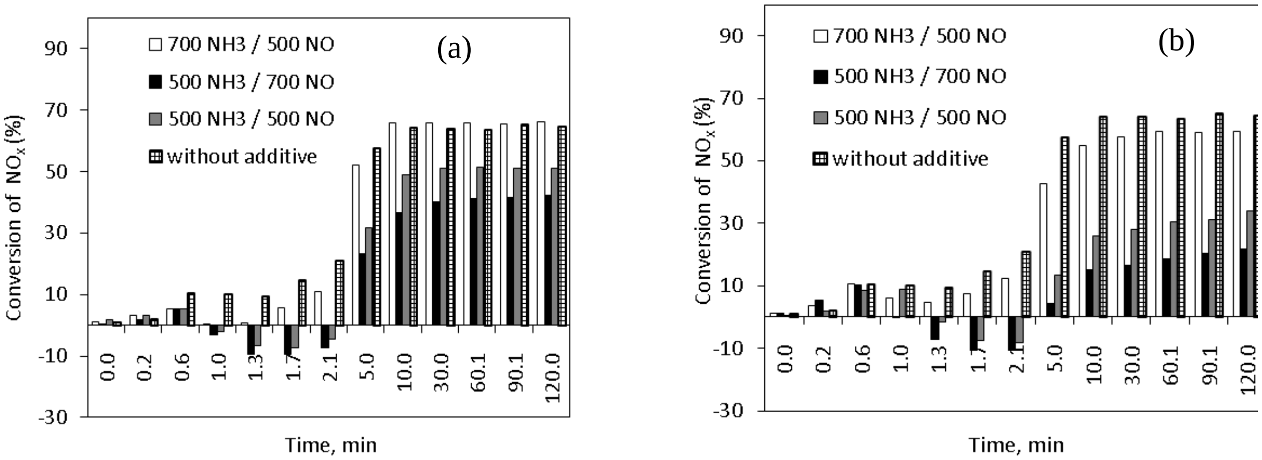

Figure 6: Effect of NH_3/NO_x on SNCR at 900 °C, a) Fe, b) $FeCO_3$. Conditions: 0.05 – 0.07 mol. % NH_3, 0.05 – 0.07 mol. % NO, 10 mol. % oxygen and 2 mol. % water vapor in N_2, total flow rate was 700 ml/min (21 °C, 101325 Pa), additive amount: 0.073 g Fe, 0.1451 g $FeCO_3$.

During all the tests of additive effects on SNCR, the amount of N_2O formed was also monitored. It was found out that none of the additives had any effect on the amount of N_2O produced - the same amount of N_2O was produced as for SNCR (without the additives).

Conclusion

Fe waste materials were tested as additives of SNCR. It was found out that Fe additives are oxidized during reaction into Fe_2O_3 and/or Fe_3O_4 and have inhibitory effect on the SNCR process, which can be explained by the ability of the oxides in low oxidation states non-selectively oxidize ammonia into nitrogen or NO_x. The negative effect of additives is reduced with increasing temperature from 700 to 900 °C and with decreasing of oxygen amount in the feed gas and depends of the extent of oxidation degree of the iron oxide - Fe oxides in higher oxidation state have lower negative effect.

Based on literature results[8] the mechanism of SNCR at real conditions of combustion facilities differs from those studied in this study in laboratory conditions, because in the real combustion chamber, CH_i and NH_i radicals from the fuel there are also present, which participate in the radical SNCR reaction. If the Fe-based additive would have positive effect in combustion facility published in the literature (iron catalyzed removal of non-carbon radicals which reduces the kinetic competition for carbon-containing radicals, thereby increasing the rate of NO_x removal[8]), the overall efficiency of additive assisted SNCR will depend on the sum of contributions of all reactions taking place in the system. For that reason, it is necessary to understand also negative effect of Fe-based additives (non-selective ammonia oxidation in the presence of Fe additives in their low oxidation states observed in this study) and ensure such conditions at which this negative effect will be minimalized. This can be done by adjusting the temperature, oxygen amount in the feed gas, NH_3/NO_x ratio or ensuring pre-oxidation of the Fe materials by oxygen by their dosing into oxygen rich area or ensuring appropriate time delay between contact of additive with oxygen, NO_x and ammonia. It is supposed that additive in the powder form will be pneumatically injected by separated additive injector. The testing of the effect of Fe-based additives in pilot plant combustion facility and thus differentiation between additive effect on SNCR without presence of radicals from the fuel and in their presence is currently in progress.

Acknowledgement

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Selektivní nekatalytická redukce NO_X amoniakem – vliv aditiv na bázi železa

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Souhrn

Selektivní nekatalytická redukce NO_x *amoniakem (SNCR) představuje principiálně jednoduchý proces snížení emisí* NO_x *a je komerčně využívána na celém světě. Nicméně vzhledem k nízké účinnosti v reálných podmínkách, je snaha najít cestu, jak účinnost SNCR zvýšit. Cílem naší práce bylo použití běžně dostupných a levných Fe aditiv - šedé litiny a sideritu (*$FeCO_3$*) - za podmínek vhodných pro SNCR ke studiu jejich katalytického účinku na proces SNCR v laboratorních podmínkách, kde nejsou přítomny radikály pocházející z paliva. Katalytický účinek aditiv na bázi železa byl testován v reaktoru s pevným ložem v přítomnosti kyslíku a vodní páry při 700 a 900 °C. Bylo zjištěno, že Fe oxidy mají inhibiční účinek na SNCR, což lze vysvětlit schopností oxidů neselektivně oxidovat amoniak na dusík nebo* NO_x*. Negativní vliv aditiv na účinnost SNCR se snižoval se zvyšující se teplotou a se snižujícím se množstvím kyslíku ve vstupní směsi a závisel na oxidačním stavu železa. Toto však může být minimalizováno úpravou teploty, množstvím kyslíku, poměru* NH_3/NO_x *nebo zajištěním oxidace Fe aditiv kyslíkem jejich dávkováním do oblasti bohaté na kyslík nebo vhodného časového zpoždění mezi kontaktem aditiva s kyslíkem a* NO_x *a amoniakem.*

Klíčová slova: *SNCR, aditivum, oxidy železa, redukce* NO_x

The use of heterogeneous photocatalysis for treatment of wastewaters containing azo dyes – effects of pH and salinity on TiO_2 zeta potential and photocatalytic activity

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Abstract

The knowledge of interrelations between catalyst zeta potential, dye adsorption, and photocatalytic performance is important for evaluating the process parameters of photocatalytic wastewater treatment. This paper deals with the experimental study of heterogeneous UV photocatalysis, used for removal of methyl orange dye from model wastewater. Photocatalytic experiments were conducted in an open batch reactor with P25 aeroxide TiO_2 as a photocatalyst and UV-A LED array as the light source. During experiments, the effect of pH and co-existing ions on the catalyst zeta potential and both the dye adsorption and degradation efficiency was studied. The adsorption of the dye onto the surface of the P25 catalyst was a very important step in the photocatalytic reaction and was strongly dependent on pH and salinity of the reaction solution. Photocatalytic decolorization was found out to be faster in acidic pH without any added sodium chloride. In contrary, the addition of sodium chloride significantly increased the decolorization efficiency in the alkaline pH. It also results from the comparison of the experimental data obtained, that the zeta potential is not a universal indicator of the degree of dye sorption as well as photocatalytic degradation on titanium dioxide.

Keywords: *heterogeneous photocatalysis, zeta potential, azo dye, waste water*

Introduction

Textile industry wastewaters, especially those from dyeing steps, usually contain high amounts of inorganic salts and organic azodye residues.[1] These dyes usually show low biodegradability and high toxicity which complicates their direct discharge into the watercourse.[2] In addition, conventional water treatment technologies are not usually designed to handle this specific class of pollutants, and their inadequate removal is commonly observed.[3,4] The residues of dye pollutants are then often discharged into surface waters, leading to the decline of water dissolved oxygen. This can lead to partial or complete water ecosystem destruction and to its eutrophication. Heterogeneous UV photocatalysis can deal with those recalcitrant contaminants, lowering their overall concentration and consequently wastewater toxicity.[5,6,7] Titanium dioxide mediated photocatalytic oxidation has been applied extensively for dye degradation studies.[5,6,8] This is mainly because of its low cost, stable nature and its optical absorption in the UV region. Photocatalytic processes have several advantages over competing processes. These are: (1) possibility of complete mineralization to harmless carbon dioxide, water, and mineral salts; (2) no waste disposal problem; (3) no manipulation with expensive oxidants is needed and (4) only mild temperature and pressure are necessary. On the other hand, the photocatalytic processes are in some cases costly and their non-selective nature often causes a relatively expensive degradation of conventional organic substances contained in treated wastewaters. Also, some intermediate degradation products can be more toxic than the original dye and the presence of inorganic salts in wastewater can significantly affect the degradation process.[9,10]

Heterogeneous photocatalysis is based on valence electrons excitation in a molecule of semiconductor catalyst by high energy photons of UV light. If the photon interacting with the valence electron has higher energy then the energy of a band gap (i.e. light of wavelength ≤ 390 nm for anatase type TiO_2), the electron is excited into the catalyst conduction band and a hole is left in the valence band, having a strong affinity for the electron. The holes can act on their own directly, or more often create hydroxyl radicals with a suitable electron donor, for example, water.[11] The hydroxyl radicals „·OH" are very reactive and aggressively attack virtually all organic compounds. The created radicals have a short lifetime, and it is advantageous if the compounds, that are supposed to be degraded, are located close to the radical's birthplace, i.e. in the vicinity of the photocatalyst particle surface, or to be directly adsorbed onto it.[12] Degradation can also take place by a self-sensitization mechanism, in which the light (often VIS) is absorbed by the dye molecule. Charge transfer from the excited dye molecule to the conduction band of the semiconductor results in the formation of an unstable dye cation radical, and an active species on the semiconductor surface that attacks the destabilized dye molecule.[13] Some authors also found that direct photolytic degradation of azo dyes can be observed, dominantly with hard VUV and UV-C light sources.[14] However, typically commercial dyes are designed to resist UV light and the direct photolysis is negligible or has a very low quantum yield.

Additionally, during the photocatalytic processes, adsorption of water, molecular oxygen, co-existing ions, and the dye onto the catalyst surface takes place. The adsorption of azo dyestuffs on the titanium dioxide surface has been previously studied by several authors.[9,15,16,17] The dye sorption is usually very fast, reaching equilibrium within 30 minutes.[15] The pH may affect the surface charge on the photocatalyst and also the state of ionization of the dye and hence its adsorption. Bouanimba et. al.[17] studied the influence of initial pH on adsorption of anionic methyl orange (MO) onto Evonik P25 titania catalyst. The pH was adjusted using sulfuric acid, hydrochloric acid, perchloric acid, nitric acid, and sodium hydroxide. In all cases, higher sorption was found in acidic than alkaline media. However, adsorption was lower when using H_2SO_4 in comparison with other acids. The effect of co-existing inorganic ions on both adsorption and photocatalytic degradation of organic compounds has been reported as negative by various researches. Dugandzic et al.[18] found a negative effect of chlorides on the decomposition of nicosulfuron, at pH 5, Guilard et al.[19] reported a negative effect of inorganic ions and correlated their inhibitive effect with the amount of dye, initially adsorbed on the titanium dioxide surface. Bouanimba et. al.[17] reported that the addition of salts such as NaCl, KCl, $CaCl_2$, Na_2SO_4, Na_2HPO_4, Na_2CO_3, and $NaHCO_3$ in the presence of TiO_2 significantly reduced MO adsorption and decolorization efficiencies. However, the addition of $BaCl_2$ appeared to enhance adsorption and degradation rate. Although the opinion that substances which are adsorbed strongly degrade faster is predominant, there are still conflicting results as summarized, for example, for various substrates, by Bhatkhande et. al.[9]

Zeta potential, or electrokinetic potential, is a nonequilibrium parameter, which affects all dispersion systems, including the used TiO_2 catalyst. It is a potential, between the slipping plane and counterion layer in surrounding bulk liquid.[11] The zeta potential value is an indicator of the double layers condition and dispersion system stability. When dispersed particles have high value, positive or negative, of zeta potential (± 30 mV is often declared as a borderline value of stability), they are repulsing each other, the creation of clusters is suppressed and the dispersion is stable. When the zeta potential is approaching zero (isoelectric point) the dispersion system is becoming unstable. The Zeta potential is generally dependent on many parameters (particle nature and concentration, pH, concentration and type of ions in solution, temperature, etc.).[20,21,22] Some of them are interconnected, so any change in one parameter has some effect on the others. The effect of pH and salinity on the zeta potential of various TiO_2 dispersions has been previously extensively studied by different authors.[23,24,25] To our knowledge, none of the works published did address systematically the relationship between zeta potential and process characteristics of the photocatalytic degradation of azo dyes.

To extend our knowledge on the interrelations between catalyst zeta potential, dye adsorption, and photocatalytic performance, the experiments were carried out with methyl orange (MO), i.e. sodium 4-{[4-(dimethylamino)phenyl] diazenyl}benzene-1-sulfonate, as a model mono-azo dye in various ionic environments. Methyl orange dye was selected for the study because of its anionic nature which corresponds to the electrostatic interactions required for the study, because it absorbs light at a wavelength greater than the illumination source wavelength, and because it is brightly colored, making it easy to detect. The experiments were performed in the range of pH in which the MO acid-base color changes don't take place. As a source of UV radiation, UV-A LEDs were used. LEDs have, in comparison to conventional UV sources, several advantages, such as higher efficiency (electric power saving), narrow range of emitted light frequencies (no direct photolysis and negligible emission of low energy light), better operational safety (no ozone and „hard“ UV production) and lower heat production. [26]

Experimental part

As a photocatalyst, the Aeroxide P25 titanium dioxide, manufactured by Evonik Industries was used. P25 is of mixed-phase TiO_2 mainly containing anatase (more than 80 %) and rutile, the two most common crystal phases of TiO_2. It consists of aggregated primary particles. The hydrophilic aggregates are several hundred nm in size and the primary particles have a mean diameter of approx. 21 nm. Particle size and density of 4000 kg/m³ lead to a specific surface of approx. 50 m²/g. In all experiments, the catalyst concentration of 1 g/l was used.

The sodium salt of methyl orange (Sodium 4-{[4-(dimethylamino) phenyl] diazenyl}benzene-1-sulfonate) manufactured by Lachema (CZ) was used as a model pollutant/dye. Absorption spectrum in a range from 190 to 750 nm was measured using DR 6000 UV/VIS spectrophotometer (Hach Lange, US) and the wavelength of maximum absorbance was determined. Then the calibration curve was constructed and used to determine the actual concentration of MO dye during degradation experiments.

All photocatalytic experiments were conducted in an open batch reactor with a volume of 250 ml, irradiated area of approximately 38.5 cm^2 and slurry depth of 8 cm. The LED UV-A light source CBM-120-UV-C14-FB365-21 (Luminus Devices, USA) was placed in the upper part at the distance of 2 cm from the surface of the reaction mixture. The module producer has declared radiation flux of 8.5 W at a peak wavelength of 365nm with a total power consumption of 32.5 W. The photocatalytic experiments were focused on the determination of the effect of pH and sodium chloride content on decolorization rate. After the photocatalyst was added to the dye solution, the produced suspension was intensively mixed for 1 hour to reach adsorption equilibrium. If needed, the suspension was adjusted by the addition of hydrochloric acid and/or sodium hydroxide. pH was monitored with the use of glass measuring electrode. The electrode was submerged into the measured mixture as briefly as possible and thoroughly rinsed with demineralized water before and after every use to prevent electrode fouling. For adjustment of sodium ions concentration, p.a. purity sodium chloride was used. Reaction mixture samples were taken in small volumes (1.8 ml) to avoid considerable changes in the reaction volume. The samples were left to sediment and centrifuged at 10 000 rpm for 10 minutes. For total organic carbon analysis, TOC/TN analyzer (SKALAR, NL) was used. Chemical oxygen demand was determined using Hach Lange LCI 500 cuvette tests. Multiple measurements were carried out under identical reaction conditions to confirm the reproducibility. The differences between duplicate measurements were less than 10%.

The adsorption of dye on TiO_2 catalyst surface was determined in the dark by using 200 mL of aqueous solution of dye at alkaline and acidic pH of 10.5 and 5.5. After 60 min of mechanical stirring, the aqueous samples were centrifuged to remove TiO_2 powder before spectrophotometric analysis.

The zeta potential/pH dependences were determined via titration of 1 g/l TiO_2 dispersion by MPT-2k auto-titrator (Malvern Instruments, UK). For adjustment, the pH 0.25 M HCl and 0.25 M NaOH were used. In some experiments, 65 mmol/l of sodium chloride was also added. Dynamic light scattering (DLS) measurements were performed using a NanoZS apparatus (Malvern Instruments, UK) operating at a wavelength of λ=633nm in backscattering mode. The average values of zeta potential, as well as hydrodynamic diameter, were calculated from 3rd order cumulant fits of the correlation functions measured at a given kinetic stage. The value of the isoelectric point (IEP) was determined from the graphical dependences obtained. All measurements were conducted at 25 ^{0}C after the TiO_2 suspension was adjusted in an ultrasonic bath for 10 min.

Results and discussion

First, preliminary experiments with diluted MO and TiO_2 catalyst irradiated with UV-A light were carried out, enabling to obtain optimum discoloration process conditions using procedures described in the paper of Kertesz [43]. The catalyst loading of 1 g/L, initial dye concentration in the range from 10 to 300 mg/l and agitation speed higher than 400 rpm were found as optimum. Experiments were also carried out in the absence of TiO_2 catalyst under UV-A irradiation. The MO dye was found as resistant to self-photolysis by UV-A light used. It means that no degradation of the model compound took place in the absence of a catalyst and true heterogeneous catalytic regime can be considered in the consequent experiments.

The measurement of the zeta potential of TiO_2 dispersion was important to understand the charge-related phenomena on the surface of the TiO_2 catalyst. The zeta potential profile of catalyst dispersion is shown in Figure 1 as the zeta potential vs. pH dependence.

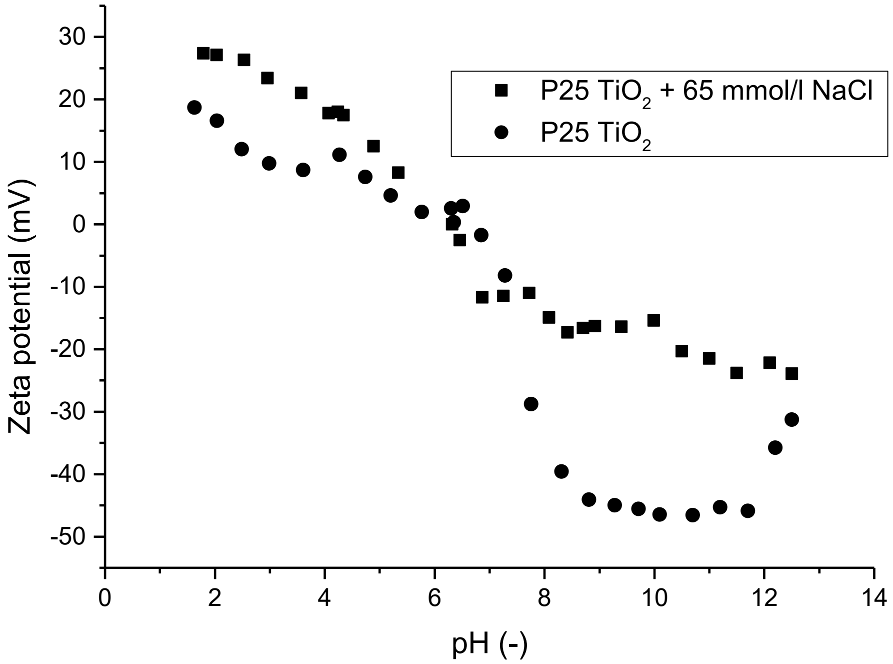

Figure 1: The dependence of zeta potential of Aeroxide P25 TiO_2 on solution pH; with and without the addition of NaCl (concentration of 65 mmol/l).

The zeta potential decreased with increasing pH and had zero value, i.e. isoelectric point (IEP), at pH=6.3. In acidic condition, the positive zeta potential of the catalyst particles was observed, while negative zeta potential was found at pHs above IEP. This is in good agreement with the results of some other authors [23,24]. Thus, the pH value of the wastewater may affect, through the surface charge, properties of TiO_2, both the size of formed catalyst aggregates and the efficiency of adsorption of dye onto the TiO_2 surface. At pH close to the IEP, the large catalyst aggregates were generated with a smaller external surface area (see Figure 2). The aggregation increases the number of particles "shadowed" by the surrounding particles in the outer layer of the aggregate. Under this condition, it is probable that the true accessibility of the inner active centers of catalyst for both the large dye ions and UV light is limited. In figure 2, we can also observe large data scattering for pH levels where zeta potential is close to zero, which makes the colloidal system highly unstable. Particle sedimentation was noticed in few instances under this conditions within several hours. Thus, for the selection of the optimal parameters of the photocatalytic degradation process, the knowledge of IEP of the catalytic system is important.

The surface charge of the particles has an effect; not only on aggregation processes but influences the adsorption of different compounds as well, especially those with ionic form. At pH values exceeding the IEP, the photocatalyst particles are negatively charged, thus making the interaction of negatively charged dye ions with the catalyst surface more difficult. On the other hand, the highest interactions can be expected at acidic pH, because the positive charges of the catalyst surface attract the dye anions.

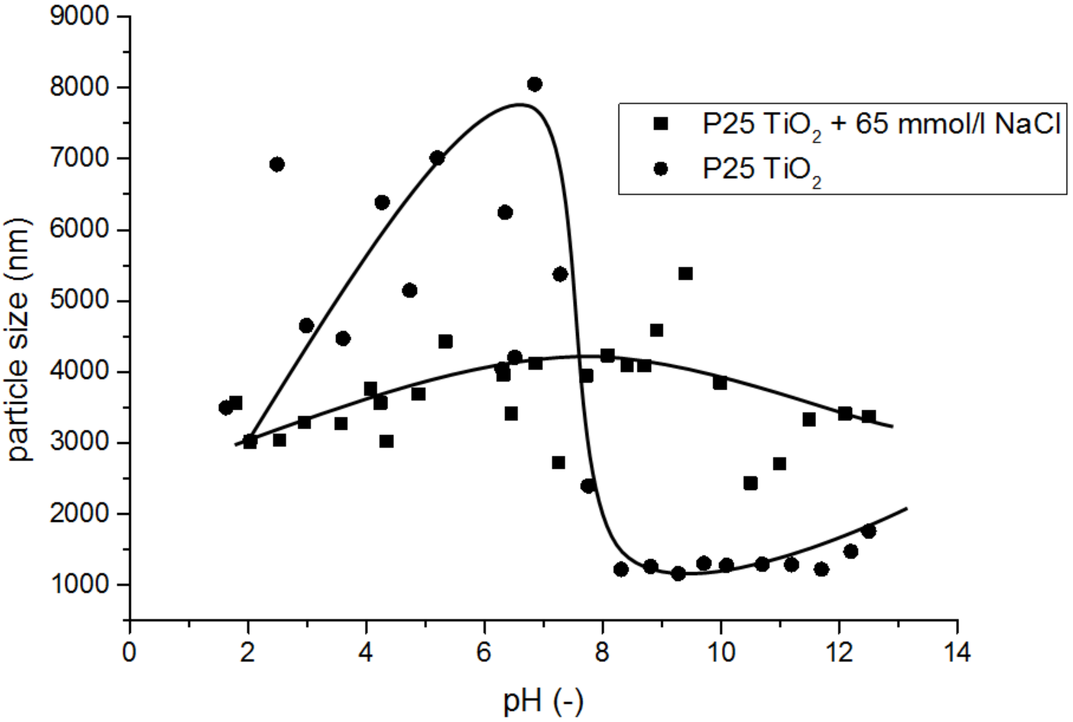

Figure 2: The dependence of P25 TiO_2 particle size on pH (concentration of P25 TiO_2 photocatalyst = 1 g/l)

Figure 1 also shows the zeta potential vs. pH dependence for catalyst dispersion modified by the addition of a constant amount of sodium chloride. It is necessary to mention, that the change of concentration of sodium and chloride ions as a result of pH adjustment of the reaction system was negligible (less than 0.2 mmol/l, in comparison with the addition of 65 mmol/l NaCl). The compensation of negative zeta potential is clearly visible at pH above the isoelectric point. In the acidic region, the value of zeta potential moves slightly to positive values. The presence of NaCl in the dispersions induces aggregation of particles dominantly in the alkaline region (Figure 2). The average hydrodynamic diameter values of aggregates in the region close to the IEP have significantly smaller scatter compared to a system without any added NaCl.

Model MO dye is one of the indicators commonly used in titrations. An azo group chromophore (-N=N-), generating color of MO, is a part of a conjugated system, here created by two substituted aromatic rings. In an alkaline solution, methyl orange is yellow, while in an acidic solution it is red. During acidification, the hydrogen ion attaches to one of the nitrogens in the nitrogen-nitrogen double bond and creates complicated H^+ delocalization over the entire dye molecule [27]. Figure 3 illustrates the dependence of relative absorbance of methyl orange solution on light wavelength for various values of pH. We can observe absorbance shift at low pH values (<4.5), manifesting as a change of the absorbance peak wavelength. As a result, it was necessary to conduct experiments in the pH range to assure acid-base color stability. According to the literature [28,17], the change of MO color takes place at pH between 3.0 and 4.4, because the dye pK_a is 3.7. For pH > pK_a, MO is in anionic form while molecular form predominates at very acidic pH (pH < pKa −1). Therefore, all following experiments were conducted at pH ranging from 4.5 to 11.5, and as Figure 3 illustrates, there is no significant change in absorbance profile in the band of experimental pH levels used.

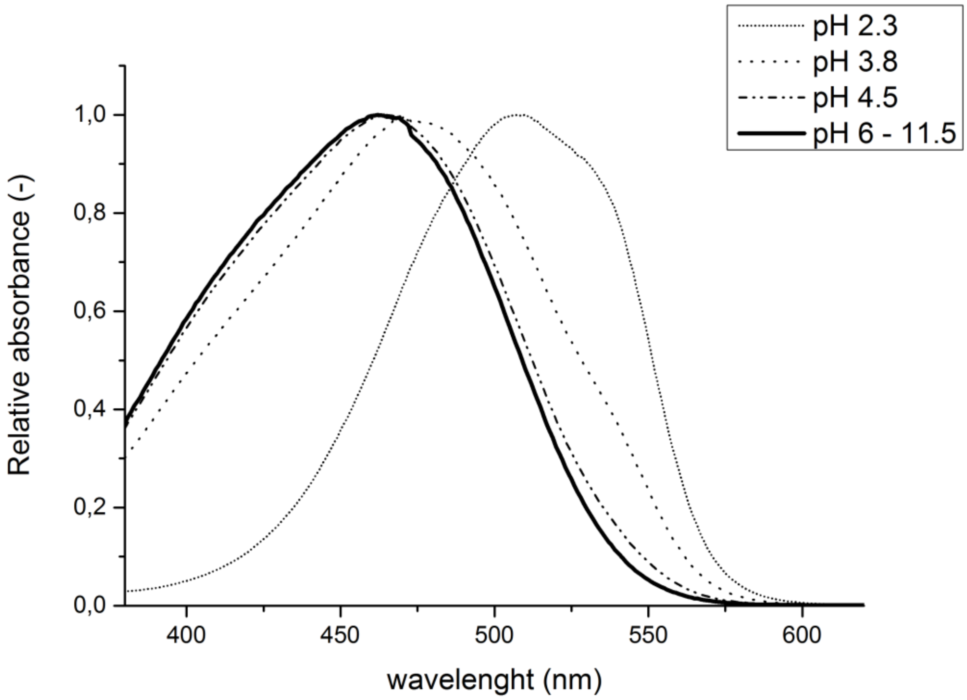

Figure 3: The dependence of MO relative peak absorbance on light wavelength at different pH values

As it has been already said, the TiO_2 photocatalytic activity can be influenced by the interaction (adsorption) of reactants on the photocatalyst surface. In order to investigate the adsorption of MO, we have studied the variation of the adsorbed amount with the equilibrium dye concentration for different values of pH and the addition of co-existing (Na^+ and Cl^-) ions. These are illustrated in Figures 4 (pH=5.5) and 5 (pH=10). The adsorbed amount of dye is relatively small, ranging from 0 to 6 mg per gram of catalyst. As can be seen, for the systems without NaCl addition, there is significantly greater sorption in acidic media than in the alkaline. This result is in good agreement with experimental data obtained for example by authors[16,17]. This effect can easily be explained taking into account that anionic species of MO are present in the solution. Considering both the negative charge of these species and the fact that the zeta potential of the P25 TiO_2 becomes positive at pH values below the IEP (see Figure1) one could incline to conclude that adsorption takes place through a simple electrostatic accumulation of the anionic species in the diffuse part of the catalyst interface double layer. However, the simple electrostatic accumulation in the diffuse part of the interface cannot explain the considerable adsorption of MO at pH higher than IEP and presence of co-existing Na^+ and Cl^- ions (see Figure 5), where the anionic MO interacts with a catalyst that has negative zeta potential. In this case, the sorption of model dye is greatly enhanced and clearly shows the highest values. This phenomenon could relate to the results of authors[38] who have found that in the alkaline region, increased co-adsorption of sodium ions at the outer plane of the Stern layer located at the catalyst surface (in that case silica nanoparticles) takes place. They found that the Stern layer compresses (becomes thinner) as the electrolyte concentration is increased. This finding provides a simple and intuitive picture of the electric double layer that explains the concurrent increase in surface charge density but decreases in zeta potential, as the electrolyte concentration is increased.

At the same time, in the acid range, the addition of NaCl to the studied system has less influence on the dye sorption process (see Figure 4). Only a slight increase in catalyst sorption capacity can be observed. This result agrees with the zeta potential of the particles, which is more positive than in the system without the addition of NaCl (Figure 1).

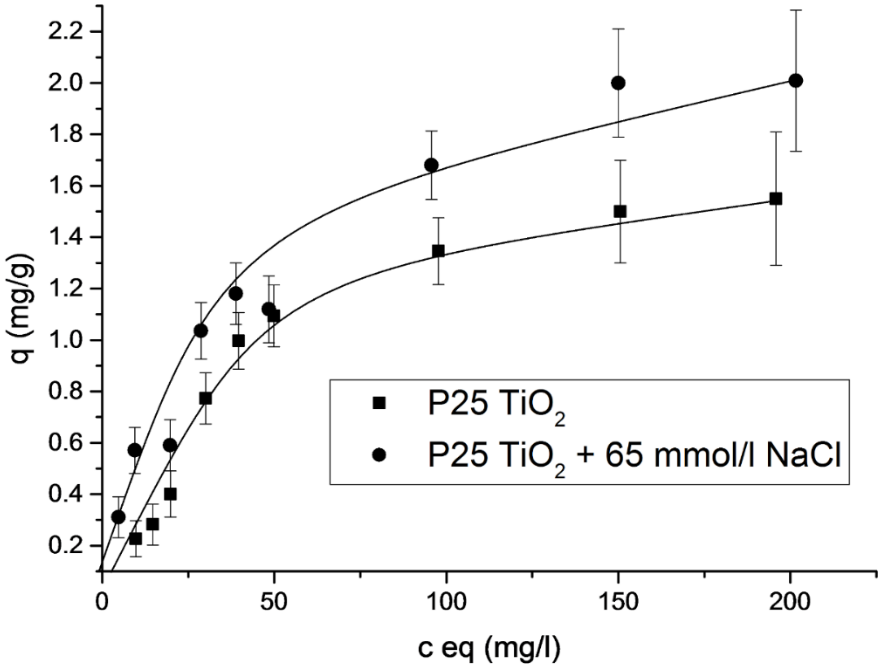

Figure 4: The dependence of the adsorbed amount of methyl orange dye q onto P25 titanium dioxide on equilibrium dye concentration c_{eq} in acidic medium with and without of sodium chloride addition. (concentration of P25 TiO_2 photocatalyst = 1 g/l).

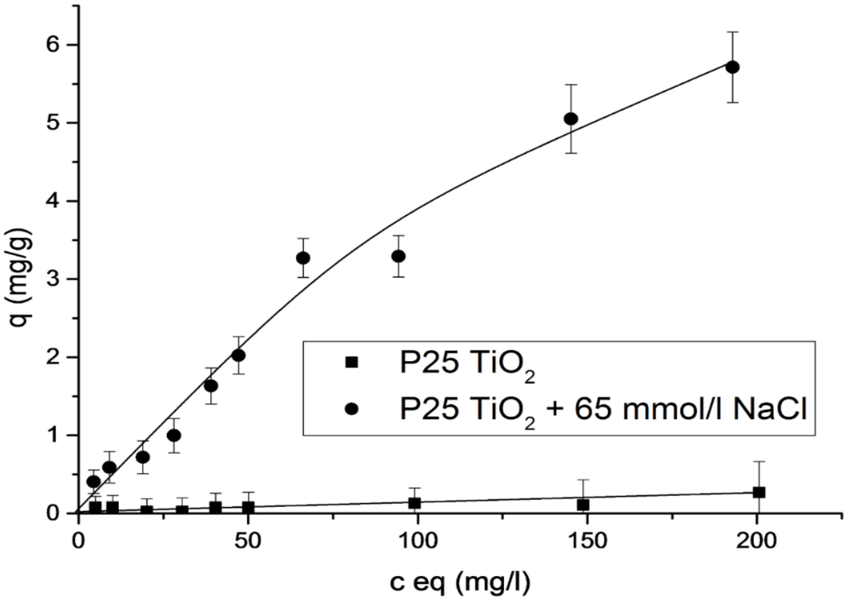

Figure 5: The dependence of the adsorbed amount of methyl orange dye q onto P25 titanium dioxide on equilibrium dye concentration c_{eq} at solution pH of 10, with and without added sodium chloride (*concentration of P25 TiO_2 photocatalyst = 1 g/l*).

The effects of pH on photocatalytic reaction are depicted in figure 6, as the time dependence of the relative methyl orange concentration for different initial values of pH.

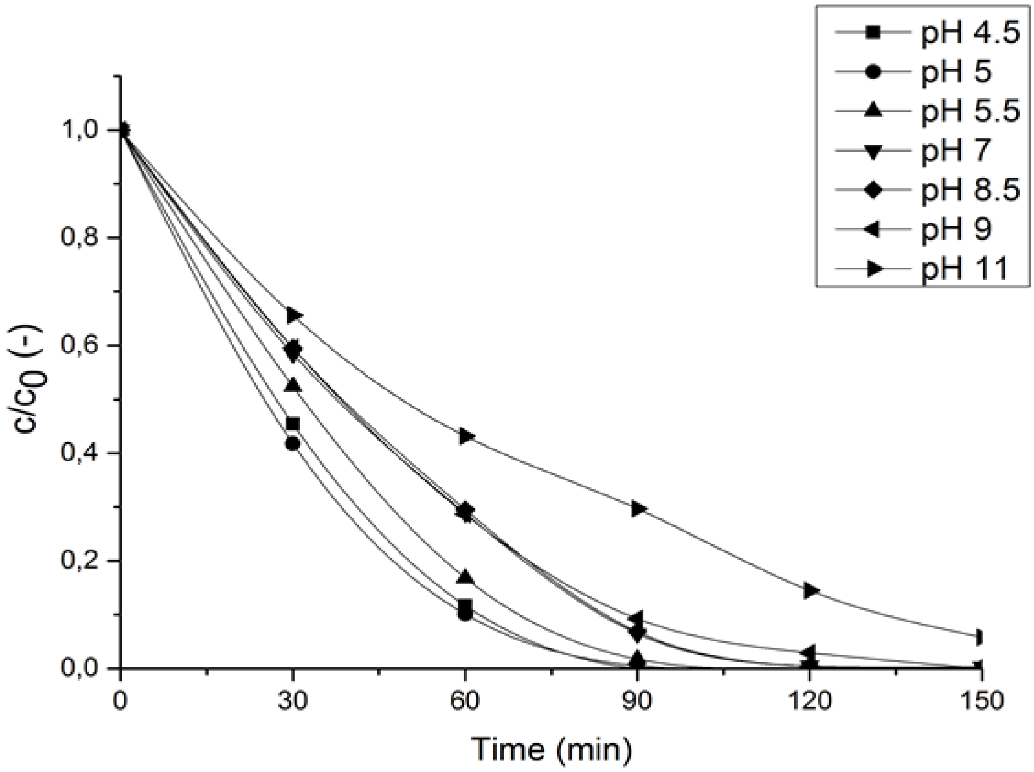

Figure 6: The dependence of the relative concentration c/c0 of methyl orange dye solution on time for different values of initial pH. (c0=50 mg/l, concentration of P25 TiO_2 photocatalyst = 1 g/l)

The results show a clear decrease of reaction rate with rising pH. The fastest decolorization was observed at the lowest experimental pH values, around 5. This is in the agreement with data published in the literature. [23,29,30] This could be because of formerly discussed adsorption of the dye onto the catalyst surface. The degradation curves at pH values ranged from 7 to 9 were observed to approach lower, but similar degradation values. The slowest kinetic was observed at pH 11, most likely as a result of the very strong coulombic repulsion [31], that exists between the TiO_2 surfaces (see Figure 1) and negatively charged methyl orange dye. The opposite trend, i.e. an increase of decolorization rate with an increase of solution pH was observed for cationic dyes by authors.[11]

The regression of experimental degradation data (Figure 7) confirmed pseudo-first-order reaction kinetics in all cases, with a decrease of apparent reaction rate constant with rising initial pH of the reaction slurry. This is in good agreement with other authors [29,32]. and with the hypothesis of an interaction between the anionic dye and photocatalyst particle. In the case of pH affected adsorption interactions, the Langmuir-Hinshelwood kinetics can be applied to heterogeneous photocatalysis, which for small initial concentrations can be simplified to the aforementioned pseudo-first order kinetic equation.[32, 33]

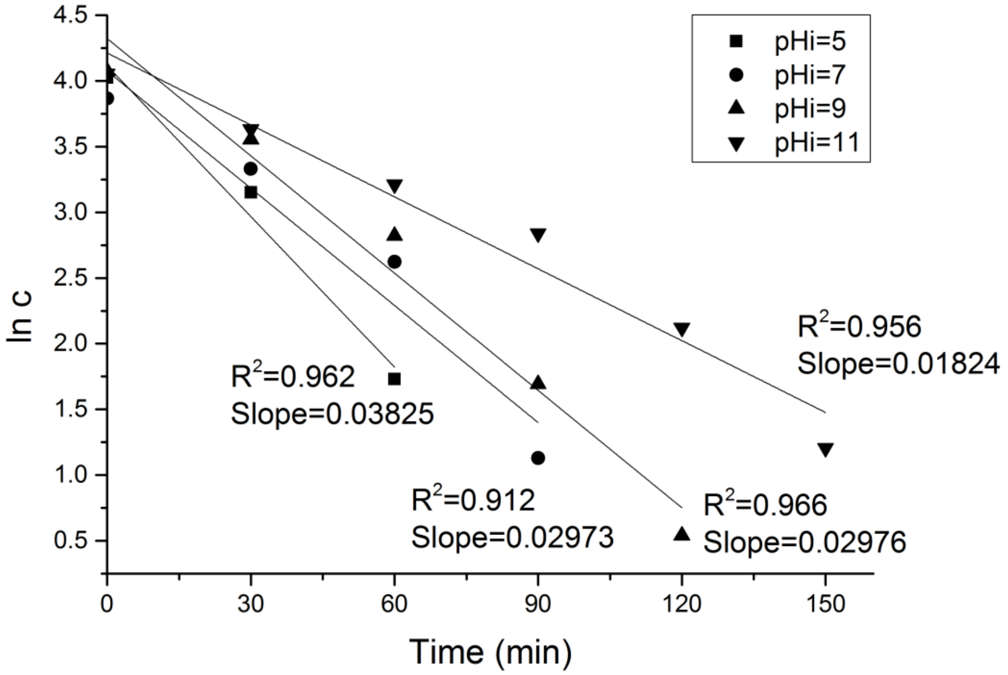

Figure 7: Linearization of experimental data at different initial pH levels, without the addition of NaCl (c_0=50 mg/l, concentration of P25 TiO_2 photocatalyst = 1 g/l).

The photocatalytic degradation of MO dye can be also affected by the presence of co-existing ions in the dispersion matrix. These ions are generally present in wastewater, thanks to salts, which are initially added to the dye solution in order to improve the dyeing process. However, on the release of wastewater, the ions become an integral part of the effluent. It follows from the experimental data depicted in Figure 8 that the addition of sodium and chloride ions had a positive effect in the alkaline region where the negative zeta potential and a high degree of sorption were indicated (see also Figures 1 and 5). In the acidic pH range, the negative effect was observed. The addition of inorganic ions [34,35,36], such as chlorides [37], into the matrix of a treated solution of dyes, was previously reported by other authors to have a negative effect. This was explained by the inhibitory effect of chloride ions on the reaction because of the scavenging of photoproduced •OH by Cl^-. The phenomenon was pronounced at acidic pH, and consequently, the decolorization was slowed.

The promotion of photocatalytic decolorization in the high salinity alkaline dispersion is a more complicated matter. It follows from our experiments, that in the case of high salinity systems, there is no correlation between the zeta potential and decolorization efficiency. But in alkaline pH, the decolorization is closely followed our sorption results (Figure 5). It is probably due to the compensation of negative zeta potential by sodium cations resulting in compression of the Stern layer and better interaction between anionic dye molecule in the diffusion layer and •OH generated on the photocatalyst particle surface. The increase in zeta potential (approximately from -60 mV to -40 mV) with increased concentration of sodium chloride in the dispersion of amphoteric nanoparticles was also observed [38], and similar preliminary experiments were performed.[39] Luo et al. [40] studied the effect of natural organic matter on the zeta potential of titanium dioxide and demonstrated an increase of zeta potential with the addition of calcium chloride, showing compression of the electric double layer. He also showed that the increase of sodium chloride concentration leads to better sorption of natural humic and fulvic acids at a pH of 8. Proposing the creation of calcium ion bridge, working as intermediate between titanium dioxide particle and natural organic matter, promoting the sorption. Mwaanga et al. [41] reported a study of sorption of natural organic matter on titanium dioxide at various pH and ionic strength. According to his results, higher ionic strength results in better sorption at alkaline pH.

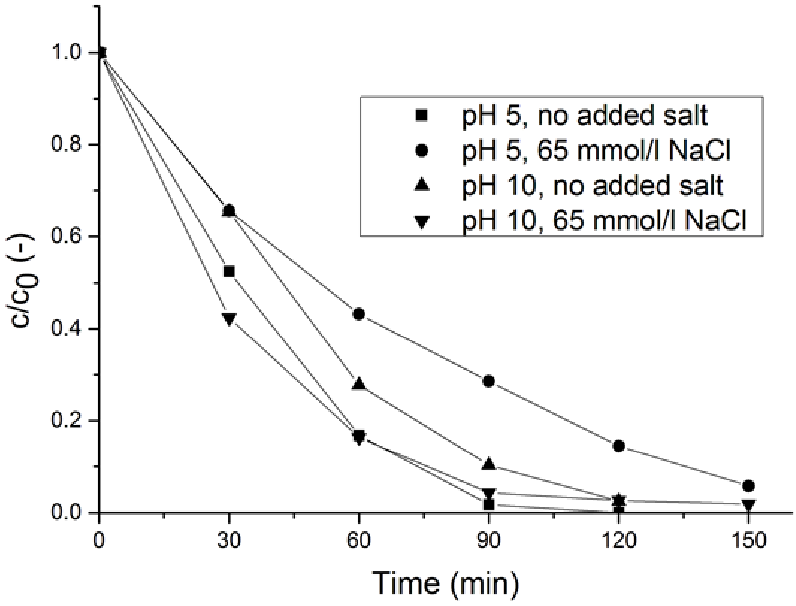

Figure 8: The dependence of relative concentration c/c0 on time for different initial pH values; with and without the addition of sodium chloride (initial concentration of dye = 50 mg/l, concentration of P25 TiO_2 photocatalyst = 1 g/l).

In order to elucidate the mechanism of the degradation, solution pH was also monitored during the experiments. The data collected are displayed in Figure 9.

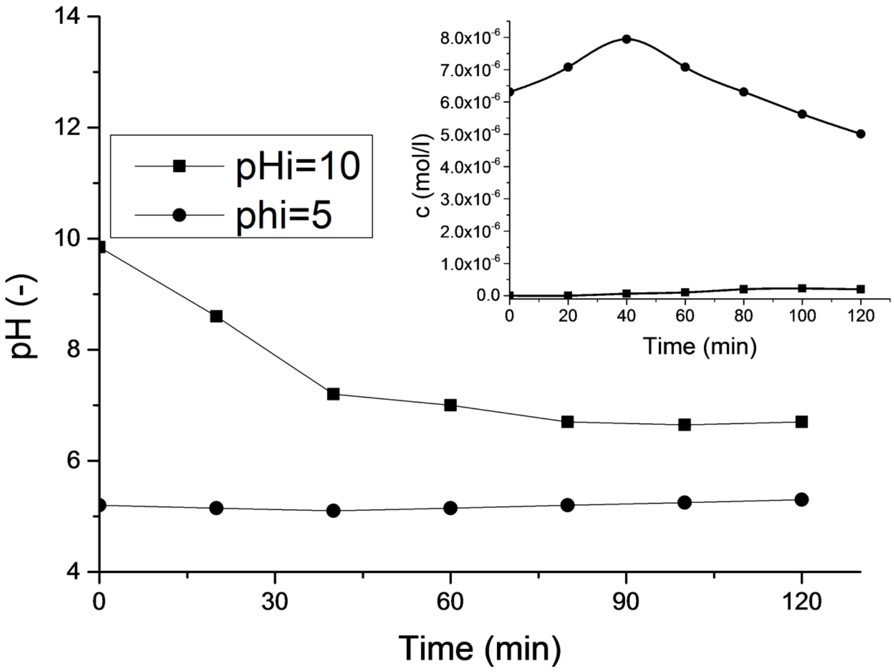

Figure 9: Change of solution pH during photocatalytic degradation of methyl orange dye (initial concentration = 50 mg/l, concentration of P25 TiO_2 photocatalyst = 1 g/l) for two different initial pH. Insert: change in H^+/H_3O^+ concentration.

For a solution with alkaline initial pH (pHi=10), a decrease from pH=10 to 6.7 was observed. It supports the assumption that hydroxyl radicals (•OH) and H^+ ions are generated by the reaction of the positive holes with water [17]. Unlike the alkaline solution, in the acidic solution (initial pH = 5), no significant pH decrease was observed. But assuming that the number of radicals and H^+ generated is comparable to the alkali region, it is obvious that the amount of H^+ ions produced is negligible, in comparison with the H^+ ions present in solution with the initial pH of 5.

The UV-VIS spectra recorded during catalytic photodegradation of model dye are presented in Figure 10. The spectrum of dye before photodegradation (t = 0 min) exhibits three main peaks at wavelengths of 464, 270 and 190 nm.

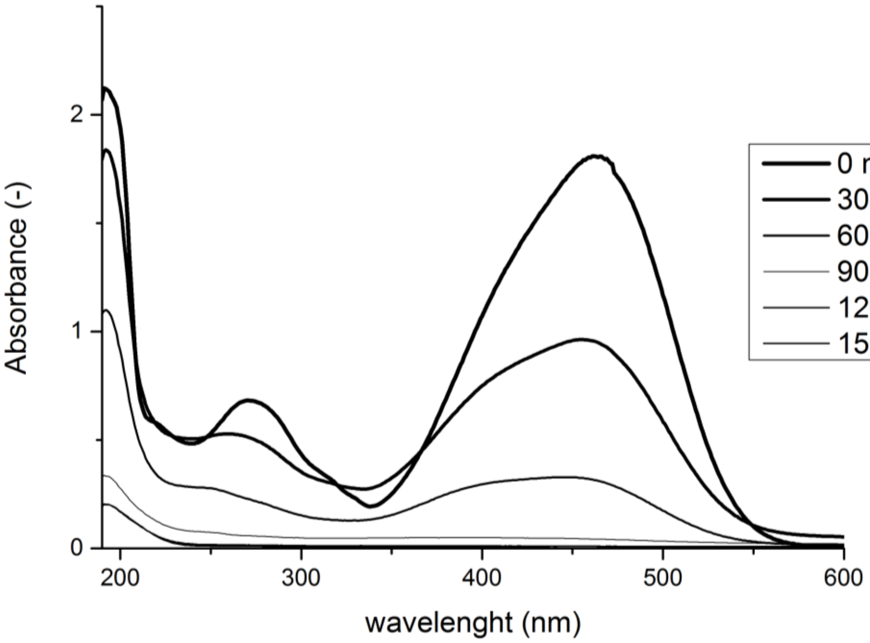

Figure 10: Absorption spectra of methyl orange dye solution during heterogeneous photocatalytic treatment at different sampling times. Initial pH= 5.5, concentration of P25 TiO_2 photocatalyst = 1 g/l

The absorption in the visible region can be attributed to chromophore containing azo linkage, whereas the bands observed in the UV region can be assigned to benzene rings present in MO molecule. It can be seen, that there is a rapid decrease of absorbance in the visible part of a spectrum, while the decline in UV range is slower. The cause of this phenomenon is that the dye molecule interaction with hydroxyl radicals results initially in cleavage of the molecule in the vicinity of the azo bond followed by the formation of molecules containing benzene rings. [10,42] This step results in discoloration of the solution, i.e. in the rapid decline of absorbance in the visible range. Then these primary reaction intermediates undergo a series of subsequent reactions which lead to the formation of aromatic acids, aliphatic acids, and finally to complete mineralization of carbon, nitrogen and sulfur heteroatoms into CO_2 and SO_4^{2-}, and NO_3^- ions, respectively. It must be emphasized that decolorization of the solution does not provide complete data on the azo-dye degradation. Therefore, monitoring of other parameters is necessary. Figure 11 presents the effectiveness of photodegradation of MO determined on the basis of changes in TOC and COD relative concentration.

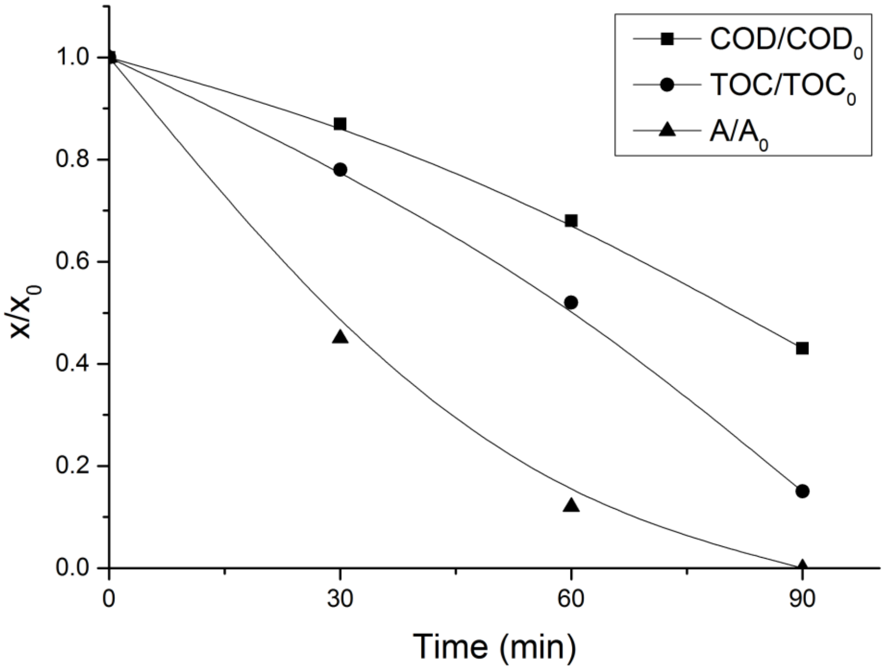

Figure 11: The time dependence of relative values of COD, TOC, and peak absorbance for 50 mg/l MO solution during photocatalytic treatment. Initial pH = 5.5, concentration of P25 TiO_2 photocatalyst = 1 g/l

It can be seen that a much slower decrease of relative COD and TOC values was observed in comparison with the decrease in absorbance at the peak wavelength. These results show that mineralization is a much slower process than simple dye decolorization.

Conclusions

The effect of pH and ionic environment (changed by sodium chloride) on the zeta potential, dye adsorption and UV/TiO_2 heterogeneous photocatalytic decolorization of an anionic methyl orange dye were studied experimentally. The effect of solution pH on P25 TiO_2 zeta potential was determined experimentally, and the obtained results are in good agreement with results previously published by other authors. Addition of sodium chloride into the mixture shifted the zeta potential towards more positive values, this shift was more pronounced in the alkaline pH range. The addition of sodium chloride also improved sorption of MO dye onto photocatalyst, especially in alkaline pH. The photocatalytic decolorization rate, without any addition of sodium chloride, was in good agreement with the sorption data and with the results published by other authors – faster decolorization in the acidic pH range. With the addition of sodium chloride, the decolorization slows down significantly for acidic pH and is improved in alkaline pH. Fastest decolorization was observed at a pH=5 (lowest experimental pH) with no sodium chloride, and at a pH of 10 with the addition of 65 mmol/l of sodium chloride. It results from the comparison of the experimental data obtained, that the zeta potential is not a universal indicator of dye sorption as well as photocatalytic degradation on titanium dioxide. The decreases of COD and TOC parameters were also monitored and were much slower in comparison to UV/VIS absorbance at the peak wavelength.

Acknowledgment

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Využití heterogenní fotokatalýzy pro úpravu odpadních vod obsahujících azo barviva – vliv pH a obsahu solí na zeta potenciál oxidu titaničitého a fotokatalytickou aktivitu

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Souhrn

Znalost interakcí mezi zeta potenciálem katalyzátoru, sorpcí barviva a výkonem fotokatalýzy je nezbytná pro hodnocení procesních parametrů fotokatalytického zpracování odpadních vod. Tento článek se zabývá experimentálním studiem heterogenní UV fotokatalýzy, použité pro odstranění barviva methyloranže z modelové odpadní vody. Fotokatalytické experimenty byly provedeny ve vsádkovém reaktoru s P25 oxidem titaničitým jako fotokatalyzátorem a UV-A LED modulem jako zdrojem záření. Během experimentů byl sledován efekt pH a přítomných iontů na zeta potenciál katalyzátoru. Taktéž byla sledována sorpce barviva a jeho degradace. Adsorpce barviva na povrch P25 katalyzátoru byl velmi významný krok ve fotokatalytickém procesu, a byla zjištěna silná závislost na pH a salinitě reakčního roztoku. Vyšší rychlost snížení barevnosti roztoku v oblasti kyselého pH byla zaznamenána v případě nulového přídavku chloridu sodného. Naopak, přídavek chloridu sodného významně zvýšil účinnost odbarvení v oblasti alkalického pH. Z porovnání získaných experimentálních dat je také patrné, že zeta potenciál není univerzálním indikátorem předpovídající sorpci barviva nebo fotokatalytickou degradaci pomocí oxidu titaničitého.

Klíčová slova: *heterogenní fotokatalýza, zeta potenciál, azo barviva, odpadní voda.*

Preparation of collagen concentrate from chicken feet

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Abstract

The meat-processing industry produces a huge and ever greater amount of involuntary by-products at slaughterhouses, which increase significantly the waste amount. In terms of poultry, these comprise feet, heads, viscera and skin - items that are rich in protein, especially collagen. The latter can be gained through a procedure that involves grinding and defatting raw material, since poultry by-products from meat-processing industry contain a wide range of fat (15 – 70 %). Indeed, it is also necessary to extract other non-collagenic matter, such as pigment and water-soluble proteins. In this study, non-collagen components were removed by treatment of chicken feet in 0.1% NaOH. Three methods of defatting of raw material (applying $NaHCO_3$, lipolytic enzyme and 10 different solvent systems) were tested. The use of solvent mixture of petroleum ether and ethanol proved to be the most efficient method of defatting chicken feet with a residual fat content of approximately 5 %. Collagen concentrate prepared this way possesses the potential to be utilized by commercial sectors, such as the food or pharmaceutical industry.

Keywords: *by-products, defatting, protein, poultry, slaughterhouse*

Introduction

The food industry has stimulated a growth through promoting flavourful items and provide a balance of protein from animal sources. Such food substances benefit consumers and producers, but also give rise to a large volume of by-products, often accounting 25 – 30 % of total production. These animal-sourced by-products could be utilized by the meat-processing industry to ensure competitiveness against suppliers of plant-based proteins[1].

According to data from the US Department of Agriculture, 8,909,014,000 chickens, 232,389,000 turkeys and 27,749,000 ducks were slaughtered in 2016. In live weight this equalled 24.5 million tons of chicken, 3.2 million tons of turkey, 86,200 tons of duck and 1,700 tons of other poultry, a total of 27.8 million tons[2].

The meat-processing industry generates unwanted by-products as a result of the trade, such as blood, bones, surplus pieces cut from meat, skin, fatty tissue, horns, hooves, limbs and guts. Ecological disposal of such waste is very expensive. Although some by-products are eaten in certain countries, in accordance with the particular national customs, elsewhere they may be considered inedible. However, such by-products possess a high content of essential amino acids, minerals and vitamins, and it would be economical to extract these where possible. For example, by-products of the animal slaughter trade sometimes find application as a component in foodsubstance, as feed for livestock or pets, and fertilizers. In addition, as a raw material, they can be utilized in the production of pharmaceuticals, biomolecules (such as protein hydrolysates, enzymes, extracts with functional properties and bioactive peptides) and chemicals[3].

Bianchi et al. studied the potential energy output of poultry by-products, which could be harnessed to produce electricity, especially in deregulated energy markets. Although a small-scale indirect steam turbine would represent a viable competitor to any of such system, it would need fossil fuels to operate. Choosing the capacity of an applicable device in relation to the corresponding amount of energy would depend on the given price of electricity and natural gas. For example, if the price is 0.06 $/kWh, a 10 MW device is recommended, without the need of fossil fuels. If the cost of electricity rises and natural gas drops in price, then equipment rated at 50 MW or more is recommended[4].

By-products originating from the poultry processing industry (such as edible tissues, bones, blood, fat, shells, unhatched eggs, discarded chickens, feathers, heads and legs) account for 22-30% of total meat production[1,5]. Notably, bedding for poultry is a by-product that itself arises through processing poultry. Mechanical separation of meat from bones results in a great deal of poultry residue, which on average contains 17% proteins (especially collagen). According to data from the FAO (Food and Agricultural Organization) from 2012, the consumption of poultry had risen by 3.6 % per year. Indeed, between the years 2000 – 2009, the quantity of chicken consumed per person per 12-month period went up from 30 to 38 kg. In 2010, around 78 million tonnes of poultry were eaten worldwide. In first-world countries, poultry by-products are incorporated into pet food (for cats and dogs), feed additives for livestock and compost for the agricultural sector; whereas, in developing countries, they are simply dumped on refuse sites[1,6].

In this context, major nutrients for animals comprise the following by-products: meat; bone and blood meal; ground plasma; hydrolysate from feathers; tallow or lard containing proteins, fats, minerals and trace elements; forms of vitamin B; and some fat-soluble vitamins[7].

To date, literature presents various procedures for removing water-soluble pigments and proteins from poultry feet. Du et al. (2013) applied the following: chicken feet were mixed with 0.5M NaOH at a ratio of 1:10 (v/v) and shaken for 6 h at 4 °C; alkaline solution was changed every 2 h[5]. In contrast, Almeida and Lannes (2013) used 4% acetic acid for 16 h at room temperature[8]. Huda et al. (2013) studying duck feet employed 5% solution of lactic acid at the ratio of 1: 8 (v/v) for 24 h at 4 – 7 °C[9].

Poultry skins contain approximately 70 % of fat[10], chicken bones contain around 20 % of fat[11] and chicken feet contain about 15 % of fat[12]. If these by-products valuable in the food or cosmetic industry, such as gelatine, are supposed to be processed further, it is desirable that fat content of these tissues is as small as possible as fat is an undesirable ingredient in gelatine. That is why, this study concerns also fat separation from chicken feet.

Since fat content of chicken feet is generally very high, it is necessary to defat them. A few studies have described deffating chicken feet or other poultry-based tissues. According to Du et al. (2013) technique for the processing of poultry heads was as follows: pure samples were mixed with 15 mM $NaHCO_3$ at a ratio of 1:4 (v/v) and mixed for 1 h at 4 °C, then centrifuged at 10,000 x g for 10 min. at 4 °C. This step was repeated 3times until no fat was observed in the sludge[5]. Soxhlet method was applied in the study of chicken skins by Sarbon et al. (2012)[13]. However, due to the complexity of the process, this method is inappropriate for practical application. Huda et al. (2013) removed the fat from the top layer by spoon at the end of the alkaline treatment of duck feet[9]. This method was found to be very inefficient.

The aims of the paper

The purpose is to process chicken feet, which are a significant source of collagen, into collagen concentrate. To achieve this, several methods of defatting of a raw material have been examined. During the process, undesirable water-soluble proteins and pigments need to be removed as well.

Materials and methods

Chicken feet

Chicken feet rich in protein are hence a suitable by-product of the poultry industry. For this experiment, they were supplied by RACIOLA Uherský Brod, s.r.o. The content of dry matter was determined by drying the feet at 103 °C until constant weight had been achieved. The proteins present were determined by Kjeldahl method[14]. The amount of collagen was calculated from the quantity of hydroxyproline (by multiplying the value by the coefficient 8[15]); the level of fat was determined by extraction according to Soxhlet, applying a two stage process with two solvents (chloroform and ethanol)[16]; lastly, the mineral content was determined by burning the sample and annealing at 650 °C for at least 1 h in a muffle furnace[16]. Each test was perfrormed in three replications; results are presented as an arithmetic mean with standard deviation.

Appliances, tools and chemicals

These comprises: a SPAR Mixer SP-100AD-B meat cutter (TH Industry RD, Taiwan), Memmert ULP 400 drying devices (Memmert GmbH + Co. KG, Germany), an LT 43 shaker (Nedform, Czech Republic), a Kern 440 - 47 electronic scale, a Kern 770 electronic analytical balance (Kern, Germany), a desiccator, a Samsung fridge-freezer (Samsung, South Korea), a metal filter sieve (seize of pores 200 μm), a PA filter cloth (pore size 200 μm), a Nabertherm muffle furnace (Nabertherm GmbH, Germany), Parnas-Wagner distillation apparatus, $NaHCO_3$, petroleum ether, ethanol, chloroform, acetone, butyl alcohol, diethyl ether, penthane, and hexane (Verkon, Czech Republic). Lipolase 100 T (lipase from *Thermomyces lanuginosus*) was produced by submerged fermentation of the genetically modified microorganism *Aspergillus oryzae* (Novozymes, Denmark), with 100 KLU/g (kilo lipase unit/g) as declared enzyme activity.

Process to convert chicken feet into a product rich in collagen

Processing chicken feet into a product boasting a high amount of collagen involves the steps shown in Figure 1.

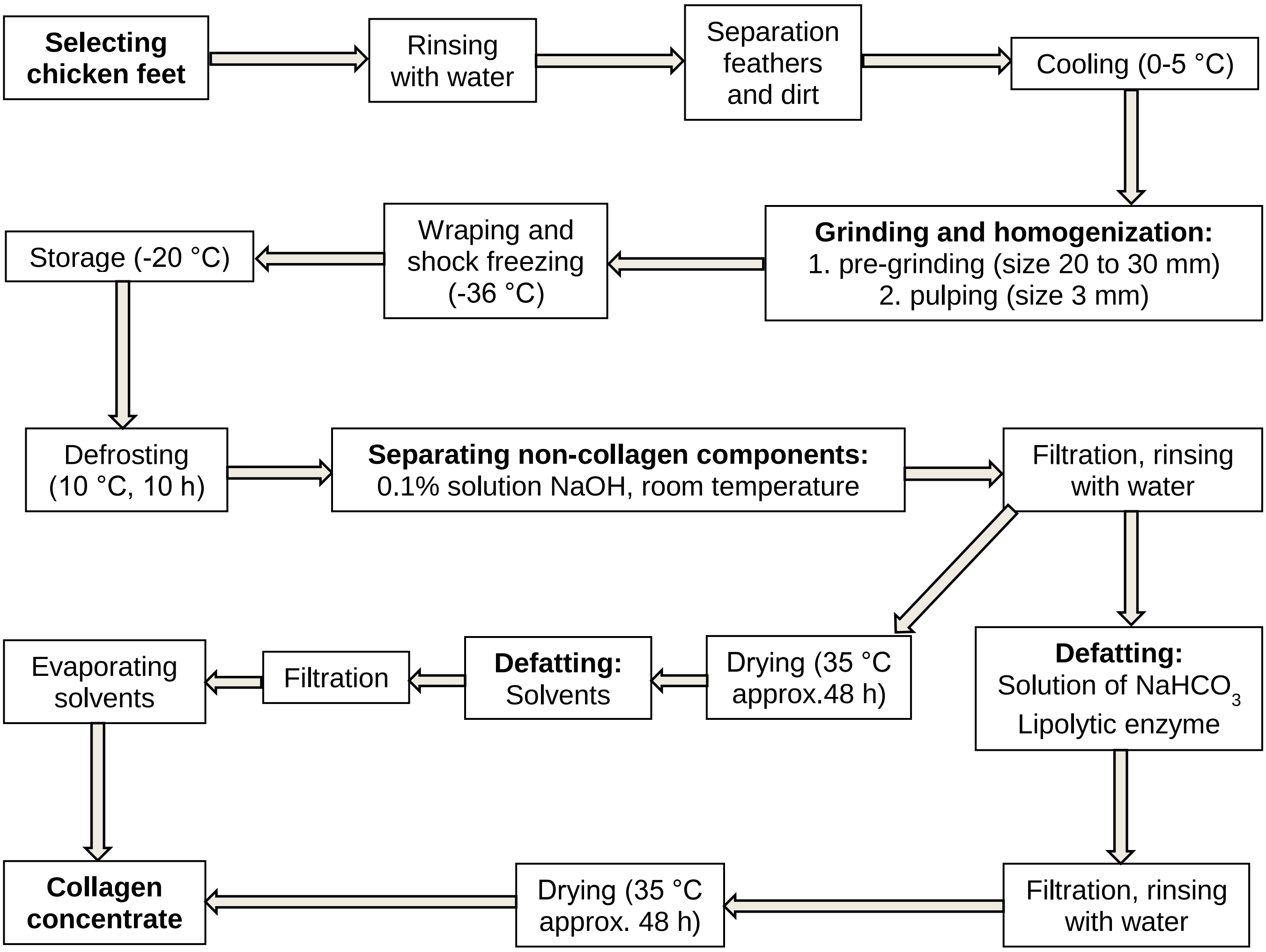

Figure 1: Flow chart of processing chicken feet into collagen concentrate

I. Grinding and homogenization of the raw material

The preparatory stage of preparing the raw material, i.e. grinding it to the desired structure for further processing, is very important. Proper conditions have to be set in order to prevent denaturation of the collagen protein during the entire purification process. Key to creating a high quality and hygienically safe product is ensuring basic hygiene conditions when obtaining the feet. A crucial aspect is to rinse said raw material in water immediately after selecting the feet intended for use. The slaughterhouse had a cleaning system in place for carrying the feet away via a pipe, in which the raw material was initial cleaned and cooled.

After purification and allowing excess water to drip off, the feet were placed in storage containers. These were then moved to chilled areas to prevent unwanted microbial growth and degradation of the feedstock, wherein the feet were stored at 0 – 5 °C for no more than 36 hours after slaughter. Homogenization, i.e. grinding up whole feet, was conducted as soon as possible after slaughter, so that the temperature of the raw material did not exceed 12°C. Due to rise in the temperature of the raw material during homogenization, it was necessary to slightly freeze it at -2 °C to -5 °C prior to the operation. Grinding required two phases, utilizing an industrial meat grinder equipped with a four-arm knife for both phases as shown in Figure 2. The initial pre-grinding stage required a kidney-shaped cutting head of size 20 to 30 mm, whereas a different cutting head, at the size of 3 mm, was employed in the second stage (pulping). Under these conditions, the final temperature of the homogenized material increased by a maximum of 3 °C. The ground and homogenized raw material was put into PE bags with walls of 150 µm in thickness. The packed raw material was then deep frozen (shock frozen) at -36 °C ± 2 °C. Said frozen raw material was then stored in the freezer at -20°C ± 2°C. Prior to the experiments, the raw material was thawed out in the refrigerator at 10 °C ± 2 °C over a 12 h period.

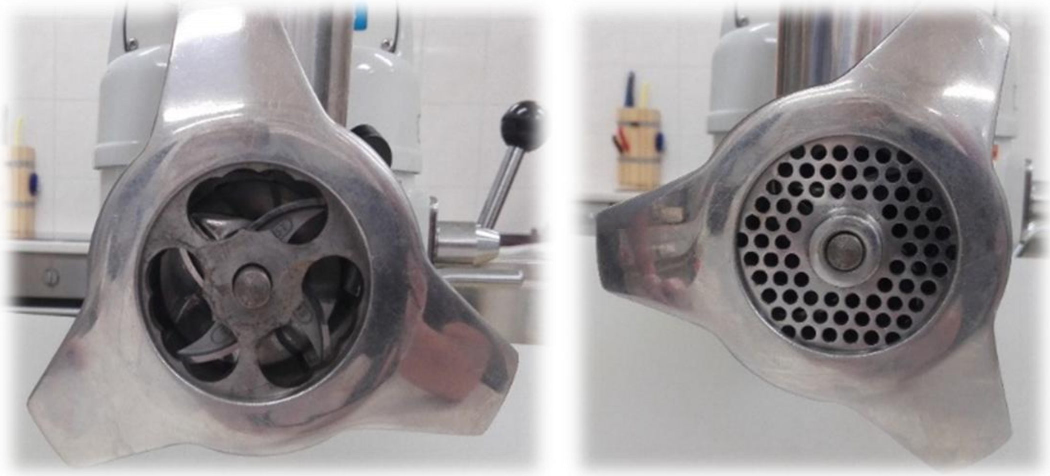

Figure 2: Details of cutting heads (kidney-shaped head on the left, cutting head of the size of 3 mm on the right)

II. Separation of undesirable non-collagenous components from the raw material

The procedure described by Du et al. (2013) with a slight modification to remove non-collagenous components was used. Once thawed, material was mixed with 0.1% NaOH solution at a ratio of 1:8 and shaken on a shaker at room temperature for 45 min. It was then filtered through a filter sieve lined with a single layer of PA cloth and rinsed with tap water. The whole process was repeated 4 times. The raw material was partially defatted during this process.

III. Removal of fat from the raw material

Three potential methods of removing fat from the raw material have been suggested herein, i.e. a use of $NaHCO_3$ solution, lipolytic enzyme or solvents. The residual fat content was determined by Soxhlet method, requiring two steps for extracting the same; the fat was extracted with chloroform for 8 h and then with ethanol for the same length of time. Each experiment was performed twice; the results are presented as an arithmetic mean.

1. Deffating with $NaHCO_3$ solution

The method described by Du et al. (2013) with a slight modification was applied. Once thawed, the chicken feet were mixed with 150 mM $NaHCO_3$ at a ratio of 1:5 (v/v) in an Erlenmeyer flask and shaken for 1 h at room temperature. Afterwards, the material was filtered through a filter sieve; the entire procedure was repeated 4times. The resultant material was then dried for about 24 h at 35 °C.

2. Deffating with a lipolytic enzyme

To this end, the authors utilized the lipolytic enzyme Lipolase 100 T. Defatting efficiency was studied by the factorial experiments 2^2 and the central experiment; the factors monitored comprised adding the enzyme and the duration of defatting. 100 g of chicken feet were mixed in an Erlenmeyer flask with 500 mL of distilled water, into which the lipolytic enzyme Lipolase 100 T was added at the amount according to the scheme of the experiments (factor A; see Table 2). The pH was adjusted to 7.0 ± 0.3. The flask was sealed and shaken in an incubator at 12 °C; shaking continued for a determined period of time, according the aforementioned scheme (factor B; see Table 2). After 1, 2 and 5 h of shaking, the pH was checked and adjusted to the prescribed value. The product (collagen concentrate) was filtered through a sieve lined with three layers of PA cloth and dried at 35 °C for 24 h.

3. Deffating with solvents

Experiments were carried out with 8 types of solvents, in addition to which a combination of 2 types of solvent was tested.

The chicken feet were dried at 35 °C in an air-circulation oven for about 48 h prior to the defatting process. Afterwards, they were mixed with the solvent or mixture of solvents at a ratio of 1:10 (v/v) in an Erlenmeyer flask; the solvent mixture was prepared at a ratio of 1:1 (v/v) of its components. The flask was sealed and shaken for 32 h at room temperature in four stages (at 3, 6, 8 and 15 h). After each period, the solvent was exchanged. The defatted material was left in the hood for 30 min. to allow the residual solvent to evaporate.

Results and discussion

Table 1 shows the composition of the chicken feet.

Table 1: Composition of the chicken feet

	Dry matter [%]	**Proteins** [%]*	**Collagen** [%]*#	**Fat** [%]*	**Minerals** [%]*
Chicken feet	35.5 ±3.0	48.3 ±0.4	82.8 ±0.7	34.8 ±0.8	16.1 ±0.2

**based on the dry weight of the raw material*   *#from total protein content*

Results of deffating:

1. Deffating with $NaHCO_3$ solution

The residual fat content of the raw material, as defatted by 15 mM $NaHCO_3$ solution, exceeded 25 %, hence was inefficient for further use of the raw material.

2. Enzyme method

The results of the experiments are shown in Table 2. The residual fat content ranged from 24 % to 28 %, which was very high value in relation to the original fat content of the raw material (approximately 35 %). The amount of enzyme added and the processing time did exert any significant effect on the efficiency of the process. Notably, Lipolase 100 T exhibited very poor defatting efficiency.

Table 2: Schedule of the experiments and deffating results

Exp. No.	**Addition of enzyme** (factor A) [%]*	**Period of deffating** (factor B) [h]	**Residual fat** [%]
1	1.0	18	26.5
2	1.0	48	28.5
3	2.5	18	26.1
4	2.5	48	26.0
5	1.75	33	23.8

** based on the dry weight of the raw material*

3. Solvent method

Table 3 shows the results of the experiments. The highest defatting efficiency of the raw material was achieved using a 1:1 (v/v) mixture of petroleum ether and ethanol, since only 5 % residual fat remained in defatted raw material. A synergistic effect was evident for mentioned solvent mixture; in contrast, the efficiency of pure petroleum ether was approximately 1.5times lower (almost 8% residual fat content), while the figure for pure ethanol was around 4 times lower (≈ 21 % residual fat).

Table 3: Chemicals applied in the deffating process and their resultant efficiency

Solvent (mixture)	**Residual fat** [%]	**Solvent**	**Residual fat** [%]
Petroleum ether+ethanol	4.97	Butylalkohol	7.66
Petroleum ether+acetone	6.41	Acetone	7.74
Pentane	6.67	Petrolether	7.93
Hexane	6.95	Choroform	8.42
Diethyl ether	7.56	Ethanol	22.2

The final product (collagen concentrate) defatted with solvent mixture petroleum ether+ethanol contains 75.0 % of collagen, 14.6 % minerals, 5.4 % of non-collagenous organic matter and 5.0 % of residual fat (based on the dry matter).

Conclusion

Chicken feet containing a large amount of collagen were cleaned, chilled, ground and homogenized. Once water-soluble proteins and pigments were removed, it was necessary to defat the raw material due to the high fat content (approximately 35 %), which involved testing various methods to discern which was the most effective. Defatting with $NaHCO_3$ solution and lipolytic enzyme both proved unsuitable because the residual fat content remaining in the raw material exceeded 25 % and 26 %, respectively. Defatting with a mixture of petroleum ether and ethanol for 32 h (the mixture was exchanged 3times) at room temperature was the most efficient method for defatting the material, wherein the residual fat content equalled approximately 5 %; the resultant product described herein is very rich in collagen. It is worth noting that the prices for solvents represent a crucial aspect for processing at an industrial scale. The current retail costs per a litre of solvents are: butyl alcohol: 17.9 EUR; diethyl ether: 10.6 EUR; pentane: 8.0 EUR; hexane: 5.9 EUR; petroleum ether: 5.5 EUR; chloroform: 5.5 EUR; acetone: 3.9 EUR; and ethanol: 2.3 EUR (source: www.verkon.cz). Since ethanol and petroleum ether rank as ones of the cheapest available, a blend of petroleum ether and ethanol would constitute the most efficient and economically viable system for defatting poultry tissues. Collagen concentrate (75.0 % of collagen) prepared from chicken feet could potentially be utilized in the food industry (as food supplements or nutrients) or in cosmetics (as moisturising agents).

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Příprava kolagenního koncentrátu z kuřecích běháků

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Souhrn

Maso-zpracující průmysl produkuje velké množství nežádoucích vedlejších jatečných produktů, které mají jen velmi malé využití, a množství těchto vedlejších produktů se neustále zvyšuje. Příkladem takového typu vedlejších produktů jsou drůbeží běháky, hlavy, vnitřnosti a kůže, které jsou bohaté na proteiny, zejména kolagen. Kolagen je získán v několika krocích, během kterých je materiál podroben procesu mletí a odtučnění, jelikož drůbeží vedlejší produkty obsahují 15 – 70 % tuku. Dále je nezbytné ostranit nekolagenní složky (pigmenty a proteiny rozpustné ve vodě). Nekolagenní složky byly odstraněny opracováním v 0,1% NaOH. Dále byly otestovány 3 způsoby odtučnění suroviny (použití $NaHCO_3$, lipolytického enzymu a 10 různých rozpouštědlových systémů). Použití směsi rozpouštědel petrolether a ethanol se ukázalo jako nejefektivbnější metoda odtučnění kuřecích běháků (zbytkový obsah tuku přibližně 5 %). Připravený kolagenní koncentrát lze využít např. v potravinářském nebo farmaceutickém průmyslu.

Klíčová slova: vedlejší produkty, odtučnění, bílkovina, drůbež, jatka

Biomass analysis applicable to energy purposes

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Summary

Grass biomass is an important part of renewable energy sources of moderate belt. Growing grass for energy increases the potential of grass-harvesting not only for industrial purposes. The aim of the new research on the use of grasses for energy purposes is the cooperation of OSEVA Development and Research Ltd. in Zubri, VSB-TUO The ENET (Bulk Solids Center) and the University of Vigo in Spain (Energetic Technology Group) is a comprehensive comparison of the treatment of selected energy crops from input products through pelletizing to final combustion test results. The subject of this study is the specific processing of four selected energy crops. Detailed description of the process of production of pellets, evaluation of their mechanical-physical properties with quality evaluation is described. Selected manufactured oatmeal pellets were further transported to the University of Vigo, where tests were carried out in a small scale biomass combustor. The first experiments aimed at optimizing the setting for alternative fuels with higher ash content (eg primary and secondary airflow). The subject of the matter of concern was also particulate matter emissions. The results were compared with commonly available wood pellets and alternative pellets made from leaves and spruce sawdust (25 : 75).

Key words: *grass biomass, pelletization, alternative fuel, particulate matter emissions*

Introduction

Grass biomass is an important part of renewable energy sources in the Czech Republic.

Seed-grasses provide farmers with market seed production and, at the same time, straw that is usable for energy purposes. At the same time, an important source of grass biomass is the mass of permanent grassland of grass and pasture, temporary grassland on arable land, technical areas and lawns. This essentially agricultural and technical biomaterial raises a question of a modern solution and economic use of this grass mass. One way that is suitable for the use of grass biomass appears to be its use for energy production. Growing grass for energy increases the potential of grass-harvesting potential for industrial purposes. Grass biomass is used for energy production in the field of OSEVA Development and Research Ltd. based in Zubri at the biogas plant in Valasske Mezirici, mainly in the form of sowing. In Frenstat pod Radhostem is production of meadow hay biopellet for heating of buildings.

The article describes the processing of grass biomass for energy use. For the tests, 4 grasses were used - the bentgrass (*Agrostis gigantea* Roth), the reed canary grass (*Phalaris arundinacea* L.), the tall fescue (*Festuca arundinacea* Schreber) and the tall oatgrass (*Arrhenatherum elatius* (L.) P. Beauv. ex J. Presl & C. Presl). After their crunching, they were processed into pellets. Mechanical and physical parameters such as mechanical resistance, hardness and more have been determined for the pellets produced. Selected pellets were tested in a small scale biomass combustor. Resulting particulate matter (PM) emissions were compared with commercially available wood pellet data as well as with alternative pellets made from leaves and spruce sawdust (25:75). Cooperation continues. Tests of other grasses are underway, and attention is focused on the issue of significant biomass ash shedding, which leads to the creation of flares in the burner or the flame section of the boiler exchanger.

Material and methods

Material

For the study were used 4 species of grass - the bentgrass, the reed canary grass, the tall fescue and the tall oatgrass. The grasses were grown separately on single-breeding sowing areas. For pelleting, the fertilized grass variant was used. In the grasses were established energy parameters (Laboratory of Geological Engineering, FMG, VSB-TU Ostrava) [1].

Figure 1 shows ash value, combustion heat and calorific values for individual grasses.

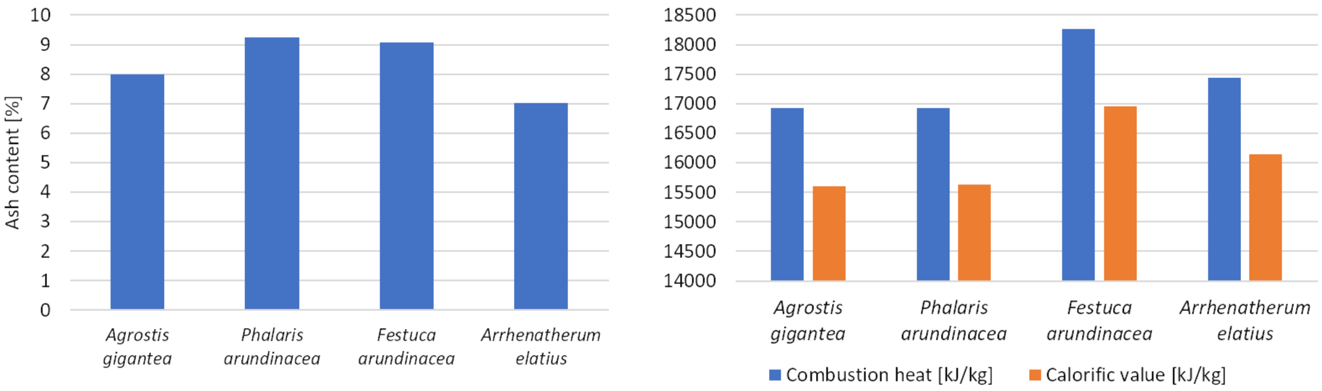

Figure 1: Energy parameters of grass [1].

For combustion tests were for comparison chosen commercially available wood pellets from spruce sawdust and biopellets made from leaves and spruce sawdust in a ratio of 25 : 75.

Grass pelletization

Dried grasses were crushed in the Green Energy 9FQ 50 hammer crusher, Pest Control Corporation. They were further pelleted on a Kahl 14-175 flatbed matrix press (Figure 2). The input grass moisture values were before the pelletization process itself adjusted to 16 % (w.b.) [1]. For all sorts of grasses were for comparison used identical pelletizing matrices. In this study, 40 kg of pellets were produced for each energy grass.

Figure 2: Pelletizing press Kahl 14-175.

Mechanical and physical properties of pellets

For the produced pellets was set moisture (EN 14774-1), mechanical resistance of pellets (D), pellet hardness (H) and moisture resistance (WI). The moisture test was repeated three times.

The mechanical resistance of the pellets (D) was measured on a Holmen NHP 1000 instrument. During the test, a sample of 100 g of pellets was circulated pneumatically at 70 mbar in a chamber with perforated cone-shaped walls for 60 seconds. After the test, the sample was sieved through a 3.15 mm sieve. Durability D was calculated as a percentage of the weight of the pellet sample after the test to the weight of the pellet sample before the [3] test. This procedure was performed in five replicate tests and the mean value was used.

The hardness of the pellet (Hardness H) was expressed as a pressure load in N units until the pellet was broken or crushed. Hardness was measured with the MultiTest 50 Manual Hardness, Sotax Tester [2]. The test was repeated ten times.

The resistance against the moisture, so called the wettability index (WI) was performed according to Equation (1) defined by [4]:

$$\mathrm{WI} = \frac{\mathrm{m_2} - \mathrm{m_1}}{\mathrm{m_1}} \times 100\ [\%] \tag{1}$$

where m_1 is the pellet weight before the test and m_2 is the pellet weight after the test. The test is to immerse the pellet in distilled water for 30 seconds. The test was repeated ten times.

Combustion

The tests have been conducted in a small-scale combustor (Figure 3). The general scheme and the different sections of the facility used to carry out these experiments is described in [5].

It is an experimental biomass combustion chamber with a vacuum system and an air supply. The combustor produces power within the range 7-12 kW_{th}.

Figure 3: Used facility.

Experimental methodology

A particle impactor with thirteen scales, DEKATI DLPI was used to measure the concentration and distribution particles. In order to avoid condensation in the gas stream, the extraction and the impactor were heated to 130 °C. The filters used in the impactor were made in the laboratory with aluminium paper, besides, they received a thermal treatment before and after each test. In this test, totalizator was not employed [6].

Results and discussions

The mechanical-physical properties of the grass pellets made of the bentgrass, the reed canary grass, the tall fescue and the tall oatgrass are presented in Table I. The grasses were first evaluated - the bentgrass, the reed canary grass, the tall fescue and the tall oatgrass. On the basis of the lowest ash value (Figure 1), ie 7.02%, was the tall oatgrass selected for further combustion. Due to the economic difficulty of transporting material to the University of Vigo in Spain, only one grass was selected in the first phase of the research. The combustion results were compared with commercially available wood pellets and biopelet of leaves and spruce sawdust in a ratio of 25:75.

Table I: The mechanical-physical properties of the grass pellets

Material of the pellet	moisture, %	D, -	H, N	WI, -
Bentgrass	5.1	99.31	189.0	11.8
Reed canary grass	4.8	99.11	85.5	11.5
Tall fescue grass	4.6	98.52	94.3	12.0
Tall oatgrass	3.8	99.19	242.9	11.5
Spruce sawdust	7.2	98.38	108.8	10.5
Leaves and spruce sawdust (25:75)	8.2	97.62	119.0	8.99

The results of the mechanical-physical properties (Table I) show a higher hardness H of the tall oatgrass pellets, whose water adsorption is, on the contrary, slightly lower than in the case of the bentgrass and reed canary grass. This may be due to different contents of lignin, hemicellulose and cellulose [7]. However, it can be stated that the produced pellets have been defined by EN 17225-6 defined values (D ≥ 97.5%, Moisture ≤ 12%). The values obtained for the parameters H and WI are not normative. For the hardness H of the pellets, compared to the pellets of other species of grass that have been measured in the before mentioned cooperation, the oat shows the highest hardness. The hardness of the pellets is an indicator of quality and higher value also predisposes a higher bulk density. The moisture resistance (WI) values were in line with the literature values [8, 9]. Moisture resistance to pellets indicates the risk of mold growth, pellets can also indicate a selection of suitable pellets such as screw feeders and others.

Some of the pellets produced were used to find optimal parameters for their combustion in experimental equipment. The repeatability of tests for fuels with high ash content (≈6%) was verified in [5]. Table II shows the summary of the pre-tests performed with their duration and optimal parameters for each alternative fuel.

Table II: Characteristics of the performed tests

Burning pelets	Ignition (min)+Stability (min)+ Shut own (min)= Total duration (min)	Primary air [%]	Secondary air [%]	Total air [m^3/h]
Tall oatgrass	45+90+15=150	30	70	20
		40	60	20
		50	50	20
Leaves and spruce sawdust (25:75)	45+90+15=150	30	70	20
		40	60	20
		50	50	20
Wood pellets	45+180+15=240	30	70	20

The duration is directly related to the ash content and it is particularly low when fuels with a high ash content are used. The same total airflow of 20 m^3.h^{-1} was always used, thus for low primary air staging, the amount of supplied air is sufficient for combustion take place without disturbances. In addition, the air staging was varied in order to study the effect of using different distributions in the results. With the grass and leaf pellets it has been possible used three different air staging. Nevertheless, with the commercial pellets (wood pellets), it was not possible used normally more than 30% of primary air, because the use of higher primary air percentages resulted in high powers, which could cause deterioration of the system components.

The facility used in this cooperation is very versatile, allowing studies of varied nature [10]. In some of these studies has been verified not only its repetitiveness with commercial fuels [6], but also with special fuels which has a high ash content too [5]. In figure 4 and figure 5, in each of the graphs have been shown the particle distribution for a different tested fuel. Within each graph, the parameter that varies is the air staging and is specified in the legend.

There are numerous studies relating to particles distribution using commercial wood pellet [11, 12]. In these studies, it has been determined that the majority of the particles generated in biomass have a diameter smaller than 1 µm. In addition, the distribution may have a unimodal or bimodal shape depending on the position of the sampling point relative to the bed. However, there are not results relative to the particles distribution for non-commercial, alternative fuels.

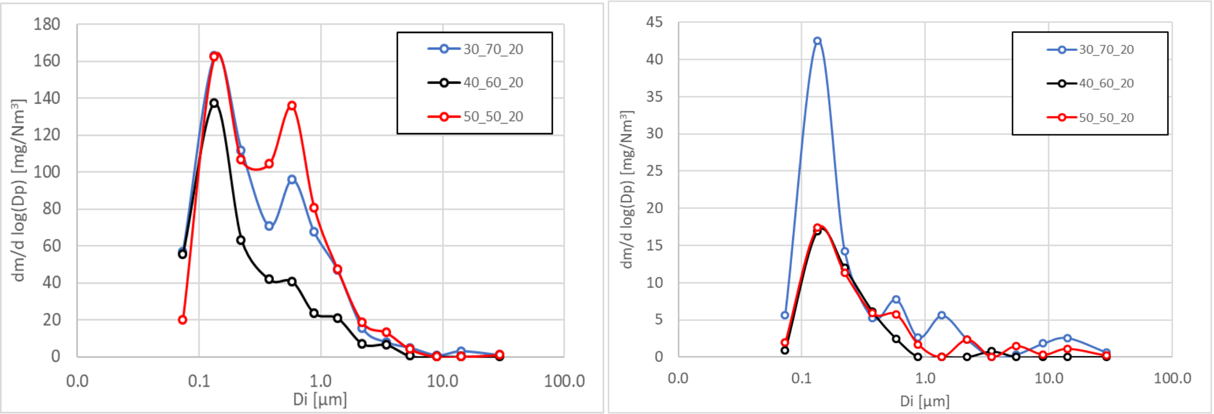

Figure 4: Particulate matter distribution for each test. The total airflow is $\dot{m}''_{air}$=0.459kg/m^{2}s. The air staging is specified in the legend. On the left tall oatgrass, on the right leave pellets. Quantity of mass (dm/dlog(Dp)) on mass median diameter (Di).

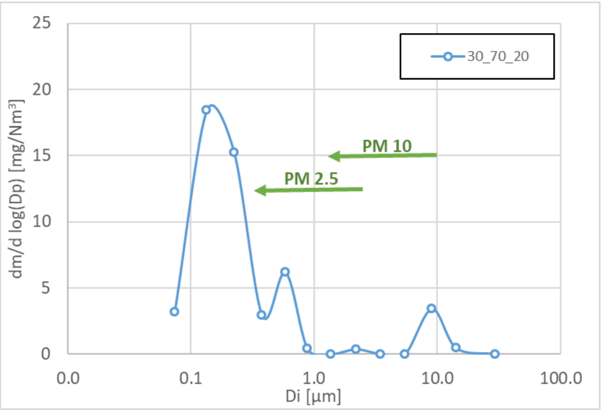

Figure 5: Particulate matter distribution for wood pellets (one test). The total airflow is $\dot{m}''_{air}$=0.459kg/m^{2}s. The air staging is specified in the legend. Quantity of mass (dm/dlog(Dp)) on mass median diameter (Di). PM 10 – particulate matter less than 10 µm, PM 2.5 – particulate matter less than 2.5 µm.

In this particular facility, using wood commercial fuel the majority of the particles are less than 1μm, and the distribution is unimodal with a particle peak between 30 – 100 nm [10]. The same results are proved in figure 5. This study allows to establish the particles size distribution for non-commercial fuel (pellets from tall oatgrass), of which there are no results so far. It can be verified that independently of the used fuel, the particles are always smaller than 1 μm. However, not all fuels have the same particle distribution shape, for leaf pellets and wood pellets is unimodal, nevertheless, for pellets from tall oatgrass is bimodal. For fuels with an unimodal distribution the particles peak is between 30 – 100 nm. As a general trend, the particle size distribution is related to the used fuel. Analysing the results, the particles diameter is always less than 1 μm, therefore, the fuel quality will be determined by the particles concentration emitted by the facility with each fuel.

Conclusion

Research on the use of grass straw from grasses grown for market seed production is very topical. Particularly due to the decrease of livestock in recent years, the areas with grass biomass suitable for alternative use have increased. Pellets represent one of the preferred forms of processing this grass biomass for biofuel. The pellets have good fuel properties, allow for trouble-free transport and handling. Therefore, the four selected energy grasses were processed into pellet form - the bentgrass, the reed canary grass, the tall fescue and the tall oatgrass. All pellets produced qualitatively conform to the required standards. Highest hardness and mechanical resistance with the lowest ash content included high grass seedlings. Therefore, it was selected for transport to the combustion test. Preliminary experiments determined the setting of the small scale biomass combustor and subsequent emission tests were carried out. The results showed the distribution of particulate matter of the tall oatgrass pellets elevated compared to commonly available wood pellets and alternative pellets of leaves and spruce sawdust (25 : 75). The particle size distribution for all tested materials was approximately under 1 μm. However, their concentration for the tall oatgrass was significant value. In the case of tall oatgrass, the shape of the distribution curve was bimodal, unlike wooden pellets and pellets from leaves and spruce sawdust (25 : 75), where it was unimodal and shifted rather to the nanometer area. At present, tests are also being carried out with bentgrass to compare the results for each species of grass.

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Analýza biomasy využitelné pro energetické účely

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Souhrn

Travní biomasa je významnou součástí obnovitelných zdrojů energie mírného pásu. Pěstování trav pro energii rozšiřuje možnosti potenciálu využití trav nejen pro průmyslové účely. Cílem nového výzkumu v oblasti využívání trav pro energetické účely je spolupráce OSEVA vývoj a výzkum s.r.o. v Zubří, VŠB-TUO Centra ENET (Bulk Solids Centre) a University of Vigo ve Španělsku (Energetic Technology Group) je komplexní srovnání zpracování vytipovaných druhů energetických travin od vstupních produktů přes zpracování peletizací až po konečné výsledky spalovacích zkoušek. Předmětem uvedené studie je konkrétní zpracování čtyř vybraných energetických travin. Detailně je popsán postup výroby pelet, vyhodnocení jejich mechanicko-fyzikální vlastností s vyhodnocením kvality. Vybrané vyrobené pelety ovsíku vyvýšeného byly dále převezeny na University of Vigo, kde proběhly testy in a small scale biomass combustor. První experimenty si kladly za cíl optimální nastavení zařízení pro alternativní paliva s vyšším obsahem popela (např. primární a sekundární průtok vzduchu). Předmětem zájmu byla také particulate matter emissions. Výsledky byly srovnány s běžně dostupnými dřevěnými peletami a alternativními peletami vyrobenými z listí a smrkových pilin (25:75).

***Klíčová slova:** travní biomasa, peletizace, alternativní palivo, particulate matter emissions*

Effect of hydrothermal pretreatment of different municipal biological wastes for biogas production

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Abstract

Sewage sludge, lawn maintenance waste, fruit/vegetable waste and food catering waste were chosen for study as typical municipal biological wastes. Hydrothermal pretreatment was used to accelerate biological anaerobic digestion for enhancement of biogas/bio-methane production from tested biowastes. Mesophilic anaerobic digestion tests were used to evaluate biogas production for original raw materials and hydrothermal treated biowastes. Laboratory batch biogasification tests were performed in duplicate with use of 3-liter glass anaerobic fermenters containing approximately 2 L of fermentation medium. The biogasification tests were conducted at a temperature of 37 ± 1 °C and stirred for 15 minutes every 2 hours. In the case of raw materials, fruit/vegetable waste and food catering waste show higher biogas/methane production than that of lawn maintenance waste and sewage sludge. After hydrothermal pretreatment at typical condition (160 °C at 0.5 h), the biogas (bio-methane) specific yields of fruit/vegetable waste, lawn maintenance waste and municipal sewage sludge increased by 7.6 (6.6), 26.5 (24.1) and 58.3 (53.2) % respectively, while for treated food catering waste the biogas (bio-methane) specific yield decreased by 4.2 (6.1) %. It seems, the lower the origin waste biodegradability, the higher the biogas/bio-methane yield increasing after pretreatment. More detailed research on this topic is desirable.

Keywords: *municipal biowaste; biogas production; hydrothermal pretreatment; specific methane yield.*

Introduction

Typical municipal biological wastes are municipal sewage sludge, lawn maintenance waste, fruit/vegetable waste and food catering waste. Municipal sewage sludge is the by-product of the waste-water treatment process (WWTP). Lawn maintenance waste includes usually short cut grass[1]. Fruit/vegetable waste is refused fruits and vegetables from households, municipal markets and catering enterprises. Food catering waste is generated from households, restaurants, hotels and canteens of schools and large companies[2].

The common characteristic of municipal biological wastes is their high environmental and health hazards[3]. There are different disposal pathways for municipal biological wastes, but anaerobic digestion technologies play the most important role because of the possibilities for renewable materials and energy utilization due to the production of biogas and digestate fertilizers[4,5].

Many studies[6,7,8,9] show that thermal pretreatment of biowaste or biomass can significantly increase biogas/bio-methane production, but only under certain processing conditions. Although municipal biological wastes are seen as prospective renewable energy sources, there are not enough the experimental results of different materials for biogas production potential, especially with and without hydrothermal pretreatment[10]. Therefore, it was necessary to assess the effect of hydrothermal pretreatment of different biological wastes for specific biogas/bio-methane yields. The aim of this study was to investigate the biogas and methane production with/without hydrothermal pretreatment of typical municipal biological wastes.

Materials and methods

As suitable objects for study, municipal sewage sludge, lawn maintenance waste, fruit/vegetable waste and food catering waste were chosen as typical municipal biological wastes. The biowaste samples for investigation were collected and prepared by removing bones, plastic and metals, crushing and homogenization by the company WEKUS Ltd., which deals with the anaerobic digestion of agricultural and municipal biological wastes using devices combining biogas production and hydrothermal pretreatment of risk biowastes. Lawn maintenance waste, fruit/vegetable waste and food catering waste were crushed into particles less than 12 mm before testing. Hydrothermal treatment was carried out in laboratory high-pressure stainless vessels heated in the electric thermo-stated oven. Liquid to solid ratio of hydrothermal treated samples was 10:1. The processing volume of reaction vessels was 500 ml. The parameters for hydrothermal treatment were 160 °C for 0.5 hour of stable heating, according to routine operating procedures of WEKUS Ltd. The cooling time of samples was at least 2 hours. After opening the reaction vessels, the samples were processed within 4 hours.

The chemical analyses of the basic characteristics of waste samples were performed according to standard procedures published in the methodological manuals of the Central Institute for Supervising and Testing in Agriculture[11,12], which are based on the world (ISO) or European Committee for Standardization (CEN) procedures. Measurement by individual instruments was performed in accordance with the manufacturers' operating procedures.

The total content of dry matter (DM) in wet samples was determined gravimetrically after drying at 105 °C to constant weight according to CSN EN 14346[13]. The content of organic dry matter in biological samples, which is the same parameter as volatile solids (VS), was determined gravimetrically after combustion at 550 °C to the constant weight of ash according to CSN EN 15169[14].

The soluble chemical oxygen demand (COD) was determined by the potassium dichromate/ferrous ammonium sulphate method according to ČSN ISO 15705[15]. Total organic carbon (C_{tot}) and total nitrogen (N_{tot}) were measured by a CHNSO elemental analyzer (vario EL Cube, Elementar Analysensysteme Ltd., Germany). Volatile fatty acids (VFAs) were measured by an isotachophoresis analyzer (Villa-Labeco Ltd., Slovakia). $N\text{-}NH_4^+$ and $P\text{-}PO_4^{3+}$ contents were measured by a capillary zone electrophoresis analyzer (Villa-Labeco Ltd., Slovakia). The pH was determined by a pH meter (Seltron Ltd., the Netherlands).

The total content of some macronutrients, namely P and S, were determined in the mineralization solution after sample decomposition using aqua regia in a closed high-pressure microwave system (microwave oven Milestone MLS-1200 Mega from Milestone Inc., Italy) with analytical determination by an inductively coupled plasma optical emission spectroscopy (ICP-OES) instrumentation (namely Integra XL, GBC Scientific Equipment Ltd., Australia) according to CISTA methods[12] and common operation procedures of the equipment.

Anaerobic digestion tests for biogas production from biomass were carried out based on the guidelines of VDI 4630[16]. Laboratory batch tests were performed in duplicate with use of the assembly of 48 pieces of 3-liter glass anaerobic fermenters containing approximately 2 L of fermentation medium. The biogasification tests were conducted at a temperature of 37 ± 1 °C and stirred for 15 minutes every 2 hours. For each reactor, the volume of biogas displaced by acidic solution was measured in a graduated cylinder. The basic composition of biogas (methane and carbon dioxide contents) was measured with a biogas analyzer and calculated to specific yields of biogas and methane at a standard temperature and pressure (STP) condition, namely at the temperature of 0 °C with a pressure of 100 kPa or 1 Bar (so-called normalized volume of gas, e.g. Nm^3 or NL). Therefore, the suitable unit for the expression of biogas or methane specific production from organic dry matter or volatile solids of anaerobic digestion feedstocks is Nm^3/t VS or NL/kg VS.

For each series of experiments, four blanks with only water and inoculum were included to measure the methane production originating from the inoculum. Usually this blank methane production was more than ten times lower than the methane production of sample and inoculum blends. The blank values were always subtracted from sample measurements. The input of the VS ratio of tested materials to an inoculum was 3:10. The inoculum was adjusted digestate from the agricultural biogas station

(Ekoenergie Vyskov, FABE, Ltd., Bitozeves), which processes maize and grass silages and animal excrements in a ratio of 10:2:1. The total solids of inoculum was 67.6 g TS per 1 kg of wet weight (ww). The VS:TS ratio of inoculum was 67.2 %, which corresponds to the value 45.4 g VS/kg ww. The total period of biogas digestion was uniformly set at 35 days. This is a sufficient time, during which the intensive phase of biogas production ended in all tested substrates. In the course of the experiments, the intensive phase of the biogas development lasted from about two to four weeks after the end of the start-up period (the so-called lag-phase), which usually takes about one to five days.

Results and discussion

Characteristics of raw biowaste materials

Biogas/bio-methane yields are determined by feedstock composition, first of all by the content and quality of biodegradable substances. Resistant solids are composed of lignin and some other non-biodegradable substances. It is commonly known that biodegradable volatile solids include sugars, starch, organic acids, cellulose, lipids and proteins. All of these substances have different specific biogas/bio-methane yields. Therefore, the knowledge of feedstock composition of individual samples allows to predict their biogas and methane production. Table 1 shows the basic composition of tested biowastes with respect to their feedstock quality for biogas production. Based on these results, it can be assumed that the highest yields of biogas/bio-methane can be expected for the food catering waste and the lowest for the municipal sludge.

Table 1: Characteristics of raw biowaste materials (%$_{WW}$)

Object	**TS (%)**	**VS (%)**	**VS/TS (%TS)**	**Fibers (%TS)**	**Lipids (%TS)**	**Proteins (%TS)**	**Ash (%TS)**	**N_{tot} (%TS)**	**P_{tot} (%TS)**	**pH**
Sewage sludge	16.2	11.4	70.4	20.3	15.79	20.4	29.56	3.27	1.864	7.74
Lawn maintenance waste	10.3	9.0	87.6	22.7	0.52	15.3	12.42	2.45	0.432	7.32
Fruit/vegetable waste	11.5	9.9	86.3	33.8	10.71	23.6	13.68	3.78	0.451	5.18
Food catering waste	20.5	18.5	90.2	18.6	32.48	23.9	9.77	3.83	0.403	4.83

Characteristics of hydrothermal treated biowaste materials

Table 2 presents the characteristics of hydrothermal treated biowaste materials. Changing the level of biodegradability of individual biowastes is reflected primarily by changing their COD values after hydrothermal treatment. The main cause is an increase of organic matters dissolving and hydrolyzing caused by that the parts of solid organic matters are liquefied in the form of low molecular weight organic compounds.

The hydrothermal treatment disrupts the raw organic compounds thus organic carbon, nitrogen and phosphorus will be released from the solid biowaste materials into the liquid phase. The total nitrogen in the liquid phase of all biowastes was relatively high, while the total phosphorus was relatively low. The highest content of both elements in the liquid phase of hydrothermal treated biowastes was in food catering waste.

The pH values tend to decrease for all hydrothermal treated materials, especially for lawn maintenance waste and municipal sewage sludge, which changed from alkaline to acid values after hydrothermal treatment. This is caused by the increase of soluble content of VFAs, amino acids and ammonia nitrogen, which could significantly affect pH changes. The highest concentration of all dissolved compounds after hydrothermal treatment was found at food catering waste and the lowest at sewage sludge. Contrary, the highest pH was at treated sewage sludge and the lowest at treated food waste (see Table 2).

Table 2: Characteristics of liquid phase of hydrothermal treated biowaste materials

Object	VFA (g/L)	COD (g/L)	TOC (g/L)	TN (g/L)	TP (g/L)	C:N:P	pH
Sewage sludge	9.12	35.2	10.14	1.82	0.224	38.2:7.32:1	5.96
Lawn maintenance waste	10.51	28.6	12.16	1.69	0.206	46.3:7.95:1	5.92
Fruit/vegetable waste	11.23	46.7	14.07	1.84	0.238	57.6:7.11:1	4.36
Food catering waste	15.86	129	61.72	3.18	0.553	111.4:5.74:1	4.18

On one side, the low-molecular organic compounds, including VFAs and amino acids, generated during hydrothermal processing are suitable substrates for biogas production, but on the other side due to pH changes the high concentration of these compounds can inhibit the activity of methanogenic bacteria. Volatile fatty acids (VFA) are short-chained organic acids such as acetic acid, propionic acid, butyric acid and valeric acid or branched isomers of them, which are the intermediate metabolites of anaerobic digestion and are the important precursors of methanization. But their enormous accumulation can disrupt this process due to direct feedback on the interaction of the different groups of micro-organisms in the biogas reactor, especially the accumulation of butyric or valeric acid and their branched isomers[5,17]. For example, Shofie et al.[18] state that acetoclastic methanogenesis is inhibited, if the propionic acid concentration reached above 1000 mg/L as COD equivalent. Vieitez and Ghosh[19] reported interrupting the process of anaerobic digestion when the concentration of VFAs exceeds 13,000 mg/L.

According to stochiometric calculation, 1.0 g of acetic acid, propionic acid, butyric acid and valeric acid were equivalent to 1.07, 1.51, 1.82 and 2.04 g COD, respectively. For tested biowastes, VFAs accounted for 36.7, 25.9, 24.0 and 12.3 % of total COD in the liquid phase of lawn maintenance waste, municipal sewage sludge, fruit/vegetable waste and food catering waste, respectively. As seen, the percentages of VFAs/COD are relatively high almost for all tested biowastes except for food catering waste.

The obtained results confirmed that the hydrothermal treatment accelerated organic substances dissolving into liquid phase resulted into increasing the values of COD, VFA and soluble organic C_{tot} and thereby improving the anaerobic biodegradation of biowaste materials.

Biogas and methane specific yields of raw and hydrothermal treated biowaste materials

Table 3 compares the results of experimental determination of biogas and methane production for raw biowaste materials and hydrothermal treated biowastes. The obtained results confirmed that hydrothermal treatment accelerated anaerobic biodegradation of biowaste materials and biogas/bio-methane production. In the case of raw materials, fruit/vegetable waste and food catering waste show higher biogas and bio-methane production than that of lawn maintenance waste and municipal sewage sludge. The highest biogas and bio-methane yields of food catering waste can be explained by its composition because of the highest lipid and protein contents in ***comparison*** with the other tested biowastes.

Table 3: Biogas and methane specific yields of raw and hydrothermal treated biowaste materials (mean ± SE)

Object	Raw biowaste materials			Hydrothermal treated biowastes		
	Biogas (NL/kg VS)	Methane content ($\%_{VV}$)	Methane (NL/kg VS)	Biogas (NL/kg VS)	Methane content ($\%_{VV}$)	Methane (NL/kg VS)
Sewage sludge	218 ± 6	64.8	141 ± 4	345 ± 8	62.4	216 ± 5
Lawn maintenance waste	392 ± 9	58.1	228 ± 6	496 ± 10	57.1	283 ± 7
Fruit/vegetable waste	436 ± 8	59.3	259 ± 5	469 ± 9	58.9	276 ± 5
Food catering waste	576 ± 10	62.6	361 ± 7	552 ± 9	61.5	339 ± 6

Different situations occur in the case of hydrothermal treated biological materials. It was found that after hydrothermal pretreatment at typical condition (160 °C at 0.5 h), the biogas specific yields of fruit/vegetable waste, lawn maintenance waste and municipal sewage sludge increased by 7.6, 26.5 and 58.3 % respectively, while for treated food catering waste the biogas specific yield decreased by 4.2 %. Correspondingly, the bio-methane specific yields of fruit/vegetable waste, lawn maintenance waste and municipal sewage sludge increased by 6.6, 24.1 and 53.2 % respectively, while for treated food catering waste the bio-methane specific yield decreased by 6.1 %.

Distefano and Ambulkar[6] reported 52 % increase in methane production for sewage sludge after thermal treatment at 175 °C. Also, Qiao et al.[8] found biogas yield increase by 67.8 % (from 202 to 339 ml/g VS) for sewage sludge and by 18.5 % (from 443 to 525 ml/g VS) for fruit/vegetable waste after hydrothermal pretreatment (170 °C, 1 h), respectively. Similarly, bio-methane yield increase by 65.8 % (from 155 to 257 ml/g VS) for sewage sludge and by 16.0 % (from 281 to 326 ml/g VS) for fruit/vegetable waste after hydrothermal pretreatment, respectively.[8] Vice versa, in the case of food waste the decreases of biogas (from 781 to 754 ml/g VS or -3.5 %) and bio-methane yields (from 531 to 491 ml/g VS or -7.5 %) were recorded after the same pretreatment (170 °C, 1 h).[8]

Municipal sewage sludge gives the highest increasing rate of biogas/bio-methane production after hydrothermal treatment, demonstrating that it greatly affects mainly the sewage sludge. It can be explained by the highest content of raw organic substances which are not easily biodegradable, but are well degradable by hydrothermal treatment resulting at intensive releasing soluble organic substances, causing higher biogas and bio-methane yields.

On the contrary, the biogas and bio-methane production for hydrothermal treated food catering waste even decreased. It can be explained by the highest content of lipids and proteins in food waste in comparison with the other materials. It seems the higher the origin waste biodegradability, the lower the change of biogas and bio-methane yields after hydrothermal pretreatment. In any case, this phenomenon deserves more detailed research in the future.

Conclusions

It was confirmed that hydrothermal pretreatment is a prospective method for acceleration of biological anaerobic digestion and enhancement of biogas/bio-methane production from typical municipal biowastes. Biogas/bio-methane yields are determined by feedstock composition, first of all by the content and quality of biodegradable organic substances. Hydrothermal treatment accelerated organic substances dissolving into liquid phase resulted into increasing the values of COD, VFA and soluble Ctot and thereby improving the anaerobic biodegradation of biowaste materials. In the case of raw materials, fruit/vegetable waste and food catering waste show higher biogas/methane production than that of lawn maintenance waste and municipal sewage sludge. Municipal sewage sludge gives the highest increasing rate of biogas/bio-methane production after hydrothermal treatment. On the contrary, the biogas/bio-methane production of hydrothermal treated food catering waste decreased. It means, the lower the origin waste biodegradability, the higher the biogas/bio-methane yield increasing after pretreatment. Given the importance of this topic, it is desirable to extend and deepen this research in the future, in particular to increase the number of test repetitions to ensure the possibility of reliable statistical evaluation and to supplement the studding of the energy balance of investigated processes.

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Vliv hydrotermální předúpravy různých komunálních biologických odpadů na produkci bioplynu

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Souhrn

Pro výzkum byly jako typické komunální biologické odpady zvoleny kaly z čistíren odpadních vod, odpady z údržby travnatých ploch, odpady po zpracování zeleniny a ovoce a odpady vznikající v provozech veřejného stravování. Hydrotermální předúprava byla použita z důvodů zintenzivnění anaerobní biologické digesce a tím i produkce bioplynu a metanu z testovaných bioodpadů. Pro vyhodnocení produkce bioplynu z původních a hydrotermálně upravených biologických odpadů byly použity vsázkové laboratorní testy mezofilní anaerobní digesce, a to s použitím třílitrových skleněných anaerobních reaktorů obsahujících přibližně 2 litry fermentačního média, vše ve dvou opakováních. Testy biozplynování byly prováděny při teplotě 37 ± 1 ° C a míchány po dobu 15 minut každé 2 hodiny. V případě odpadů z ovoce a zeleniny a provozoven veřejného stravování byla zjištěna vyšší produkce metanu než u odpadů z údržby travnatých ploch a kalů z komunálních čistíren odpadních vod. Po hydrotermální předúpravě při typických podmínkách (teplota 160 °C po dobu 30 min) se produkce bioplynu (metanu) zvýšila u odpadů ze zeleniny a ovoce o 7,6 (6,6) %, z údržby travnatých ploch o 26,5 (24,1) % a z kalů komunálních čistíren odpadních vod o 58,3 (53,2) %, zatímco u předupravených odpadů z veřejného stravování se výnos bioplynu (metanu) nezvýšil, ale dokonce poklesl, a to o 4,2 (6,1) %. Zdá se, že čím nižší je biodegradabilita neošetřených odpadů, tím vyšší je nárůst výtěžnosti bioplynu a metanu po předúpravě. Podrobnější výzkum tohoto tématu je žádoucí.

Klíčová slova: *komunální bioodpady; produkce bioplynu; hydrotermální předúprava; specifická výtěžnost metanu.*

The Influence of Secondary Raw Materials on Tobermorite Formation in Calcium-Silicate Composites

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Abstract

The physical-mechanical properties of calcium-silicate composites depend on their microstructure, which itself, in autoclaved aerated concrete especially, depends on the formation and morphology of the calcium hydrosilicate phases. The main one of these phases is tobermorite, which is what this paper is focused on. Two secondary raw materials representing two main groups of by-products are discussed. Namely, these are fluidized bed combustion fly ash and slag produced by the incineration and power plants. Studying the utilisation of secondary raw materials has become a necessity for both environmental and financial reasons. Selected raw materials were mixed with lime only. In this way, the conditions eliminating the effects of other impurities were ensured. The material's molar ratio of calcium oxide to silicon dioxide was 0.73 and 1.0. The material samples were then autoclaved at two temperatures (170 and 190 °C) and three different hydrothermal durations (4, 8 and 16 hours). The results indicate that slag appears to be promising material. Samples containing slag reached the same compressive strength as reference samples at 190°C with a molar C/S ratio of 0.73.

Keywords: *Tobermorite, calcium-silicate composite,* fluidized bed combustion fly ash*, slag*

Introduction

Calcium-silicate composites are made with pure materials such as quicklime and silica sand. Nowadays these materials are becoming still more difficult to obtain. Their sources can suffer from contamination and their extraction is becoming more expensive, which in turn raises the price of the final product. This generates the need to re-use and recycle various waste materials. It is the usage of secondary raw materials that is currently receiving much attention. This concerns mainly pozzolanic silica materials such as fly ash or slag.[1, 2]

FBC ash

This paper focuses on two secondary raw materials - fluidized bed combustion fly ash (FBC) and slag. FBC ash is a combustion by-product from fluidised bed combustion with the addition of milled limestone. Adding milled limestone is a method of flue-gas desulphurisation. The coal combustion temperature ranges between 800 and 900°C. There are certain variations taking place during the combustion process, which cause instabilities in the mineral composition of the ash. Chemical composition and mineralogy may vary as well. This complicates the utilisation of FBC ash and requires constant observation of the properties.[3] FBC ash seems viable mainly because of its high content of reactive aluminosilicates.

FBC ash can often be used as aggregate instead of silica sand. Some research shows that FBC ash can help reduce bulk density in aerated concrete, and a 25% to 50% replacement can improve its compressive strength. Kurama et al. claim that a substitution of the silicate components reduces thermal conductivity. FBC ash consists of crystalline and amorphous phases. The amorphous phase is what gives the material its pozzolanic properties.[2]

Slag

Slag (HPS) is inorganic waste produced by burning coal in a fluidised bed combustor. It can be a valuable source of alternative aggregate for concrete. One of the reasons for considering slag as a secondary raw material is preserving the environment and cutting down on landfilling. An important property of slag is its high content of silicon dioxide. It is also characteristic by non-homogeneity and a high content of impurities. Mineralogical analyses have shown that aside from the amorphous phase, slag also contains mullite, anorthite, melilite, calcium and clay rocks, magnetite, and gypsum. It may be contaminated by unburned coal and sulphur compounds. These impurities can cause concrete to suffer from volume changes.[4]

There are currently too few studies that describe the use of slag as a secondary raw material. Replacing the silicate component in concrete with slag or other calcium-silicate composites is still largely an unexplored area. In this respect, slag shows great promise and is worth investigating.

Microstructure

So far studies have focused only on the hydrothermal reactions during the synthesis of tobermorite and other CSH phases while using very pure primary raw materials such as quicklime and silica sand. However, tobermorite synthesis using secondary raw materials needs researching as well and is addressed in this paper.

In commercially available products made with lime, silica sand, hydrated lime, and water these components partly react under hydrothermal conditions, producing calcium silicate hydrate (CSH). The strength of calcium-silicate products hardened by autoclaving comes from CSH phases, which bind the silicate particles together. The hydrothermal treatment of calcium silicate products is generally done at temperatures of 150°C to 220°C and steam pressure of 0.8-1.6 MPa over 3 to 10 hours.[5]

The hydrothermal reaction produced by the action of pressurised steam transforms the calcium silicate hydrate into tobermorite, and thereby improves the strength of the composite. Prolonged autoclaving slowly transforms tobermorite to xonotlite, which, when detected, indicates wrong autoclave hardening and can be detrimental to the composite's properties.[1, 5]

Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) is a natural layered mineral. It is the primary component of autoclaved calcium-silicate, such as sand-lime bricks, autoclaved aerated concrete, thermal insulation boards, or similar products. It is also used as an adsorber. This is thanks to the stabilised thermal properties of materials at high temperatures and a large specific surface area with high porosity.[1, 6, 7, 8, 9] There are several morphologies of tobermorite, namely fibers and platelets.

Materials

The goal of this research was to study the formation of tobermorite in a calcium-silicate composite in dependence on the choice of the silicate compound and hydrothermal conditions. The experiments were performed at different hydrothermal conditions and with different molar ratios of calcium oxide to silicon dioxide (henceforth C/S). At first, two secondary materials and one reference compound (i.e. silica sand) were chosen. The next step involved measuring the basic properties of the raw materials so as to optimise the mixture formulae and set the conditions for the hydrothermal reactions. After that samples could be made, and their microstructure studied.

Raw materials

The determining criterion for the choice of the raw materials was their SiO_2 content, which was amorphous in both cases. The materials selected for the experiments were silica sand, FBC ash, and slag (HPS). They were then tested for basic properties.

Properties of the materials

The first basic property to be tested was chemical composition. Drawing on the knowledge of calcium oxide and silicon dioxide content it was possible to design the mixtures. Table 1 shows the properties of material as results of the chemical composition analysis. Another property that may affect the formation of tobermorite is the specific surface area. It was measured together with bulk density and water absorption. Bulk density was measured using an AccuPyc II 1340 helium pycnometer. The specific surface area was determined by the Blaine permeability method in accordance with ČSN EN 196-6. Water absorption was measured as the 24-hour difference between the mass of the wet and dry material.

Table 1: Properties of the materials

Raw material	**Oxide content [%]**			**Bulk density [kg/m^3]**	**Specific surface area [m^2/kg]**	**Water absorption [%]**
	SiO_2	**CaO**	**Al_2O_3**			
Quartz sand	92.91	0.23	2.53	2700	308	30.8
FBC	38.05	17.67	24.67	2740	390	192.9
HPS	50.00	3.42	23.40	2610	298	35.3

Reactivity of lime was measured using the Dewar vessel. The test was performed in accordance with ČSN EN 459-2.

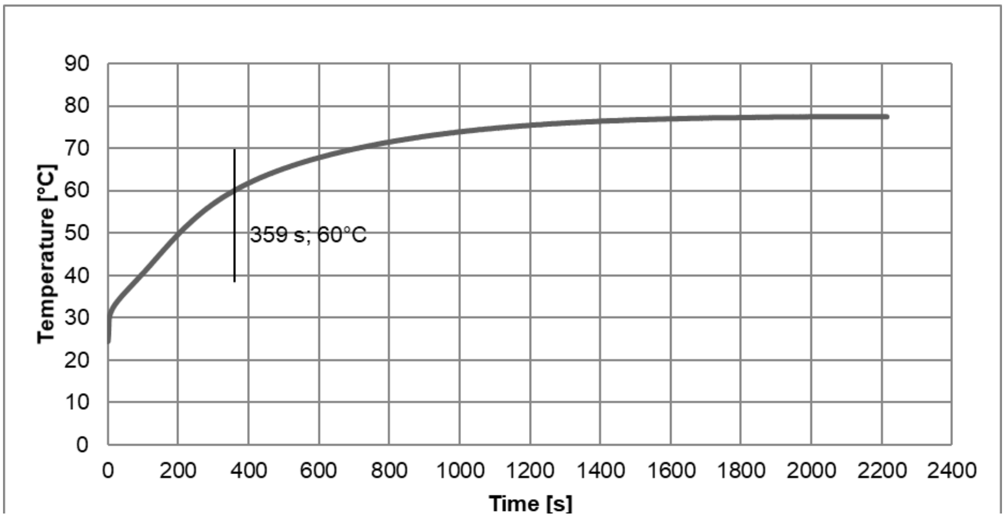

Figure 1: Reactivity of lime

The reactivity of the lime was set at 359 s (Figure 1), that is 5 minutes and 59 seconds, as the time at which the hydration temperature reached 60°C. According to ČSN EN 459-1, such lime is specified as CL 90 - Q (R5).

Methods

As said above the mixtures needed to be optimised based on their chemical composition. The goal was to design the mixtures in such a way that the molar C/S ratio was 0.73 and 1.00. The choice of these particular ratios is based on limit values at which tobermorite should form. Figure 2 shows the raw material ratios.

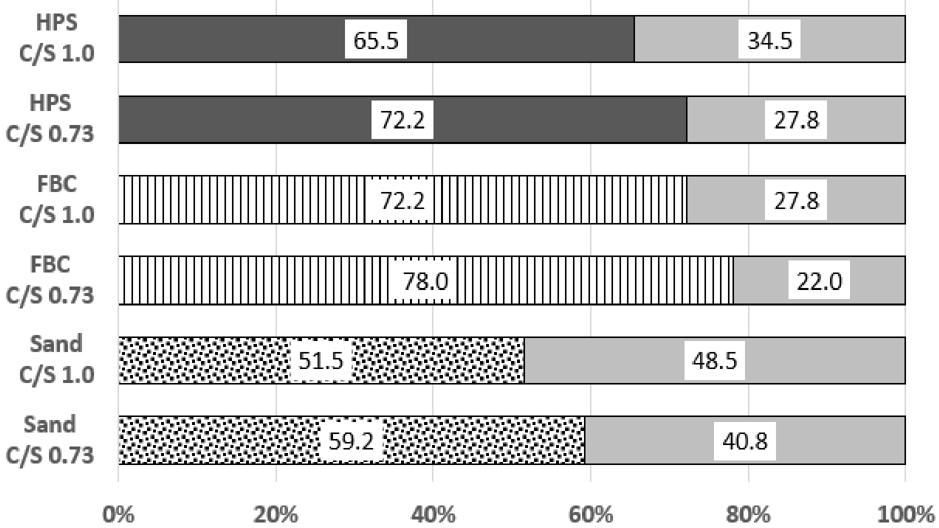

Figure 2: Mixtures (percentage share) of the raw materials; silica raw material – left side, lime – right side

Sample preparation

Lime, the silicate materials, and water were mixed to a slurry, which was poured into moulds. The Samples had the dimensions of 20×20×100 mm. After demoulding, the samples were left to mature for 24 hours. After that they were autoclaved at 170 °C and 190 °C at a holding time of 4, 8 and 16 hours. The choice of the temperatures and holding time is based on silicon dioxide solubility and the conditions of tobermorite formation. The hydrothermal conditions were created using small autoclaving capsules (Figure 3), which consisted of a Teflon lining (300 ml) encased in a steel sleeve. To ensure they are airtight, the capsules are closed with a double seal. Only one specimen was placed in each vessel. It was positioned on a disc under which was poured an amount of water corresponding to 10 % of the lining's capacity. The sample had to be kept from contact with the water underneath. Then, the capsules were sealed. The tightness of the seal was verified after autoclaving when the capsules were weighed to see whether they had lost any mass. To begin the autoclaving process, the capsules were placed in a dryer which could deliver the required temperature for the required time.

Microstructure

Once autoclaved, the samples were extracted from the capsules and dried at 40°C until their mass had stabilised. In order to study their microstructure, the surface layer of the samples needed to be removed and the cores thus obtained were milled in a vibration mill. The resulting powder was sifted using a 0.5 mm sieve. Larger particles that remained were milled again. The powder was finally milled in an isopropanol solution down to a maximum particle size of 20 µm using a McCorne XRD mill. When the suspension had dried the samples could be placed in the holders of an Empyrean Panalytical X-ray diffractometer. This X-ray diffractometer has an angular reproducibility of < 0.0002° and 2θ linearity equal or better than ±0.01°. The output of this analysis was XRD diagrams. This examination was supplemented by SEM imaging.

Figure 3: Autoclaving capsules

Results and discussion

The influence of secondary raw materials on tobermorite formation was studied by a microstructure examination. This study was supplemented with test results of physical-mechanical properties and SEM imaging.

The influence of secondary raw materials on physical-mechanical properties

The specimens were tested for bulk density and compressive strength. It should be noted that the measured values were only to supplement the study of microstructure. The samples were small and intended for tobermorite synthesis; they were not composites that would possess correctly measurable compressive strength and bulk density.

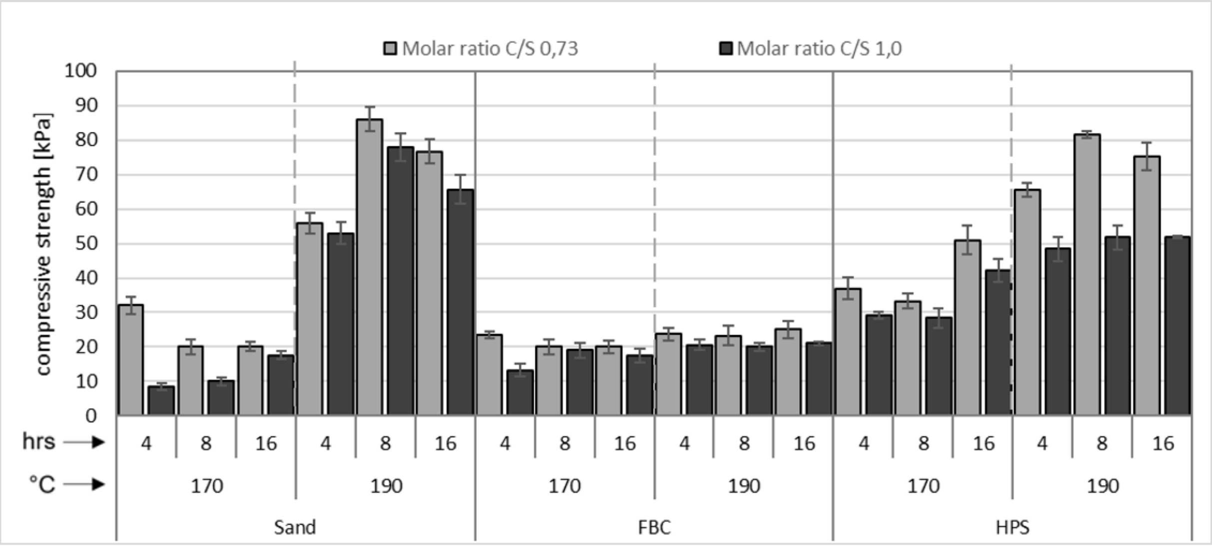

Figure 4: Compressive strength of samples with lime and silica raw material

The experiment compared the influence of a representative of FBC ash and a representative of slag. It was found that FBC ash caused a decrease in compressive strength. The strength decrease was almost entirely proportional to autoclaving temperature, time, and the C/S ratio. Samples containing slag reached the same compressive strength as reference samples at 190 °C with a molar C/S ratio of 0.73. In fact, their compressive strength was higher than that of the reference autoclaved at 170 °C. The reason is the amorphous aluminosilicate, which is more soluble than the crystalline oxide contained in sand. Better solubility results in better reactivity, which allows CSH phases to form at 170 °C.

The results also show that samples with a molar C/S ratio of 0.73 reached better compressive strength than the sample with a C/S ratio of 1.0. The reason is the high content of calcium oxide in the samples with a higher molar ratio.

The influence of secondary raw materials on microstructure

The influence of secondary raw materials on microstructure was studied primarily by XRD analysis. This analysis was supplemented by SEM images. The main parameter of the microstructure study was tobermorite peak intensity in XRD analysis diagrams. The effect of the raw materials and autoclaving mode on the crystallization and quality of the tobermorite was monitored. The quantification of tobermorite will be dealt with by follow-up research in the future. The data of tobermorite peaks was then converted into a graph.

Besides tobermorite, other phases were found in the samples. In the samples with quartz sand, most quartz and portland minerals were found. An increase in autoclave temperature led to dissolution of quartz and portlandite in favour of tobermorite. Tobermorite was formed in a sample with quartz sand at a temperature of 190°C, which was sufficient for the solubility of quartz. In samples with FBC ash and HPS, tobermorite, portlandite, and very low quartz were also found. Furthermore, the α-C2SH phase was detected in sample with FBS ash.

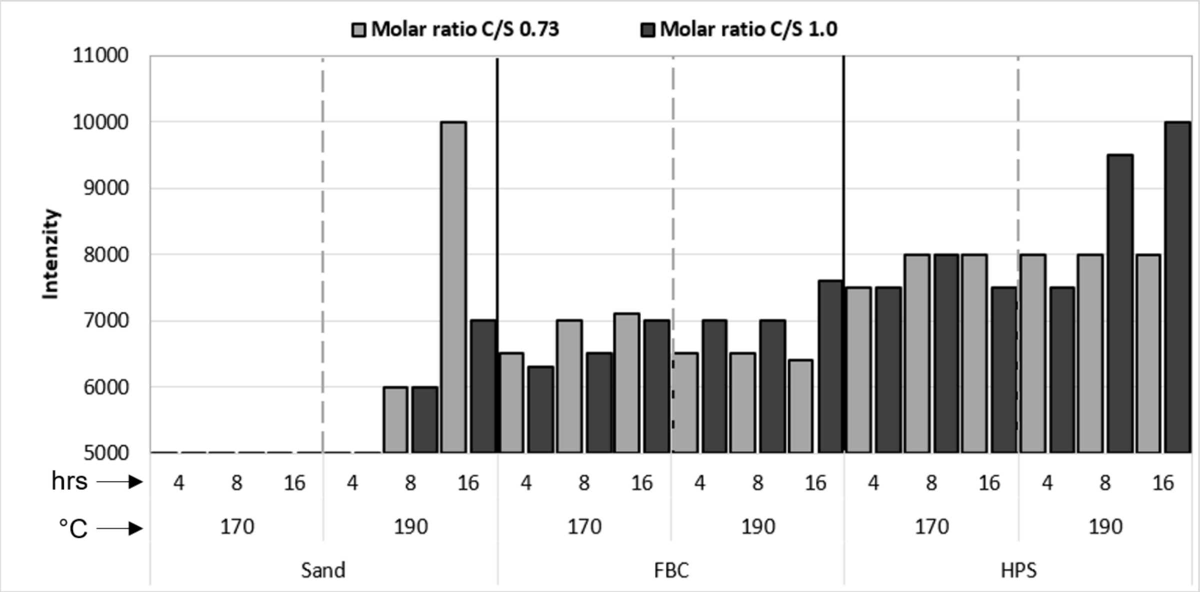

Figure 5: Intensity of tobermorite according to XRD

The tobermorite peak intensity in the sample with FBC ash was nearly constant at 170 °C and 190 °C and every autoclaving time. This is due to the high solubility and reactivity of amorphous silicon dioxide. In terms of microstructure, autoclaving at 170°C for 4 hours is sufficient for tobermorite formation in lime and FBC ash samples. It is important to remember that strength is still very low at this time and temperature. The samples also contained portlandite. It was present at the molar C/S ratio of 1.0. This caused a surplus of CaO in the sample. It was thus proved that FBC ash has a negative effect on compressive strength in large-amount substitutions[2]. In this case it was a 100% replacement and so a drop-in strength was to be expected.

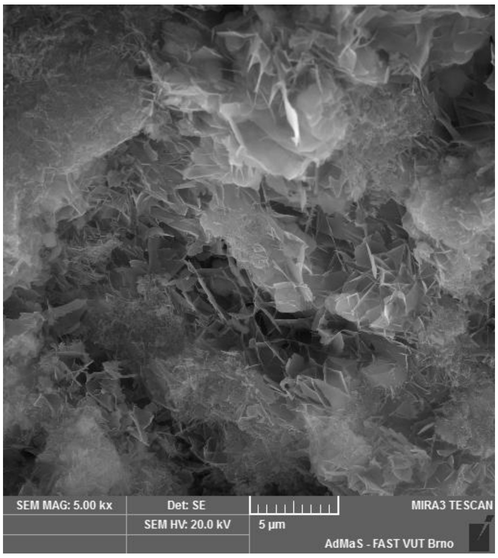

Figure 6: Image from SEM analysis - sample with FBC ash with a molar C/S ratio of 0.73 autoclaved at 190 °C for 8 hours.

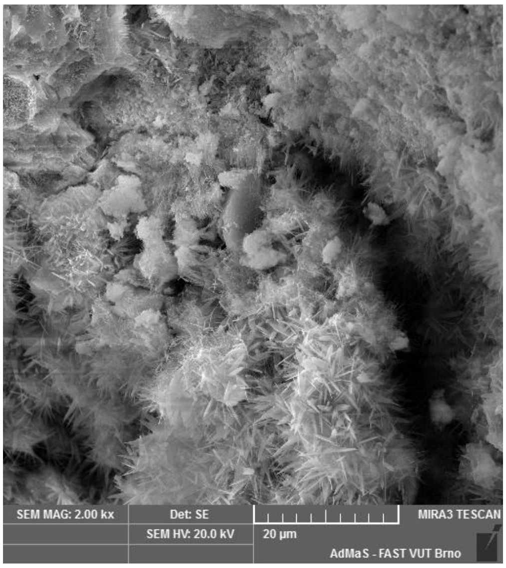

Figure 7: Image from SEM analysis - sample with HPS with a molar C/S ratio of 0.73 autoclaved at 190° C for 8 hours.

The SEM images (Figure 6) show that tobermorite content is not very high. It occurs locally and has a plate-like habit. This could be the cause of the low compressive strength[5].

The differences in tobermorite peak intensity in samples made with slag are greater, especially when autoclaved at 190°C. The longer autoclaving time caused greater tobermorite crystallisation. This fact is in accordance with the values of compressive strength, which in samples with slag were similar to those of the reference samples. The slag contained 12 % more SiO_2 than the FBC ash. This is the reason why tobermorite could form at a greater magnitude. The SEM images (Figure 7) show that tobermorite covered most of the surface of the aggregate. Furthermore, it had a lath-like habit, which provided a better bond between the particles and by extension higher compressive strength.

Conclusion

This investigation brought interesting findings. It compared the basic influence of FBC ash and slag on the properties and microstructure of calcium-silicate composites. It was a basic comparison of an alternative source of a silicate raw material for autoclaved aerated concrete manufacturing. The influence of the molar C/S ratio was also observed.

- It was found that the higher molar C/S ratio of 1.0 is unsuitable. It delivers lower compressive strength.
- FBC ash reduces compressive strength in samples with a 100% replacement for sand. Plate-like tobermorite was identified. No influence of the autoclaving temperature and time was found.
- The replacement of sand with slag increased compressive strength and was conducive to tobermorite formation with increasing autoclaving temperature and time.

The results show that slag is a more promising raw material for calcium-silicate composite manufacturing. This basic investigation will be expanded by research into the influence of slag in different replacement percentages or particle sizes.

Acknowledgements

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Vliv druhotných surovin na tvorbu tobermoritu vápenosilikátového kompozitu

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Souhrn

Fyzikálně mechanické vlastnosti vápenosilikátových kompozitů jsou dány jejich mikrostrukturou. Mikrostruktura těchto kompozitů, zejména pak autoklávovaného pórobetonu, je závislá na tvorbě a morfologii vzniklých kalcium hydrosilikátových fází. Hlavním zástupcem těchto fází je pak tobermorit. A právě tvorbou tobermoritu se zabývá tento článek. V článku jsou zkoumány dvě druhotné suroviny, které byly vybrány jako zástupce dvou hlavních skupin druhotných surovin. Jedná se o fluidní popílky a o škváry z termálních procesů. Studie využitelnosti potenciálu druhotných surovin se v dnešní době stává skoro nutností, a to z hlediska ekologického tak ekonomického. Vybrané suroviny byly míchány pouze s vápnem. Takto byly zajištěny podmínky pro studii bez vlivu dalších příměsí. Poměr suroviny byl volen s molárním poměrem oxidu vápenatého ku oxidu křemičitém 0,73 a 1,0. Vzorky byly dále autoklávovány, a to při dvou teplotách (170 a 190 °C) a třech různých délkách hydrotermální výdrže (4, 8 a 16 hodin). Dle získaných údajů se škvára jeví jako perspektivnější materiál.

Klíčová slova: *Tobermorit, vápeno-silikátový kompozit, fluidní popílek, škvára*

The Influence of Secondary Raw Materials on the Microstructure and Physical-Mechanical Properties of Autoclaved Aerated Concrete

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Abstract

Using secondary raw materials is both eco-friendly and cost-effective. Great amounts of secondary raw materials are produced in the power industry by solid fuel combustion. There are two types of ashes, high temperature fly ash and fluidised bed combustion ash in this industry. As opposed to high temperature fly ash, the fluidised bed combustion ash generated by the more energy-efficient and modern combustion is still little used. High-temperature incineration also produces a slag beside fly ash, which has potential for use in aerated concrete. For this reason, research is focused on fluidised bed combustion fly ash, fluidised bed combustion bottom ash and slag. The aerated concrete composite was developed using a laboratory autoclave operating at 190 °C over a 7-hour holding time. The secondary raw materials amounted to 10 %, 30 %, and 50 % of the aerated concrete. While fresh, the mixtures were tested for rheologic properties by the flow table test. The results showed a dependence of rheological properties on the content of fluidised bed combustion fly and bottom ash. The research showed that a 10% content of secondary raw materials is to no detriment to physical properties. The influence of secondary raw materials on the microstructure was examined by X-ray diffraction analysis and compared to the peak intensity of the tobermorite which is the carrier of the autoclaved aerated concrete. The intensity peak of the sample with 10% admixture of fluidised bed combustion fly and bottom ash comparable to the reference sample and corresponded to the results of the physical properties.

Keywords: *Autoclaved aerated concrete, fluidised bed combustion fly ash, fluidised bed combustion bottom ash, slag, rheology*

Introduction

The market dominance of large companies is a source of pressure to manufacture the best possible aerated concrete at the lowest possible cost. Current trends prefer the replacement of a part of primary raw materials with by-products without making any substantial changes to the manufacturing process. Reducing the autoclaving time is generally a good step, since autoclaving is a costly process.

Fly ash is the finest coal combustion residue that is caught in separators. Their particles range within 0.001 – 1 mm.[1] Fly ash is a heterogeneous mixture of particles of varying shape, size, and chemical composition. [3, 4] Aside from fly ash, traditional high-temperature combustion also produces slag. Slag is of a coarser fraction and current studies show that a partial replacement of silica sand by slag results in a pozzolanic reaction, producing tobermorite.[2, 5]

Fluidised bed combustors burn crushed fuel suspended in an upstream of hot air and combustion gases in a way that causes the fuel particles to burn away slowly. The ash thus produced is lifted to a certain height where the combustor opens to a greater width and causes the gas velocity to drop down to the suspension velocity. The particles remain suspended in this position. Solid combustion residue must be prevented from fusing, which means that maximum temperatures must not exceed the temperature of ash softening. Combustion takes place at 850 °C. Fluidised bed combustion produces ash that can be divided by particle size into fly ash and bottom ash. **Fluidised bed combustors ash (FBC ash)** does not suffer from particle elongation, it remains porous, has a layered structure, and a large specific surface area. FBC ash contains a high amount of SO_3, mainly in the form of anhydrite. Its properties are similar to gypsum, which is why no addition of it should be required for the manufacturing of aerated concrete if FBC ash is present. Calcium oxide contained in the ash is both the reactive CaO and non-reactive $CaSO_4$ as far as the hydrothermal reaction is concerned. They also contain a reactive mineral phase, which may give FBC ash its pozzolanic properties.[2, 6, 7, 8]

Experiment

Raw materials

The primary raw materials were lime, cement, and sand. The samples were made with cement I 52.5 N. It is a Portland cement with a clinker content of 95 – 100 % and 0 – 5 % of other components. The lime is described by ČSN EN 459-1 as *"Construction lime"* CL 90-Q (R5, P1). The silica sand had a higher alkali content, but enough silicon dioxide (92.91 wt. %). FBC ash is produced in heating plants and has a high content of aluminium oxide, iron oxide, and calcium oxide.

The experiment used fluidised bed combustion fly ash (FBCFA), fluidised bed combustion bottom ash (FBCBA), and slag as raw materials. FBCBA and slag had the fraction of 0-8 mm. This is why they were milled in a ball mill to a specific surface area of approx. 300 m^2/kg. This value was determined on the basis of the particle size of the sand. The raw materials were tested for chemical composition (Table I), specific density, and water absorption (Table II).

Table I: Chemical composition of the secondary raw materials

Raw materials	**Chemical composition [%]**				
	SiO_2	**CaO**	**Na_2O**	**Al_2O_3**	**SO_3**
FBCFA	38.05	17.76	0.3	24.67	5.44
FBCBA	38.40	12.99	0.39	24.60	5.40
Slag	51.00	4.37	-	22.44	1.11

Table II: Physical properties of the secondary raw materials

Raw materials	**Specific density**	**Specific surface area**	**Water absorption**
	[kg/m^3]	**[m^2/kg]**	**[%]**
FBCFA	2740	390	192.9
FBCBA	2510	250	130
Slag	2610	298	35.3

Mixture formula and AAC sample preparation

The reference mixture was adopted from an existing AAC manufacturing technology. This mixture was then mixed with 10 %, 30 %, and 50 % of a secondary raw material. The amount of water was adjusted to maintain a flow value of 25 cm. This flow value was used for samples on which the compressive strength, bulk density and microstructure were determined. The results of the flow value of the sample mixture are shown separately in the section „rheology".

A plasticiser was added to a pre-heated silica-sulphate slurry, at 40 ± 1 °C, and mixed for 5 seconds. Pre-homogenised lime, cement, and the secondary raw materials were then added and left to mix for 45 seconds. After that, the walls of the mixer were cleaned and an aluminium suspension was added. The mixture was mixed for 60 seconds; the entire mixing process did not take longer than 120 seconds. The fresh mixture was poured in moulds and left to harden in a dryer at 40 °C for 24 hours. After that the samples were extracted from the moulds.

Table III: Reference mixture

Raw materials	Reference	Unit
Lime	40	[kg/m^3]
Cement	60	
Sand	371	
Gypsum	13	
Aluminium powder	0.450	
Plasticiser	0.396	

Autoclaving took place in a laboratory autoclave at 190 °C and a 7-hour holding time. The dissolution temperature of silica sand at hydrothermal conditions is 180 °C. To ensure the correct hydrothermal conditions at the centre of the samples, the holding temperature was set to 190 °C. Tobermorite formation and hardening of the material is determined not only by the autoclaving temperature but also by time. The time of 7 hours was based on a real industrial manufacturing technology. Figure I shows the entire autoclaving process.

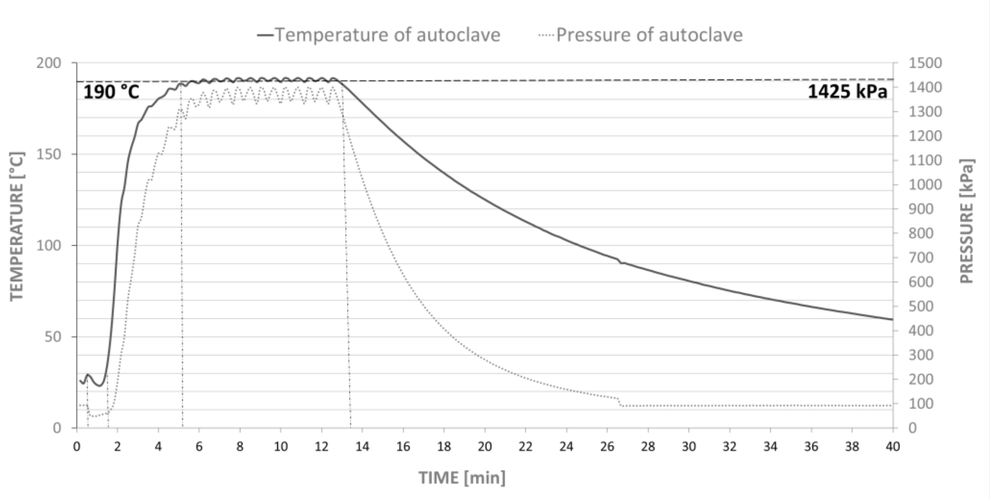

Figure I: Autoclaving at a 7-hour holding time

Results and discussion

Rheology

FBCFA has the highest water consumption, which is caused by its high-water absorption and a high CaO content.

The results indicate that the addition of FBCFA and FBCBA has a similar effect on consistency. This is due to their similar water absorption, the value of which exceeds 100%. As could be expected, a greater amount of ash mixed with the same amount of water caused the flow value to decrease. A higher content of ash results in a descending dependence of the flow value on the water-solid ratio.

The addition of slag did not appear to affect the mixture’s rheology. A higher content of this material caused no change in water consumption. This is due to the fact that the surface of slag particles is sealed, making them much less absorbent.

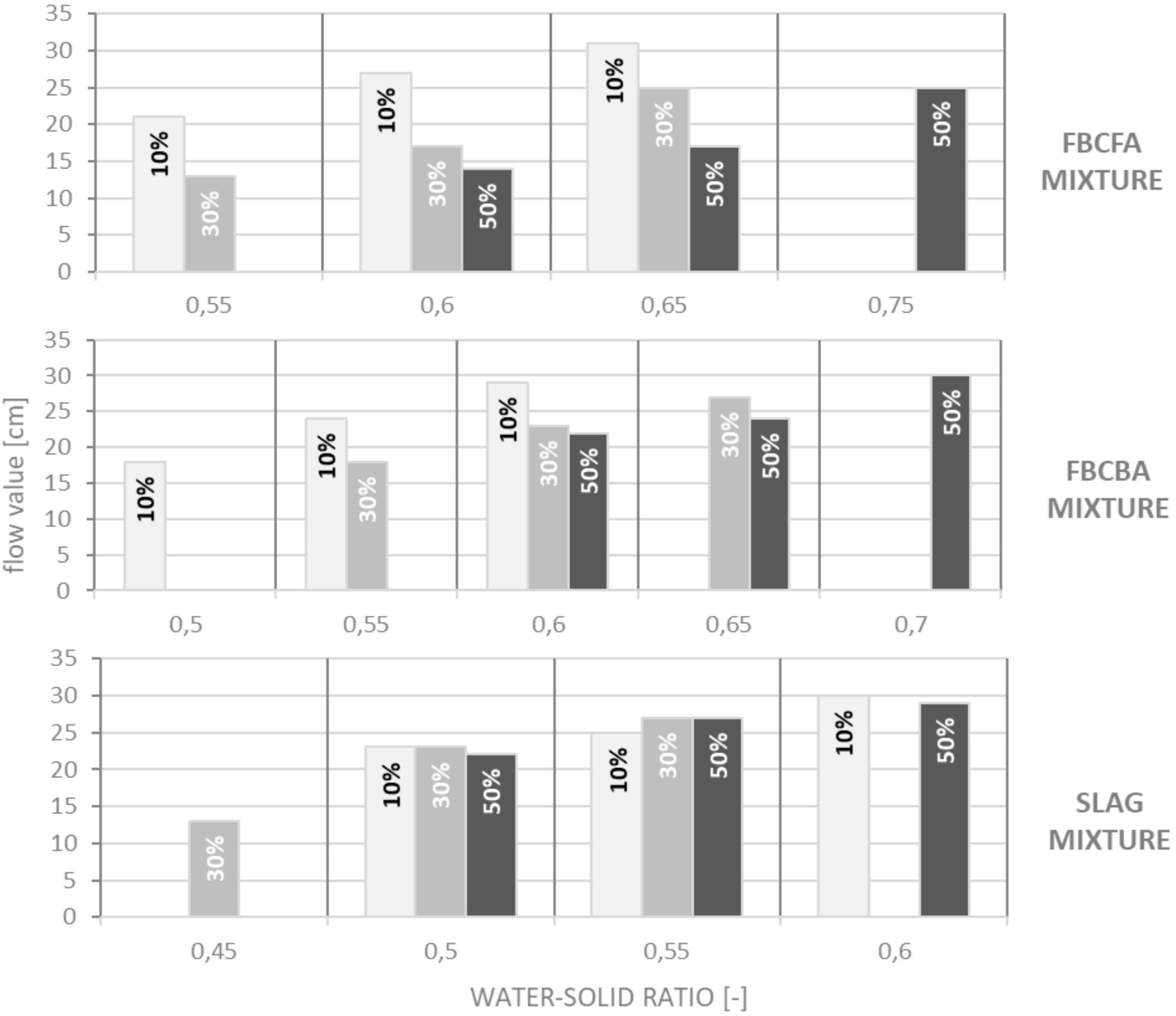

Figure II: The dependence of the flow value on water-solid ratio in mixtures with a 10%, 30%, and 50% addition of FBCFA, FBCBA, and slag.

The results indicate that the flow value does not depend on water content alone, but also on the specific surface area, water absorption, and chemical composition. At a higher content of CaO, water is consumed during hydration, which also raises the mixture's temperature and affects the flow value.

To flow value of 25 cm, it is necessary to use different water contents. Used water-solid ratios are displayed in Table IV.

Table IV: Water-solid ratio of mixtures with a 10%, 30%, and 50% addition of FBCFA, FBCBA, and slag

Mixture		Water-solid ratio [-]
FBCFA	10 %	0.57
	30 %	0.65
	50 %	0.75
FBCBA	10 %	0.55
	30 %	0.62
	50 %	0.65
Slag	10 %	0.55
	30 %	0.52
	50 %	0.52

Compressive strength

Figure III shows a chart of compressive strength and constructiveness coefficient for samples with a 10%, 30%, and 50% addition of secondary raw materials. In the figure III, you can see error bars that indicate a compression strength measurement relative error. The relative error of the coefficient of constructiveness is displayed numerically in the graph. Compressive strength and bulk density were tested according to ČSN 73 1350 Testing of autoclaved aerated concrete. The constructiveness coefficient represents a ratio between compressive strength *(f_c)* and bulk density (*BD*). It is identified as K_k and is calculated as follows:

$$K_k = \frac{\overline{f_c}}{BD} \cdot 100$$

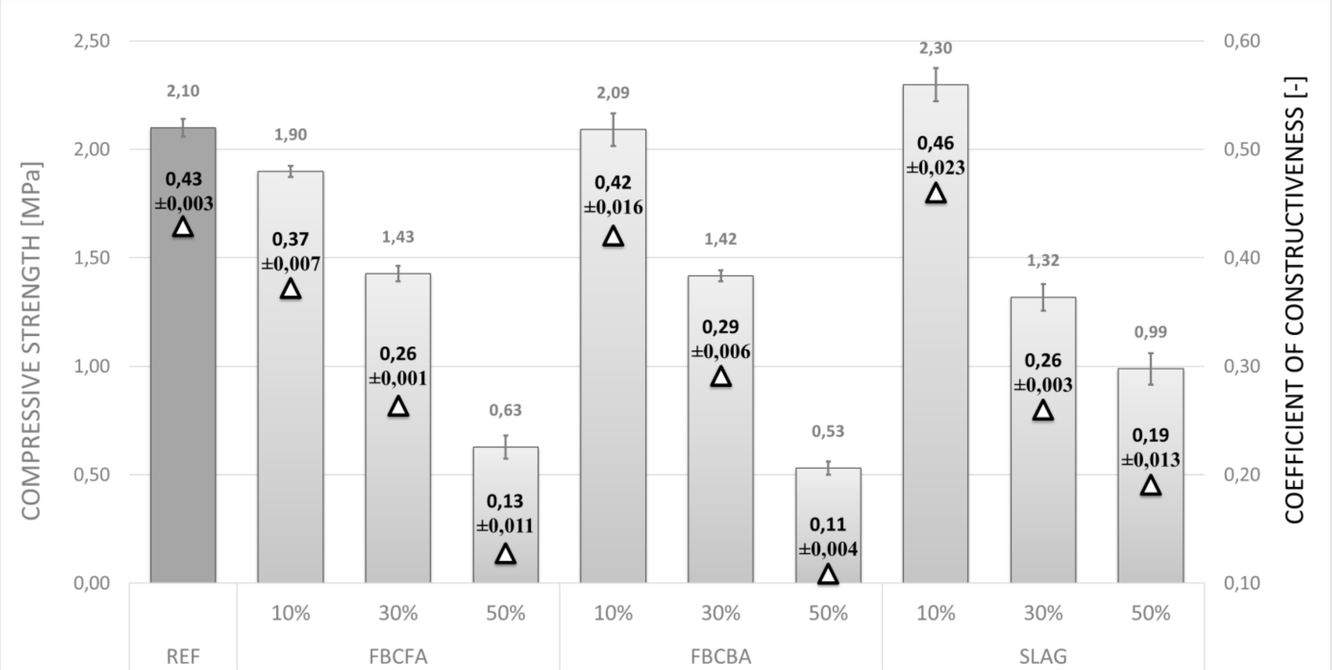

Figure III: Compressive strength (column) and constructiveness coefficient (triangle) of samples with a 10%, 30%, and 50% addition of FBCFA, FBCBA, and slag

In samples with 10% of FBCFA the constructiveness coefficient and compressive strength were 13% and 10% lower respectively when compared to the reference. The coefficient decreased as the content of secondary raw materials increased. A 30% addition reduces strength by 32 %, and with a 50% addition strength drops by up to 70 %.

After autoclaving for 7 hours the samples with a 10% addition reached similar values of strength and the constructiveness coefficient as the reference. The coefficient is 2% lower and compressive strength is only 0.1 MPa lower in samples with a 10% addition of FBCBA. In the case of a 30% content of FBCBA the strength drops by 32 %. The sample with 50 % of FBCBA had compressive strength 75 % lower.

A 10% addition of FBCBA results in the same strength as the reference while in samples with 10 % FBCFA it dropped only by 10 %. At a higher content it is more difficult for tobermorite to form, most likely because of the reactivity of silicon dioxide, which does not have enough calcium hydroxide for the reaction. The poorer tobermorite crystallisation in these samples then brings about a decrease in strength, in some by up to 75 % when compared to the reference.

The sample with a 10% addition of slag exceeded the strength of the reference by 9%. However, at higher contents strength begins to markedly decrease again. At a 30% addition strength is 37 % lower than in the reference, and 53 % at 50 %. The sample containing slag had better strength thanks to a higher content of silicon dioxide. Unlike fly ash, slag forms at temperatures above 1000 °C, producing sintered, less reactive particles. The lower reactivity caused strength to improve due to a better ratio of silicon dioxide to calcium hydroxide.

Microstructure

The samples' microstructure was examined by x-ray diffraction analysis using the device Empyrean Panalitical (Cu-cathode λ=1.540598 for Kα 1). X-ray diffraction analysis was measured on cores of samples that were milling to a size less than 20 µm with the addition of isopropanol in an XRD McCorne mill and then dried. Angular reproducibility is <0,0002° and 2theta linearity over whole range is enqual or better than ± 0,01°. Additionally, the reference sample was analysed by scanning electron microscope TESCAN MIRA3 XMU. Representative fragments of dried samples of approximately 5 × 5 × 5 mm were selected for scanning electron microscopy. A thin layer of gold 300 – 400 Å was applied to the samples using the Quorum Q150r. Figure IV and figure V shows the results.

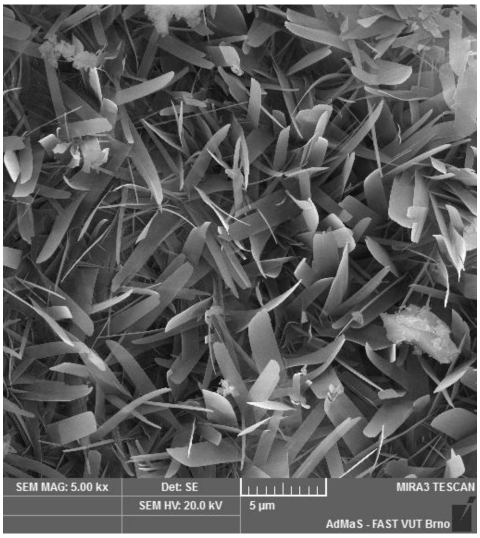

Figure IV: SEM image of the reference sample

The reference sample contains plate-like tobermorite crystals. Between them there is non-crystalline calcium hydrogen silicate gel.

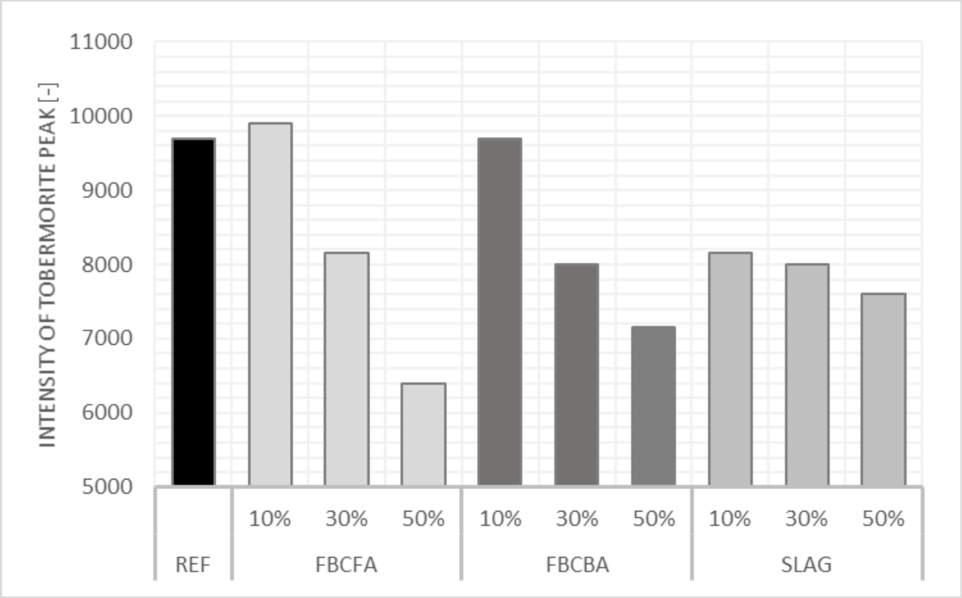

Figure V: Tobermorite peak intensity of samples measured by X-ray diffraction analysis

The samples were observed for tobermorite peak intensity. Crystals formed at high intensity have better structure. The sample with a 10% addition of FBCFA reached a more intense peak than the reference. At higher FBCFA amounts the intensity begins to decrease.

The sample with 10% of FBCBA likewise exhibited a more intense tobermorite peak than the reference. Much like FBCFA, samples with a higher FBCBA content suffer a dramatic decrease in tobermorite peak intensity.

The addition of fly and bed ash is viable only up to 10%. This content is conducive to tobermorite formation. FBCFA and FBCBA consist of porous alumino-silicate particles, which are amorphous. This is why these ashes react well with $Ca(OH)_2$ at hydrothermal conditions and produces tobermorite. These ashes also contain a greater amount of aluminium oxide, which is favourable to tobermorite formation.

The sample with the addition of slag reached a lower tobermorite peak intensity than the reference. Unlike the materials containing fly ash, however, the tobermorite peak intensity decreases by a negligible degree. As said above, slag is not as reactive, which is why a higher content causes neither a substantial decrease, nor increase.

Conclusion

The investigation has proved that the use of fluidised bed combustion ash and slag can be used for the above-described purpose. The highest compressive strength was measured in the sample with a 10% addition of slag. Samples with 10% of fly and bed ash reached similar strength as the reference. Tobermorite crystallisation with a 10% content of the two ashes is comparable to the reference sample.

It can thus be said that the following replacements by secondary raw materials can be made without a detriment to the properties of the aerated concrete:

- 10% addition of FBCFA
- 10% addition of FBCBA
- 10% addition of slag.

Further research will focus on testing other secondary raw materials and their combinations so as to achieve the greatest possible substitution of primary raw materials. Another goal will be to observe the influence of rheology on the macrostructure of the samples.

Acknowledgements

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Vliv druhotných surovin na mikrostrukturu a fyzikálně mechanické vlastnosti autoklávovaného pórobetonu

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Souhrn

Využívání druhotných surovin má pozitivní vliv z hlediska ekologických i ekonomických aspektů. Vysoká produkce druhotných surovin vzniká v energetickém průmyslu při spalování tuhých látek. V tomto odvětví vznikají dva druhy popílků, vysokoteplotní a fluidní. Fluidní popílky vzniklé při energeticky výhodnějším a modernějším fluidním spalováním jsou na rozdíl od vysokoteplotních popílků stále málo využívané. Při vysokoteplotním spalování vzniká vedle úletového popílku také škvára, která má potenciál pro využití v pórobetonu. Z tohoto důvodu je výzkum zaměřen na fluidní popílky a škváry.

Pórobeton s příměsí druhotných surovin byl vyvíjen v hydrotermálních podmínkách laboratorního autoklávu při 7hodinové izotermní výdrži na 190 °C. Druhotné suroviny jsou využity jako 10%, 30% a 50% příměs v pískovém pórobetonu. Na čerstvé surovinové směsi byly stanoveny reologické vlastnosti pomocí zkoušky rozlitím. Výsledky ukázaly závislost reologických vlastností na množství příměsi fluidního úletového a ložového popele, škváry. Výzkum ukázal, že využití 10% příměsi druhotných surovin neovlivní fyzikální vlastnosti vzorků. Vliv druhotných surovin na mikrostrukturu byl zkoušen pomocí rentgenové difrakční analýzy a byly porovnány intenzity píku tobermoritu, který je nositelem pevností pórobetonu. Intenzity u vzorku s 10 % příměsi úletového a ložového popele byly srovnatelné s referenčním vzorkem a korespondují tak s výsledky fyzikálních vlastností.

Klíčová slova: *Pórobeton, fluidní úletový popílek, fluidní ložový popel, škvára, reologie*

Stability of blast furnace slag in the demineralized water

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Summary

Blast furnace slag represents waste product from the metallurgy which is commonly utilized in the construction industry as well as it is studied in the form of fine particles as potential material for removal of heavy metals ions from solutions. Milled blast furnace slag causes significant increase of the pH value of the suspension in the contact with demineralized water as well as soluble silicates (mainly due to hydrolysis), Ca(II) and Mg(II) ions are released to the solution. The reaction of CaO present in the material takes place in the early stages of contact with water, mainly Ca(II) ions are released to the solution. Hydrolysis and silicates release take place mainly after 24 hours of contact time. Equilibrium is reached after 7 days of contact. The ratio slag mass:water volume has negligible influence on the final pH value of the solution after contact but the amounts of released components (soluble SiO_2*, Ca(II) and Mg(II)) increase with increasing amount of water towards the constant mass of slag. Particle size has significant influence on the interaction of slag with demineralized water. The change of pH value as well as amount of released species increase with decreasing particle size. Only slight interaction between slag and water occurs for particles >0.5 mm, thus it can be stated that the material is relatively stable. Milling of slag to the form of fine particles (<0.5 mm) leads to the strong interaction with water, significant changes of solution pH values and release of the high amount of soluble* SiO_2 *and Ca(II) ions were observed. Temperature has significant influence on the interaction of slag with water as well. Temperature influences mainly the hydrolysis of silicates. The released amounts of soluble* SiO_2 *and Ca(II) ions increase significantly with increasing temperature kept during contact. Interactions of phases containing Mg(II) are not influenced by temperature. Finely milled blast furnace slag can be stabilized by addition of* Al_2O_3 *and subsequent thermal treatment at least at 900 °C. The hydrolysis of silicates is primarily supressed by treatment but the Ca(II) is bound stronger in the structure after the treatment as well.*

***Keywords**: blast furnace slag, stability, leaching, stabilization, demineralized water*

Introduction

Utilization of waste material plays important role in the research of environmental protection nowadays.[1,2,3] Slags represent industrial waste material which originates in the metallurgical industry as well as in the waste incinerator facilities[4,5]. Metallurgical slags can be divided to ferrous and non-ferrous metals production slags.[1,4,6,7] Slags formed in the pig iron (blast furnace slag) and steel (steelmaking slag) production play the most important role in the industrial as well as research utilization.[5,7,8,9]

Blast furnace slags represent material based mainly on the silicate minerals and containing higher amount of Ca(II) and Mg(II) in the structure. Exact elemental and mineralogical composition depends on the batch of the blast furnace and on the type of further processing (e.g. process of cooling). Slowly cooled blast furnace slags are crystalline but slags quickly cooled in the water stream (granulated) are more amorphous.[4,7,10] Blast furnace slags are subject to hydrolysis processes which depend on their structure (crystalline phases). Hydrolysis process leads to increase on solution pH value and it could strongly influence the utilization of slag.[2,7]

Slags are the most often used in the construction industry as backfilling material or as replacement of Portland cement in the concretes. They are often alkali-activated for the utilization as binder in concretes.[2,8] Present research deals with utilization of various slags as potential sorption materials for waste water purification as well.[10,11,12] Slags can be used for adsorption of heavy metals ions[10,11,12], phosphates[13,14], ammonia[15] or organic dyes[16]. All types of blast furnace slags' utilization are strongly affected by the hydrolysis of structure.[7] It is beneficial in the case of alkali-activation which leads to the formation of the Calcium-silicate-hydrate gel with improved binding properties due to hydrolysis of material.[2,8] Hydrolysis can cause problems by the backfilling utilization due to release of various compounds to the solution and changes in the properties of slag and it strongly affects the mechanism of adsorption on the slags.[7] Slags can be partially stabilized by alkali-activation and formation of concrete or by thermal treatment.[2,8]

Presented work deals with interactions of blast furnace slag in the aqueous environment and with stabilization of the slag structure. The leaching of blast furnace slag by demineralized water was realized to describe the pH value changes and release of selected elements/ions (Si, Ca, Mg) in the dependence of time, slag dose, slag's particle size and temperature during contact. Further the treatment of slag by the Al_2O_3 and high temperatures with aim to stabilize the slag's structure was performed.

Experimental part

Blast furnace slag utilized in all experiments was kindly provided by ArcelorMittal Ostrava a.s. (Czech Republic) Slag was milled in the laboratory mill IKA M20 (IKA – Werke GmbH & Co. KG, Staufen, Germany) and sieved through 0.8 mm sieve prior the experiments. Slag was characterized by X-ray fluorescence (XRF) and X-Ray powder diffraction (XRD) analyses. Both analyses were supplied by Nanotechnology centre, VŠB-Technical university of Ostrava. The influences of contact time, ratio slag mass:water volume, slag's particle size and temperature during contact were investigated. Times 4, 24, 48 hours, 5, 7 and 14 days were selected for contact time experiment. 0.5 g of slag was weighted to the Erlenmeyer flask and 100 mL of demineralized water was added (ratio slag:water 1:200). Suspensions were occasionally stirred. The suspensions were filtered after the given contact time. The selected ratios for slag:water experiment were 1:50, 1:100, 1:200 and 1:400 (mass of slag:volume of demineralized water). Contact time was set to 24 hours. After that suspensions were filtered. The slag's particle size effect on the stability of studied material was studied for size ranges <0.05 mm, 0.05 - 0.5 mm, 0.5 – 5 mm, 5 – 10 mm. Ratio slag:water was 1:200. Suspensions were occasionally stirred and they were filtered after 24 hours.

All previous experiments were carried out at laboratory temperature. The effect of temperature was studied for temperatures 4, 26, and 80 °C. The ratio slag:water was selected 1:200 and contact time was 24 hours. Suspensions were occasionally stirred as in the previous experiments and they were filtered after 24 hours. Filtration of all samples was carried out by vacuum filtration with membrane filters Pragopor 6 (pore size 0.4 µm, Pragochema Ldt., Prague, Czech Republic). The pH values of all filtrates were measured at the WTW InoLab 720 pH meter equipped by WTW SenTix 41 electrode (WTW, Weilhiem, Germany). Content of dissolved SiO_2 in all leachates was determined by the UV-VIS spectrometry (Varian Cary 50, Varian, USA) after reaction with ammonium molybdate on the wavelength 430 nm. Contents of Ca, Mg and Fe in the solutions after contact with slag were determined by atomic absorption spectrometry (Varian AA240FS, Varian, USA). The wavelengths were 422.7 nm for Ca determination,202.6 nm for Mg determination and 372.0 nm for Fe determination. For atomization was utilized air-acetylene flame. The highest limit of quantification (LOQ) of the utilized methods was 0.05 mg/L. Raw blast furnace slag was modified by addition of Al_2O_3 (5 – 25 % w/w, supplied by Lachema Brno, Czech Republic) and subsequent thermal treatment at 800, 900 and 1000 °C in the laboratory furnace (LAC, Rajhrad, Czech Republic) for 2 hours. Prepared samples were then leached by demineralized water (ratio 1:200, contact time 24 hours). The pH value of the filtrates and content of released SiO_2, Ca, Fe and Mg were determined by the above mentioned methods. All experiments were realized in two parallel assessments.

Results and discussion

Results of XRF analysis of the used blast furnace slag confirm the silicate-based character. Content of SiO_2 was the slag is 38.2 % (w/w). Al_2O_3, CaO and MgO form other major components of the used slag with contents 7.2 % (w/w), 37.3 % (w/w) and 12.7 % (w/w) respectively. Contents of other elements were below 1 % (w/w) so the properties of slag are mainly influenced by Si, Al, Ca and Mg. XRD analysis shows that slag is composed by gehlenite, akermanite, merwinite, forsterite, calcite and calcium oxide. The XRD analysis confirms that slag is composed mainly by silicate-based minerals. Mineralogical composition could influence the stability of material in the aquatic environment as calcium oxide exhibit high reactivity in water and silicates can be subject to hydrolysis processes.

Time dependence of pH value change of the solution after contact with slag is depicted on the Figure 1. The initial pH value of the demineralized water was 6.14. Fast increase of the pH value to the value 9 can be seen after 4 hours of contact. The maximum pH value 10 was reached after 7 days of contact of slag and demineralized water. Very slight decrease was registered after 14 days of contact. It can be stated that major processes causing the changes of solution parameters are fast. After the initial phase of reaction the equilibrium is reached after 7 days.

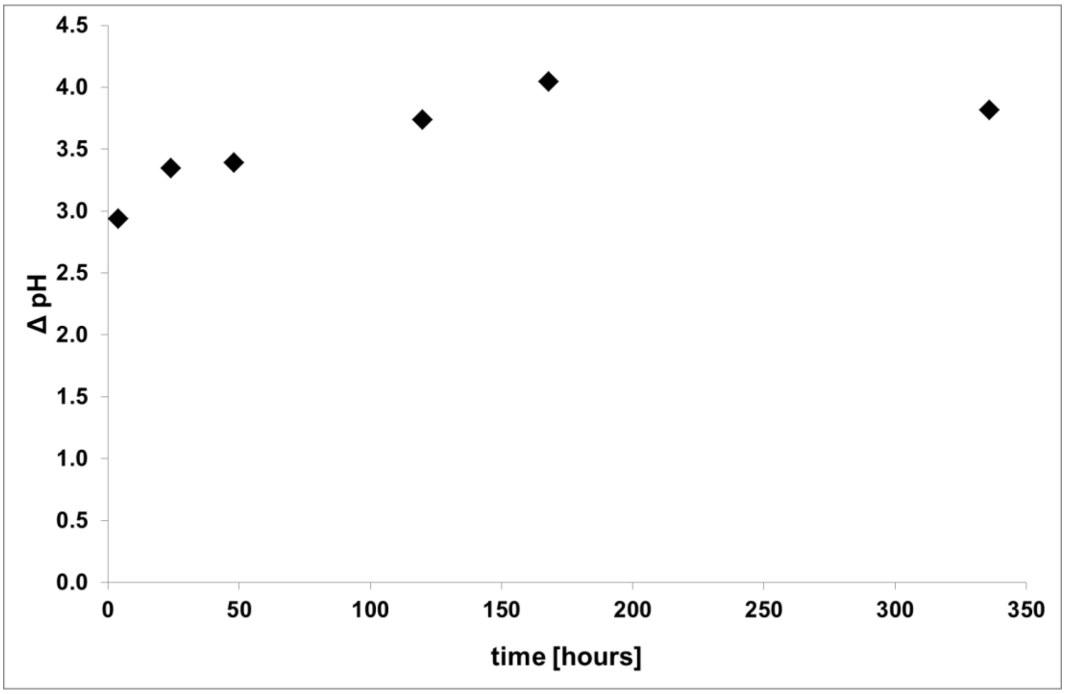


Figure 1: Dependence of pH value change on the contact time of slag with demineralized water

During the reaction of slag with demineralized water various compounds are released to the solution. Amounts of soluble silicates expressed as SiO_2, Ca, Mg and Fe ions were observed. The concentrations of Fe in all solutions from all experiments were under the limit of quantification of the utilized method (0.05 mg/L) and therefore the data for Fe are not shown in the figures. Very low concentrations of Fe in the leachates are probably caused by low amount of Fe in the initial slag (0.4 % w/w according to XRF analysis). Data for time dependence of released compounds' amounts (SiO_2, Ca(II) and Mg(II)) are shown on the Figure 2. The amount of leached magnesium was practically constant during the examined time period. The value oscillated between 0.5 and 0.8 mg/g. Obtained values of leached Mg were much lower compared to SiO_2 and Ca(II). Magnesium is probably bound in more stable minerals in the comparison to Ca(II). Contents of leached SiO_2 and Ca(II) correspond to the data obtained for changes of solutions' pH value. The increase of content of both substances during the 7 days is evident from the Figure 2. The content of leached Ca(II) after 4 hours is higher than after 24 and 48 hours. In the initial stage of interaction the calcium oxide probably react with water, which leads to the fast increase of pH value and Ca(II) ions are released to the solution due to partial dissolution of CaO. Then Ca(II) ions can react with other components of solution or with slag, which leads to the slight decrease of Ca(II) content in the solution. Small amount (around 1.1 mg/g) of SiO_2 is released during the first 24 hours. Soluble silicates (SiO_2) are probably released due to hydrolysis of silicate minerals contained in the slag. Silicon is probably released in the form of silicate anion and it can probably contribute to the pH value increase as the silicic acid belongs to the weak acids and can bind H(I) ions from the water molecules. The amounts of Ca(II) and soluble silicates (SiO_2) increase further in the time, which is probably caused by hydrolysis of silicate minerals containing both species. It can be stated that minerals containing magnesium are more stable compared to minerals containing Ca(II) in the blast furnace slag. Dissolution of CaO leads probably the interaction in the initial stage, then the hydrolysis of silicate minerals takes place. Predominant leaching of Si and Ca from the slags in the aquatic environment was reported by van Zomeren et al.[17]

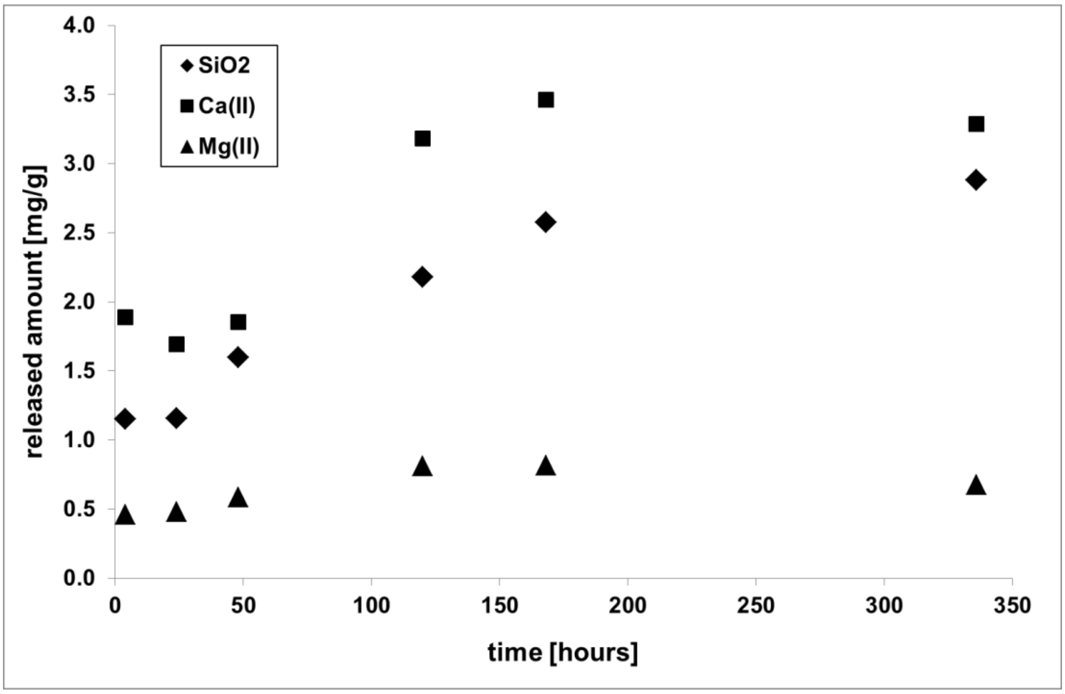


Figure 2: Dependence of released amounts of selected species on the contact time of slag with demineralized water.

The ratio slag mass:water volume has no significant effect on the changes of pH value of the solution after contact of slag with water in the contact time 24 hours (Figure 3). The pH value very slightly increases with the decreasing water volume added to 1 g of slag. The pH value of the solutions after filtration was from 9.5 to 10.

Despite the negligible differences in the change of the solutions' pH values, the amounts of released species vary at the studied ratios. Concentrations of the monitored substances in the solutions increase with decreasing amount of water added to slag but the released amounts related to the 1 gram of slag exhibit opposite trend. The released amounts of soluble silicates (SiO_2), Ca(II) and Mg(II) decrease with decreasing amount of added demineralized water. It could be stated that slag is more stable when exposed to lower volume of water. If constant mass of slag reacts in lower amount of water, the equilibrium of hydrolysis as well as the maximal solubility of some compounds contained in the slag (e.g. CaO) is probably reached earlier compared to higher amount of water. If the slag is exposed to high amount of water, its structure is probably more eroded, which could lead to changes of other properties as well.

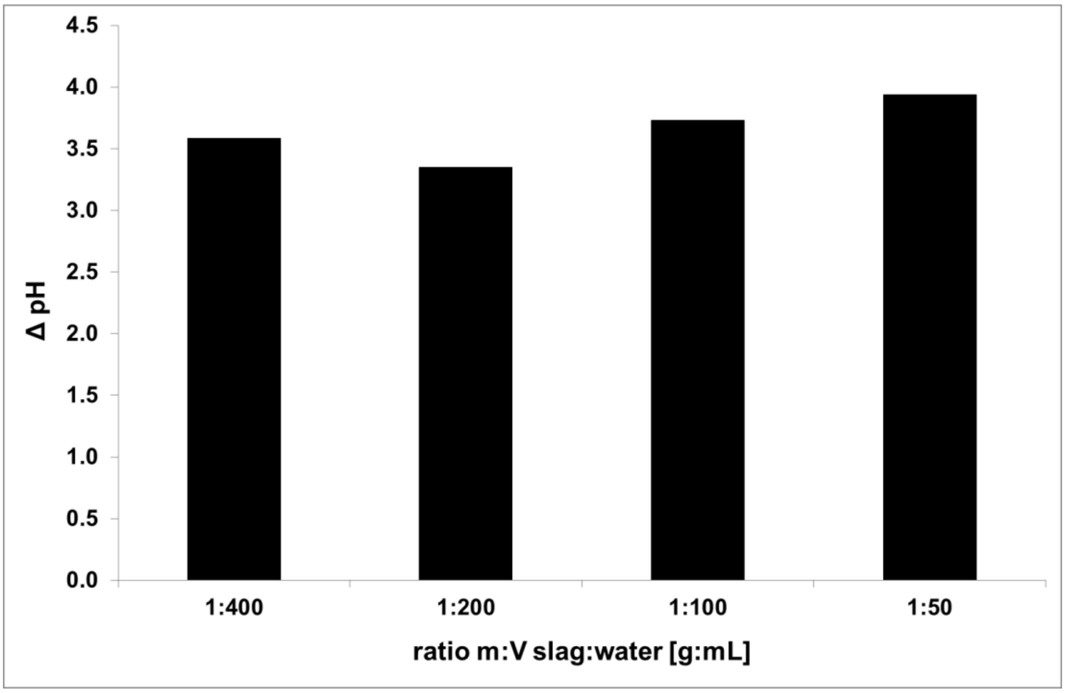


Figure 3: Changes of the pH value during contact of slag with demineralized water dependent on the slag:water ratio.

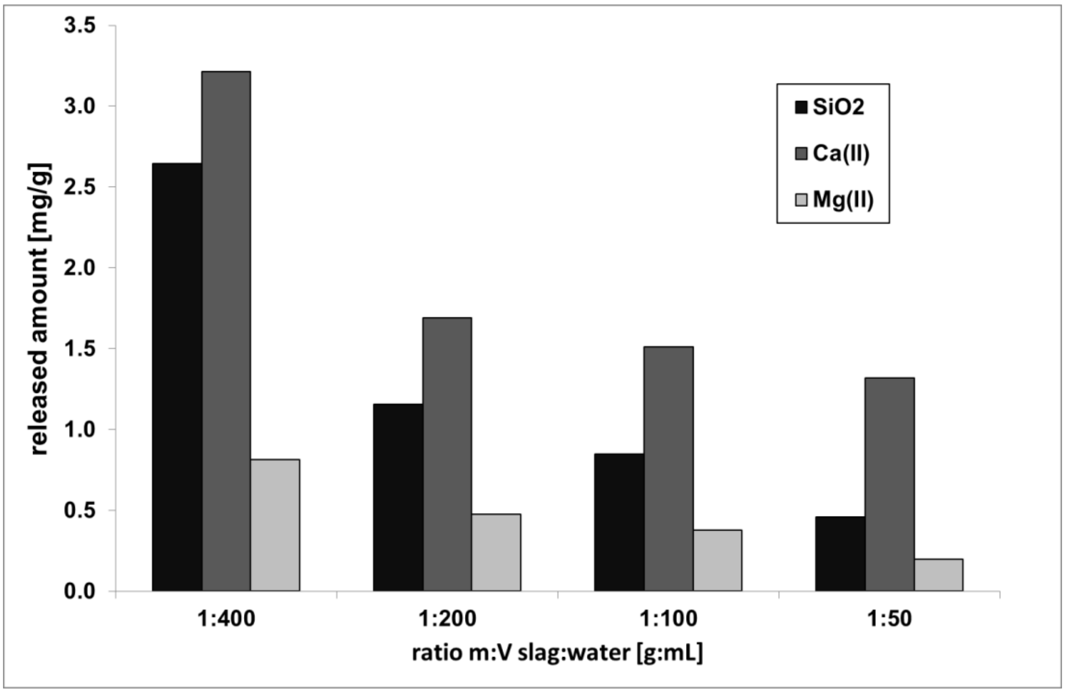


Figure 4: Released amounts of selected species during contact of slag with demineralized water dependent on the slag:water ratio.

Particle size of slag significantly influences the pH values of solutions after contact as well as the amounts of released species (Figure 5). The pH value changes increase with decreasing particles size. The increase about 0.7 pH units for slag with particles in the range 5 – 10 mm was observed in the comparison to 4.8 pH units for slag with particles < 0.05 mm. Only small changes were observed in the released amounts of Mg(II) for particular ranges of particle size. It is evident from the Figure 5 that only small amount of monitored species was released to the solution for big particles (5 – 10 mm) and Ca(II) forms the majority of released species. The released amounts of studied species significantly increase with decreasing particle size of slag for Ca(II) and SiO_2. Smaller particles exhibit higher surface area accessible to the interaction with demineralized water and thus reduction of the particle size of slag leads to the increase of amounts of released species which can cause bigger increase of the pH value of solution after contact with slag.

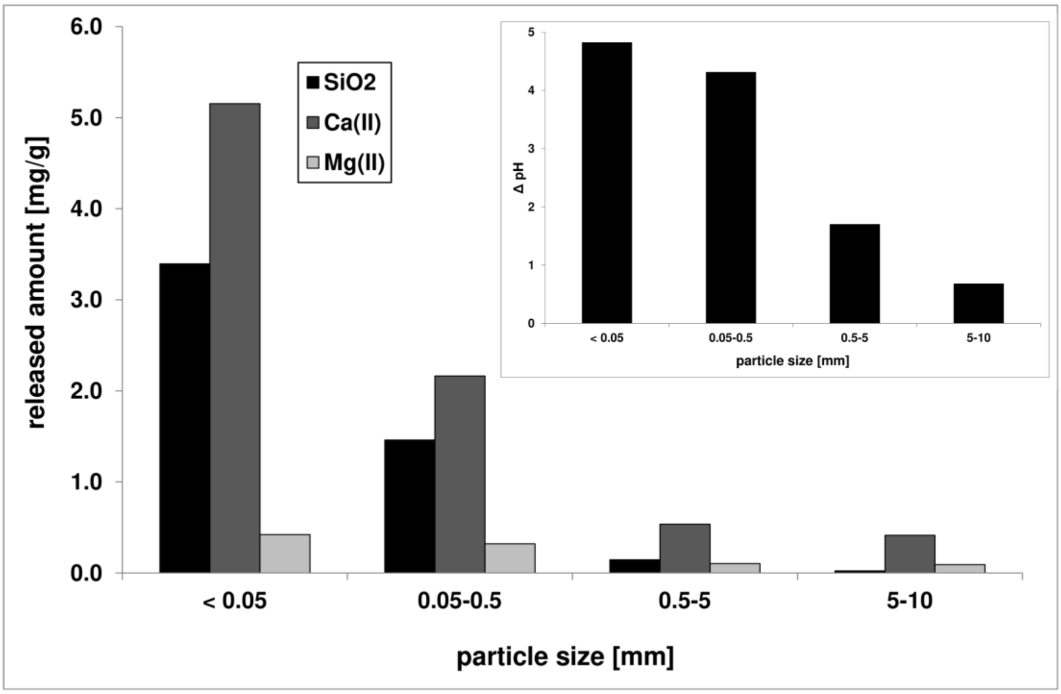


Figure 5: Released amounts of selected species and changes of pH values during contact of slag with demineralized water dependent on the particle size of slag.

The pH values of solutions after contact with slag vary only about ± 0.2 pH units in the case of various temperatures kept during contact. It can be stated that temperature has negligible effect on the pH value change. The released amounts of monitored species in the dependence on temperature kept during contact are depicted on the Figure 6. Increasing temperature leads to the increase of amounts of released species except of Mg(II). It can be stated that Mg(II) is bonded in the more stable minerals in the slag compared to Ca(II). The ratio of released SiO_2:Ca(II) vary with temperature as well. Higher amount of Ca(II) ions was released from the slag at 4 and 26 °C compared to SiO_2 content in the solution.

Opposite situation occurs at temperature 80 °C, the soluble SiO_2 content is higher compared to Ca(II) content. The increasing temperature affects mainly the soluble SiO_2 content in the solutions after contact with slag. Various types of soluble silicate structures probably originate by various temperatures, which can be concluded from the negligible differences of pH values of solutions after contact with slag. The change of pH value is probably caused by CaO reaction with water and by bonding of H(I) in silicic acid as it was concluded earlier. Thus the change of pH value during contact of slag with water could increase with increasing content of SiO_2 and Ca(II) in the solutions. However, the pH values of the leachates are practically the same at different temperatures. The increasing temperature probably leads to forming of more complex (more cross-linked) silicates in the solution which bond less of H(I) ions and thus they cause lower increase of the pH value.

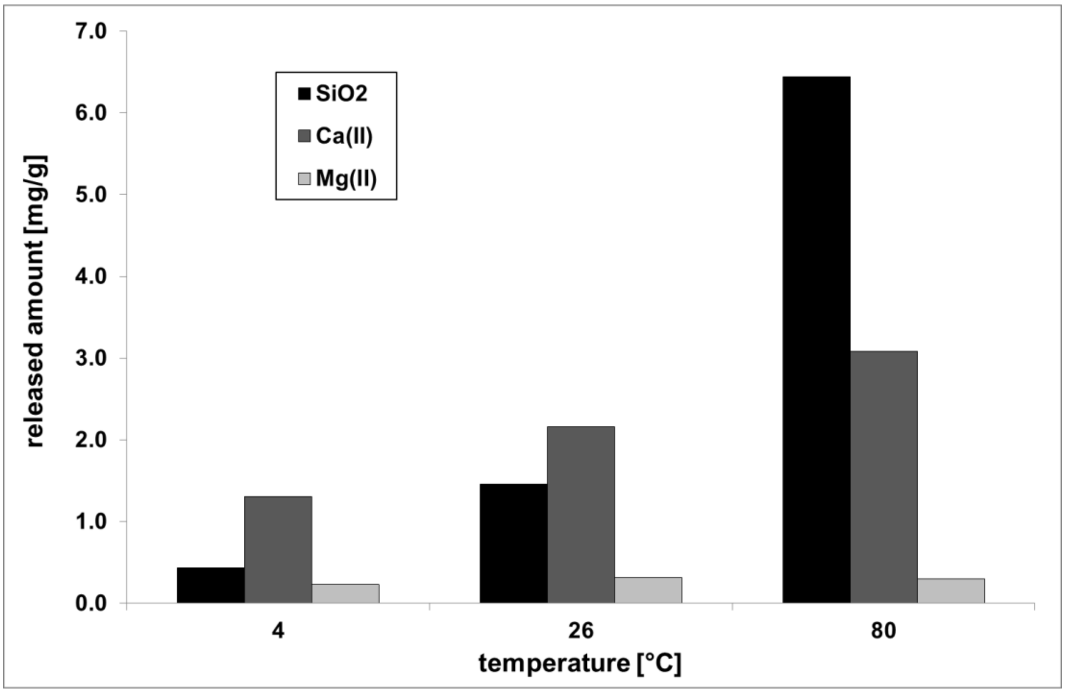


Figure 6: Released amounts of selected species during contact of slag with demineralized water dependent on the reaction temperature.

It can be beneficial to stabilize the slag prior the utilization e.g. in application as adsorbent or as backfilling material for special purposes. The stabilization can be made by change of mineralogical composition resulting to more stable minerals. Silicon is often combined with aluminium in natural relatively stable minerals[18]. Utilized blast furnace slag was mixed with various amounts of Al_2O_3 and mixtures were thermally treated at 800, 900 and 1000°C with the aim to recrystallize minerals which contain almost part of the added Al_2O_3 after treatment. Behaviour of treated slags in the aquatic environment from the sight of solutions' pH value changes after 24 hours of contact time is depicted on the Figure 7.

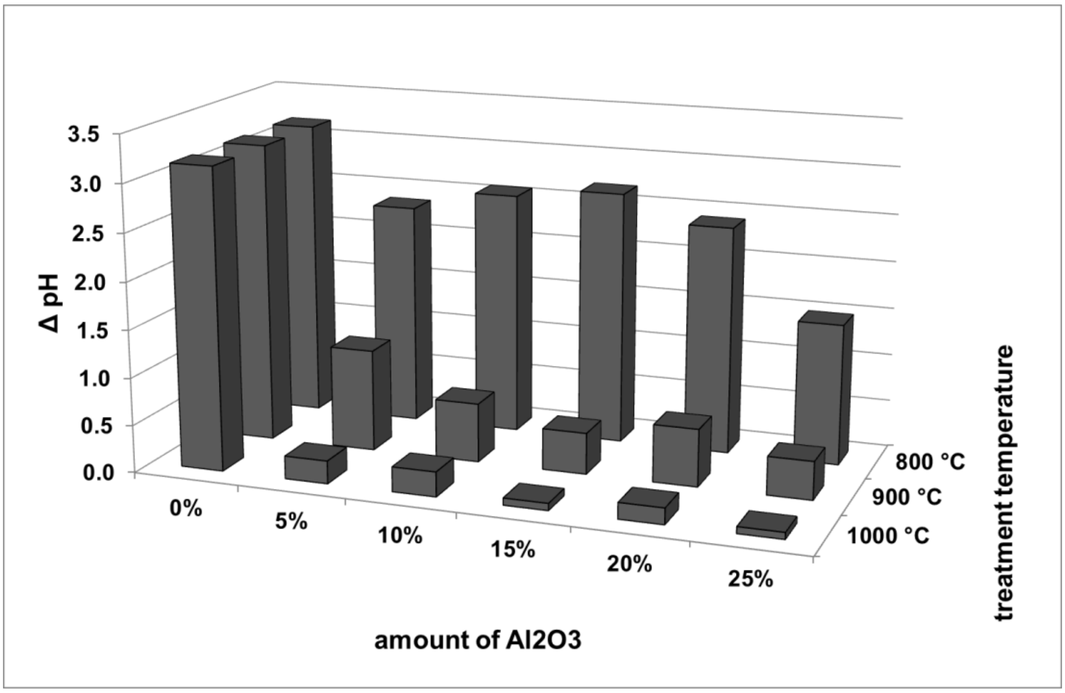
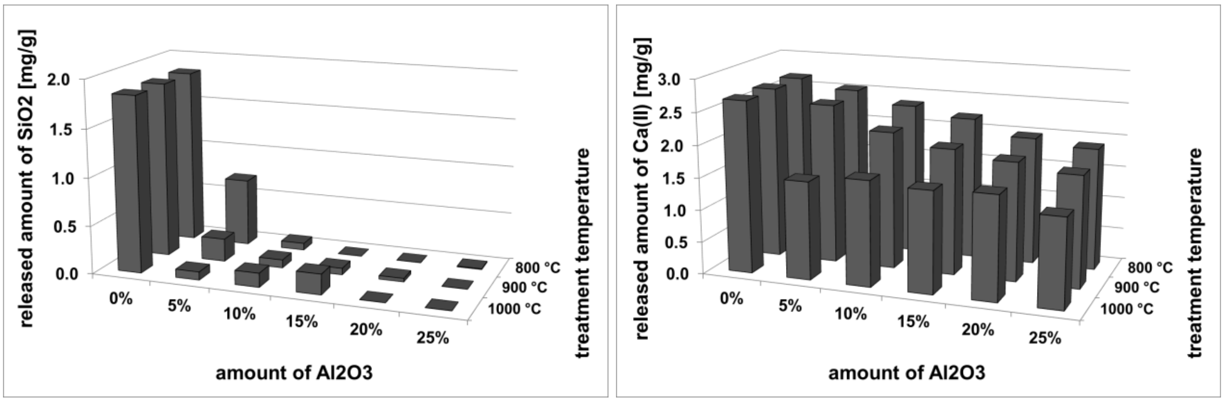


Figure 7: Changes of the pH values during contact of slags modified by various doses of Al_2O_3 and by various temperatures with demineralized water.

It is evident that thermal treatment of raw slag without Al_2O_3 addition has only slight effect on the stabilization of material. The pH value change of the solution after contact with raw slag without treatment in the previous part was about 3.4 pH units and the change of the solutions' pH value for thermally treated slags was about 3.2 pH units in the case of all used temperatures. Treatment temperature 800 °C is not enough high to cause the incorporation of aluminium to the minerals forming the slag. Thus the stabilization effect of Al_2O_3 addition is not sufficient from the sight of pH values changes in the case of treatment temperature 800 °C. The stability of materials treated at 900 °C increases with increasing amount of added Al_2O_3. Addition of 5 % w/w Al_2O_3 causes the decrease of change of solution's pH value from 3.2 units to 1 pH unit. Further increase of added amount of Al_2O_3 leads to decrease of pH value change to the 0.5 pH unit. Addition of Al_2O_3 and thermal treatment at 1000 °C leads to stable material already from low additions (5 % w/w) of Al_2O_3. The change of pH values of solutions after contact of slag with Al_2O_3 treated at 1000 °C with demineralized water was around 0.2 pH units.

Influence of the addition of Al_2O_3 and subsequent thermal treatment on the released amount of SiO_2 and Ca(II) is depicted on the Figure 8. Released amounts of Mg(II) were negligible (0.35 mg/g for slags without Al_2O_3 addition and thermally treated and around 0.1 mg/g for slags with added Al_2O_3 and thermally treated) therefore the data are not presented here. Addition of Al_2O_3 and thermal treatment lead to stabilization of silicate minerals contained in the slag, which could be concluded from the Figure 8a. Addition of 5 % w/w of Al_2O_3 leads to very significant decrease of released amount of soluble silicates (SiO_2). The effect on the released amount of Ca(II) (Figure 8b) is not so significant compared to data for soluble silicates (SiO_2) but the amount of released Ca(II) decreases with increasing amount of added Al_2O_3 and with increasing temperature of thermal treatment. It can be concluded that proposed treatment of slag by Al_2O_3 addition and subsequent thermal treatment leads primarily to the stabilization of silicate minerals towards the hydrolysis probably by forming more stable aluminosilicates with higher negative charge caused by isomorphic substitution of Al for Si. More negatively charged minerals bind stronger cations such as Ca(II) [18]. CaO is less affected by treatment but the treatment helps to diminish the change of solution's pH value especially at higher treatment temperatures. Ca(II) is probably bind in new minerals after treatment which do not cause pH value increase (they are not subject to hydrolysis processes or reaction with water). The increase of the pH value of solutions after contact of slags treated at 800 °C with demineralized water is probably caused by reaction of CaO instead of hydrolysis of silicate minerals.



a **b**

Figure 8: Released amounts of SiO_2 (a) and Ca(II) (b) during contact of slags modified by Al_2O_3 and various temperatures with demineralized water.

Conclusion

The stability of blast furnace slag in the aquatic environment is serious problem for the utilization of slags. Blast furnace slag is composed mainly by silicate minerals and CaO. These compounds can react with water and they can change the properties of solution after contact as well as properties of slag itself can be affected by water. The significant increase of the pH value can be observed shortly after mixing of slag with water. Then the pH value further increases and the equilibrium of interaction processes is reached after 7 days of contact. During the contact mainly soluble forms of silicates and Ca(II) are released to the solution. CaO probably influences the pH value in the initial stages of reaction with water. Hydrolysis of silicates contained in the slag takes place mainly after 24 hours of contact with water. The silicates containing Ca(II) seem to be less stable in the comparison with minerals containing Mg(II). The ratio slag mass:water volume plays only minor role from the sight of pH values changes. It was found out that despite the slight differences in the changes of pH values the slag exposed to lower volume of water was less hydrolysed (lower amounts of soluble silicates (SiO_2), Ca(II) and Mg(II) were released) compared to higher volumes of added water. The particle size of slag plays significant role in reaction between slag and demineralized water. Lowering the particle size leads to stronger interaction with higher increase of the pH value of solution after contact with slag and higher amount of released SiO_2 and CaO.

The temperature kept during the contact of slag with demineralized water has significant influence as well. Increasing temperature leads to significant increase of released amount of soluble SiO_2 as well as to the increase of released amount of Ca(II) ions. Temperature changes lead probably to forming of various soluble silicate structures, which affects the pH values changes caused by contact of slag with water. Blast furnace slag can be stabilized for special purposes by addition of Al_2O_3 with subsequent thermal treatment of the material. Thermal treatment at 800 °C is not sufficient for incorporation of aluminium to the structure of slag's minerals and thus for stabilization of slag. The stabilization effect of Al_2O_3 and thermal treatment at 900 and 1000 °C is evident already for addition of 5% w/w of Al_2O_3 to the slag. Added Al_2O_3 primarily interacts with silicates contained in the slag probably by forming more stable aluminosilicates. The amount of released soluble SiO_2 decreases orderly after addition of Al_2O_3 and thermal treatment. The amount of released Ca(II) ions decreases with increasing addition of Al_2O_3 and with increasing treatment temperature. It is presumable that Ca(II) is bound in the more stable minerals after treatment because release of Ca(II) to the solution does not lead to increase of the solution's pH value. It was confirmed that proposed stabilization procedure can lead to the materials based on slag and stable in the aquatic environment.

Acknowledgements

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Stabilita vysokopecní strusky v demineralizované vodě

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Souhrn

Vysokopecní struska představuje odpadní materiál z metalurgického průmyslu, který je dále ve velké míře využíván ve stavebnictví a je také studován v jemně disperzní formě jako potencionální materiál pro odstraňování těžkých kovů z roztoků. Rozemletá vysokopecní struska při kontaktu s demineralizovanou vodou způsobuje velký nárůst hodnoty pH suspenze, přičemž jsou do roztoku uvolňovány rozpustné silikáty (pravděpodobně v důsledku hydrolýzy) a dále vápenaté a hořečnaté ionty. V počátečních fázích kontaktu dochází pravděpodobně k reakci přítomného CaO, kdy jsou do roztoku uvolňovány především vápenaté ionty. Hydrolýza a uvolňování silikátů se projevuje ve větší míře až po 24 hodinách kontaktu, přičemž rovnovážného stavu je dosaženo až po 7 dnech kontaktu. Poměr množství struska:přidaný objem vody má zanedbatelný vliv na výslednou hodnotu pH roztoku po kontaktu se struskou, avšak s rostoucím množstvím vody vůči konstantní navážce strusky narůstá uvolňované množství všech sledovaných komponent (rozpuštěný SiO_2*, Ca(II) a Mg(II)). Velký vliv na interakci strusky s demineralizovanou vodou má velikost částic. S klesající velikostí částic strusky narůstá velikost změny hodnoty pH a také uvolněné množství sledovaných komponent. U částic větších než 0,5 mm dochází jen ke slabé interakci s demineralizovanou vodou, materiál je tedy relativně stabilní. U jemně pomleté strusky (velikost částic < 0,5 mm) dochází ke značným změnám hodnoty pH roztoku po kontaktu se struskou a rovněž dochází k uvolnění většího množství* SiO_2 *a Ca(II) z materiálu. Vliv na interakci vysokopecní strusky s demineralizovanou vodou má také teplota. Teplota ovlivňuje především hydrolýzu silikátů. S rostoucí teplotou značně narůstá uvolněné množství* SiO_2 *ze strusky. S rostoucí teplotou dochází také k nárůstu uvolněného množství Ca(II) iontů, interakce fází strusky obsahujících vázané Mg(II) ionty nejsou teplotou téměř ovlivněny. Jemně pomletá vysokopecní struska může být stabilizovaná přídavkem* Al_2O_3 *s následnou tepelnou úpravou alespoň při 900 °C. Úprava primárně způsobuje potlačení hydrolýzy silikátů, ale ovlivňuje také vazbu Ca(II) ve struktuře.*

Klíčová slova: *vysokopecní struska, stabilita, loužení, stabilizace, demineralizovaná voda*

Landfilling and incineration as LDPE bubble foil life-cycle laste stage

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Abstract

The subject of the research was focused on a partial model of the life cycle of production and disposal of the bubble foil. The production process of the bubble film is evaluated from the feedstock use stage which presents low density polyethylene, until two scenarios of disposal of the finished product – incineration and landfilling which, in Slovakia and in some countries, more used comprared to recycling. The modeling of the environmental impacts of the production was carried out in accordance with the STN EN ISO 14040: 2007 standard using the GaBi Education database 2017 software. The impacts of different end-of-life scenarios are compared with indicators as: global warming potential, acidification potential, eutrophication potential, ozone depletion potential and photochemic ozone creation potential. In almost every evaluated impact category production of LDPE presents higher value. The incineration has the largest share of global warning potential (28.61 kg CO_2 eq.). Emissions which are generated by incineration are not dangerous for the environment and human health. The results of the comparative LCA study show that in almost every evaluated impact categories incineration has higher value than landfilling.

Key words: *Life cycle assessment, bubble foil, low density polyethylene, incineration, landfilling*

Introduction

The research have been focused on modeling of life cycle assessment of plastic bubble foil composed by LDPE (low-density polyethylene) as a kind of plastic packaging material.

In the modern era, plastics play a vital role in our daily life activities due to the fact that plastic is lightweight, non biodegradable and low cost. Worldwide plastic production has been growing as these materials are replacing glass and metal. Today, an average person living in Western Europe or North America consumes 100 kilograms of plastic each year, mostly in the form of packaging. Plastic wastes disposal can be done by various methods such as landfill, incineration, mechanical and chemical recycling but these are restricted due to some environmental, economic and political problems[1].Among them, disposal of plastic waste in environment is considered to be a big problem due to its very low biodegradability and presence in large quantities[2].

Our research was aimed at a packaging material, becasue it is a fundamental element of almost every manufactured product. Because of the relatively short life cycle of many consumer products, the volume of packaging on the market is almost exactly equal to the volume of packaging waste[3].

LDPE is a thermoplastic made from the monomer ethylene[4].

Recycling and incineration are the usual aspects of recovery methods in the case of thermoplastic polymers. The incineration presents some problems like the production of toxic gases and the residue ash which contains lead and cadmium. Recycling presents advantages such as reduction of environmental problems and saving both material and energy[5].

Within the consumer packaging sector, the low density polyethylene (LDPE) and the high density polyethylene (HDPE) are most commonly used, followed by polypropylene (PP) and polyethylene terephthalate (PET). For agricultural applications and non-consumer packaging, LDPE is the most used material.

Within the total packaging market, plastic films like shrink and stretch films (10.8%), shopping bags (3.3 %) and other flexible packages (26.1%) can be found. Siracusa et al. (2011) have studied the environmental impact of multilayer polymer film from food packaging during the entire life cycle of the product. They analysed two films composed of LDPE and polyamide (PA) with different thickness (70 and 90 mm). On one hand, they concluded that plastic pellet production from raw material is the process with the worst environmental impact compared to film converting process, mainly due to resource saving[6].

Disposing of the waste to landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs and the poor biodegradability of commonly used polymers[7].

For the assessment we worked through the method of Life Cycle Assessment (LCA), as it is seen as a suitable instrument for the evaluation of the environmental impacts of a product or an activity through its entire life cycle. LCA is definned as a compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.The product system consists of a set of processes, all focused on the fulfilment of the required function. The result of a life cycle assessment is expressed in terms of “potential” effects. These potential effects are indicators for the real effects on local, regional and global level[8]. Life Cycle Assessment method presents a model considering the net environmental impact based on the selection of materials that naturally support long-term management of energy sources[9,10,11]. A significant number of publications have explained the use of LCA; using comparisons of different waste management scenarios in order to quantify the environmental burdens and benefits of different proposals[12].

Experimental part

The prosesses were analysed in a factory in Slovakia (Central Europe). On the basis of the process balance, the life-cycle evaluation model was created for production and end-of-life of bubble foil. The study was conducted following the procedure indicated by the European standards series ISO 14040.

The inventory is based on data obtained from the factory, where the LCA study and data from the GaBi diabase were realized. For the life cycle impact assessment of the production of bubble foil GaBi Education database 2017 software and the weak point analysis and CML method were used.

Definition of the goal and scope

The goal of LCA study was to compare two types end-of-life of bubble foil (incineration, landfilling). The aim of this study is to assess the environmental impact of different end-of-life scenarios of the bubble foil used in Slovakia and many other countries. The subject of the assessment is bubble foil produced from granulated LDPE. It has a special type of shape, 100% recyclable two-layer polyethylene foil (Table 1) with air bubbles that is used as wrapping material in the dispatch and shipping of goods. The function of the system is to provide packaging material to protect sensitive goods for impact. Since the bubble foil is used as a packaging material for various products, the assessed life cycle of the bubble foil does not include the use phase. Because of this reason a declared unit was chosen instead of a functional unit, which represents 11.1 kg of bubble foil. The declared unit 11.1 kg represents one standard pack of buble foil, i. e. 150 m^2. Production time is 8.5 minutes and consumption of LDPE granulate is 11.50 kg. System boundaries are defined as “ cradle to grave“ (figure 1). All relevant life cycle flows, processes and phases are included in the study: production processes of LDPE granulate and bubble foil and end-of-life scenarios. The distribution and use phases were not included in the system.

Table 1: Technical parameters of the bubble foil

Flat weight	50 g/m^2
Thickness	80 μm
Bubble diameter	10 mm
Bubble height	4 mm
Foil width	1 000 mm

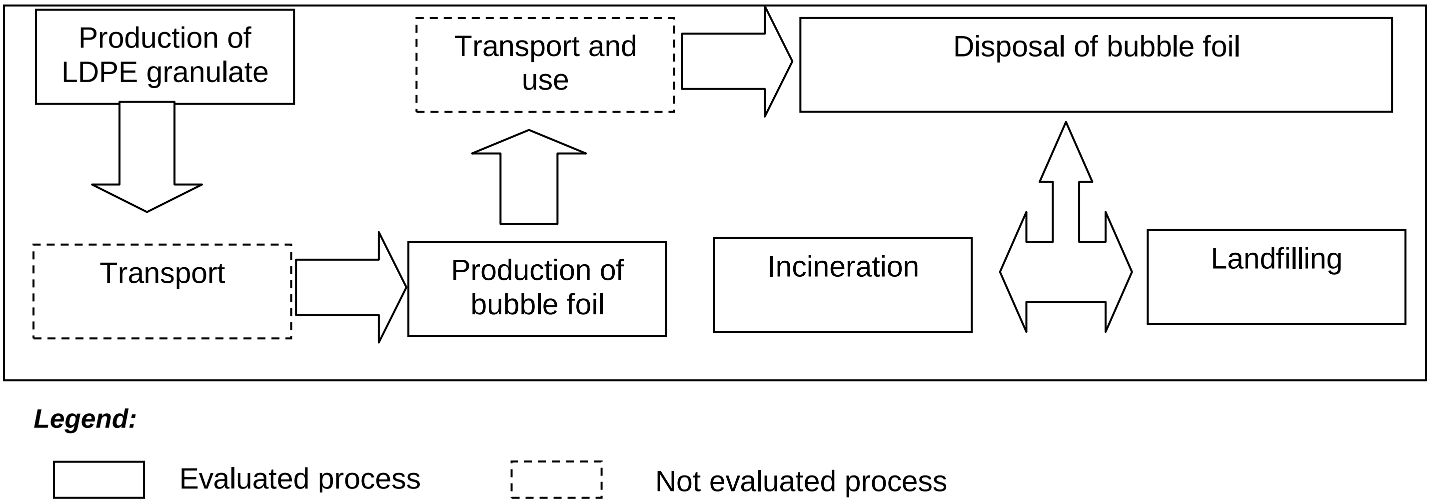

Figure 1: System scheme for the LCI of the bubble foil

Life Cycle Inventory Analysis

The production process of bubble foil consists of bubble foil extrusion and finishing. The basic input raw material of the production proces is represented by LDPE in the form of waxy granules. The low-density polyethylene used in the production of the bubble foil represents a special type which is produced by high-pressure ethylene polymerization. This type of low density polyethylene consists almost entirely of carbon and hydrogen elements. Under normal conditions it does not pose any adverse effects on human health, it is biologically inert. It is an allochthonous substance with a very slow disintegration in the environment, it is insoluble in water, therefore in the aquatic environment it is biologically inactive and does not pose a threat to groundwater. It is suitable for recycling and can be effectively destroyed by incineration, while incineration under ideal conditions (temperature and / or air sufficiency) is almost complete (> 99 %) to produce carbon dioxide and water, waste is reduced producing 43 MJ of energy per kg of polyethylene[13].

Production process

The bubble foil machine used in the stated company is called the Automatic Line for Bubble Foil Production (Figure 2) consisting of an injection press, a feeding roll device and a foil winder.

Figure 2: Automatic line for bubble foil production

The blown film extrusion process is used to manufacture bubble foil. The granulated low density polyethylene is introduced into the reservoir, subsequently to the extruder, where it is heated to 110 °C - temperature when it is melted. The molten material from the extruder, is „blown out“ on the shaping rolls. Bubbles are formed on one layer of the foil with vacuum and sticking the second layer will cause the air to close. The formed bubble foil is air cooled, subsequently stretched and finally winded.

The main inputs in the proces are polyethylene low density granulate and electrical energy (in the LCA study, only material flows are included in the Life Cycle Impact Assessment). Plastic waste is produced in the form of residues or as a defective product. All data in manufacturing phase are presented in Table 2.

Table 2: Input and output of manufacturing proces of bubble foil

Material	**kg**
Polyethylene low density granulate	11.5
Waste	**kg**
Plastic waste	0.4
Product	**kg**
Bubble foil	11.1

End-of-life

As already presented in *Definition of the goal and scope* two different processes are included in the end-of-life study that are present in Slovakia: incineration and landfilling. The following limitations are listed in the presented LCA study: absence of primary data of end-of-life proces (addressed waste disposal companies in Slovakia do not record separate data on waste) and limits of the used software. We used average data for EU28.

In the case of incineration proces the “Plastic packaging in municipal waste incineration“ process was used in GaBi numerical model. The data set represents an average European waste-to-energy plant for the thermal treatment of municipal solid waste with typical technology used in Europe to meet the legal requirements. Environmental impacts for waste collection, transport or any pretreatment of the waste are not included in the data set. Two different incineration models - one with a wet and one with a dry flue gas treatment and different NO_x – removal technologies are mixed to represent the appliance of different systems in Europe.

For the landfill process “Plastic waste on landfill“ process was used in GaBi education database 2017. The data set represents a typical municipal waste landfill with surface and basic sealing meeting European limits for emissins. Collection, transport and pre-treatment are not included. Only environmental impacts of the landfill proces occurring within 100 years are considered.

Results and Discussion

The study was conducted comparing the same type of bubble foil, in terms of production technologies and material used, but with different end-of-life scenarios: incineration and landfilling.

Life Cycle Impact Assessment

The impact assessment of all inputs and outputs was performed using weak point analysis of inputs and outputs and CML (Centre for Environmental Studies, Leiden, Netherland) method. CML is a method for the impact assessment (LCIA) in a LCA. Life cycle impact assessment translates emissions and resource extractions into a limited number of environmental impact scores by means of so-called characterisation factors. Environmental impacts of different end-of-life scenarios are compared with environmental indicators as: global warming potential, acidification potential, eutrophication potential, ozone depletion potential and photochemic ozone creation potential.

The results of the balance of weak and strong input and output sites showed that incineration and landfilling consumes material resources in the same amount (cca. 14 300 – 14 600 kg), of which, in particular, renewable resources are consumed (Table 3). Among all outputs the highest values are represented by emissions to fresh water produced mainly during bubble foil production. We see a slight increase in emissions to air in case of incineration. Emissions into the air are formed in the largest amount of inorganic emissions (43.2 %). Negligible quantity is formed by heavy metals, radioactive emissions, organic emissions (especially VOCs), and particulate matter. Harding, Dennis, von Blottnitz, Harrison (2007) compared the partial life cycle of plastic products, including products made of low density polyethylene LDPE. They conclude that a considerable amount of water is required for their production, resulting in increased waste water production. The production of air emissions, compared to waste water generation is negligible in the production of LDPE plastic products. The increase in emissions to air is caused by end-of-life models – in particular incineration[14].

Table 3: Weak point analysis from elementary flows

	Incineration (%)			Landfilling (%)		
	Production	Disposal	Total	Production	Disposal	Total
Flows	17.6	82.4	100.0	35.9	64.1	100.0
Resources	17.0	40.6	57.66	34.6	31.4	66.0
Deposited goods	0.01	0.20	0.21	0.02	0.8	0.82
Emissions to air	0.63	8.14	8.77	1.27	0.63	1.9
Emissions to water	0.0004	33.38	33.38	0.0009	31.3	31.3
Emissions to agricultural soil	-	-6.22E-9	-6.22E-9	-	-1.95E-9	-1.95E-9
Emissions to industrial soil	-	0.0004	0.0004	-	0.001	0.001

The results of the life cycle assessment of 11.1 kg of bubble foil, as a characterization, show that the overal greatest impact is global warning potential (Table 4).

Table 4: Characterization profil of 11.1 kg of bubble foil

	Incineration	**Landfilling**
Global warning potential, kg CO_2-eq	52.70	24.90
Acidification potential, kg SO_2-eq	0.10	0.09
Eutrophication potential, kg PO^{3-}_4-eq	6.34E-3	8.04E-3
Ozone depletion potential, kg R11-eq	1.09E-9	2.02E-12
Photochem. Ozone creation potential, kg Ethene-eq	0.01	0.01

The results of LCA study of the bubble foil are calculated to absolute value in the particual groups of impact. The two different scenarios is compared on the level of functional unit. In all results (impact factors) the share of production is the same. We mainly follow the impact factor of the end-of-life. Deeper analysis of the resuls show that the impact of incineration compared to production is slightly higher.The greatest overall impact on global warming potential (Figure 3) is presented by processing incineration (incineration: 28.61 kg CO_2 eq.,). During perfect incineration polyethylene is burned almost completely. Emissions that are generated are not dangerous to the environment and human health[14]. The production of bubble foil produces 24,1 kg CO_2 eq. Greene (2011) found that the production of 1,500 plastic bottles of LDPE produces 0.04t CO_2 eq. and from the lifecycle from gate to grave, LDPE has the largest share of the global warming potential indicator.[15]

In case of landfilling, polyethylene is inert, it does not release gases or other compounds known to pollute water resources[16]. The CO_2 production is minimal in our LCA analysis (0.82 kg CO_2 eq.).

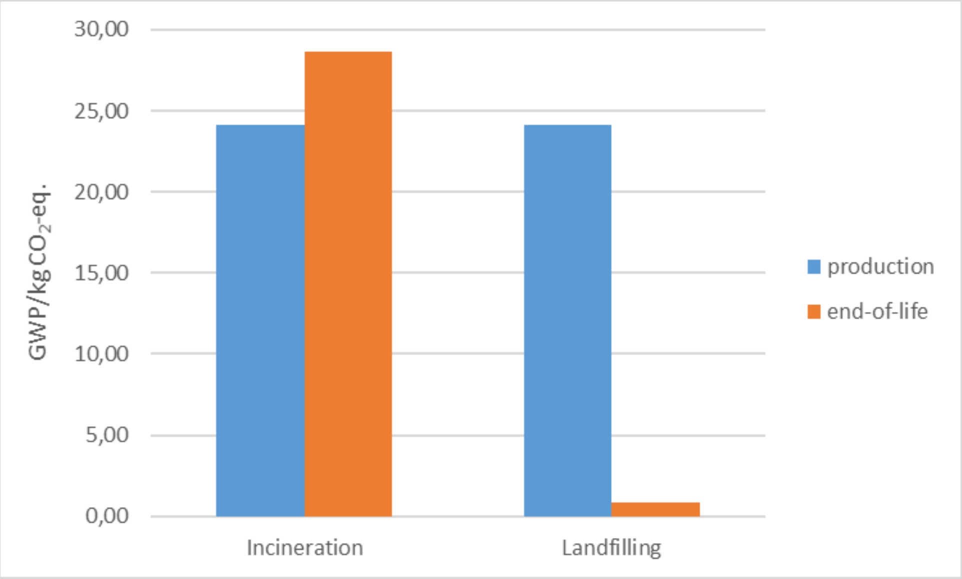

Figure 3 Global warning potential for 11.1 kg of bubble foil

In Table 5 impact in all studied categories are presented for incineration scenario in share of life cycle phases (production, end-of-life). In the case of incineration scenario the biggest share in all indicators represents production. The end-of-life proces (incineration) has minor share (maximum value in acidification potential 0.007 kg SO_2 eq.).

Table 5: Other indicators for incineration of bubble foil

	Acidification potential (kg SO_2 eq.)	**Eutrophication potential (kg PO^{3-}_4 eq.)**	**Ozone depletion potential (kg R11 eq.)**	**Photochemic ozone creation potential (kg Ethene eq.)**
Production	9.00E-2	6.00E-3	0.0E+0	1.00E-2
Incineration	7.00E-3	3.00E-4	1.0E-9	3.00E-4

The landfilling has a minor share in AP, EP, ODP and POCP indicators (table 6) with the share from 0,002 (AP, EP) to 2.10^{-12} (ODP). Only in case of acidification and eutrophication potential indicator, the value is higher. In the case of bubble foil end-of-life in landfills, which are present for more than thousand years in the evironment, bubble foil may break down into smaller particles that may continue to pollute the soil and water. Guo (2012) demonstrated in his study that packaging material from LDPE led to an increase in environmental burdens, because it has a higher impact on eutrophication, human and aqua eco-toxicity[17]

Table 6: Other indicators for landfilling of bubble foil

	Acidification potential (kg SO_2 eq.)	**Eutrophication potential (kg PO^{3-}_4 eq.)**	**Ozone depletion potential (kg R11 eq.)**	**Photochemic ozone creation potential (kg Ethene eq.)**
Production	9.00E-2	6.00E-3	0.0E+0	1.00E-2
Landfilling	2.00E-3	2.00E-3	2.00E-12	3.00E-4

If we normalize results with respect to bubble foil mass and calculate all impact categories for 11.1 kg of bubble foil the results look promising for landfilling. In almost every evaluated impact categories incineration has higher value than landfilling (table 7). Incineration, compared to landfilling shows a higher share of global warming potential indicators (52.7 kg CO_2 eq.). We could observe that landfilling has the largest share of eutrophication potential (0.008 kg PO^{3-}_4 eq.). The indicator of acidification potential is almost balanced for both evaluated end-of-life scenarios. In all other impact categories values of landfilling are in average still below values of incineration (table 7). This plastic waste usually has a high level of contamination with dirt, organic material and adhesives, etc. As a result, in most countries, LDPE plastic waste is currently either incinerated for energy recovery or landfilled.

Table 7: Normalized results of 11.1 kg of bubble foil

	Global warning potential (kg CO_2 eq.)	**Acidification potential (kg SO_2 eq.)**	**Eutrophication potential (kg PO^{3-}_4 eq.)**	**Ozone depletion potential (kg R11 eq.)**	**Photochemic ozone creation potential (kg Ethene eq.)**
Incineration	5.27E+1	1.00E-1	6.00E-3	1.00E-9	1.00E-2
Landfilling	2.49E+1	9.00E-2	8.00E-3	2.00E-12	1.00E-2

Conclusions

Post-consumer LDPE (low-density polyethylene) plastic foils recovered from municipal solid waste are considered difficult to recycle. In Slovakia and other countries, incineration or landfilling of waste bubble foil is therefore preferred. It was also necessary to consider the fact that separate plastic containers contain many impurities that are no longer usable. The use of recycling is considered in the case of plastic waste from companies whose waste is more polluting and containing mainly polyethylene films[18].

The LCA of these two ways of waste removal bubble foil has been performed. For the analysis, specific data from LDPE bubble foil production were used. In the article the life cycle assessment study of two scenario end-of-life of bubble foil is presented: incineration and landfilling. The production process was assessed. GaBi Education software was used for numerical modelling of the life cycle phase. Functional unit was one standard pack of bubble foil from LDPE granulate. The biggest impact in all monitored indicators comes from granulate production proces. The production of the LDPE granulate and the following products has a significant impact on global warming potential (24.1 kg CO_2 eq.).

End-of-life scenario has a considerable impact on global warming potential in the case of incineration compared to landfilling (incineration: 28.61 kg CO_2 eq., landfilling: 0.82 kg CO_2 eq.). The acidification potential and eutrophication potential are slightly significant for evaluated end-of-life scenarios of bubble foil, but these values are very low (incineration: 0.003 of EP, 0.007 of AP, landfilling: 0.002 of AP and EP). The other evaluated indicators have a negligible impact for both end-of-life scenarios. LDPE bubble foil is environmentally friendly, can be disposed of by landfilling or by incineration, which does not produce environmentally harmful substance.

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Skládkovanie a spaľovanie ako posledná etapa životného cyklu LDPE bublinovej fólie

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Abstrakt

Predmetom výskumu je čiastočný model životného cyklu výroby a zneškodnenia bublinkovej fólie. Hodnotený je výrobný proces bublinkovej fólie od použitia vstupnej suroviny, ktorou je polyetylén s nízkou hustotou po dva scenáre zneškodnenie hotového produktu – spaľovanie a skládkovanie, ktoré sú na Slovensku a v niektorých iných krajinách viac využívané. Modelovanie environmentálnych vplyvov výroby sme realizovali v zmysle normy STN EN ISO 14040:2007 využitím GaBi Education database 2017 software. Vplyv rôznych scenárov konca životného cykla (spaľovanie, skládkovanie) sa porovnávajú s ukazovateľmi: potenciál globálního otepľovania, potencial acidifikácie, potenciál eutrofizácie, potenciál poškodenia ozónu a potenciál tvorby fotochemického ozónu. Takmer v každej hodnotene kategórii dopadov proces výroby LDPE predstavuje vyššiu hodnotu. Spaľovanie má najväčší podiel na potenciály globálního otepľovania (28.61 kg CO_2 *eq.). Produkované emisie nie sú nebezpečné pre životné prostredie a ľudské zdravie. Z výsledkov komparatívnej LCA štúdie vyplýva, že spaľovanie má takmer vo všetkých kategóriá vyššiu hodnotu ako skládkovanie.*

Kľúčové slová: *Hodnotenie životného cyklu, bublinková fólia, polyetylén s nízkou hustotou, spaľovanie, skládkovanie*

Environmental policy and electromobility in European Union

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Summary

Globalization trends affect the growth of road passenger and freight transport, which has a positive impact to meet the quality needs of the population, but has a negative impact on the environment. At present, is being developed and applied technology to reduce the negative effects of transport and automotive on the environment. The company exerts pressure on automotive companies to develop cars with the lowest emissions. This trend is strongly supported by the European Union, which wants automakers to stimulate new measures to invest in new technologies to reduce CO_2 *and* NO_x *emissions. However, the direction and priorities of developed and applied technologies are also dependent on economic developments, political and legislative factors. In the contribution we are focusing on the development of electric vehicles, we analyse their sales in the European Union, and on the example of Slovakia we say that income-dependent electric mobility is being explored, while trying out the opportunities offered today by renowned carmakers. The disappointment is that, as with conventional drives, even more environmentally friendly ones declare only results from laboratory conditions, which can significantly affect the more burgeoning of ecological means of transport. Considering the amount of the purchase price of electric vehicles in Slovakia, it is more likely that the buyer will continue to favour classic cars for quite a long time, although hybrid and clean electric vehicles are already more efficient in terms of fuel costs.*

Keywords: *Transportation, electric vehicles, emissions, investment intensity.*

Introduction

The European Union's environmental policy is one of the Union's youngest policies and is currently one of the most discussed and can be said to be even the most progressive. As a follow-up to environmental policy, we will address the issue of reducing emissions in transport. Transport is the only sector in which greenhouse gas emissions have been rising since 1990. It produces 26 % of greenhouse gas emissions in the European Union, which is more than it produces industry, energy, buildings, agriculture or waste management. Three quarters of transport emissions are generated on the road. From transport emissions, 44.5 % of passenger cars and 18.8 % of heavy-duty vehicles are dispensing. The European Environmental Agency states that transport emissions in the European Union have increased by 23 % by 2015. In Slovakia the trend was the opposite, the amount of CO_2 produced decreased by 0.6 %

In 2011, the European Commission published the Transport Strategy 2050 and the White Paper on Transport. The basic idea of both documents is the creation of solutions for a competitive, resource efficient transport system, addressing the problem of resource constraints and Europe's dependence on these resources, reducing CO_2 emissions, unsustainable traffic safety and fragmentation of land, traffic congestion and traffic noise. European transport should consume less energy, use cleaner energy and improve efficiency in the use of both existing and newly built transport infrastructure. The White Paper has four main objectives to be met by 2050. One of the objectives is the first objective is to use sustainable low-carbon fuels in air transport and at least 40 % reduce emissions from shipping, 50 % of medium-haul transport from road transport for rail and waterborne transport, reduce CO_2 emissions from transport by 60 % compared to 1990 and gradually reduce the ban on conventional fuel vehicles entering city centres. These objectives are further specified for urban, suburban and long-distance transport.

If transport emissions are not radically and rapidly reduced, there is no chance of meeting the goal set by the Paris Climate Agreement. The extent and intensity of transport have long exceeded the sustainable level and the problems that transport naturally causes can only be solved by its radical limitations. Modern civilization, however, is not willing to reduce transport, but to introduce technological innovation. While technological innovation in transport is only mitigating and degrading its negative consequences, energy and climate considerations are of the utmost importance and need to be maximized. A key issue that focuses on innovation is the fundamental replacement of fossil fuels for renewables so as to reduce as much as possible greenhouse gas emissions from transport. The original plans of the European Commission to reduce CO_2 emissions in transport are being shot with the discomfort of car manufacturers as well as environmental organizations. Automotive have labelled them as very strict or incomprehensible. The European Parliament is currently debating a new proposal that supports more and more electric cars to reduce car emissions by 15 % by 2025 and 30 % by 2030 compared to 2021 and includes a ban on sales other than cars without emissions. The contribution will focus on electro mobility, the advantages and disadvantages of electric vehicles as well as their efficiency.

Transport and its contribution to environmental pollution

The growth of road passenger and freight transport has not only positives but also negatives, with the greatest impact on the environment. At present, numerous technologies are therefore being developed and applied to reduce the negative effects of transport and automobile on the environment. The amount of pollutant emissions in transport is related to the fuel consumption, which adversely affects the technical condition of the fleet operated, the use of the means of transport and the load on the transport infrastructure. The company exerts pressure on car companies to develop cars with the lowest emissions. This trend is strongly supported by the European Union, which wants automakers to stimulate new measures to invest in new technologies to reduce CO_2 emissions. The main idea of investing in cars with new types of engines, especially electric cars, is also a shift away from the use of fossil fuels.

Electric cars are not new vehicles. They are even older than gasoline cars. The first electric vehicle appeared on the road in 1873 and its constructor was the Englishman Robert Davidson. The first petrol-powered motor vehicle appeared on the road twelve years later. Already in 1887 there were 100 electric taxis in London. In 1900, some 4,000 vehicles were registered in the US, of which 40 % were steam engines, 38 % electric vehicles, and 22 % gasoline powered vehicles. After 1900, the mass development of combustion engines and electric cars failed to compete with the gasoline car and the oil era of the automobile. The operation of petrol cars was trouble-free between 1900 and 1973, as the price of oil was low and easily available. During this period, there was no interest in alternative drives and the reason for something new to develop, but in view of increasing emissions, the first European emission standard for passenger cars was introduced in 1970. The first serious problem for gasoline (diesel) cars occurred at the beginning of the 1970s during the oil crisis. The price of oil has risen from US $ 3.29 in 1973 to US $ 11.58 in 1974. In addition to rising oil prices, import embargos have been introduced, and in some countries a fuel allocation per person has been introduced. Another serious problem occurred in the 1980s, when measurements showed an increase in air pollution, which also contributed to car transport and very cheap oil during this period. In the 1980s, there was an increasing focus on alternative fuels and electromobility.[1]

The first emission limits in the automotive industry were based on voluntary agreements between car manufacturers and the European Commission. In 1992, the EURO 1 emission standard was introduced, requiring a changeover to unleaded petrol and the universal fitting of gasoline catalytic converters to reduce carbon monoxide (CO) emissions. The new start for electric cars occurred in 1996, when the EURO 2 standard was introduced, further reduced the carbon monoxide emission limit and also reduced the combined threshold for unburnt hydrocarbons and nitrogen oxides for petrol and diesel vehicles. EURO 2 has introduced various emission limits for petrol and diesel. In 1997, Toyota Prius was introduced on the Japanese market. In 2000, it became the first mass-produced hybrid vehicle in the world and is currently the best-selling hybrid vehicle with 3.9 mil. sold pieces.

Table 1: Euro emissions standards EURO 1 and EURO 2

EURO 1 emission limits	**EURO 2 emission limits (petrol)**
CO – 2.72 g/km (petrol and diesel) **HC+ NOx –** 0.97 g/km (petrol and diesel) **PM –** 0.14 g/km (diesel only)	**CO –** 2.2 g/km **HC+ NOx –** 0.5 g/km **PM –** no limit
	EURO 2 emission limits (diesel)
	CO – 1.0 g/km **HC+ NOx –** 0.7 g/km **PM –** 0.08 g/km
EURO 3 emission limits (petrol)	**EURO 4 emission limits (petrol)**
CO – 2.3 g/km **HC –** 0.20 g/km **NOx –** 0.15 **PM –** no limit	**CO –** 1.0 g/km **HC –** 0.10 g/km **NOx –** 0.08 **PM –** no limit
EURO 3 emission limits (diesel)	**EURO 4 emission limits (diesel)**
CO – 0.64 g/km **HC+ NOx –** 0.56 g/km **NOx –** 0.50 g/km **PM –** 0.05 g/km	**CO –** 0.50 g/km **HC+ NOx –** 0.30 g/km **NOx –** 0.25 g/km **PM –** 0.025 g/km
EURO 5 emission limits (petrol)	**EURO 6 emission limits (petrol)**
CO – 1.0 g/km **HC –** 0.10 g/km **NOx –** 0.06 g/km **PM –** 0.005 g/km (direct injection only)	**CO –** 1.0 g/km **HC –** 0.10 g/km **NOx –** 0.06 g/km **PM –** 0.005 g/km (direct injection only) **PM –** 6.0x10 ^11/km (direct injection only)
EURO 5 emission limits (diesel)	**EURO 6 emission limits (diesel)**
CO – 0.50 g/km **HC+ NOx –** 0.23 g/km **NOx –** 0.18 g/km **PM –** 0.005 g/km **PM –** 6.0x10 ^11/km	**CO –** 0.50 g/km **HC+ NOx –** 0.17 g/km **NOx –** 0.08 g/km **PM –** 0.005 g/km **PM –** 6.0x10 ^11/km

Source: https://www.theaa.com/driving-advice/fuels-environment/euro-emissions-standards

Due to the existence of emission agreements, the emissions produced by automotive transport have been greatly reduced until 2004, when the cartels were no longer willing to voluntarily reduce their emissions. The most significant progress in reducing emissions was achieved during the period of EURO 0 and EURO 1, with developments in all the areas shown in Figure 1. The most significant progress can be seen in NOx, where there was a 98 % improvement. In the particle area, the improvement was 97 % and 95 % in HC. Production of CO_2 emissions also decreased significantly by 89 %. For CO_2 emissions, we can also note the fact that there has been almost no reduction in CO_2 emissions since the introduction of EURO 4. Automobile manufacturers argue that they do not have technologies that would significantly improve the situation and require less stringent CO_2 limits. [2, 3]

Since 2010, the first mandatory EURO 5 standard has been in force. For EURO 5, limits have been set for CO_2 140 g / km. The current EURO 6 standard is still the toughest standard, has reduced the CO2 production limits by an additional 10g / km and has introduced a number of novelties to the automotive industry. It came into force on 1 September 2014. Cars built after 2014 had to have a mandatory start-stop system that, when standing in the engine, shuts down the engine to reduce emissions and thus reduce the CO_2 production to 95g / km (from today's 130g / km) by 2020.[3]

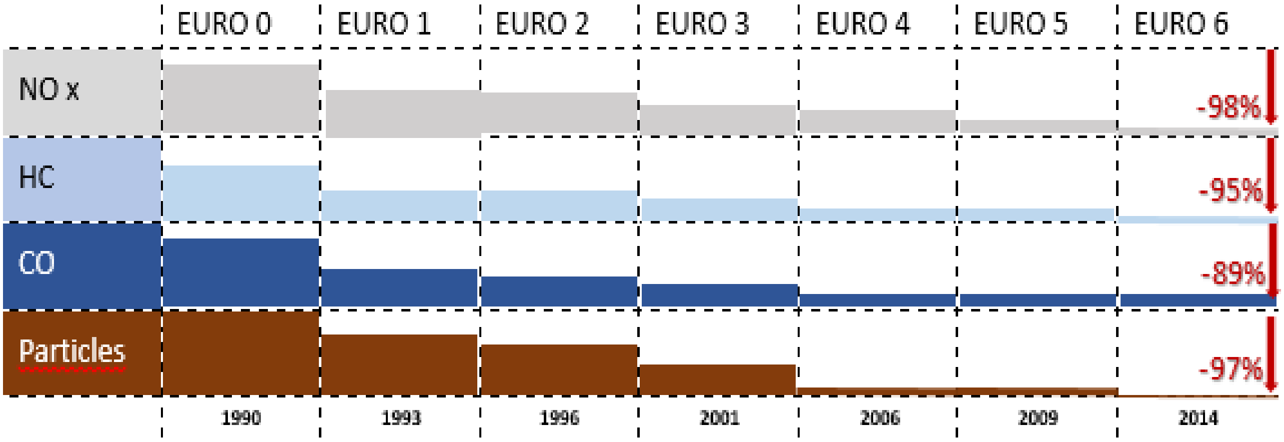

Figure 1: Progress in emissions from EURO 0 to EURO 6
CO = Carbon Monoxide, **NOx** = Oxides of Nitrogen **HC** = Hydrocarbons **PM** = Particulate matter
Source: processed by http://image.slidesharecdn.com/renaulttruckspresentation2014en-140321131359-phpapp01/95/renau lt-trucks-presentation-40-638.jpg?cb=1395407876

Results and discussions

In the European Union and in individual countries, the production of electric vehicles has already been promoted for a number of years, which is intended to meet the objectives of the Europe 2050 strategy. An electric vehicle is a vehicle exclusively powered by an electric motor powered by an electric energy storage battery. Batteries are charged externally from the electrical system or can be recharged using an internal combustion engine or fuel cell system. Electric cars include an electric car (electric car, electric vehicle, electric car), a passenger or truck, a bus, an electric motorcycle, an electric bicycle.

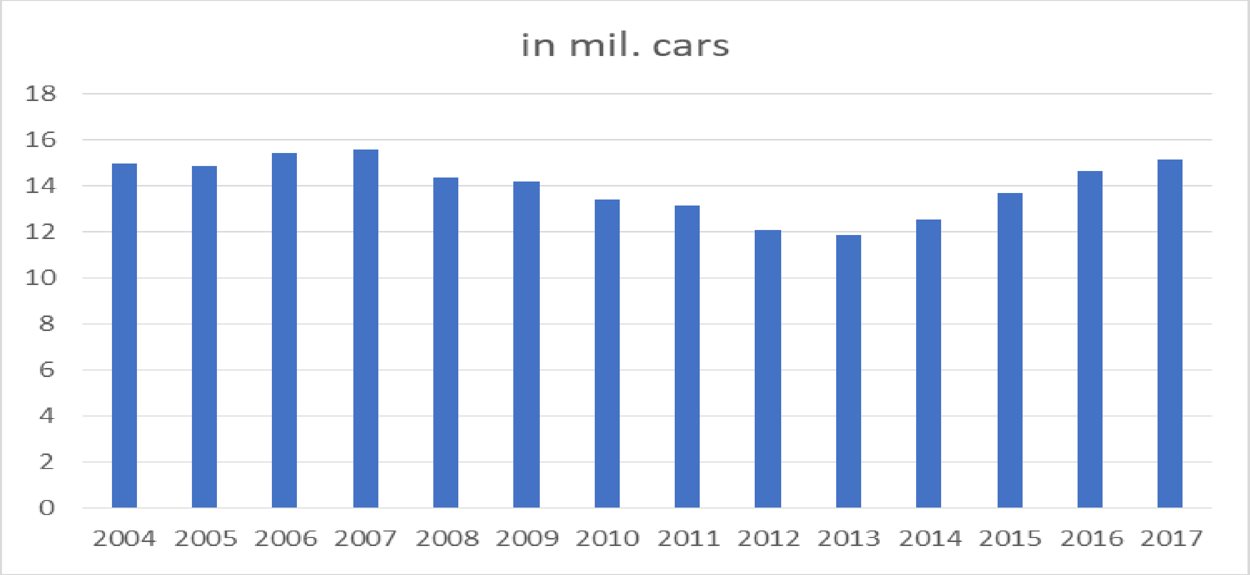

Figure 2: Car selling progress in European Union
Source: CARSALESBASE.COM. European car sales analysis February 2018 – brands. 2018
http://carsalesbase.com/european-car-sales-analysis-february-2018-brands/

In 2017, record sales of 2016 were overtaken, when 15,137,732 units were sold, representing a 3.39 % increase over the previous year. This is a massive increase in sales, as sales in 2013 were 11,873,302 cars. An average of 14 million cars are sold annually since 2004. Sales of hybrid vehicles (51.81 %), plug-in hybrid vehicles (28.90 %) also grew significantly. The reason these types of drives grew by a double digit number is country support and more progressive technology. The growth in sales of cars using only the combustion engine was 2 %.[4] In 2017 97,571 electric vehicles were sold in the European Union.[5] In the second quarter of 2018, demand for alternatively-powered vehicles in the European Union grew significantly (+44.3 %), mostly driven by hybrid (+49.2 %) and battery electric (+45.5 %) car sales. Overall, 72,168 electrically-chargeable cars were registered in the EU from April to June 2018, or 43.8 % more than in the same period one year ago. Demand for LPG and NGV vehicles also increased strongly – up 35.2 % in the second quarter of the year – mainly thanks to a notable uplift of natural gas-fuelled car registrations (+139,8 %). Among the five key EU markets, APV registrations saw the highest increases in Spain (+79.4 %) and Germany (+72.1 %). Demand for alternatively-powered vehicles also continued to post strong growth in France (+43.4 %), the UK (+42.3 %) and Italy (+20.7 %). On a global scale, electric cars have only a negligible share of automotive transport (0.2 %), but their number will grow rapidly in the years to come. In connection with the low number of electric vehicles beside the direct financial support, political support in the form of concessions in parking systems, road taxes, motorway tolls, the possibility of driving electric vehicles in reserved lanes and other benefits for electric car owners is necessary.

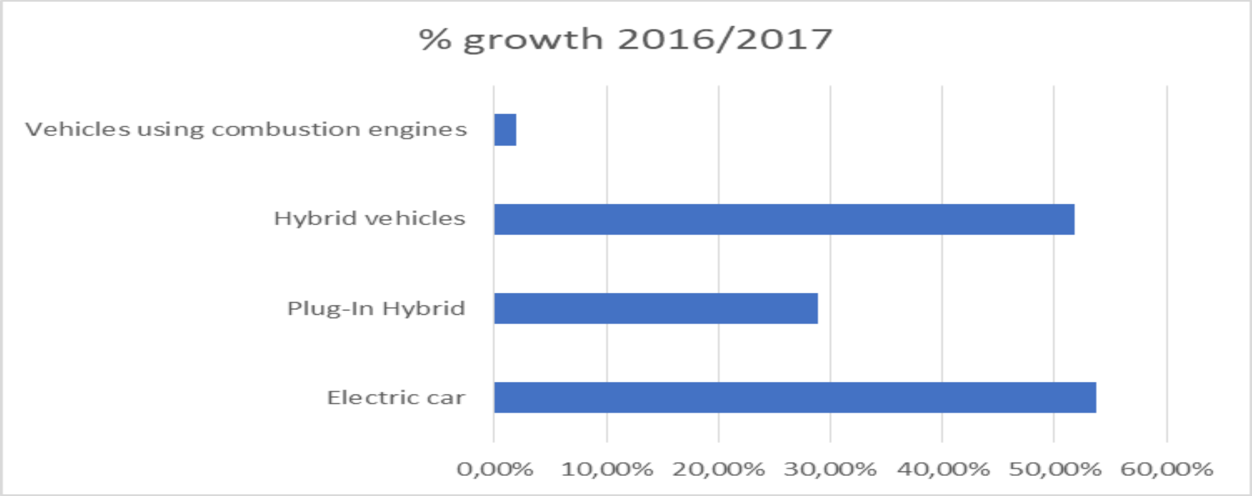

Figure 3: Number of registered cars in EU countries by car type

Source: own figure processed by https://www.best-selling-cars.com/europe/2017-full-year-europe-electric-hybrid-vehicle-sales-per-eu-efta-country/

According to the International Energy Agency (IEA), the sale of electric cars is currently concentrated in ten countries - China, the United States, Japan, Canada, Norway, Britain, France, Germany, the Netherlands and Sweden. These countries in the past accounted for up to 95 % of the global electro mobility market. The absolute largest market for China in China in 2016, where more than 200 million electric double-wheeled vehicles and 300,000 electric buses are the global leader in electrification.[7]

Apart from the disadvantages of the electric car, there is a problem with lithium-ion batteries that are the basis for the operation of mobile phones, notebooks of electric cars and other electrical equipment. Currently these batteries are indispensable because they are not an adequate substitute for them. Lithium reserves are not infinite, and the sites are concentrated in Bolivia, Argentina and Chile. There are up to 50 % of the world's property in Bolivia, 25% in Argentina and Chile, and 25 % around the world.[8]

Limited stock lithium companies are constantly working on developing a new type of battery. Research also raises the need to increase the range, weight and cost of batteries. The battery system today weighs approximately 290 Kg. It consists mainly of lithium, graphite, cobalt, aluminium and magnesium. Battery life after warranty is most likely to show a certain drop in capacity compared to new batteries, but in most cases no battery replacement or battery cells replacement will be required because manufacturers expect to have as long life as the electric vehicle itself. In Figure 4 we can see the development of the prices of two currently most expensive and unbraked commodities for the production of batteries in electric vehicles. Prices in each year are as of 31 January. Both cobalt and palladium prices were relatively stable between 2014 and 2015 and fell sharply in 2016. In 2018, the price of cobalt increased by 116 % and its price exceeded 75,000 USD / tonne. However, after the Dieselgate case, carmakers reported massive investments in electric cars, and the cost of these commodities has softened several times. The price of palladium has risen by 206 % in 2 years and the cobalt price has risen by as much as 366 %. Car makers have claimed that mass production will lead to a gradual decline in the price of electric vehicles. And here we are faced with the problem of the high price of electric cars, which is based on the price of the battery and its production costs, which are growing sooner.[11]

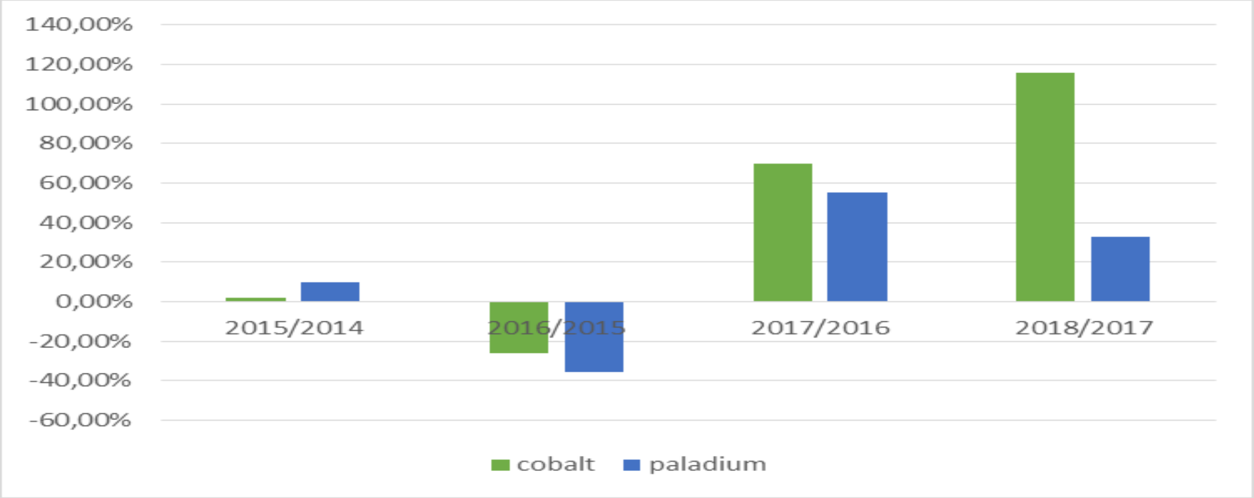

Figure 4: Price change of key commodities

Source: own figure processed by https://www.investing.com/commodities/palladium-historical-data

By 2020, the assumption is to increase the share of electric car sales in global sales from the current 2.5 % to 6 % and by 2030 to 25-40 % by 2030. This means, however, that even despite the attempt to ban the production and sale of combustion engines, they will continue to dominate over a few years over electric motors. However, the changes will also require improvement and expansion of the recharging infrastructure, increased electro mobility, recharging of the battery and, of course, lowering the high price of vehicles.

In some countries, the infrastructure of charging stations is poorly built. Without the construction of new charging stations, it is not possible to expect increased demand for electric vehicles. In Figure 5, we can see the number of built-in charging stations and number of charging stations per 1,000 citizens in the selected countries of the European Union. We divided the countries into 3 groups, namely the eastern European countries and countries of the Balkans (Latvia, Bulgaria, Hungary, Croatia, Slovakia, Slovenia, Poland, Austria and the Czech Republic). Furthermore, the Nordic countries (Finland, Sweden and Denmark) and countries that strongly support green energy (Norway, France and the Netherlands). In the first group of countries Austria has the most charging stations per capita. They have very weak infrastructure in Latvia, where there are only 74 charging stations and Bulgaria 94. The second group of states are Nordic countries where charging stations are being built at a faster rate than in Eastern European countries and countries in southern Europe. Finland has twice as many charging stations as in Slovakia. In Denmark, the number of charging stations is 2,582 and in Sweden even 4,733. The third group of countries, including France, the Netherlands and Norway, is slightly different in relation to environmental protection. In France, green technologies are preferred. Currently there are 16,331 charging stations in France. More than 2,000 are planned to be built by 2020. In Norway, 10,350 charging stations (up to 1,000 people far more than France) and the Netherlands have 32,875 charging stations. Both countries have a common goal, and by 2025 – 2030 (the Union's goal is 2050), they want to ban the sale of cars for fossil fuels. It should also be remembered that these two countries are among the world leaders in the sale of electric vehicles. This fact helped to hire massive state support and excellent infrastructure.[12]

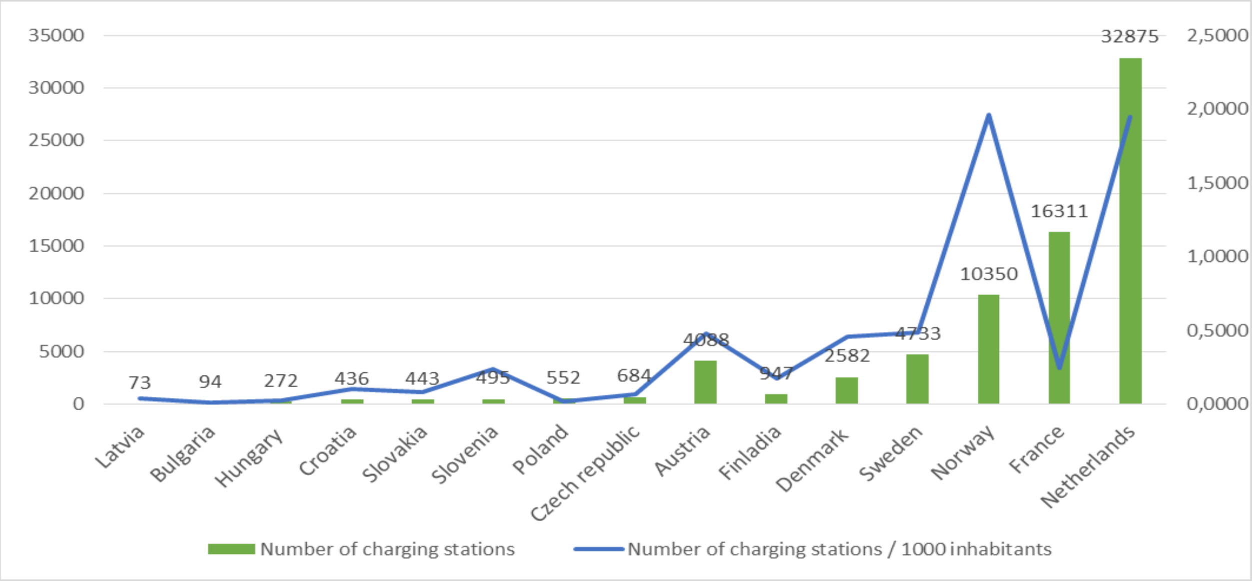

Figure 5: Number of electromobile charging stations and number of charging stations per 1,000 citizens in selected countries

Source: processed by http://www.eafo.eu/electric-vehicle-charging-infrastructure

Certainly, not unified charging connections must also be mentioned. In practice, this means we have different types of terminals for charging. If you are the owner of a vehicle such as the BMW i3 and want to charge your car on a Tesla stand it is not possible. This is a major problem to be solved at the beginning of the European Union's promotion of electro mobility. Similarly, as mobile phone manufacturers once agreed, each manufacturer would not have a different type of charger (the only exception was and still is Apple). It would be ideal to resolve the 'gentlemen' agreement 'to agree on a single type of voluntary agreement.[13]

Electro mobility support and interest in electric cars in Slovakia

State support for electro mobility in the form of a financial contribution to the purchase of a vehicle started in Slovakia on November 11, 2016. The state created a € 5.2 million electric mobility finance package. He contributed 5 mi to this package. € Recycling Fund and € 0.2 million. € Automotive Industry Association. Subsidies for the purchase of a new electric vehicle amount to € 5,000 and for hybrid and plug-in hybrid vehicles of € 3,000. The main condition for the purchase of the vehicle was that the vehicle was first registered and the vehicle was classified as M1 (passenger cars) or N1 (small trucks up to 3.5 tons). Not only private individuals, but also entrepreneurs, municipalities and cities, could apply for the contribution.[14] It was initially expected that the amount of 5.2 mil. € is exhausted in one year. However, assumptions have not been fulfilled. From November 11, 2016 to November 8, 2017, only 1,885 million € were spent. A total of 445 applications were recorded, of which 275 applications were for electric vehicles and 170 for hybrid and plug-in hybrid vehicles. On the basis of the decision of the Government of the Slovak Republic, the time to withdraw the allocated financial volume was extended until 30 June 2018. If the funds are not used up to a set date, the balance will be used for the construction of new charging stations for electromobiles.[15]

According to data from the Automobile Industry Association of the Slovak Republic, Slovaks requested subsidies for 523 electric vehicles and 266 plug-in hybrids. This means that the state has contributed a total of € 3,413,000 to motorists for 789 cars. In 2015 only 188 electric vehicles and plug-in hybrids were registered. A further 434 vehicles were added in 2016. After launching the subsidy program in November 2016, interest in subsidies increased, and in 2017 there were 2,178 new registrations, which represented a year-on-year increase of more than 400 %. Increased interest continued in the first half of 2018 when there were 1,427 new registrations. In total, there are almost 4,300 electric and plug-in hybrid cars registered in Slovakia. During the funding period, the Slovaks were most interested in

Nissan's electric models, namely Nissan Leaf, which sold 175 units and the Nissan ENV 200, which sold 66 units. In terms of plug-in hybrid cars, the most sold Mercedes-Benz GLC 350 e was 60 units, the Mitsubishi Outlander PHEV 27 units and the Hyundai Ioniq Plug-in Hybrid 26 units.[17]

Currently, in order to replace the state support scheme for electromobility, the Ministry of Environment of the Slovak Republic has announced a scheme for the municipality to which is allocated 1 mil. € and which should support the procurement of around 30 electric cars. Public sector support, with a contribution of 95% of the purchase price of the vehicle, is a great disparity in the efficiency of spending compared to the end-user scheme for the general public. The purchase of electric cars in Slovakia is mainly affected by the monthly cost of electric, gasoline and diesel cars. Based on the Car Cost Index, which compares ownership and operation costs for all types of cars in 21 European countries, Slovaks have an electric car monthly up to € 955 per month, with only € 597 in Hungary, the lowest amount among European Union countries. The average monthly cost in the European Union for electric cars is € 819 (see Figure 6).[16] The analysis of May 2018 has shown that riding on electric cars is becoming cost-competitive in several European countries, in particular due to the disadvantage of in-car engines. Since the price of electric cars is higher than gasoline or diesel cars, the difference between the purchase price and the selling price in the future is also greater. But by gradually lowering the purchase price, the value of depreciation should decrease, while fuel savings will be maintained. The cost of using electric cars is lower than in the case of cars with a combustion engine in Norway and the Netherlands. In Belgium and the UK, the difference in overall costs is rapidly decreasing. The cost of electric cars varies greatly by country. In Poland, the ownership and operation of an electrified car monthly is € 448, in Italy € 761. The cheapest country for using a gasoline car 353 € and a diesel car 363 € is Romania. When analysing the monthly costs of electric, gasoline and diesel cars in V4 countries, the cost of electric cars is highest in the Slovak Republic 955 € and in the Czech Republic it is 800 €. (Figure 7)

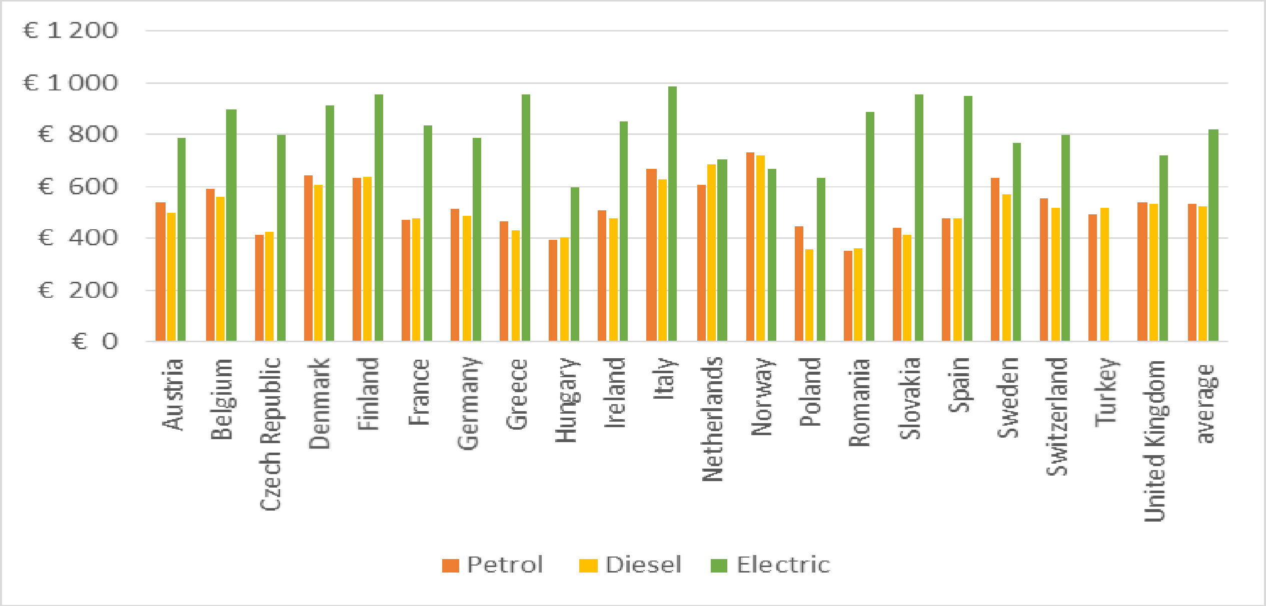

Figure 6: Monthly operation expensies by car type in EU countires
Source: processed by https://www.leaseplan.com/corporate/news-and-media/newsroom/2018/car%20cost%20index

The monthly cost of diesel cars is highest in the Czech Republic of 425 €, the lowest in Poland is 359 € and the monthly cost of gasoline cars is the lowest in Hungary of 393 €. Overall, the cost of their operation is the highest in the Slovak Republic. Costs are calculated based on fuel / energy consumption data reported by manufacturers. Owners of electric cars pay higher taxes, on average 131 € / month, mainly due to higher road tax and VAT, as there is a higher purchase price of the vehicle. In the case of combustion engines it is slightly more than 100 €.

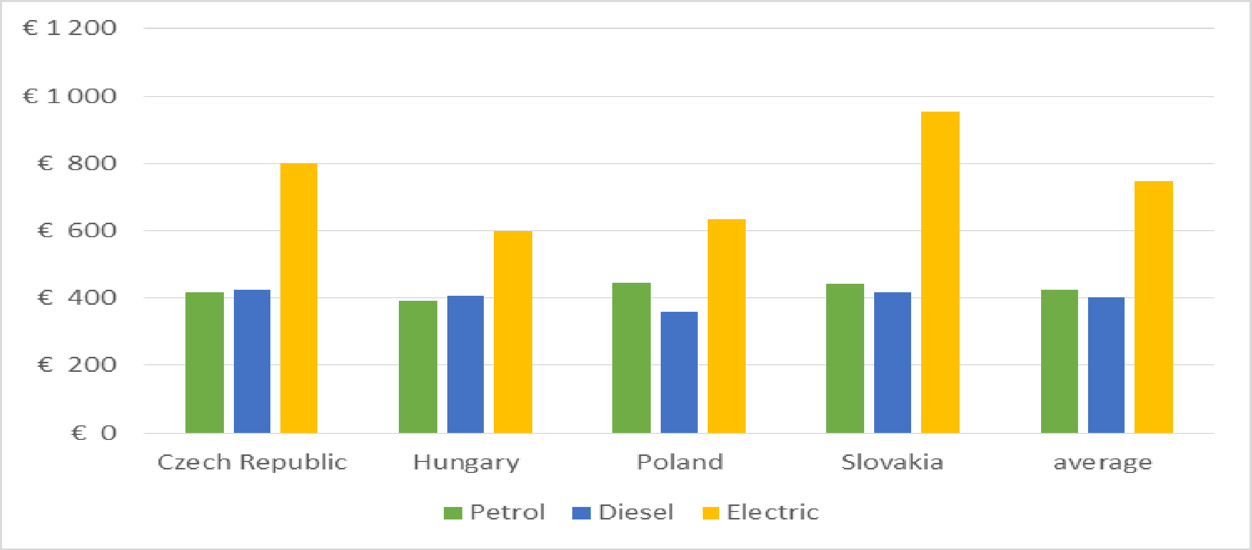

Figure 7: Average monthly costs by car type in V4 countires (in €) [16]
Source: own figure

In the paper, we note that there is a low interest in the purchase of an electric car in Slovakia. In the survey, we examined the reasons for this low interest on the selected sample of 35 – 40 year olds from the Bratislava region. A survey of 365 respondents found that for 42.4 % of respondents there was a high price barrier for electric car procurement, 31.4 % of respondents had a problem with electric cars driving range, 22.5 % of respondents saw a problem in the lack of charging stations in remote municipalities from the economic center and 3.7 % of respondents give other reasons.

To test the real efficiency of electric cars, we took test trips on the Mercedes Benz E350e borrowed vehicle. According to the label, we would assume that it is a electric power-driven vehicle, but in this case it is a plug-in hybrid - a petrol engine + electric motor. The manufacturer reports an average consumption of 2.1 – 2.5 l / 100 km and an electric range of about 40 km. With these parameters, the vehicle appears to be highly efficient and excellent for managers, but also as a family vehicle. In our test we travelled through the city (Bratislava) and then a longer route to Banska Bystrica and back. In pure urban traffic, we've set the vehicle on an electric drive to measure real-life driving. In any case, we did not get to the declared values, but the actual mileage was 18 – 21 km, then the vehicle went into the hybrid, respectively petrol mode. When driving outside the city, we used a hybrid drive, a combination of an electric drive and a gasoline. The bus to the fully charged battery and the refuelling 40 litre tank was around 620-650km with an average consumption of about 4.5 l / 100 km. Of course, we also tried to drive outside the city on a pure gasoline propulsion along with recharging batteries and their subsequent use in the city. Consumption, of course, rose to about 6 – 6.5 l and the batteries were recharged after approximately 100 – 120 km. The vehicle uses a petrol engine powered alternator to recharge, on the one hand, it recovers energy while braking and at the same time also converts the residual heat to electricity.

We can say that the value of the manufacturer far outweighs the reality, but the drive itself would be greatly usable in today's conditions for people coming to the city to work – at home in the garage I will charge the vehicle and on arrival to work it will be charging there as well as for longer journeys, where we do not have to rely on electric drive, but we will use gasoline. It is the ideal solution that helps reduce emissions in cities and at the same time solves the shift from classic engines (gasoline / diesel) to new, more environmentally friendly ways of motoring. The tested model had a relatively low mileage, but there are competing vehicles on the market with a real surge of electric drive with the same concept - the hybrid plugin. For example, the BMW 350e has a real dazzle in the city on a pure electric drive of about 28 – 30km and the total ride is about 650 – 680 km. The great advantage of a hybrid vehicle plug-in is its ability to recharge at home as well as in electric cars as well as at commercial recharging stations that are gradually increasing and still relatively many of them available for free or at a minimum charge.

Conclusions

The transportation sector is one of the largest employers, on the other hand, it is the biggest polluter of the environment. In the paper, we looked at electromobility, which, according to the European Transport Strategy 2050, should be one of the important steps to reduce emissions in cities. According to the strategy, in the cities until 2050 only electric cars should be driven, where the most emissions are produced in city hubs. Electromobility is a very important topic in the European Union and Slovakia over these months and should be seen not only as an ordinary substitution for conventional cars, but also as one of the pillars of the autonomous mode of transportation, since it will be carried out according to the requirements of the customers. What is primarily related to the needs of people who share the idea of a shared economy, singles live and therefore either do not need to own a car, or they can carry a small electric car. The reason why people will want to buy electric cars will also be the fact that the European Commission has adopted new legislation to change the use of motorways throughout the European Union. Highway tolls will take into account the type of vehicle and will be particularly advantageous for electric cars. Finally, we can state that the electrification of the transport sector offers the opportunity to use energy produced from renewable sources, thereby reducing dependence on oil, electric vehicles emitting lower levels of carbon dioxide and air pollutants, thus contributing to decarbonisation of road transport and improvement of air quality.

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Environmentálna politika Európskej únie a elektromobilita

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Súhrn

Globalizačné trendy vplývajú na nárast cestnej osobnej a nákladnej dopravy, čo má pozitívny vplyv na kvalitu uspokojovania potrieb obyvateľov, no má negatívne dopady životné prostredie. V súčasnosti sú preto vyvíjané a aplikované technológie zamerané na znižovanie negatívnych vplyvov dopravy a automobilizmu na životné prostredie. Spoločnosť vyvíja tlak na automobilové spoločnosti, na vývoj automobilov s čo najnižšími emisiami. Tento trend je silne podporovaný Európskou úniou, ktorá chce výrobcov automobilov novými opatreniami stimulovať práve k investíciám do nových technológií na zníženie emisií CO_2 *a NOx. Smerovanie a priority vyvíjaných a aplikovaných technológií sú však závislé aj od ekonomického vývoja, politických a legislatívnych faktorov. V príspevku sa venujeme vývoju elektromobilov, analyzujeme ich predaj v Európskej únii a na príklade Slovenska uvádzame, že je elektromobilita závislá od príjmov, zároveň sme si vyskúšali možnosti, ktoré dnes ponúkajú renomovaní producenti áut. Sklamaním je, že rovnako ako pri klasických pohonoch, aj pri ekologicky šetrnejších deklarujú iba výsledky z laboratórnych podmienok, čo môže výrazne ovplyvniť razantnejší nástup ekologických dopravných prostriedkov. Vzhľadom na výšku kúpnej ceny elektrických vozidiel na Slovensku je pravdepodobnejšie, že kupujúci budú aj naďalej uprednostňovať vozidlá na klasický pohon, hoci hybridné ako aj čisté elektrické vozidlá sú už z hľadiska nákladov na palivo efektívnejšie.*

***Kľúčové slová**: Doprava, elektromobily, emisie, investičná náročnosť.*

How can calculation methods affect a common EU target for municipal waste recycling?

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Abstract

The paper discusses municipal waste strategies for approaching the European Union (EU) recycling targets that were set out in the Commission Decision (2011/753/EU) focused on establishing rules and calculation methods for these targets. We analyse the calculation of recycling targets for municipal waste in 2010 – 2015 by using four calculation methods for the EU member states. We try to assess the differences in interpretations of the EU municipal waste (MW) definitions and the impact that the different recycling rate calculation methods may have on final recycling figures. We discuss significant inconsistencies in the data collection methods as well as interpretations of the definition of MW used to support the decision of the European Parliament from 14 March 2017 claiming that the calculation of recycled MW should be based on one harmonised method that would prevent member states from reporting scrap[1] as recycled waste.

***Keywords:** municipal waste; household waste, mixed municipal waste, recycling rates, recycling calculation methods, circular economy*

Introduction

The European Commission's 2015[1] Circular Economy Action Plan, adopted by the European Parliament on 14 March 2017 regarding the proposal for a directive of the European Parliament and of the Council amending Directive 2008/98/EC on waste COM(2015)0595 – C8-0382/2015 – 2015/0275(COD) brought new challenges for municipal waste (MW) management in Europe, which had become increasingly complex over the last decade[2]. This complexity is to some extent caused by the introduction of additional facilities for pre-treating waste, mainly mechanical biological treatment, and for sorting for recovery. There are also some legal requirements for increasing the recovery of certain waste streams, resulting in increasing cross-order transportation of waste for recovery. Moreover, on 14 June 2018 new waste package has been published in official journal of the European Union with deadline for entry into force 5 July 2020.

Waste policies and targets set at the European Union (EU) level include minimum requirements for managing certain waste types. The most relevant targets for MW are: the Landfill Directive's[3] landfill diversion targets for biodegradable MW; the Packaging and Packaging Waste Directive's[4] recycling targets; and the Waste Framework Directive's (WFD) target[5] for recycling and preparing for reuse (more precisely, the target applies to specific types of household and similar waste). EU member states can choose from among four different methods to monitor their progress towards the most recent target[6]; each monitoring method establishes rules and calculation methods for verifying compliance with the target (a) in Article 11(2) of the WFD, i.e. the target of recycling 50 % of municipal waste by 2020 (55 % by 2025, 60 % by 2030 and 35 % by 2035). In addition, stricter rules for calculating recycling rates will

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[1] Scrap is the discarded or rejected material from an operation suitable for reprocessing.

help to better monitor real progress towards the circular economy. The comparability of available EU member state data and indicators may be limited in some cases. There are differences in MW definitions, reported waste types, and data processing. For example, some member states only include waste from households, whereas others may include similar waste from commercial activities and offices[7-10]. Depending on national waste management and waste data collection systems, the approaches for MW data collection established in the member states vary to a large extent, thus hampering data comparability across countries.

We analyse the definitions of MW applied by EU member states. Some member states have changed their definition of MW over time, and recycled amounts can be calculated differently depending on whether they include the weight of materials collected but discarded during the recycling process[7,9]. We present an analysis of the calculation of recycling targets for MW in 2010 – 2015 using the four calculation methods outlined in the EC Decision[6] for all EU member states. We try to assess the differences in interpretation of the EU MW definitions[5-6,11] and the impact that different recycling rate calculation methods may have on the final recycling values presented by Eurostat[1]. We discuss significant inconsistencies in the data capture and the interpretation of the definition of MW to support the decision of the European Parliament (EP) from 14 March 2017[12] on four Directives[4-5,13] concerning waste management, mainly waste from households and small firms, representing 8 % of total waste. These plans produced by the EP are the first step towards creating a circular economy[14] in which products are designed to facilitate reuse. The key issues include how ambitious the targets should be for recycling rates[6], and how much to limit landfilling, which is probably the most harmful method of waste disposal. The following research questions were set:

RQ1: How does the definition of MW affect the results of recycling targets?

RQ2: How do calculation methods affect the target for municipal waste recycling?

The paper is structured to present answers to these two research questions: the first sub-chapter provides a concise description of the material and the scientific methods used, focusing on data and sources. The second part of the paper contains the evaluation and exact description of the achieved results and their discussion with previously published papers. Furthermore, we outline the need for further solutions, and the importance of developing this field in research society, and practice. The concluding part of the paper provides a concise summary of the most important findings in relation to the paper focus.

Materials and Methods

The research was carried out on data collected for 2010 – 2015. The sample consists of the 28 EU 28 member states, as well as Norway, Switzerland, and Iceland.

European Waste Classification for Statistics and European List of Waste

Waste statistics data were collected in the EU on the basis of an OECD/Eurostat joint questionnaire (JQ) until the adoption of Regulation (EC) 2150/2002[15-16], the Waste Statistics Regulation. Municipal waste (MW) includes household waste and similar waste explained in detail in Annexes I and II[11,17-18] from origination, collecting, and waste materials[2].

To understand how consistently the definition of MW is applied across the 28 EU member states, an analysis was carried out[7,10] to compare the situation in the member states, focusing on which materials each member state includes in its definition of MW and on their recycling rate calculations (Table 1).

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[2] The most comprehensive definition for statistics on MW is still the simple definition provided by the OECD/Eurostat JQ (Eurostat, 2016): Municipal waste covers household waste and waste similar in nature and composition to household waste.

Table 1: Waste materials included in the national definitions of MW

Main Material Category	*Material Subcategory*	*Country*
Residual waste, bulky waste	Reused products	Finland, Ireland
	Material recyclables (paper and cardboard, textiles, plastics, glass, metals, and other recyclables, such as wood waste)	EU-28
	Packaging waste from the private sector	EU-28 except for the Czech Republic, Estonia, Finland, France, Germany, Latvia and Romania
	Biowaste (food waste and garden waste)	EU-28
	Hazardous household waste	EU-28 *except* for Cyprus
Waste from municipal services comprises the following fractions:	Street sweepings	EU-28
	Biowaste (garden and park waste, maintenance of roadsides, cemetery waste)	EU-28
	Kitchen and canteen waste	EU-28
Waste from commerce and trade, small businesses, office buildings and institutions	Collected by households or by municipal services	EU-28
	Collected by private sector	EU-28 *except* for Latvia, Netherlands and Spain
Other waste from municipal services	C&D waste	Romania
	Waste from municipal sewage networks and treatment	Germany, Romania

Source: Greenfield, 2015 and authors

The Waste Statistics Regulation obliges the member states to report statistical data on waste generation and waste treatment according to the European Waste Classification for Statistics (EWC-Stat). The EWC-Stat is a mainly substance-oriented aggregation of the waste types defined in the European List of Wastes (LoW)[5]. The result is a 1:n - relationship between EWC-Stat and LoW which allows for the unambiguous conversion of the waste types classified according to the LoW into the EWC-Stat waste categories. The transposition table between the EWC-Stat and the LoW is established in Annex III of the (EC) 2150/2002[15-16], the Waste Statistics Regulation[16]. The EWC-Stat categories that have to be reported to Eurostat are set out in section 2 of Annexes I and II[10]. Whereas the Waste Statistics Regulation stipulates that the EWC-Stat has to be used for reporting the data to Eurostat, it does not prescribe a specific classification to be used for data collection. Countries may use any waste classification as long as they can produce the defined formats in the quality required. In practice, most of the countries collect their data according to the LoW and convert it subsequently into the required EWC-Stat categories based on the transposition table in Annex III of the Waste Statistics Regulation[10]. The direct use of the EWC-Stat for data collection is applied only by few countries. For the countries that use the EWC-Stat for data collection, the guidance document[2] is particularly help in clarifying which wastes are covered by the defined reporting categories.

Recycling target calculation methods

To verify compliance with the MW target set in Article 11(2)(a) of the WFD[5], EU member states would apply a recycling target to one of the following:

1) the preparation for reuse and recycling of paper, metal, plastic, and glass household waste;
2) the preparation for reuse and recycling of paper, metal, plastic, glass household waste, and other single types of household waste or similar waste from other origins;
3) the preparation for reuse and recycling of household waste;
4) the preparation for reuse and recycling of municipal waste.

The EC Decision[6] specified the use of one of four calculation methods for the calculation of the recycling target:

1) Calculation method 1 (in %):

Recycling rate of paper, metal, plastic, and glass household waste =
(Recycled amount of paper, metal, plastic, and glass household waste)
/ (Total generated amount of paper, metal, plastic, and glass household waste)

2) Calculation method 2 (in %):

Recycling rate of household and similar waste =
(Recycled amount of paper, metal, plastic, and glass waste and other single waste streams from households or similar waste streams)
/ (Total generated amount of paper, metal, plastic, and glass waste and other single waste streams from households or similar waste)

3) Calculation method 3 (in %):

Recycling rate of household waste =
(Recycled amount of household waste)
/ (Total household waste amounts excluding certain waste categories)

4) Calculation method 4 (in %):

Recycling of municipal waste =
(Municipal waste recycled)
/ (Municipal waste generated)

Results and discussion

The possibility of using four calculation methods regarding the 2020 recycling target for MW is maintained mainly because of legal certainty and to minimize any short-term disruption to the waste management plans adopted by several EU member states. The method used to determine the recycling rate differs for every EU member state[7,9-10].

Table 2 summarizes these methods for 28 EU member states, Norway, Switzerland, and Iceland. This table does not cover the potential of recycling materials from mixed municipal waste (MMW). There is a great deal of additional recycling potential in the MMW (mainly the household waste) produced by member states. The additional recycling potential concerns particularly separately collected paper and cardboard, plastic, and biowaste. Member states calculate this potential with different weights. Table 2 shows that methods 2 and 4 have been adopted by 23 of the 31 states of the European Free Trade Association (EFTA) that were considered. Focusing on the aspect of certain waste types similarity to household waste, Eurostat's Guidance on municipal waste data collection[11] offers an option allowing the scope of MW to be expressed in terms of the European LoW[18].

Table 2: Methods of calculating MW recycling rate in different countries of the European Free Trade Association in 2015

Method 1	**Method 2**	**Method 3**	**Method 4**	**Method**
Recycling rate of paper, metal, plastic, and glass household waste [%]	**Recycling rate of household and similar waste [%]**	**Recycling rate of household waste [%]**	**Recycling of municipal waste [%]**	**Currently not signed up to one of the four methods**
Ireland Malta	Austria Croatia Cyprus Czechia Estonia France Greece Hungary Italy Lithuania Poland Portugal Romania Slovakia Sweden	Bulgaria Luxembourg United Kingdom	Belgium Denmark Finland Germany Latvia Netherlands Slovenia Spain	Norway Switzerland Iceland
2	15	3	8	3

Source: EEA (2015) and authors

This option is based on the principle that the scope of MW includes household waste and similar waste types generated by sources other than households, regardless of whether municipalities or private actors are responsible for their collection. Recent experience demonstrates that a relevant number of member states include amounts of mixed municipal waste (MMW) (i.e. LoW code 20 03 01) from all business economy sector - NACE Rev. 2[19] activities in the MW data (group 38 of NACE). Furthermore, one can argue that the overall target is to reduce the unsorted MMW or residual household waste (RHW), regardless of its origin. If this is to be done, it is consistent to cover the separately collected fractions from all origins as well. Source-segregated material fractions found in residual household waste (EWC-Stat/version 4 code 10.1) are considered as mis-sorted waste fractions. Housing types are divided into single-family and multi-family houses. Here, the term ‘single-family house’ corresponds to households with their own residual waste bin, while ‘multi-family house’ corresponds to households sharing residual waste bins, e.g. common containers in blocks of flats. Therefore, the starting point for the waste types to be included are the waste codes listed in Chapter 20 of the LoW, with some additions from subchapter 15 01[18]. When discarded items are handed over to the waste management system, they are classified as a certain waste type, ideally by 6-digit codes according to the LoW[18] or another (national) classification. The weight and code are usually registered at the weighbridge of a waste management facility. Thus, the key to any definition of MW is certainly the material classification of the waste, since this classification best determines its similarity to household waste ‘in nature and composition’.

The scope of recycled MW materials is based on selected LoW codes, which are specified in Table 3 along with EWC-Stat/Version 4 codes for recycling target calculation, as member states have to submit an annual national waste report based on the Waste Statistics Regulation[16]. Member state implementation reports on MW recycling targets should comply with the specific requirements set out in Annexes I and II[6], see Table 3. However, member states may use different weights for collected waste materials (specified by LoW codes). Eurostat has collected and published data on MW since 1995. These data are widely used for comparing MW generation and treatment in different countries, and indicators relevant to MW are used to monitor European waste policies[20]. The data on MW expressed in kilograms per capita are part of a set of indicators compiled annually to monitor the EU’s sustainable development strategy[2].

Table 3 Municipal waste materials and relevant LoW and EWC-Stat/Version 4 codes for calculation methods 1, 2, and 3 of Annex II (EC, 2011)

Waste materials	*LoW code according to (EC, 2011)*	*EWC-Stat codes according to (EC, 2002, 2010)*
Paper and cardboard	20 01 01, 15 01 01	07.2
Metals	20 01 40, 15 01 04	06
Plastic	20 01 39, 15 01 02	07.4
Glass	20 01 02, 15 01 07	07.1
Biodegradable kitchen and canteen waste	20 01 08	09 (excl. 9.11, 9.3)
Biodegradable garden and park waste	20 02 01	09 (excl. 9.11, 9.3)
Non-biodegradable garden and park waste	20 02 02, 20 02 03	12 (excl. 12.4, 12.6)
Wood	20 01 38, 15 01 03	07.5
Textiles	20 01 10, 20 01 11, 15 01 09	07.6
Batteries	20 01 34, 20 01 33*	08.41
Discarded equipment	20 01 21*, 20 01 23*, 20 01 35*, 20 01 36	08 (excl. 08.1, 08.41)
Other municipal waste	20 03 01, 20 03 02, 20 03 07, 15 01 06	10.1, 09 (excl. 9.11, 9.3)

Source: (EC, 2011; Eurostat, 2012)

Table 4: Municipal waste generated by country in selected years in kilograms per capita

	1995	*2000*	*2005*	*2010*	*2015*
EU-28	-	521	515	504	477
EU-27	473	523	517	505	477
Belgium	455	471	482	456	419
Bulgaria	694	612	588	554	419
Czechia	302	335	289	318	316
Denmark	521	664	736	-	789
Germany	623	642	565	602	625
Estonia	371	453	433	305	359
Ireland	512	599	731	624	-
Greece	-	412	442	532	-
Spain	505	653	588	510	434
France	475	514	530	533	502
Croatia	-	262	336	379	393
Italy	454	509	546	547	486
Cyprus	595	628	688	689	638
Latvia	264	271	320	324	433
Lithuania	426	365	387	404	448
Luxembourg	587	654	672	679	625
Hungary	460	446	461	403	377
Malta	387	533	623	601	624
Netherlands	539	598	599	571	523
Austria	437	580	575	562	560
Poland	285	320	319	316	286
Portugal	352	457	452	516	-
Romania	342	355	383	313	-
Slovenia	596	513	494	490	449
Slovakia	295	254	273	319	329
Finland	413	502	478	470	500
Sweden	386	428	477	439	447
United Kingdom	498	577	581	509	485
Iceland	426	462	516	481	:
Norway	624	613	426	469	421
Switzerland	600	656	661	708	725

Source: Eurostat[22-26]

Table 4 shows municipal waste generation by EU and EFTA countries expressed in kilograms per capita. To illustrate the trends, Table 4 shows generated MW for selected years, covering the period 1995 to 2015.

Using data from Eurostat, we can calculate the recycling of MW by country in kilograms per capita and the MW recycling rate by country as a percentage of generated MW in the period 2010-2015 (Table 5).

Table 5: Shared recycling of MW by EFTA countries in kilograms per capita [kg/citizen] and as a percentage of total MW [%] in 2010 – 2015

Country	***2010***		***2011***		***2012***		***2013***		***2014***		***2015***	
	kg/ cit.	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*
EU-28	124	24.6	128	25.7	130	26.8	128	26.8	134	28.1	137	28.7
EU-27	125	24.8	129	25.8	131	26.9	129	26.9	135	28.1	137	28.7
Ireland	200	32.0	188	30.5	181	30.8	-	-	-	-	-	-
Malta	32	5.2	46	7.8	45	7.7	48	8.1	45	7.4	42	6.7
Calculation method 1	***116.0***	***18.6***	***117.0***	***19.2***	***113.0***	***19.3***	***48.0***	***8.1***	***45.0***	***7.4***	***42.0***	***6.7***
Austria	152	27.1	137	23.8	139	23.9	142	24.5	144	25.5	144	25.7
Croatia	12	3.3	29	7.5	51	13.2	54	13.2	56	14.4	64	16.3
Cyprus	74	10.7	85	12.6	81	12.3	81	13.1	83	13.5	85	13.3
Czechia	43	13.6	47	14.8	63	20.6	65	21.3	70	22.6	81	25.5
Estonia	31	10.1	44	14.5	40	14.0	37	12.7	95	26.6	89	24.7
France	95	17.8	111	20.6	110	21.1	111	21.5	112	22.1	112	22.3
Greece	78	14.7	75	14.9	79	15.6	-	-	-	-	-	-#
Hungary	64	15.9	66	17.2	84	20.9	81	21.4	94	24.3	98	25.9
Italy	103	18.8	120	22.8	121	23.9	122	24.8	127	26.1	126	25.9
Lithuania	14	3.4	81	18.2	87	19.6	88	20.4	91	21.1	103	22.9
Poland	47	14.8	31	9.7	33	10.3	39	13.3	57	21.1	75	26.4
Portugal	59	11.3	56	11.5	52	11.5	57	12.9	74	16.2	-	-
Romania	8	2.6	9	3.3	8	3.3	11	4.2	13	5.2	14	5.7
Slovakia	18	5.7	19	6.2	26	8.4	20	6.6	16	5.1	25	7.6
Sweden	151	34.4	149	33.1	147	32.7	150	33.4	146	33.4	145	32.4
Calculation method 2	***63.3***	***13.6***	***70.6***	***15.4***	***74.7***	***16.8***	***75.6***	***17.4***	***84.1***	***19.8***	***89.3***	***21.1***
Bulgaria	136	24.5	122	24.0	103	22.3	108	25.1	94	21.2	80	19.0
Luxembourg	183	27.0	188	28.4	182	27.7	174	28.4	178	28.4	178	28.4
United Kingdom	129	25.3	129	26.2	128	26.9	132	27.4	132	27.3	132	27.2
Calculation method 3	***149.3***	***25.6***	***146.3***	***26.2***	***137.7***	***25.6***	***138.0***	***27.0***	***134.7***	***25.6***	***130.0***	***24.9***
Belgium	153	33.6	155	33.9	144	32.2	138	31.6	141	33.0	143	34.3
Denmark	-	-	213	27.3	203	25.7	205	26.0	212	26.9	215	27.3
Finland	92	19.7	110	21.8	109	21.5	94	19.0	87	18.0	141	28.1
Germany	**275**	**45.6**	**288**	**46.1**	**293**	**47.4**	**286**	**46.6**	**300**	**47.6**	**299**	**47.8**
Latvia	28	8.8	30	8.6	41	13.7	71	20.2	85	23.4	92	21.2
Netherlands	142	24.8	137	24.2	131	23.9	126	23.9	125	23.7	129	24.6
Slovenia	**99**	**20.2**	**126**	**30.3**	**131**	**36.3**	**116**	**28.0**	**126**	**29.0**	**208**	**46.4**
Spain	90	17.6	81	16.7	91	19.5	70	15.5	76	16.9	73	16.8
Calculation method 4	***32***	***5.2***	***46***	***7.8***	***45***	***7.7***	***48***	***8.1***	***45***	***7.4***	***42***	***6.7***
Norway	*111.0*	*20.4*	*118.0*	*22.3*	*122.0*	*24.8*	*119.5*	*23.7*	*126.2*	*24.7*	*140.5*	*27.3*
Switzerland	125	26.5	121	24.9	124	25.9	116	23.4	110	26.1	110	26.2
Iceland	239	33.7	238	34.6	241	34.8	236	33.6	238	32.6	231	31.9

Source: Authors based on Eurostat [22-26]

It will be very difficult for most European countries to reach the 50% recycling target in 2020 when the recycling rate for the EU-28 was 28.7 % in 2015: linear extrapolation suggests the rate will be 32.6 % in 2020. This is especially likely to be true if Eurostat[11] does not recommend adding the amount of composted or fermented MW to the recycling rate. The exception among European countries is Germany; its high recycling rates will enable it to reach a 50 % recycling rate in 2020.

Table 6: Shared recycling and composting of MW by EFTA countries in kilograms per capita [kg/citizen] and as a percentage of total MW [%] in 2010 – 2015

Country	*2010*		*2011*		*2012*		*2013*		*2014*		*2015*	
	kg/ cit.	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*	*kg/ cit.*	*%*
EU-28	193	38.3	197	39.6	202	41.5	202	42.2	209	43.7	215	45.0
EU-27	194	38.5	198	39.8	203	41.7	203	42.4	211	43.9	216	45.2
Ireland	223	35.7	222	36.1	215	36.6	-	-	-	-	-	-
Malta	32	5.2	53	9.0	57	9.7	48	8.1	45	7.4	42	6.7
Calculation method 1	***127.5***	***20.5***	***137.5***	***22.6***	***136.0***	***23.2***	***48.0***	***8.1***	***45.0***	***7.4***	***42.0***	***6.7***
Austria	**334**	**59.4**	**325**	**56.7**	**335**	**57.7**	**334**	**57.7**	**319**	**56.3**	**319**	**56.9**
Croatia	15	4.0	32	8.3	57	14.7	61	14.9	64	16.5	71	18.0
Cyprus	74	10.7	85	12.6	89	13.6	90	14.6	104	17.0	115	17.9
Czechia	50	15.8	54	17.0	71	23.2	74	24.2	79	25.4	94	29.7
Estonia	55	18.2	71	23.3	54	19.1	52	17.9	112	31.3	102	28.3
France	186	34.9	199	36.9	197	37.8	199	38.6	199	39.2	199	39.5
Greece	91	17.1	91	18.0	98	19.3	-	-	-	-	-	-
Hungary	79	19.6	84	22.0	102	25.5	100	26.4	118	30.5	121	32.2
Italy	170	31.0	187	35.5	194	38.4	194	39.4	207	42.5	212	43.5
Lithuania	20	4.9	89	19.9	104	23.5	120	27.8	132	30.5	149	33.1
Poland	68	21.4	56	17.5	63	19.6	71	24.2	87	32.3	121	42.5
Portugal	97	18.7	98	20.1	118	26.1	114	25.8	138	30.4	-	-
Romania	40	12.8	31	11.7	37	14.8	34	13.2	33	13.1	32	13.1
Slovakia	29	9.1	32	10.3	41	13.3	33	10.8	33	10.3	49	14.9
Sweden	211	48.1	213	47.3	212	47.2	219	48.7	218	49.9	215	48.0
Calculation method 2	***101.3***	***21.7***	***109.8***	***23.8***	***118.1***	***26.3***	***121.1***	***27.4***	***131.6***	***30.4***	***138.4***	***32.1***
Bulgaria	136	24.5	133	26.2	116	25.0	123	28.5	102	23.1	123	29.4
Luxembourg	316	46.5	308	46.4	310	47.4	285	46.6	299	47.7	302	48.0
United Kingdom	205	40.2	207	42	203	42.6	208	43.3	211	43.7	211	43.5
Calculation method 3	***219.0***	***37.1***	***216.0***	***38.2***	***209.7***	***38.3***	***205.3***	***39.5***	***204.0***	***38.2***	***212.0***	***40.3***
Belgium	**250**	**54.9**	**248**	**54.3**	**237**	**53.1**	**230**	**52.7**	**228**	**53.2**	**223**	**53.4**
Denmark	-	-	324	41.5	333	42.1	341	43.2	356	45.1	365	46.3
Finland	154	32.8	176	34.8	169	33.3	161	32.5	157	32.5	203	40.6
Germany	**376**	**62.5**	**394**	**63.0**	**403**	**65.2**	**392**	**63.8**	**414**	**65.6**	**413**	**66.1**
Latvia	30	9.4	34	9.7	47	15.8	91	25.9	98	27.0	116	26.7
Netherlands	**281**	**49.2**	**278**	**49.1**	**271**	**49.4**	**263**	**49.8**	**268**	**50.9**	**271**	**51.7**
Slovenia	**110**	**22.4**	**148**	**35.6**	**152**	**41.9**	**144**	**34.8**	**156**	**36.0**	**242**	**54.1**
Spain	149	29.2	130	26.7	139	29.8	147	32.5	138	30.8	144	33.3
Calculation method 4	***183.3***	***34.3***	***193.3***	***36.5***	***196.8***	***39.2***	***199.7***	***39.9***	***205.2***	***40.5***	***231.5***	***45.4***
Norway	198	42.1	194	39.9	190	39.8	194	39.2	178	42.2	180	42.8
Switzerland	**357**	**50.5**	**345**	**50.1**	**347**	**50.0**	**358**	**51.0**	**391**	**53.5**	**382**	**52.7**
Iceland	100	20.9	125	25.3	144	28.0	155	29.9	160	29.7	-	-

Source: Authors based on Eurostat [22-26]

Germany's recycling rates are driven by its waste management policy and initiatives. EU legislation under the WFD[5], for example, sets the policy framework and targets for recycling in Germany, which was one of the first European countries to limit landfilling and introduce schemes for collecting packaging waste, bio-waste, and waste paper separately. The shared recycling and composting or fermentation rates for MW in European countries in the period 2010 – 2015 is shown in Table 6.

For 2015, the recycling and composting or fermentation rates for MW vary between member states considerably, ranging from 66.1 % in Germany to 6.7 % in Malta. The EU-28 average was 45.2 %. The variations reflect differences in applied technologies, but depend also on how MW is collected, sorted, and managed. Linear extrapolation suggests the average EU-28 rate would reach 51.8% in 2020. In 2015, five EU member states achieved the WFD's 50 % EU recycling target; nevertheless, they did so by including biowaste, which was composted/fermented in the calculations: Austria (56.9 %) (method 2), Germany (66.1%), Belgium (53.4 %), Slovenia (54.1) and the Netherlands (51.7 %) (method 4). Table 6 also shows that methods 3 and 4 have higher average recycling rates than methods 1 and 2. Member states using method 4 in particular have higher recycling rates. Only Latvia has a recycling rate lower than 30 % (26.7 %).

Table 7 shows the sum of household and similar waste generated by households by year in waste categories 10.1 defined by EWC-Stat 4[15-17], and shows this sum as a percentage of total generated MW.

Table 7: Waste generated by households in EU countries by year (in EWC-STAT 4 waste categories 10.1) in kilograms per capita and as a percentage of total MW generation

Country	*2010*		*2012*		*2014*	
	kg/ cit.	*% of MW*	*kg/ cit.*	*% of MW*	*kg/ cit.*	*% of MW*
EU-28	275	62.9	260	61.2	243	59.1
Belgium	147	26.9	174	31.6	169	33.6
Bulgaria	324	67.9	262	69.5	274	73.9
Czechia	258	81.1	241	78.2	231	74.5
Denmark	334	52.2	336	56.4	316	52.1
Germany	197	44.4	194	42.8	192	42.1
Estonia	122	37.8	128	38.8	153	41.7
Ireland	303	79.9	287	79.5	256	77.6
Greece	413	88.4	377	85.7	363	87.7
Spain	413	82.9	380	83.7	365	84.1
France	278	61.5	270	59.0	252	58.6
Croatia	-	-	246	88.2	238	86.9
Italy	361	65.9	309	61.3	275	56.4
Cyprus	-	-	119	22.8	86	17.7
Latvia	187	56.5	301	50.5	208	58.4
Lithuania	244	60.0	261	66.2	256	64.6
Luxembourg	222	45.0	208	44.3	197	45.1
Hungary	236	82.5	220	81.5	260	87.0
Malta	278	77.0	233	65.4	236	65.4
Netherlands	265	48.4	253	47.8	236	46.7
Austria	180	32.5	196	41.1	198	40.6
Poland	220	94.0	228	93.1	181	83.4
Portugal	470	91.3	413	91.8	410	90.5
Romania	220	86.3	186	82.3	176	91.7
Slovenia	247	69.6	174	55.8	134	49.1
Slovakia	270	84.6	255	83.3	258	80.6
Finland	160	51.1	178	55.6	138	46.9
Sweden	230	53.4	241	54.8	173	40.2
United Kingdom	261	57.2	238	55.3	229	53.4

Source: Authors based on Eurostat [22-26]

Household and similar waste (EWC-STAT 4 code 10.1) present the sum of the amount of waste corresponding to the following LoW codes: 20 03 01 mixed municipal waste; 20 03 02 waste from markets; 20 03 07 bulky waste; 20 03 99 municipal wastes not otherwise specified; 20 03 03 street-cleaning residues. The data summarised in Table 7 concerning waste generated by households is considered to be RHW and mostly consists of mixed municipal waste (LoW code 20 03 01) and bulky waste (LoW code 20 03 07). It reflects the large potential for increasing the MW recycling rate in several EU member states with respect to the composition of collected MMW, which is mostly disposed of via landfilling[3].

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[3] Landfilling of waste makes no sense in a circular economy and can pollute water, soil and air. By 2035 the amount of municipal waste landfilled must be reduced to 10% or less of the total amount of municipal waste generated.

Conclusions

There are large differences among EU member states with respect to their waste management performance, particularly regarding the recycling of MW. On 14 March 2017 the EP proposed that the member states that recycled less than 20% of their MW in 2013 (see Table 5), and were not considered at risk of failing to achieve the target of preparing for the reuse and recycling of at least 55% of their MW by 2025, should be given additional time to comply with the preparations for the reuse and recycling targets established for 2025[21]. Those member states could also be given additional time to comply with the preparations for the reuse and recycling targets established for 2030, if they are not considered at risk of failing to achieve the target of reusing and recycling at least 60% of their MW by 2030[21]. In light of average annual progression rates observed in member states over the past fifteen years, those member states would need to increase their recycling capacity to the levels that are well above past averages to meet those targets. In order to ensure that steady progress towards the targets is made and that implementation gaps are tackled in time, member states that are given additional time should meet interim targets and establish implementation plans, the effectiveness of which should be assessed by the EC on the basis of defined criteria. In new waste package have been identified in the monitoring framework which will be continuously updated on the website dedicated to monitoring framework. The ten indicators are: EU self-sufficiency for raw materials, green public procurement, waste generation, food waste, overall recycling rates, recycling rates for specific waste streams, contribution of recycled materials to raw materials demand, trade in recyclable raw materials, private investments, jobs and gross value added and patents.

Germany, with high recycling rates that would enable it to reach the 50% recycling rate by 2020, is an exception among European countries. Germany’s recycling rates are driven by its waste management policy and initiatives. EU legislation under the WFD[5], for example, sets the policy framework and targets for recycling in Germany, which was one of the first European countries to limit landfilling and to introduce schemes for collecting packaging waste, bio-waste, and waste paper separately.

Despite separate collection, a lot of recyclables still end up in RHW/MMW, see Table 7. With high-quality sorting, especially optical sorting, a considerable amount of materials can be sorted from the residual waste and subsequently recycled and reprocessed into secondary raw materials. Member states should thus also take measures to ensure that waste that is not separately collected is sorted.

In order to ensure the uniform calculation of data on preparations for reuse and recycling targets, the EC should adopt detailed rules on the determination of recognised preparations for reuse operators, deposit-refund schemes, and final recycling operators, including specific rules on waste collection, traceability, verification, and reporting, as well as on the quality criteria for metals that have been recycled in conjunction with incineration or co-incineration. To calculate whether the preparations have been made for reuse and recycling targets, and after the adoption of the harmonised calculation method, EU member states should be able to consider using ways of recycling metals that take place in conjunction with incineration or co-incineration, such as energy recovery[21].

Compliance with the obligation to set up separate collection systems for paper, metal, plastic[4], glass, textile, and biowaste is essential to achieving the agreed reuse and recycling rates in EU member states. In addition, biowaste should be collected separately and recycled in order to contribute to an increase in preparations to meet target reuse and recycling rates, and to the protection of dry recyclable materials from contamination, as well as to prevent incineration and landfilling. Therefore, research on possible collection and recycling systems for other waste streams and new materials should be encouraged and intensified.

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[4] Single use plastic directive requires mandatory to produce beverage containers composed of at least 35% of recycled plastic by 2025 content; collecting up to 90 % of bottles in 2025; plastic ban in certain products; labelling requirements; fishing gear producer responsibility; obligations for producers (focus EPR) and Awareness-raising measures.

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Jak mohou metody výpočtu ovlivnit společný cíl EU pro recyklaci komunálního odpadu?

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Souhrn

Článek se zabývá strategií komunálního odpadu pro dosažení cílů recyklace Evropské unie (EU), které byly stanoveny v rozhodnutí Komise (2011/753 / EU) zaměřeném na stanovení pravidel a metod výpočtu těchto cílů. Analyzujeme 4 metody výpočtu recyklačních cílů komunálního odpadu v období 2010 - 2015 pro členské státy EU. Snažíme se zhodnotit rozdíly mezi interpretacemi definic komunálního odpadu a dopadů, které mohou mít různé metody výpočtu míry recyklace na konečné údaje o recyklaci. Diskutujeme významné nesrovnalosti v metodách sběru dat a interpretacích definice komunálního odpadu, které byla použita k podpoře rozhodnutí Evropského parlamentu ze dne 14. března 2017 a nového balíčku z 14 června 2018, podle něhož by výpočet recyklovaného komunálního odpadu měl vycházet z jedné harmonizované metody, která by členským státům bránila v hlášení výmětu jako recyklovaného odpadu.

***Klíčová slova:** komunální odpad, domácí odpad, směsný komunální odpad, miry recyklace, metody výpočtu recyklace, oběhové hospodářství.*

Vliv znečištění PET na teplotní okrajové podmínky při výrobě polymerbetonu

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Souhrn

Zpracování polyethylentereftalátu (PET) do polymerbetonu představuje alternativní metodu recyklace. Byl porovnán vliv znečištění polyethylentereftalátu (PET) na teplotní okrajové podmínky při výrobě takového polymerbetonu. Nečistoty (příměsi polyolefinů) neměly vliv na teplotu tání, avšak hrály významnou roli při tepelné degradaci. V inertní atmosféře znečištění zvyšovalo tepelnou degradaci, zatímco v oxidační atmosféře (na vzduchu) dokázalo v určitých případech vzorky tepelně stabilizovat.

Klíčová slova: recyklace, odpad, polyethylentereftalát (PET), polymerbeton.

Úvod

Během posledních let po celém světě dramaticky vzrostla produkce plastového odpadu. Tento jev je způsoben skutečností, že plasty zaujímají mnoho výhodných vlastností vzhledem k ostatním materiálům. Podle odhadů se v roce 2020 předpokládá, že objem výroby plastů na světě bude ve výši 400 milionů tun ročně, a pro rok 2050 dokonce více než 700 milionů tun. Bohužel se většina těchto materiálů spotřebuje pro jednorázové aplikace, jako jsou obalové produkty, které často končí v odpadu. Ekologická likvidace plastových odpadů je nezbytná nejen v České republice, a proto je nutné najít efektivní řešení využití plastů. Současný systém nakládání s odpady vychází ze zásad v hierarchii dle priorit: předcházení vzniku odpadu, opětovné použití výrobků, recyklaci a kompostování, energetické využití a skládkování[1].

Jedním z nejběžnějších plastů je polyethylentereftalát (PET). Jedná se o lineární semikrystalický termoplastický polyester s excelentními mechanickými vlastnostmi. Vyniká odolností vůči chemikáliím, vysokou pevností a rázovou houževnatostí, nízkou váhou, průhledností a snadnou recyklovatelností. Nejčastěji se používá k výrobě syntetických vláken a obalových lahví. Vedle široce používané mechanické recyklace PET, probíhá výzkum na různé metody chemické recyklace PET[2]. PET produkty se v přírodě rozkládají pomalu, až čtyři století. Dlouhou dobu byly považovány za nedegradovatelné za normálních podmínek, protože nebyl známý žádný organismus, který by konzumoval jeho poměrně velké molekuly. V letošním roce byl objeven enzym produkovaný bakterií *Ideonella sakaiensis*, který byl účinný při degradaci/recyklaci PET. Bohužel mechanismus degradace zatím není známý[3].

Zajímavou alternativou recyklace PET je jeho využití v polymerbetonu[4]. V roce 2016 byla navržena a zkonstruována technologická linka pro výrobu dílců z odpadních termoplastů a vhodných plniv, kde byl jako plnivo zvolen odpadní PET. Plastový odpad neprocházel čistícím ani separačním procesem před samotným zpracováním. Jako plnivo bylo použito drobné kamenivo frakce 0 – 4 mm. Cílem tohoto článku je posoudit vliv znečištění PET na teplotní okrajové podmínky při výrobě takového polymerbetonu.

Experimentální část

Materiály

Byly použity tyto materiály: pomletý odpadní špinavý PET (obsahoval 4 hm. % příměsí polyolefinů ve formě kousků víček a etiket), pomletý vyčištěný PET (zbavený polyolefinů na základě rozdílné hustoty), pomletý čistý PET z firmy PETKA CZ, a.s., a umytá a čistá PET lahev, která byla označena jako referenční vzorek.

Diferenciální skenovací kalorimetrie (DSC)

DSC měření byla provedena na přístroji DSC Discovery od firmy TA Instruments v teplotním rozmezí 30 až 300 °C. Rychlost ohřevu i chlazení byla 10 °C/min. Byly provedeny 2 ohřevy. V průběhu prvního ohřevu byla smazána teplotní historie vzorku. K vyhodnocení tepelných procesů sloužil druhý ohřev. U každého vzorku byly provedeny 3 měření, výsledky byly zprůměrovány a byly vypočteny směrodatné odchylky.

Termogravimetrická měření (TGA)

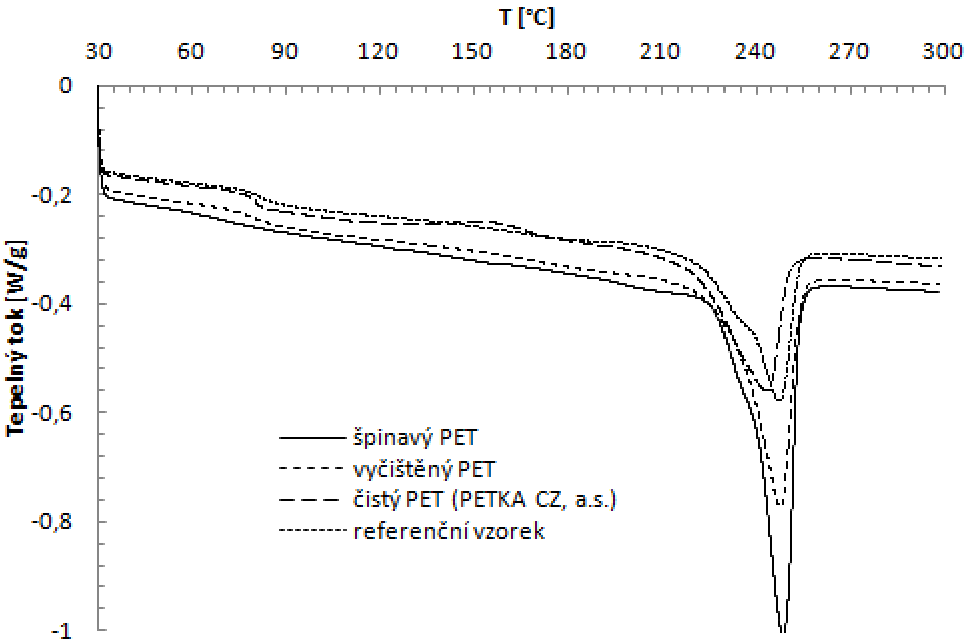
TGA měření byla provedena na přístroji TGA Q500 od firmy TA Instruments v dusíkové nebo oxidační atmosféře. Rychlost ohřevu byla 10 °C/min. PET vzorky byly podrceny. Dále bylo provedeno izotermní měření při teplotách 260 °C a 300 °C v inertní a oxidační atmosféře. Vzorek byl zahřátý na požadovanou teplotu (260 °C nebo 300 °C) a po 2 hodiny byla udržována teplota konstantní. Po celou dobu byl zaznamenáván úbytek hmotnosti. Čas, po který bylo nutné vzorek zahřívat na požadovanou teplotu, byl vzatý jako t_0 a od zbývajících časů byl odečten. Taktéž úbytek hmotnosti, který byl zaznamenán při dosažení cílové teploty, byl odečten od ostatních zaznamenaných hodnot.

Výsledky a diskuse

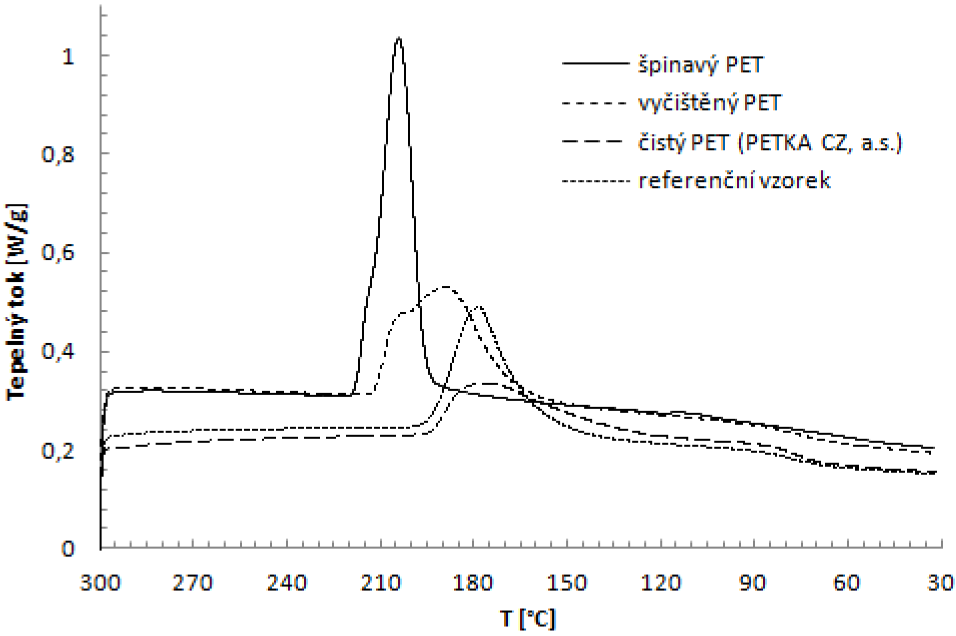
K tomu, aby se porovnal vliv nečistot na teplotní okrajové podmínky PET, byly provedeny DSC a TGA analýzy. Výsledky DSC měření byly shrnuty do Tabulky 1. Průběh prvního DSC měření pro 2. ohřev a 2. chlazení byly uvedeny v obrázku 1 a 2. Teploty tání při 1. ohřevu byly u všech vzorků téměř totožné, pouze se lišil o 3 °C referenční vzorek. U teploty tání při 2. ohřevu čistý PET z firmy PETKA, a.s., vykazoval asi o 3 °C nižší teplotu tání než ostatní vzorky. Nejednalo se však o dramatické změny. Většinou je trend opačný, nečistoty lehce snižují teplotu tání. Naměřené hodnoty jsou v souladu s obecně známými daty[5]. Minimální teplota zpracování je 255 °C. U chlazení měření ukázala, že špinavý vzorek vykazuje teploty krystalizace o asi 20 °C vyšší než čisté vzorky. Teploty krystalizace jsou silně závislé na podmínkách chlazení, a proto se jako určující uvádí teploty tání.

Tabulka 1: Výsledky DSC měření

Vzorek	**Teplota tání [°C]**		**Teplota krystalizace [°C]**	
	1. ohřev	**2. ohřev**	**1. chlazení**	**2. chlazení**
Špinavý PET	248,4 ± 0,6	247,4 ± 1,0	205,4 ± 0,8	203 ± 1,2
Vyčištěný PET	248,6 ± 0,3	247,3 ± 0,7	186,7 ± 1,3	186,2 ± 2,1
Čistý PET (PETKA CZ, a.s.)	248,6 ± 0,2	244,3 ± 0,3	182,1 ± 2,2	177,6 ± 2,5
Referenční vzorek	251,7 ± 0,9	247,8 ± 0,1	180,2 ± 0,2	178,0 ± 0,1



Obrázek 1: DSC měření 2. ohřev

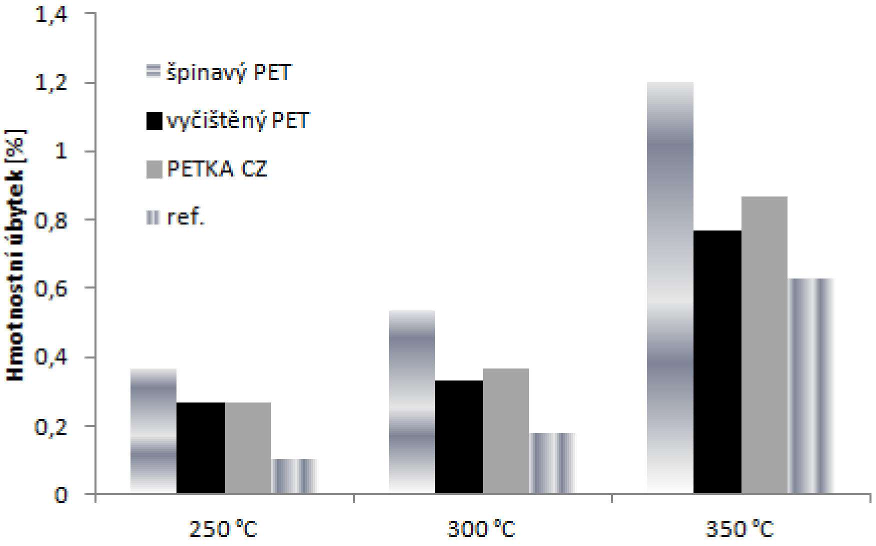


Obrázek 2: DSC měření 2. chlazení

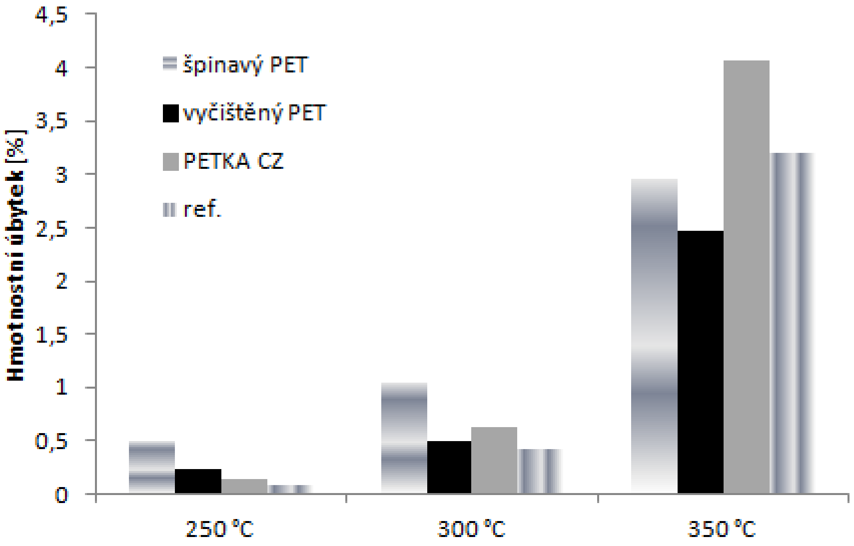
Výsledky TGA měření v inertní atmosféře jsou zobrazeny na obrázku 3, zatímco v oxidační atmosféře na obrázku 4. Při 250 °C v inertní atmosféře se ukázalo, že nejméně stabilní byl špinavý PET, naopak nejvíce stabilní byl referenční vzorek (čistá PET lahev). Stejný trend byl patrný i při vyšších teplotách. S rostoucí teplotou hrálo výraznou roli znečištění. Vyčištěná PET oproti špinavé PET vykazovala nižší hmotnostní úbytky (hmotnostní úbytek vyčištěného vzorku představoval asi 3/5 úbytku v případě špinavého vzorku při 350 °C).

Při 250 °C v oxidační atmosféře byl nejstabilnější referenční vzorek, zatímco nejméně stabilní byl špinavý vzorek. Při 300 °C byla situace obdobná, opět nejméně stabilní byl špinavý vzorek, zatímco nejstabilnější se jevil referenční vzorek. Při 350 °C došlo k zajímavému jevu, nejméně stabilní se stal vzorek z firmy PETKA, a.s. a referenční vzorek. Vyčištění PET pomohlo vzorek tepelně stabilizovat. Při 350 °C už však byly hmotnostní úbytky značné, a proto jako mezní teplota zpracování byla stanovena teplota 300 °C. V oxidační atmosféře byly hmotnostní úbytky vyšší než v inertní atmosféře.

Na základě DSC a TGA měření byla navržena izotermní TGA měření při teplotách 260 °C a 300 °C. Teplota 260 °C byla zvolena proto, aby bylo zajištěno, že PET bude plně roztavený. Teplota 300 °C byla zvolena, protože se jednalo o hraniční teplotu, kdy nastává degradace vzorku.



Obrázek 3: TGA měření různých PET v inertní atmosféře



Obrázek 4: TGA měření různých PET v oxidační atmosféře

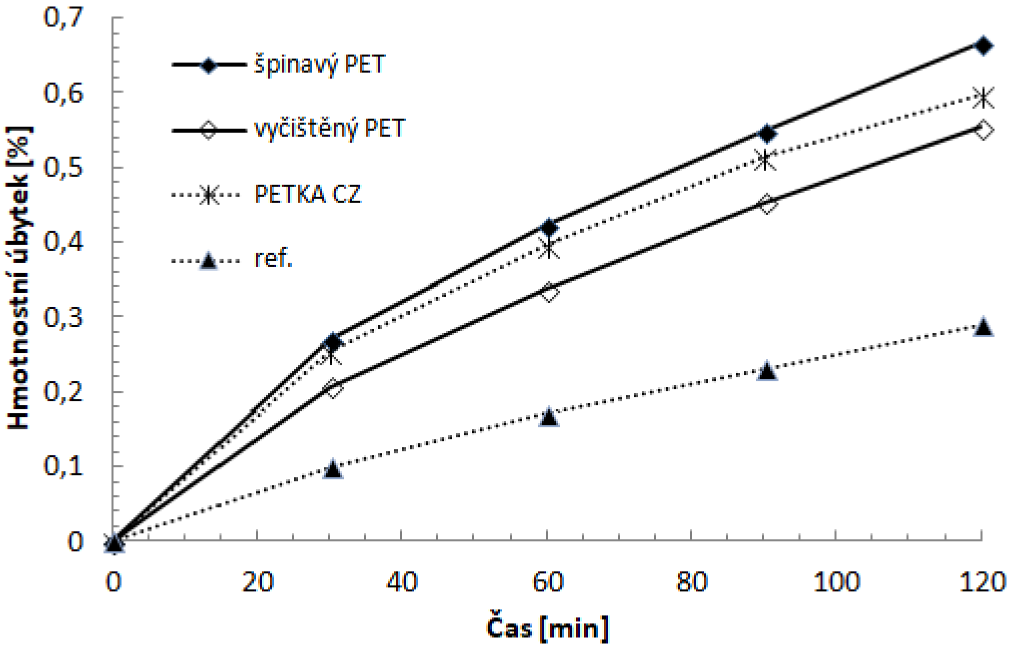
Nejdříve byla provedena izotermní měření vybraných vzorků PET při 260 °C v inertní (obrázek 5) a v oxidační (obrázek 6) atmosféře. Hmotnostní úbytky s přibývajícím časem rostly. Při 260 °C v inertní atmosféře měla nejnižší hmotnostní úbytky referenční PET, naopak nejvyšší úbytky vykazovaly špinavý PET. Když byla PET drť vyčištěna, tak došlo k poklesu hmotnostního úbytku, avšak hmotnostní úbytky nebyly nižší než u čistého referenčního PET. Z výsledků vyplývá, že v inertní atmosféře při 260 °C dochází u znečištěných PET k vyšším úbytkům hmotnosti, avšak po 120 min byly tyto úbytky hmotnosti pod 1 %.

Opačný trend byl pozorován při 260 °C v oxidační atmosféře. Referenční a čistý PET z firmy PETKA CZ, a.s. vykazovaly vyšší hmotnostní úbytky než špinavý vzorek. Promytí znečištěných vzorků způsobilo o něco vyšší hmotnostní úbytky než v případě špinavého vzorku. Nečistoty na vzduchu tepelně stabilizovaly PET. V oxidační atmosféře byly ztráty hmotnosti poměrně výrazné, po 120 min ubylo až kolem 8 % hmotnosti vzorků.

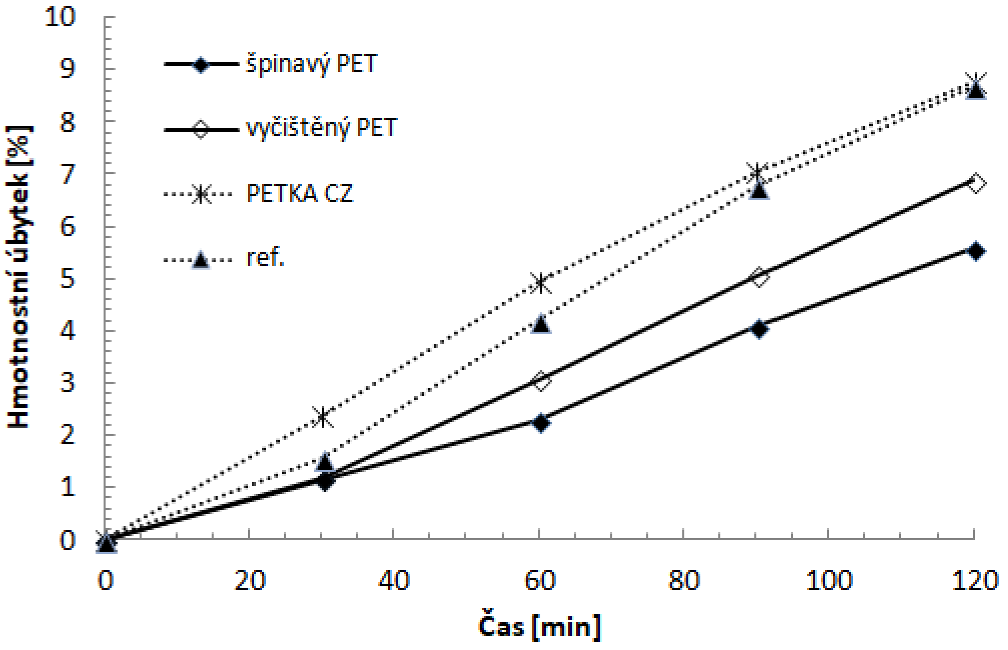
Poté byla provedena izotermní měření vybraných vzorků PET při 300 °C v inertní (obrázek 7) a v oxidační (Obrázek 8) atmosféře. Hmotnostní úbytky s přibývajícím časem rostly rychleji než při teplotě 260 °C. Při 300 °C v inertní atmosféře měla nejnižší hmotnostní úbytky čistý PET z firmy PETKA CZ, a.s. a referenční PET, naopak nejvyšší úbytky vykazoval špinavý PET. Když byla PET drť vyčištěna, tak opět došlo k poklesu hmotnostních úbytků, avšak hmotnostní úbytky nebyly nižší než u čisté referenční PET. Z výsledků vyplývá, že v inertní atmosféře při 300 °C dochází u špinavých PET k vyšším úbytkům hmotnosti, avšak po 120 min byly tyto úbytky hmotnosti pod 5 %.

Při izotermních měření při 300 °C v oxidační atmosféře docházelo k poměrně vysoké degradaci. Nejlepších výsledků dosáhl referenční PET, naopak nejhorší výsledky ukázal PET z firmy PETKA CZ, a.s. Otázkou však zůstává, nakolik jsou výsledky objektivní. U všech měření byl hmotnostní úbytek po 60 minutách přes 5 %. Důležité je zmínit, že špinavý PET vykazoval lepší tepelnou stabilitu než vyčištěný.

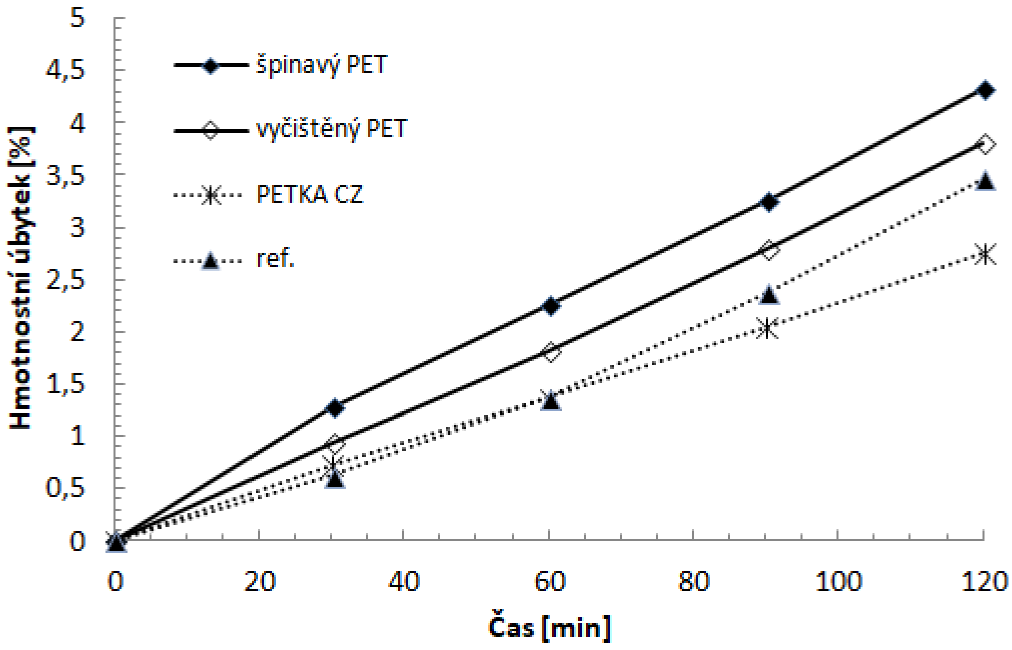
Výsledky odhalily, že na tepelnou stabilitu má vliv jednak teplota a volba atmosféry, ale také znečištění PET. V inertní atmosféře znečištění způsobuje vyšší úbytky, avšak na vzduchu dokáže vzorky tepelně stabilizovat.



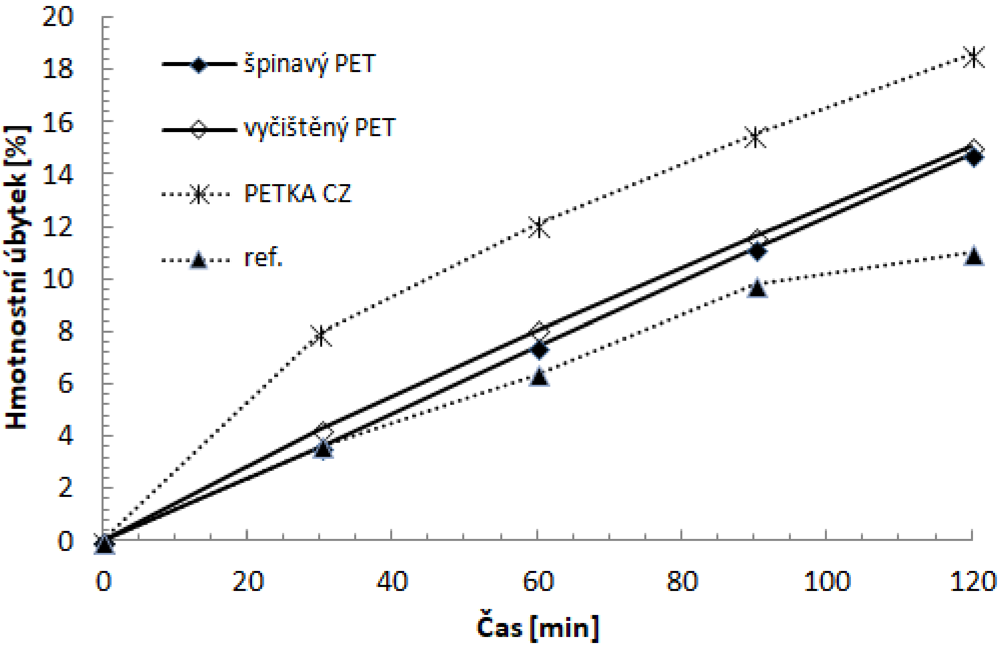
Obrázek 5: Izotermní TGA měření při 260 °C v inertní atmosféře (dusík)



Obrázek 6.: Izotermní TGA měření při 260 °C v oxidační atmosféře (vzduch)



Obrázek 7: Izotermní TGA měření při 300 °C v inertní atmosféře (dusík)



Obrázek 8: Izotermní TGA měření při 300 °C v oxidační atmosféře (vzduch)

Závěry

Teplotní okrajové podmínky zpracovatelnosti čistého a špinavého PET byly stanoveny na 255 – 300 °C. Optimální teplota zpracovatelnosti byla stanovena na 260 °C. Na teplotu tání nemělo znečištění téměř žádný vliv. V inertní atmosféře znečištění zvyšovalo tepelnou degradaci, zatímco v oxidační atmosféře (na vzduchu) v případě izotermních měření dokázalo vzorky tepelně stabilizovat. V inertní atmosféře při 260 °C byly po 120 min úbytky hmotnosti pod 1 %, zatímco v oxidační atmosféře byly až kolem 8 %. V inertní atmosféře při 300 °C byly po 120 min úbytky hmotnosti pod 5 %, avšak v oxidační atmosféře byly po 60 min nad 5 %. V praxi se PET nezpracovává v inertní podmínkách, ale doba, kterou PET stráví v extrudéru je 2 – 4 min. Příměsi polyolefinů v PET drti se nezdají být na základě výsledků našich měření nežádoucí.

Poděkování

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The influence of PET pollution on thermal boundary conditions in polymer concrete production

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Summary

The processing of polyetylene terephthalete (PET) into polymer concrete represents an alternative method of recycling. The effect of PET pollution on the thermal boundary conditions in the polymer concrete production has been compared. Impurities (polyolefine admixtures) didn't affect the melting temperature, however Theky played a crucial role in thermal degradation. The pollution increased thermal degradation in inert atmosphere, whereas in air atmosphere the pollution stabilized samples in certain cases.

***Keywords**: recycling, waste, polyetylene terephthalate (PET), polymer concrete.*

Experimentální ověření množství tepla uvolňovaného při aerobní fermentaci biologicky rozložitelných odpadů

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Souhrn

Klíčovým faktorem pro praktické využití biologického dosoušení biologicky rozložitelných odpadů a biomasy je zjištění množství využitelného tepla produkovaného mikroorganismy během fermentačních procesů. V minulosti byly publikovány určité hodnoty, nicméně zpravidla s odlišnými materiály, a ne zcela jasnými podmínkami měření. Z tohoto důvodu je experimentální ověření využitelného tepelného výkonu jedním z klíčových úkolů pro návrh prakticky využitelného zařízení pro využití biologického dosoušení bioodpadů a biomasy zejména pro výrobu tuhého alternativního paliva z těchto materiálů. Experimentální měření bylo prováděno v jednoúčelovém experimentálním reaktoru prostřednictvím měření množství odebíraného tepla z reaktoru.

Klíčová slova: *bioodpad, tuhé alternativní palivo, tepelný výkon fermentace*

Úvod

Procesy aerobní fermentace je možné úspěšně využít pro tzv. biologické dosoušení biomasy, tedy redukci vlhkosti materiálu působením mikroorganismů a tepla vedoucí k odparu vlhkosti a jejímu odvedení z materiálu. Mikroorganismy působící v materiálu jednak rozkládají organickou hmotu, čímž činí odpar a odvod vlhkosti jednodušším a jednak svým metabolismem produkují teplo, které také pozitivně působí při odparu vlhkosti. Tyto skutečnosti lze úspěšně použít pro sušení biologicky rozložitelného materiálu a biomasy. Biologické sušení a dosoušení využívá energie biologických procesů v materiálu pro pokrytí energetické potřeby pro odpar vody. Současně mikroorganismy působí pozitivně na změnu struktury materiálu a usnadnění uvolnění vázané vody v buněčných stěnách a zlepšuje dynamiku sušení.

Cooney[1] hovoří o produkci tepla 4 Whg_{O2}^{-1} využitého mikroorganismy. Svoboda, Evans[2] o 4,03 $kWhkg_{O2}$ využitého bakteriemi. Jedná se nezávisle na sobě o dvě velmi podobné hodnoty. Při známých koncentracích kyslíku vstupujícího a vystupujícího aerifikačního média (vzduchu) je možné pomocí dynamického respiračního indexu zkalkulovat spotřebu kyslíku mikroorganismy a provést přepočet na tepelný výkon. Veličina Dynamický respirační index (DRI) byla zavedena v souvislosti s potřebou hodnocení biologické stability odpadních materiálů. Z rozdílných koncentrací kyslíku před a po průchodu materiálem, objemu vzduchu a množství materiálu je možné vypočítat spotřeba O_2 v miligramech na gram sušiny měřeného materiálu za hodinu (mg $O_2kg_{VS}^{-1}h^{-1}$). Pro potřeby následných experimentů byl původní vzorec publikovaný Adanim[3] zjednodušen na

$$DRI = \frac{\dot{m}_v \cdot 3600 \Phi x_{O2}}{m_s} 10^6 [\mathrm{mg}\, O_2 kg_{vs}^{-1} h^{-1}] \qquad ,$$

kde $\dot{m}_v [kgs^{-1}]$ je průtok vzduchu při provětrávání, Φx_{O2} je střední rozdíl relativních koncentrací O_2 na vstupu a po průchodu materiálem [-], $m_s[kg]$ je hmotnost sušiny v experimentálním reaktoru.

Pro vybrané materiály uvádí Adani a Habart[4] rozsah DRI pro bioodpady 2000 až 5000 $mgO_2kg_{VS}^{-1}h^{-1}$, pro stabilizovaný materiál hodnotu DRI <1 000 $mgO_2kg_{VS}^{-1}h^{-1}$. Při spojení obou výše uvedených hodnot, tedy DRI pro bioodpady a produkci tepla při fermentačních procesech (Y) se dostáváme na teoretickou hodnotu tepelného výkonu 20,15 kW při DRI 5000 $mgO_2kg_{VS}^{-1}h^{-1}$ a Y=4,03 $kWhkg_{O2}$ na tunu suchých spalitelných látek v materiálu. Uvážíme-li popelnatost a vlhkost běžného biologicky rozložitelného odpadu ve výši cca 20 % hm. popelovin a relativní vlhkosti cca 60 %, pak získáme hm. podíl suchých spalitelných látek cca 35 % v celkovém vlhkém, vstupním materiálu – zakládce. Při přepočtu na hmotnost zakládky je to pak tedy 7,05 kW na tunu zakládky. Při DRI 2000 $mgO_2kg_{VS}^{-1}h^{-1}$, tzn. na spodní hranici výše uváděného rozsahu je to pak 2,8 kWt^{-1} (na tunu zakládky).

Sardinsky[5] uvádí celkovou produkci 3 375 000 Btu (British thermal unit), 290 $kgCO_2$ a 47 l vody v odparu během 21denního cyklu kompostovacího procesu v 1 tuně zakládky o 50% vlhkosti), tzn. 6 696 $Btuh^{-1}$. Po převodu energie na jednotky SI (1 btu = 1 055 J = 0,309 Wh) se jedná o průměrný tepelný výkon 1,96 kWt^{-1}.

Vemmelund a Berthelsen[6] uvádí 550 kcal za hodinu na 1 m^3 kompostované zemědělské kejdy, tzn. výkon 639 Wm^{-3}. Při objemové hmotnosti cca 950 kgm^{-3} a sušině cca 20 % se jedná o 672 Wt^{-1} kejdy, tzn. 3 363 Wt^{-1} sušiny.

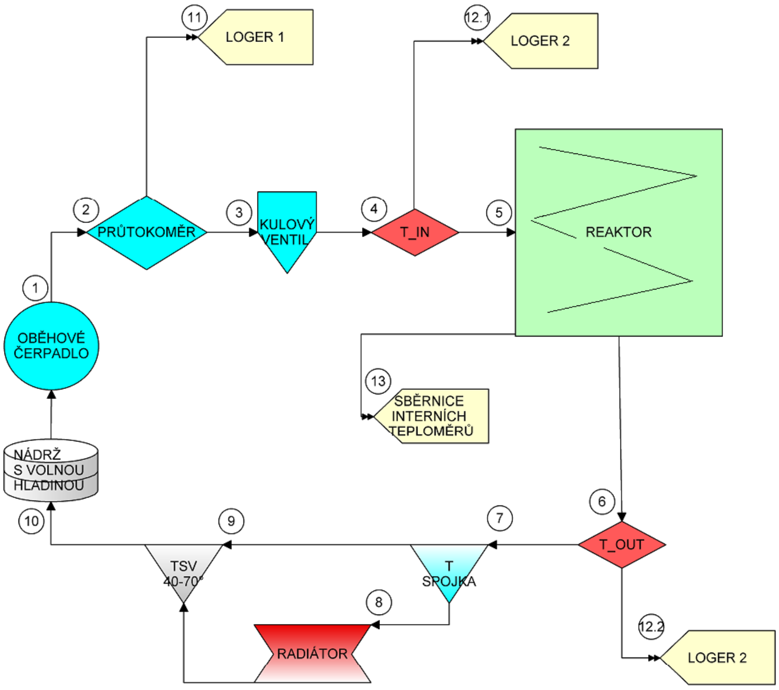
Všechny v literatuře nalezené výsledky jsou v korelaci. Nicméně s ohledem na plánovaný vývoj specifického zařízení, dobu od publikování výše uvedených výsledků, odlišné zpracovávané materiály a specifika odpadu a klimatických podmínek v ČR bude vhodné provést experimentální měření v reálných podmínkách.

Experimentální část

Cílem experimentu bylo experimentálně stanovit měrný tepelný výkon biologických procesů při aerobní fermentaci biologicky rozložitelného odpadu. Měření je založené na principu řízeného odebírání tepelné energie z aktivní vsázky BRO při zachování optimálních teplot uvnitř vsázky.

Popis měřící soustavy

Měřicí soustava (obrázek 1) pracuje na principu kalorimetru, kde reaktor tvoří izolovaný uzavřený box, z něhož je výměníkem odebíráno teplo vyvíjené biologickými procesy vsázky. Pro dostatečný přísun kyslíku pro aerobní procesy je soustava vybavena nuceným diskontinuálním provzdušňováním.



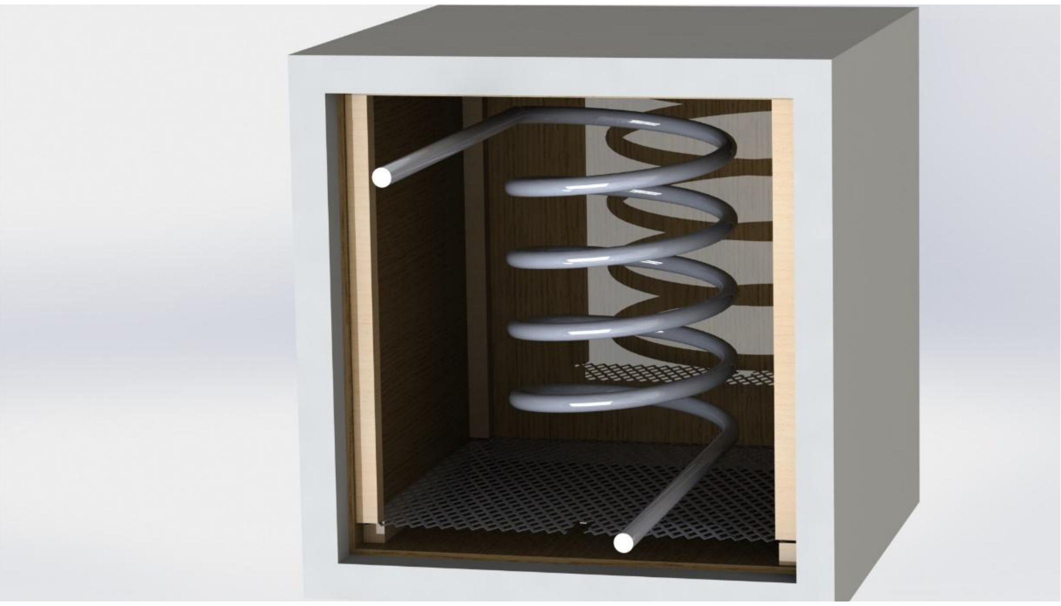
Obrázek 1: Blokové schéma měřicí soustavy

1. Oběhové čerpadlo WEBERMAN typ 24-40 180 – 0,2-3,5 m^3h^{-1}; výtlak 3,8m
2. Průtokoměr ENBRA typ řady EV (logický signál po průtoku 1 l)
3. Kulový ventil chladícího média
4. Odporový teplotní snímač SENSIT Pt1000/3850 typ TR130A-35 G3/4“/OK30
5. Výměník tepla v reaktoru–vícevrstvá trubka Pex-al-pex 26x3 mm; délka 20 m
6. Viz odrážka 4.
7. T spojka 1“
8. Chladič – interiérový radiátor; rozměry 1800×500×100
9. Termostatický směšovací ventil VTA 322 30-70 °C 1“
10. Vyrovnávací nádrž s volnou hladinou cca 11 l
11. Logger S7021 – Dvoukanálový záznamník s čítacím a binárním vstupem
12. Logger S0121 – Dvoukanálový záznamník teploty s dispejem
13. Vpichovací radiové teploměry – Codet s.r.o. BRNO

Další vybavení:

- Kancelářský notebook pro sběr dat.
- Ventilátor pro provětrávání 0,3 m^3s^{-1} při jmenovitém tlaku 300 Pa.
- Topná spirála pro temperování soustavy při startu 0,5 kW.
- Čisticí prostředek Savo pro úpravu vody.

Experimentální box



Obrázek 2: 3D vizualizace experimentálního boxu

Reaktor tvoří korpus z OSB stavebních desek tloušťky 18 mm o rozměrech 1,25×1,25 m. (v rozích jsou výztuhy z dřevěných trámků.) Vrchní a čelní strana je odnímatelná. Bedna je zaizolována stavební polystyrenovou izolací o tloušťce 140 mm.

Účinný objem reaktoru (maximální objem vsázky)

$$V = 1{,}232 \cdot 1{,}232 \cdot 0{,}9 = 1{,}37 m^3$$

Odhad ztráty tepla vnějším povrchem reaktoru

Byl proveden jako kvalifikovaný odhad sdílení tepla soustavou do okolí. Ztrátový výkon Q_z byl zkalkulován metodou sumy prostupů tepla jednotlivými stěnami na 184,6 W.

Provzdušňovací systém

Provzdušňování je realizováno ventilátorem, který vhání vzduch do prostoru pod vsázkou. Prostor v bedně tvoří perforovaný plech podepřený paletou, který zároveň slouží jako nosič vsázky. Plech má otvory 10x10 mm. Pro zabránění zkratovitého proudění vzdušiny okolo stěn, je na plech položen podél stěn pás fólie (cca 100 mm). Odvod vzdušiny z reaktoru je realizován průchodkou se zpětnou klapkou na vrchní straně bedny (průměr 100 mm).

Provzdušňování je diskontinuální a je v činnosti po sepnutí časového relé. Nízkotlaký ventilátor je použit ze vzduchotechniky (štítkové parametry: průtok 0,3 m^3s^{-1} při tlaku 300 Pa).

Obrázek 3: Pohled na měřící soustavu

Postup měření

Byla použita běžná zakládka pro kompostování v pásových hromadách připravena na kompostárně Vícenice u Náměště nad Oslavou a převezena k měření. Složení zakládky – tráva 60 %, dřevní štěpka 20 %, sláma 10 %, listí 10 %.

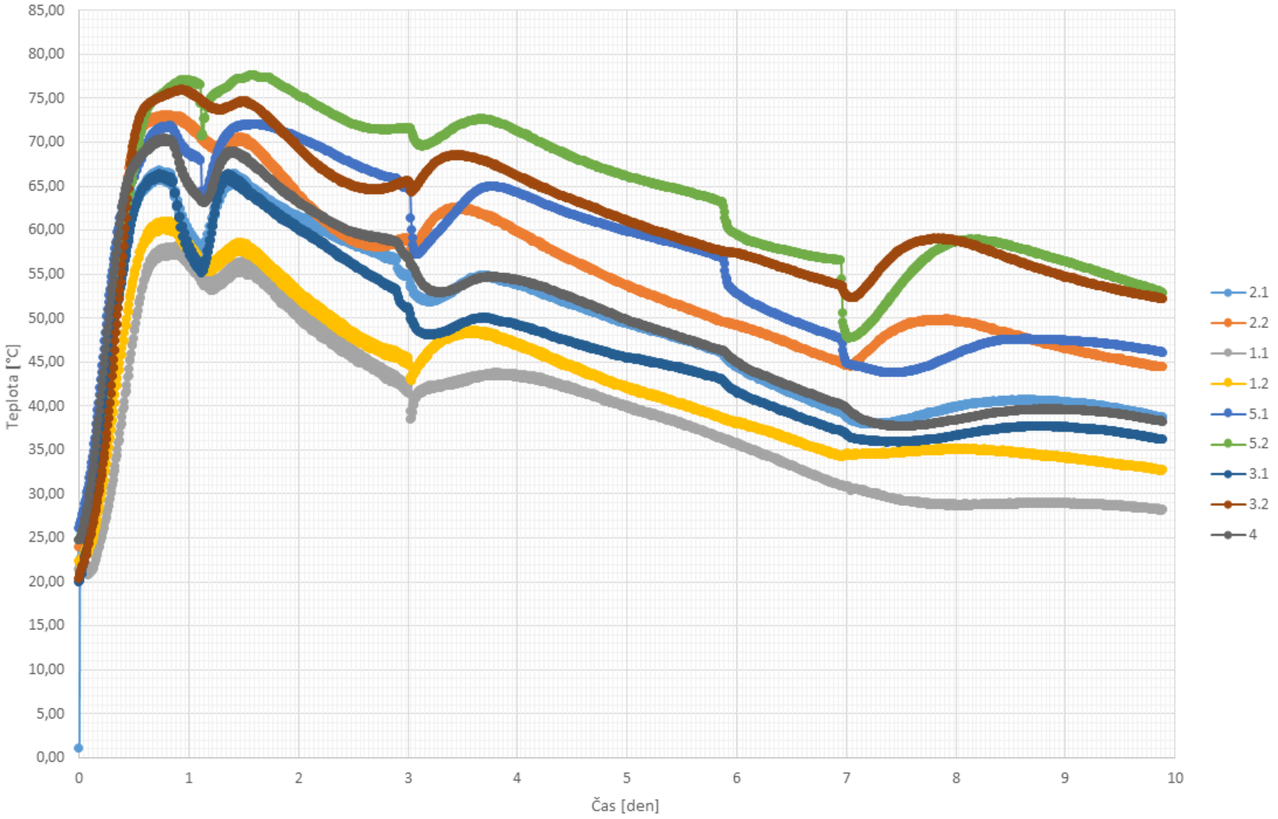
Měrná hmotnost materiálu $\rho = 520 kgm^{-3}$.

Obrázek 4: Umístění zakládky a výměníku

Patronem tohoto čísla je Ústav technologie stavebních hmot a dílců Fakulty stavební VUT v Brně

Měření 1

Měření mělo za cíl prokázat funkčnost soustavy a poukázat na nedostatky. Zároveň mělo posloužit jako zkouška k osvojení si měření a chování dílčích prvků soustavy.

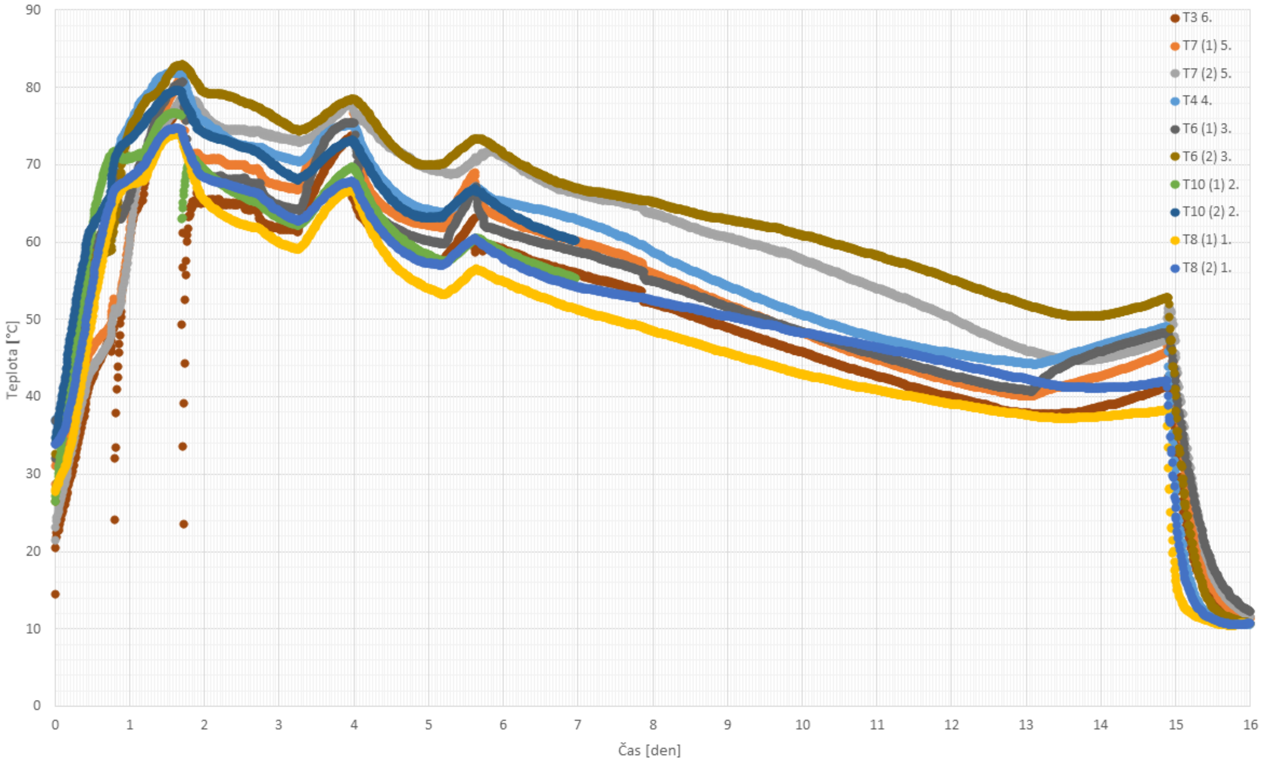


Obrázek 5: Průběh teplot uvnitř reaktoru během měření 1

Měření prokázalo funkčnost soustavy. Při měření byl pozorován únik vzduchu netěsnostmi horního víka v době mezi provětráváním, což zcela neeliminovalo ani jeho zatížení. Tento jev způsobuje komínový efekt reaktoru a také snižování hustoty vzduchu po provětrání vlivem zvyšující se teploty (z teploty v hale na cca 60 °C) a vlhkosti vzduchu. Řešením tohoto jevu byla instalace výměníku do prostoru v reaktoru nad vsázku při následujícím měření 2. Instalace výměníku částečně řeší i intenzivní odvod vlhkosti provětráváním z reaktoru. Byl použit náporový chladič z osobního automobilu (zdroj likvidace autovraků). Při rozebírání zakládky byl materiál velmi suchý, až na lokální místa a horní vrstvu.

Obrázek 6: Instalace chladiče při měření 2

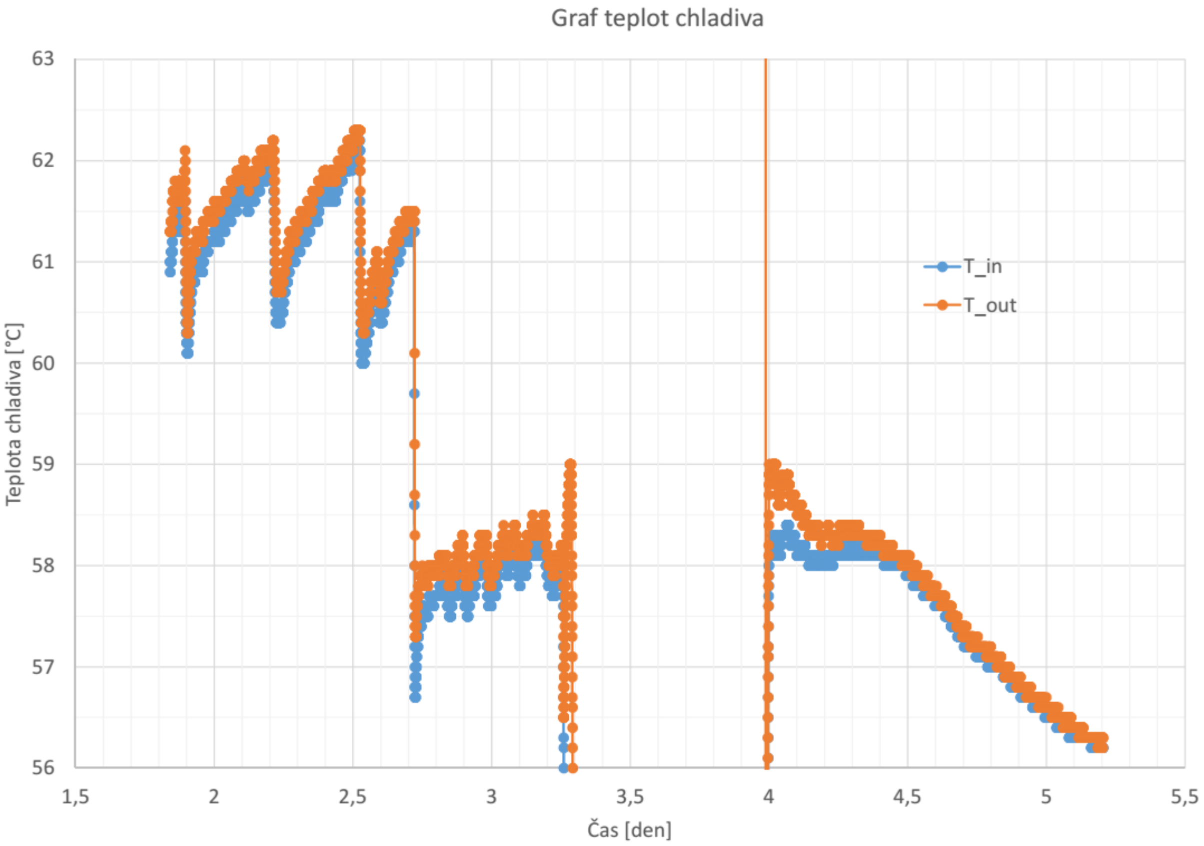
Měření 2



Obrázek 7: Průběh teplot uvnitř reaktoru během měření 2

Volba reprezentativních dat

Během měření se vyskytly nepředvídané komplikace s výpadky elektrické energie vlivem poruchy regulace na sousedící vodní elektrárně vzhledem k nízkému vodnímu stavu. Výpadky lze pozorovat jako nárůst teplot v reaktoru, viz obrázek 7. Z pohledu vývinu tepla v reaktoru je důležitá především úvodní termofilní fáze po najetí. Proto bude diskutován pouze následující časový úsek od počátku do šestého dne.



Obrázek 8: Přiblížení reprezentativních dat pro výpočet vývinu tepla z druhého měření

Měřený úsek 1

Je v časovém úseku od 1,84 dne do 2,72 dne, celkem 0,88 dne. Průtok chladiva byl stabilní bez kolísání a průměr logovaných minutových hodnot je $\dot{m}_{ch} = 0{,}311 kgs^{-1}$. Tento úsek reprezentuje plně vyvinutou termofilní fázi.

Měřený úsek 2

Je v časovém úseku od 4,41 dne do 5,2 dne, celkem 0,79 dne. Průtok chladiva byl stabilní bez kolísání a průměr logovaných minutových hodnot je $\dot{m}_{ch} = 0{,}308 kgs^{-1}$. Tento úsek reprezentuje proces ke konci termofilní fáze.

Výsledky a diskuse

Výpočet vývinu tepla aerobními fermentačními procesy

Výpočet koresponduje s daty z časových úseků měření 2. Detailní kalkulace nejsou s ohledem na rozsah publikace publikovány a jsou spolu s primárními daty z měření k dispozici u autorů.

Výpočet výkonu z kalorimetrického měření

$$P_{Qk} = c_p(T_{stř}) \cdot \Delta T \cdot \dot{m}_{ch}[kW] \ ,$$

kde T_{inp} a $T_{out}[°C]$ jsou naměřené vstupní a výstupní teploty chladiva, $c_p(T_{stř})[kJkg^{-1}]$ tepelná kapacita vody, $\dot{m}_{ch}$ průtok chladiva, $\Delta T = T_{out} - T_{inp}[°C]$ a $T_{stř} = \frac{T_{inp}+T_{out}}{2}[°C]$ střední teplota chladiva

Vypočtený výkon kalorimetru je následující.

Měřený úsek 1 $P_{Qk} = 316\ W$

Měřený úsek 2 $P_{Qk} = 76\ W$

Výpočet výkonu z provětrávání experimentálního bioreaktoru

$$P_{Qp} = (i_{out} - i_{inp}) \cdot \dot{m}_v \cdot 1000[W]$$

kde stavové veličiny vzduchu při měření jsou $T_{inp} = 15°C; \varphi_{inp} = 50\%; i_{inp} = 28{,}53 kJkg^{-1}$ a i_{out} stanovena na základě $\varphi_{out} = 100\%$ a T_{out} dle měření dle [7].

Vypočtený výkon kalorimetru je následující.

Měřený úsek 1 $P_{Qp} = 126{,}5\ W$

Měřený úsek 2 $P_{Qp} = 142{,}3\ W$

Výpočet středního výkonu fermentačních procesů

$$P_{QBRO} = P_{Qk} + P_{Qp}[W]$$

Měřený úsek 1$P_{QBRO} = 316 + 126{,}5 = 442{,}1W$

Měřený úsek 2$P_{QBRO} = 76 + 142{,}3 = 218{,}3W$

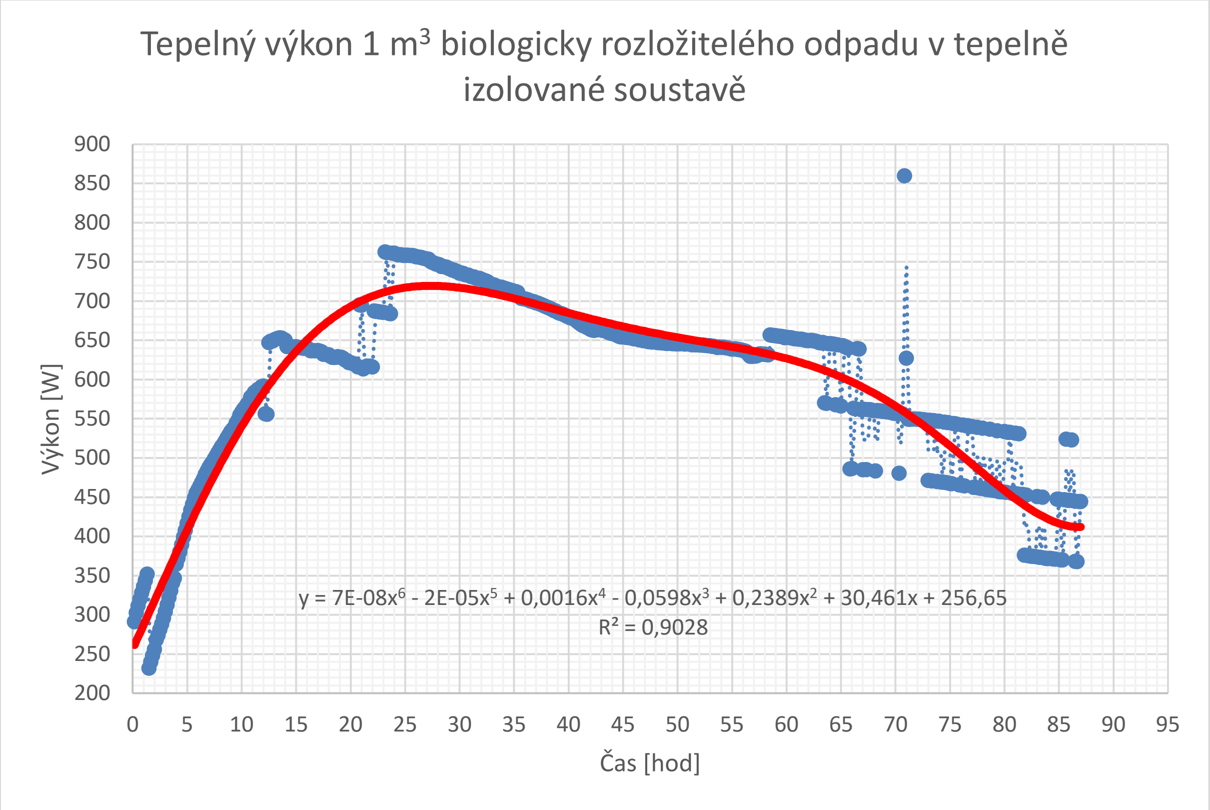
$$P_{QBRO} = \frac{2}{3}P_{QBRO}^{usek1} + \frac{1}{3}P_{QBRO}^{usek2} = \frac{2}{3}442{,}1 + \frac{1}{3}218{,}3 = 367{,}5\ W \approx 370\ W$$

Jelikož objem vsázky druhého experimentu byl dle výšky hladiny vsázky $V = 1{,}01m^3$je tento výkon vztažen právě na tento objem a na hmotnost sušiny 212 kg. Korekce na 2/3 úseku 1 a 1/3 úseku 2 jsou voleny pro zohlednění dynamiky termofilní fáze a váhy jednotlivých částí.

Pokud bychom zahrnuli do celkového vývinu tepla i odhad sdílením tepla experimentálního reaktoru do okolí výsledný celkový vývin tepla by byl následující.

$$P_{QBRO}^{+ztrata} = P_{QBRO} + P_{Qz} = 367{,}5 + 184{,}6 = 552{,}1\ W$$

Celková data z experimentů byla promítnuta do grafu a proložena křivkou – znázorňují experimentálně stanovený tepelný výkon fermentačních procesů biologicky rozložitelných odpadů.



Obrázek 9: Experimentálně stanovený tepelný výkon fermentačních procesů biologicky rozložitelných odpadů

Při srovnání s výsledky obdobných experimentů z literatury – konkrétně Vemmelund, Berthelsen [6] - 550 kcalm^{-3} při kompostování zemědělské kejdy s nuceným provětráváním – tzn. 639 Wm^{-3}, při objemové hmotnosti cca 950 kgm^{-3} a sušině cca 20 % se jedná o 672 Wt^{-1} kejdy, tzn. 3 363 Wt^{-1} sušiny. Tímto je potvrzeno, že dosažený výsledek je řádově srovnatelný a správný.

Dosažené výsledky v experimentálním reaktoru, který věrně simuluje reálné podmínky, prokazuje dále technicky využitelný vývin tepla fermentačními procesy.

Závěry

Provedená měření průkazně experimentálně stanovila skutečnou hodnotu vývin fermentačního tepla modelové zakládky v experimentálním boxu. Byla použita běžná zakládka pro kompostování v pásových hromadách připravena na kompostárně Vícenice u Náměště nad Oslavou a převezena k měření. Složení zakládky – tráva 60 %, dřevní štěpka 20 %, sláma 10 %, listí 10 %. Celková hmotnost sušiny zakládky v 1 m^2 objemu měřicího boxu byla 212 kg.

Celkový střední tepelný výkon byl experimentálně změřen na hodnotu 367,5 W. Kdy byl složen z výkonu v rámci termofilní fáze a následného poklesu teploty. Celková doba trvání experimentu byla 6 dní. Střední výkon v prvních 4 dnech byl 442,18 W, ve zbývajících dnech 218 W, což svědčí o významném poklesu po projití termofilní fáze. Střední výkon 370 W je však objektivním výsledkem. S uvážením tepelné ztráty sdílením do okolí, která byla zkalkulována na 185 W byl střední tepelný výkon materiálu 552 W na 212 kg sušiny. Celkový výsledek tohoto experimentu tedy je **2603 W t^{-1}** sušiny materiálu.

Zobecněný výsledek pro energetickou bilanci biologického dosoušení biomasy s využitím fermentačního tepla s uvážením průměrně 40 % sušiny běžné zakládky je střední tepelný výkon termofilní fáze aerobní fermentace běžné kompostářské zakládky **1041 Wt^{-1}** zakládky stanovený měřením tzn. obecně **1 kW na 1 tunu zakládky.** Tento výsledek je slibný pro další vývoj zařízení pro využití biologicky rozložitelného odpadu pro výrobu tuhého alternativního paliva v průmyslové praxi.

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Experimental research of the amount of usable heat of biodegradable waste aerobic fermentation processes

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Summary

A key factor for the practical use of biological drying of biodegradable waste and biomass is to determine the amount of usable heat produced by microorganisms during fermentation processes. Some values have been published in the past, but usually with different materials and not very clear measurement conditions. For this reason, the experimental verification of usable thermal power is one of the key tasks for the design of a practically usable facility bio drying of biowaste and biomass, in particular for the production of solid alternative fuels from these materials.

Keywords: *biodegradable waste, aerobic fermentation, heat production*

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Pohľad samospráv na vybrané otázky nakladania s komunálnym odpadom

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Súhrn

Európska únia si v rámci rozvojových stratégii stanovila za cieľ v oblasti obehového hospodárstva dosiahnuť maximálne materiálovo-energetické využitie odpadu s minimalizáciou jeho zneškodňovania. Slovenskej republike sa už dlhšie nedarí plniť tieto ciele a v rámci porovnania krajín Európskej únie je na posledných miestach v oblasti zhodnocovania odpadu vrátane komunálneho odpadu. V tejto súvislosti príspevok napomáha identifikovať príležitosti a bariéry efektívneho zhodnocovaniu komunálneho odpadu, pričom vychádza z dotazníkového prieskumu zameraného na samosprávy v Slovenskej republike. Výsledkom vyhodnotenia prieskumu je zistenie postoja predstaviteľov samospráv k životnému prostrediu, ako aj návrh opatrení, ktorých realizácia by prispela k zvýšeniu úrovne triedenia komunálneho odpadu v slovenských mestách a obciach.

Kľúčové slová: *komunálny odpad, zhodnocovanie odpadov, zneškodňovanie odpadov, skládkovanie, samospráva, dotazníkový prieskum*

Úvod

Odpad vzniká ako vedľajší produkt výroby a poskytnutia služby. Vzniká v súvislosti s každou aktivitou človeka. S rozvojom konzumnej spoločnosti rastie objem vyprodukovaného odpadu vrátane komunálneho odpadu (KO), a tým sa zvyšuje miera znečisťovania životného prostredia (ŽP). Ročná produkcia odpadu v Európskej únii predstavuje približne 2,5 miliárd ton odpadu. Z toho takmer 10 % tvoria komunálne odpady. S veľkým objemom odpadov prichádza ďalší problém, ktorým je spôsob nakladania s odpadom.

Znečisťovanie životného prostredia v dôsledku tvorby odpadov je možné redukovať dvoma spôsobmi. Vývinom dokonalejších a ekonomicky výhodnejších bezodpadových technológií alebo organizovaným zberom odpadov spolu s ich ekologickým zhodnocovaním a recykláciou.[1]

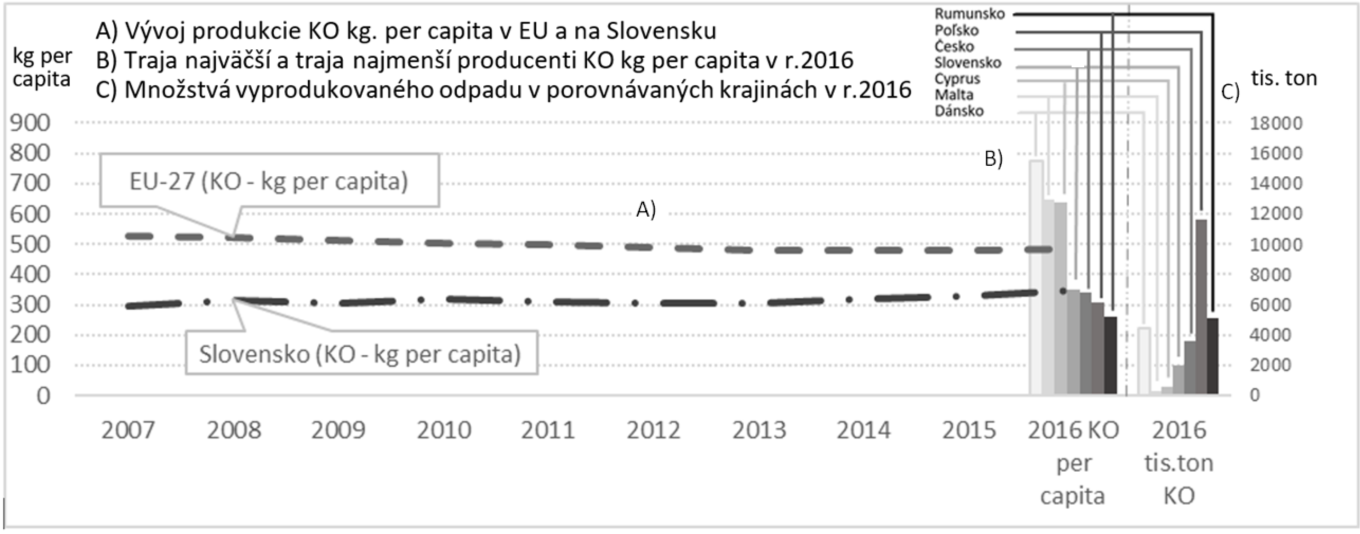
Jednotlivé štáty Európskej únie sa snažia o znižovanie produkcie komunálneho odpadu vo väzbe na *„Hierarchiu odpadového hospodárstva“.* Smernica Európskeho parlamentu a Rady 2008/98/ES, ktorá sa premietla aj do slovenskej legislatívy[2], uvádza, že: *„hierarchia odpadového hospodárstva je záväzné poradie týchto priorít:*

a) predchádzanie vzniku odpadu,
b) príprava na opätovné použitie,
c) recyklácia,
d) iné zhodnocovanie, napr. energetické zhodnocovanie,
e) zneškodňovanie“.

Na základe tejto hierarchie prijímajú jednotlivé členské štáty opatrenia, ktoré budú viesť k čo najlepšiemu environmentálnemu výsledku. Odkloniť sa od hierarchie odpadového hospodárstva je možné iba pre určité toky odpadov *„ak je to odôvodnené úvahami o životnom cykle výrobku vo vzťahu k celkovým vplyvom vzniku a nakladania s takým odpadom*“, ako to vyplýva zo zákona o odpadoch.[3]

Vyprodukované množstvo komunálneho odpadu pripadajúceho na jedného obyvateľa v členských krajinách EÚ začala väčšina európskych krajín znižovať od roku 2008 a EÚ aj naďalej vytvára tlak na znižovanie KO a zvyšovanie zhodnocovania už vzniknutého odpadu[4] (graf 1).

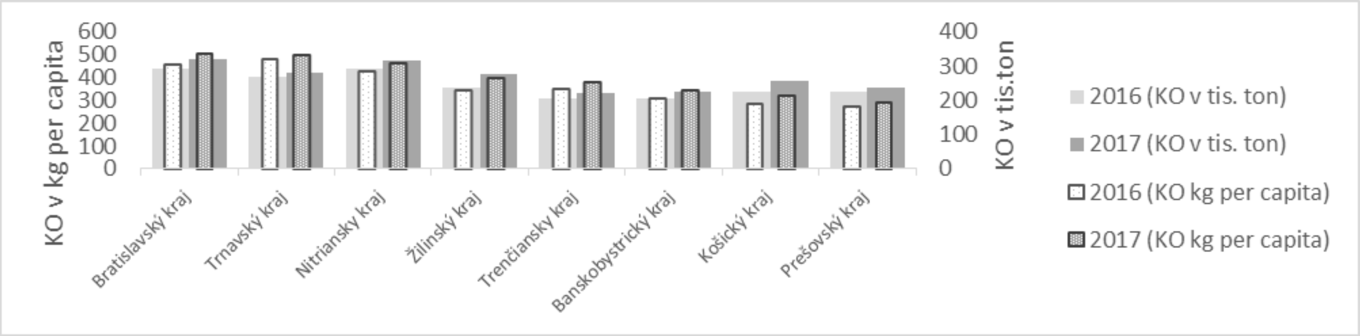
Graf 1: Vývoj produkcie KO v kg per capita v EÚ a v šiestich krajinách EÚ a celkom v tis. ton



Na Slovensku od roku 2013 bol zaznamenaný nárast produkcie komunálneho odpadu. V roku 2016 sa vyprodukovalo 1 954 tis. ton KO, v prepočte na jedného obyvateľa je to 348 kg ročne, a v roku 2017 to bolo spolu 2 137 tis. ton, pričom produkcia KO na obyvateľa vzrástla na 392,98 kg za rok.

Medzi regiónmi Slovenska sú výrazné rozdiely v produkcii komunálneho odpadu (Graf 2)^{5}. V roku 2017 bolo najviac KO celkom aj na obyvateľa produkovaného v Bratislavskom kraji a najmenej KO na obyvateľa je produkovaného v Prešovskom kraji. Medziročne sa produkcia KO zvýšila.

Graf 2: Produkcia KO v regiónoch Slovenska v kg na obyvateľa ročne a celkom v tisícoch ton



Nakladanie s komunálnym odpadom

Okrem vzniku komunálneho odpadu je potrebné venovať pozornosť aj otázke, ako sa nakladá s komunálnym odpadom. Odpad sám o sebe a nesprávne nakladanie s ním výrazným spôsobom poškodzuje životné prostredie. Primárne poškodzovanie životného prostredia a rovnako zdravia ľudí, či riziko kontaminácie je spôsobené nevhodným uskladňovaním odpadu. Sekundárne poškodzovanie životného prostredia súvisí s potrebou získavania nových zdrojov pri výrobe produktov. Objem spotrebovaných (často neobnoviteľných) zdrojov môže byť znížený správnym zhodnocovaním odpadu, ktoré by viedlo k opätovnému použitiu zdrojov získaných zo zhodnoteného odpadu. Za environmentálne najvhodnejší spôsob zhodnocovania odpadu je považovaná recyklácia materiálov, ktorá predstavuje uplatnenie princípov obehového hospodárstva, ktoré chce dosiahnuť Európska únia.

Vo väčšine európskych krajín sa najviac komunálneho odpadu skládkuje alebo spaľuje. Cieľom politiky EÚ je znížiť mieru skládkovania v európskych krajinách, nakoľko je skládkovanie považované za environmentálne najnevhodnejšiu formu nakladania s komunálnym odpadom.

Cieľom EÚ a každého členského štátu je zvyšovať mieru recyklácie komunálnych odpadov ako efektívneho spôsobu nakladania s komunálnym odpadom. V roku 2016 dosahovalo z krajín EÚ najvyššiu mieru recyklácie Nemecko, kde sa recyklovalo až 48,11 % celkového spracovaného komunálneho odpadu. Ostatné krajiny výrazne zaostávajú. V EÚ dosiahla priemerná miera recyklácie v roku 2016 29,80 %, pričom Slovensko dosiahlo úroveň 23 % vrátane kompostovania[6]. Najmenšie množstvo z celkového spracovaného odpadu sa recykluje v Rumunsku (7,40 %) a na Malte (7,84 %).

Kým v roku 2013 z celkového množstva vyprodukovaného KO na Slovensku bolo 27,78 % zhodnoteného, 70,56 % zneškodneného a 1,65 % komunálneho odpadu bol zhromaždeného[7], v roku 2016 na Slovensku sa celkovo zhodnotilo 33,20 % komunálneho odpadu, z toho 35,75 % materiálovo, 30,32 % energeticky, 32,77 % kompostovaní a 1,14 % iným spôsobom. Najviac komunálneho odpadu bolo zhodnoteného v Bratislavskom kraji (64,77 %) a najmenej v Trenčianskom kraji (22,17 %)[8].

Z regionálneho hľadiska vyššie percento zhodnoteného komunálneho odpadu ako celoslovenský priemer v roku 2016 vykazuje Bratislavský kraj (64,77 %) a Košický kraj (51,82 %). Z celkového zhodnoteného KO bolo materiálovo zhodnotených 35,75 %, pričom najväčší podiel materiálového zhodnotenia z celkového zhodnoteného komunálneho odpadu vykazoval Žilinský kraj (55,89 %). Celoslovenský podiel energetického zhodnotenia komunálneho odpadu z celkového zhodnoteného KO v uvedenom roku predstavoval 30,32 %. V Bratislavskom kraji to bolo 66,02 % a v Košickom kraji 56,85 %, v ostatných krajoch to bolo menej ako 3 %. Je potrebné zdôrazniť, že na Slovensku sú prevádzkované dve spaľovne KO, a to v Bratislave a v Košiciach.

Najviac KO (v roku 2016 až 66%) končilo na skládkach. Aj tu boli zaznamenané regionálne rozdiely. V Bratislavskom kraji to bolo len 30,65 %, v Košickom kraji 47,85 % a v ostatných krajoch to bolo v intervale od 71 % do 78 % z množstva KO vyprodukovaného v regióne. Je potrebné brániť sa tomuto negatívnemu stavu, najmä zvyšovaním miery triedenia odpadu. Európska komisia stanovuje pre Slovensko cieľ do roku 2020 recyklovať najmenej 50 % odpadu z domácností. Je otázne, či sa podarí tento cieľ pri súčasnom stave naplniť.

Európsky parlament v apríli roku 2018 schválil ambiciózne ciele: do roku 2025 zvýšiť mieru recyklácie komunálneho odpadu na 55 % a do roku 2035 na 65 %[9]. Ďalším ambicióznym cieľom je dosiahnuť, aby od roku 2035 na skládkach neskončilo viac ako 10 % odpadu.

Úroveň recyklácie odpadov je vo veľkej miere ovplyvnená politikou a cieľmi recyklácie a sociálnymi normami, pretože tieto iniciujú stimuly a efekty recyklácie[10]. Jedným z dôležitých faktorov úspechu pri implementovaní preventívnych opatrení vzniku KO a zvyšovaní miery recyklácie KO sú postoje obyvateľov v otázkach nakladania s KO, vnímanie následkov kontaminácie ŽP odpadmi aj legislatívne opatrenia[11], pričom výskum v Taliansku preukázal, že motivácia jednotlivcov nekoreluje s ich správaním vplývajúcim na zvyšovanie podielu recyklovateľnej časti KO, ale správanie zodpovedné za minimalizáciu množstva vyprodukovaného KO je závislé jedine na vnútornom presvedčení[12]. Čím viac poznatkov o vplyve KO na ŽP obyvatelia majú a zároveň veria zmyslu opatrení zvyšujúcich mieru recyklácie, tým sú ochotnejší spolupracovať a triediť odpad[13]. Signifikantným faktorom zvyšovania miery recyklácie je tiež otázka ceny, keďže za netriedený odpad domácnosti musia platiť[14], a úspešným programom znižovania produkcie nezhodnocovaného KO sa javí jeho množstevné spoplatnenie[15]. Prieskum zameraný na správanie, vnímanie a postoje ľudí v otázke znižovania KO hlavne medzi občanmi zastupujúcimi obec, ktorí majú vedomosti o administratíve a realizácii nakladania s KO v obci, je témou aj nášho príspevku.

Cieľ, metodika a vyhodnotenie prieskumu

Cieľom nášho príspevku je zhodnotiť postoje a vnímanie otázok životného prostredia a komunálneho odpadu občanmi so zameraním sa na kompetentných zástupcov samospráv, čo považujeme popri legislatívnych opatreniach za vplyvný faktor úrovne nakladania s komunálnym odpadom v Slovenskej republike a na základe dotazníkového prieskumu vykonaného v rámci samosprávy na Slovensku navrhnúť opatrenia, ktoré by prispeli k postupnému znižovaniu ukladania tohto odpadu na skládky odpadov a intenzifikovali jeho materiálové zhodnocovanie.

Výsledky prieskumu vychádzajú z primárne zistených údajov počas riešenia projektu VEGA č. 1/0582/2017, v rámci ktorého bol v roku 2018 (v období od mája do septembra) realizovaný e-mailový dotazníkový prieskum zameraný na otázky nakladania s komunálnym odpadom.

Dotazník bol distribuovaný v elektronickej podobe využitím formulárového nástroja spoločnosti Google. Oslovené boli počas niekoľkých týždňov všetky mestá, ich mestské časti a obce (ďalej len obce) na Slovensku s dostupnou e-mailovou adresou. Žiadali sme ich o spoluprácu pri získavaní informácií o spôsoboch nakladania s komunálnym odpadom a triedenom zbere a o ďalšiu distribúciu dotazníkov. Celkovo bolo v prvej etape, nasledujúcej po pilotnom testovaní dotazníka, rozposlaných 2927 jedinečných e-mailov na prevažne verejne dostupné adresy zástupcov slovenských obcí, miest a mestských častí (pár desiatok adries pochádzalo zo súkromných zdrojov členov projektového tímu), e-mailové adresy dvoch obcí neboli dohľadateľné. Priebežne sme rozosielali správy na alternatívne e-mailové adresy alebo boli oslovené osoby vo verejnej správe telefonicky, a to v prípade, keď sme zistili, že e-mail je nedoručiteľný na žiadnu nám známu adresu, alebo keď bol e-mail vymazaný bez prečítania a zaznamenania odpovede oslovenej obce v zbernej tabuľke formuláru Google. V druhej etape sme opätovne rozoslali e-maily na adresy úradov, z ktorých sme odpovede v primeranom čase nezískali.

V prvej májovo-júnovej etape sme oslovením všetkých 2927[16] úradov (Celkový počet obcí bez mestských častí, vrátane Bratislavy a Košíc ako celku: 2890, celkový počet mestských častí: Bratislava (17), Košice (22), celkový počet miest: 140, celkový počet vidieckych obcí: 2750 (vrátane 3 vojenských obvodov)).

V júlovej etape, v ktorej bola návratnosť vyššia, sme opätovne odoslali 2438 výziev samosprávam s funkčnými e-mailovými adresami (44 úradov nebolo v konečnom dôsledku kontaktovaných vôbec pre nefunkčnú, resp. neznámu e-mailovú adresu).

Spolu za celú dobu sme od všetkých respondentov získali 1114 odpovedí, ale neopakujúcich sa odpovedí od zástupcov samospráv s poznatkami o nakladaní s komunálnym odpadom odpovedalo spomedzi všetkých obcí, miest a mestských častí 947 úradov, čo je 32,23%-ný podiel počtu všetkých samosprávnych úradov obcí, miest a mestských častí. Dvaja kompetentní respondenti neuviedli svoju lokalitu, budeme ich zahŕňať len do analýz nezávislých na špecifikovaní konkrétnej obce. Odpovede a obce, ktoré boli v dotazníku zastúpené viacnásobne boli korigované váhami tak, aby bola v súčte obec zastúpená iba raz. Pri rôznych odpovediach za príslušnú obec vstupujúcich do analýz do rôznych kategórií, ak početnosť v kategórii nadobudla rozmer desatinného čísla, bolo toto číslo zaokrúhlené.

Simultánne prebiehal a prebieha dotazníkový prieskum medzi náhodnými, resp. navzájom si odporúčajúcimi občanmi prostredníctvom problematike venovanej internetovej stránky, na ktorú smerovali zdieľané odkazy Facebooku, či príspevku v dvoch tlačených periodikách a niekoľkých obecných novinách. Zber týchto dát ešte trvá, preto podrobnejšie porovnanie postojov, vnímania a činov v oblasti životného prostredia a komunálneho odpadu bežných občanov budeme vyhodnocovať po skončení zberu tohto druhu dát v decembri.

Otázky, ktoré dotazník obsahoval z oblasti triedenia komunálneho odpadu boli zamerané na osobné názory, postoje a správanie sa ako aj všeobecnú časť s údajmi o respondentoch a bydlisku slúžiacich pre kategorizáciu odpovedí. Respondenti boli požiadaní, aby odpovede na otázky vzťahovali na miesto bydliska (trvalého alebo prechodného), kde platia poplatky za komunálny odpad a v ktorom sa počas roka najčastejšie zdržujú.

Pre pracovníkov samospráv so znalosťou problematiky nakladania s komunálnym odpadom bola venovaná osobitná časť, ktorá sa respondentom, ktorí nie sú zamestnaní v rámci samosprávy, nezobrazovala. Otázky, na ktoré sme sa pýtali, nebudú po vyhodnotení za jednotlivé obce verejne dostupné, len súhrne za okresy, kraje a celé Slovensko, na analýzu a modelovanie však súhrnné či priemerné údaje nestačia, preto sme požadovali od respondentov konkrétne uvedenie miesta bydliska, resp. pracoviska obecného, mestského či miestneho úradu, ak bolo odlišné od miesta bydliska. Tento údaj vyvolávajúci obavy z možnej identifikácie respondenta a zo zverejnenia osobných údajov mohol spôsobiť nižšiu návratnosť dotazníkov.

V tomto príspevku boli vyhodnocované otázky, ktorých analýza a potvrdenie štatistickej významnosti záveru vyplývajúceho zo štatistického testu hypotetických predpokladov bola založená na testoch hypotéz o zhode podielov výskytu javov v dvoch súboroch. Podmienka náhodnosti zastúpenia respondentov vo výberovej vzorke nebola zabezpečená uplatnením štandardizovaných postupov, ale len na báze subjektívneho rozhodnutia avšak reprezentantov celej populácie 2927 zástupcov obcí, miest a miestnych úradov, okrem 46 z nich, ktorých e-mailové adresy boli buď neexistujúce alebo nefunkčné. Dlhodobé problémy informatizácie samosprávy sú však možné len pri malých obciach, a teda súhrnné výsledky nemôžu byť ovplyvnené, preto je takéto obmedzenie vzniku výberovej vzorky akceptovateľné. Nenáhodnosťou výberu môžu byť výsledky skreslené, odklon však minimalizuje relatívne vysoké - viac ako 30%-né zastúpenie populácie samospráv.

Vykonané testy zhody podielov skúmaných znakov v dvojiciach porovnávaných súborov sú založené na asymptotickom prístupe z dôvodu dostatočne veľkého počtu respondentov, a teda zabezpečujúcom primeranú silu testov. Početnosti a podiely sú korigované váhami tak, aby jedna obec bola zastúpená za samosprávu iba raz.

V každom teste bola základná hypotéza H_0 formulovaná ako zhoda podielov výskytu skúmaného znaku v súbore, t. j. H_0: $\pi_1 = \pi_2$ a alternatívna hypotéza túto zhodu popierala, t. j. H_1: $\pi_1 \neq \pi_2$, resp. konkretizovala jednoznačnú situáciu H_1: $\pi_1 < \pi_2$ podiel výskytu testovaných odpovedí je v rámci samospráv väčší) alebo H_1: $\pi_1 > \pi_2$ (podiel výskytu testovaných odpovedí je v rámci samospráv menší). Testy boli realizované na hladine významnosti $\alpha = 0{,}5$, t. j. bola akceptovaná 5% pravdepodobnosť štatistickej chyby prvého druhu, že bude zamietnuté tvrdenie hypotézy H_0, ktoré je v skutočnosti pravdivé. Štatistické testy boli vykonané pomocou štatistického softvéru (GRETL 2018c – GNU Regression, Econometric and Time-series Library).

Vzhľadom na úspešné riadenie záležitostí odpadového hospodárstva na obecných úradoch očakávame a v tomto príspevku otestujeme predpoklad osobného zmýšľania, uvedomenia, postojov a činov reprezentantov obcí v oblasti komunálnych odpadov. V analýzach nevyhodnocujeme názorové zastúpenie v populácii vzhľadom na nereprezentatívne zastúpenie skupín respondentov, zaujímajú nás skôr relatívne prevažujúce štatisticky významné rozdiely v porovnávaných skupinách. V príspevku otestujeme pravdivosť siedmych tvrdení a na záver zhrnieme odporúčania v súvislosti so zlepšením situácie v odpadovom hospodárstve.

Pozorované a testované predpoklady:

Predpoklad 1: Pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom častejšie deklarujú záujem o súčasný stav a budúcnosť životného prostredia ako ostatní účastníci prieskumu zaradení v skupine bežných občanov.

Predpoklad 2: Pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom častejšie vnímajú kvalitu životného prostredia lepšie ako ostatní účastníci prieskumu zaradení v skupine bežných občanov (a). Pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom pracujúci v obci, v ktorej majú trvalé bydlisko častejšie vnímajú kvalitu životného prostredia pozitívnejšie ako pracovníci samosprávy, ktorí majú pracovný pomer na úrade samosprávy v inej obci (b).

Predpoklad 3: Vnímanie kvality životného prostredia pracovníkmi z miest je častejšie horšie ako v prípade pracovníkov z obcí.

Predpoklad 4: Pracovníci samosprávy zodpovední za oblasť nakladania s KO sa častejšie zapájajú do aktivít minimalizujúcich množstvo vyprodukovaného komunálneho ako bežní občania.

Predpoklad 5: U pracovníkov samosprávy je vyššia miera záujmu o minimalizovanie množstva vyprodukovaného KO ako u občanov alebo u pracovníkov samosprávy s bydliskom v inej obci.

Predpoklad 6: Ste dostatočne motivovaní k triedeniu odpadu?

Predpoklad 7: Menšie obce do 1000 obyvateľov sa častejšie spájajú s inými samosprávami alebo organizáciami pri jednaní o cenách a iných otázkach ako väčšie obce.

Výsledky a diskusia

Predpoklad 1. Pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom častejšie deklarujú záujem o súčasný stav a budúcnosť životného prostredia ako ostatní účastníci prieskumu zaradení v skupine bežných občanov.

Vyšší záujem o súčasný stav a budúcnosť životného prostredia je sumarizovaný odpoveďami na otázku „Zaujímate sa o súčasný stav a budúcnosť životného prostredia?“ „Áno – aktívne (venujem tomu svoj čas a peniaze)“ + „Áno – často aj aktívne“ + jedna otvorená odpoveď „Zaujímam sa intenzívne o budúcnosť nášho životného prostredia“. Skupina je označená názvom „Vyšší záujem“. V druhej skupine nazvanej „Menší záujem“ boli zaradení respondenti odpovedajúci (Áno – pasívne (keď nepomáham, aspoň neškodím) + Áno, niekedy + Nejako bolo, nejako bude + Ja sa nebudem obmedzovať kvôli neistej budúcnosti, žijem teraz). Skupiny respondentov pozostávali z respondentov zo samospráv kompetentných v otázkach KO a druhou skupinou boli bežní občania, ktorí v pracovnom vzťahu nemajú kompetencie ohľadom KO. Početnosti a podiely odpovedí sú v nasledujúcej tabuľke.

Tabuľka 1: Zaujímate sa o súčasný stav a budúcnosť životného prostredia? (samospráva/občania)

Záujem/Súbor respondentov (počet, podiel)	**Kompetentní pracovníci samosprávy**		**Občania bez znalosti problematiky KO**		**Občania pracujúci v samospráve**		**Občania nepracujúci v samospráve**	
Vyšší záujem	809	0,8545	83	0,7194	24	0,7059	59	0,725
Nižší záujem	138	0,1455	33	0,2806	10	0,2941	23	0,275
Spolu	947	1	116	1	34	1	82	1

Nulová hypotéza: podiely v populáciách sú rovnaké verzus podiel záujmu je vyšší u kompetentných pracovníkov samosprávy ako u bežných občanov.

1. Zástupcovia samosprávy: $n_1 = 947$, $\text{podiel}_1 = 0{,}8545$; 2. Občania: $n_2 = 116$, $\text{podiel}_2 = 0{,}7194$

Testovacia štatistika: $z = (0{,}8545 - 0{,}7194) / 0{,}0360852 = 3{,}74392$

Jednostranná p-hodnota = $9{,}059 \cdot 10^{-5}$.

Jednostranná p-hodnota $9{,}059 \cdot 10^{-5} \ll \alpha = 0{,}05$, preto zamietame nulovú hypotézu o zhode, konštatujeme štatistickú významnosť výsledku, že podiely sa nerovnajú, a teda pracovníci samospráv sa častejšie vo vyššej miere zaujímajú o stav životného prostredia ako občania nepracujúci oficiálne s informáciami o komunálnom odpade.

Rozdiely v záujme o životné prostredie medzi občanmi bez znalostí problematiky KO pracujúcimi v rámci samosprávy a mimo samosprávy nie sú štatisticky významné, pracovníci samosprávy bez kompetencií ohľadom KO preukazujú dokonca nižší záujem o životné prostredie ako bežní občania zapojení do tohto prieskumu.

Záujem o životné prostredie určite zvyšujú poznatky, skúsenosti a zodpovednosť pracovníkov samosprávy za riešenia v oblasti komunálneho odpadu, čo môžeme overiť v ďalších krokoch výskumu vo vzťahu k veku, vzdelaniu a iným ukazovateľom.

Predpoklad 2: Pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom častejšie vnímajú kvalitu životného prostredia lepšie ako ostatní účastníci prieskumu zaradení v skupine bežných občanov (a), pričom častejšie vnímanie lepšej kvality životného prostredia očakávame tiež u pracovníkov samosprávy, ktorí majú v obci pracoviska aj bydlisko v porovnaní s tými, ktorí na pracovisko dochádzajú.

Pri teste tohto predpokladu sme analyzovali otázku: „Aká je podľa Vás kvalita životného prostredia vo Vašom meste/obci?“ s možnými odpoveďami: „Veľmi dobrá“ + „Dobrá“ + „Primeraná“ + pozitívna vlastná odpoveď = „Dobrá kvalita“ a „Na hranici akceptovania“ + „Horšia“ + „Veľmi zlá“ + negatívna vlastná odpoveď, ktorá sa do konca zberu dát ani nevyskytla = „Zlá kvalita“.

Kvalitu životného prostredia v mieste bydliska považujú za dobrú zástupcovia samospráv a občanov v podiele a počte, ako je uvedené v tabuľke 2a a nasledujúcom teste zhody podielov.

Tabuľka 2a: Aká je podľa Vás kvalita životného prostredia vo Vašom meste/obci? (samospráva/občania)

Kvalita/Súbor respondentov (počet, podiel)	**Kompetentní pracovníci samosprávy**		**Občania bez znalosti problematiky KO**	
Dobrá kvalita ŽP	871	0,9197	98	0,8448
Zlá kvalita ŽP	76	0,0803	18	0,1552
Spolu	947	1	116	1

Medzi kompetentnými pracovníkmi z n_1 = 947 samospráv, ktorí reflektovali na dotazník, vyššiu kvalitu životného prostredia vníma 871 pracovníkov, čo je podiel_1 91,97% pracovníkov.

Medzi občanmi bez znalosti problematiky KO, či už pracujúcimi v rámci samosprávy alebo inde, je tiež vnímaná vyššia kvalita životného prostredia relatívne vysoká, hoci nižšia ako v prípade kompetentných pracovníkov samosprávy, a to zaokrúhlene p_2 = 84,5 percentami občanov. Otestujeme, či je tento rozdiel štatisticky významný.

Nulová hypotéza: podiely v populáciách sú rovnaké, alternatívna hypotéza: podiel výskytu pozitívneho hodnotenia ŽP v populácii kompetentných pracovníkov samosprávy je vyšší.

Testovacia štatistika: $z = (0{,}9197 - 0{,}8448) / 0{,}0279353 = 2{,}68119$
Jednostranná p-hodnota zamietajúca nulovú hypotézu = 0,003668.
Jednostranná p-hodnota $0{,}003668 < \alpha = 0{,}05$ nás vedie k zamietnutiu nulovej hypotézy, konštatujeme štatistickú významnosť rozdielu, a teda pracovníci samospráv sú reálne častejšie vo vyššej miere spokojní s kvalitou životného prostredia v porovnaní s bežnými občanmi bez znalosti problematiky KO.

K predpokladu 2b, že pracovníci samosprávy zodpovední za oblasť nakladania s komunálnym odpadom pracujúci v obci, v ktorej majú trvalé bydlisko, častejšie vnímajú kvalitu životného prostredia pozitívnejšie ako pracovníci samosprávy, ktorí majú pracovné poslanie na úrade samosprávy v inej obci, nás viedla úvaha o vplyve dodatočných informácií z poznania agendy v inej obci a úsilia pracovne vynakladaného pre inú ako vlastnú obec. Myslíme, že čím viac poznatkov a kompetencií človek má, tým je spokojnejší, v súlade so závermi ohľadom predpokladu 2a.

Početnosti odpovedí kompetentných pracovníkov samosprávy sme rozlíšili podľa toho, v akej obci majú trvalé bydlisko, či v obci, kde zároveň na samospráve pracujú alebo v obci odlišnej. Uvádzame ich spolu s podielmi vyjadrujúcimi spokojnosť s kvalitou životného prostredia v obci bydliska v tabuľke 2b.

Tabuľka 2b: Aká je podľa Vás kvalita životného prostredia vo Vašom meste/obci? (bydlisko a pracovisko so zhodnou verzus odlišnou adresou obce)

Kvalita/Súbor respondentov (počet, podiel)	**Pracovisko samosprávy v obci s trvalým bydliskom**		**Pracovisko samosprávy je v inej obci ako je obec trvalého bydliska**	
Dobrá kvalita ŽP	770	0,9255	101	0,8783
Zlá kvalita ŽP	62	0,0745	14	0,1217
Spolu	832	1	115	1

Nulová hypotéza: podiely v súboroch dát respondentov v oboch skupinách sa rovnajú, alternatívna hypotéza: podiel v prvej populácii respondentov s bydliskom aj pracoviskom v jednej obci je väčší ako v druhej populácii.

1. populácia: Zástupcovia samosprávy s bydliskom a pracoviskom v obci: $n_1 = 832$, $\text{podiel}_1 = 0{,}9255$

2. populácia: Zástupcovia samosprávy s inou obcou bydliska a pracoviska: $n_2 = 115$, $\text{podiel}_2 = 0{,}8783$

Testovacia štatistika: z = (0,9255 - 0,8783) / 0,0270257 = 1,74649

Jednostranná p-hodnota = 0,04036

Jednostranná p-value = 0,04036 < α = 0,05 nám umožňuje zamietnuť H_0, konštatujeme štatistickú významnosť rozdielu, a to, že podiely sa nerovnajú, a pracovníci samospráv častejšie považujú kvalitu životného prostredia za lepšiu ako občania nepracujúci s informáciami o komunálnom odpade. P-hodnota sa ale blíži ku hodnote vymedzujúcej hranicu nezamietania a zamietania platnosti nulovej hypotézy, preto pre uistenie sa v platnosti záveru by bolo prínosné poznať odpovede od viacerých kompetentných respondentov ohľadom komunálneho odpadu, ktorí majú bydlisko a pracovisko na samospráve v odlišných obciach.

Predpoklad 3: Vnímanie kvality životného prostredia pracovníkmi z miest je častejšie horšie ako v prípade pracovníkov z obcí.

V nadväznosti na predchádzajúci predpoklad nás zaujíma aj vplyv prostredia mestského verzus vidieckeho na vnímanie kvality životného prostredia, keďže hoci najmä mladí ľudia často opúšťajú vidiecke obydlia a sťahujú sa do miest očakávajúc lepšie možnosti, čo vidieť na postupnom vyľudňovaní najmä od väčších miest vzdialenejších obcí, v súčasnosti je hlavne medzi finančne zabezpečenými ľuďmi prejavujúci sa opačný smer sťahovania sa z mesta do vidieckych sídiel uprednostňujúc ticho a prírodu a celkovo priaznivejšie životné prostredie.

Vnímanie kvality životného prostredia sme ponechali v pôvodných zoskupeniach z predchádzajúceho predpokladu deklarujúcich dobrú a horšiu (zjednodušene súhrnne pomenovanú zlú) kvalitu životného prostredia, súbory respondentov boli tvorené mestským obyvateľstvom a obyvateľstvom, resp. pracovníkmi samospráv s bydliskom charakteru obce. Početnosti a podiely sú korigované váhami tak, aby jedna obec bola zastúpená iba raz a sú v nasledujúcej tabuľke č. 3.

Tabuľka 3: Aká je podľa Vás kvalita životného prostredia vo Vašom meste/obci? (mesto/obec)

Kvalita/Súbor respondentov (počet, podiel)	**Bydlisko v meste**		**Bydlisko v obci**	
Dobrá kvalita	93	0,8774	876	0,9154
Zlá kvalita	13	0,1226	81	0,0846
Spolu	106	1	957	1

Nulová hypotéza: podiely výskytu odpovedí zo škály „Dobrá kvalita“ sa v oboch populáciách rovnajú:, alternatívna hypotéza: podiely výskytu odpovedí zo škály „Dobrá kvalita“ sa v populáciách nerovnajú a v prvej populácii (mesto) je podiel nižší H_1: $\pi_1 < \pi_2$.

Respondenti s bydliskom v mestách: $n_1 = 106$, podiel_1 tých, ktorí uvádzajú dobrú kvalitu ŽP = 0,8774
Respondenti s bydliskom v obci: n= 957, podiel_2 tých, ktorí uvádzajú dobrú kvalitu ŽP = 0,9154
Testovacia štatistika: z = (0,8774 - 0,9154) / 0,0290578 = -1,30774
Jednostranná p-hodnota = 0,09548

Jednostranná p-hodnota = 0,09548 nie je menšia ako α = 0,05, nemôžeme preto zamietnuť nulovú hypotézu, t. j. podiely odpovedí uvádzajúcich vnímanie kvalitného ŽP sú v populáciách mestských obyvateľov a vidieckych obyvateľov s najväčšou pravdepodobnosťou zhodné, obe skupiny vnímajú kvalitu ŽP rovnako, túto kvalitu charakter bydliska neovplyvňuje.

Predpoklad 4: Pracovníci samosprávy zodpovední za oblasť nakladania s KO sa častejšie zapájajú do aktivít minimalizujúcich množstvo vyprodukovaného komunálneho odpadu ako bežní občania? (a) Častejšie takúto aktivitu očakávame u pracovníkov samospráv, ktorí v obci pracoviska majú aj bydlisko (b).

Tabuľka 4: Robíte niečo preto, aby ste minimalizovali množstvo vyprodukovaného komunálneho odpadu? (samospráva/občania)

Aktivita/Súbor respondentov (počet, podiel)	**Kompetentní pracovníci samosprávy**		**Pracovisko samosprávy v obci s trvalým bydliskom**		**Pracovisko samosprávy je v inej obci ako je obec trvalého bydliska**		**Občania bez znalosti problematiky KO**	
Aktívni respondenti	919	0,9704	810	0,9736	109	0,9478	111	0,9569
Pasívni respondenti	28	0,0296	22	0,0264	6	0,0522	5	0,0431
Spolu	947	1	832	1	115	1	116	1

Pre analýzu tohto predpokladu testujeme podiel kladnej odpovede na otázku „Robíte niečo preto, aby ste minimalizovali množstvo vyprodukovaného komunálneho odpadu?“ Spomedzi pracovníkov samospráv so znalosťami otázok komunálneho odpadu vysoké percento z nich uvádza, že sa zapája do aktivít minimalizujúcich množstvo vyprodukovaného komunálneho odpadu (97,0%, bežných občanov 95,7%), podiely sú veľmi podobné a rozdiely nie sú štatisticky významné ani pri rozlišovaní medzi pracovníkmi samospráv s bydliskom v obci samosprávy a bydliskom v inej obci. Vyčíslenie je dostupné v tabuľke č. 4. Testy 4a a 4b neodhalili vyššiu aktivitu niektorých respondentov a z dôvodu štatistickej nevýznamnosti testy zhody podielov neuvádzame.

Predpoklad 5: U pracovníkov samosprávy je vyššia miera záujmu o minimalizovanie množstva vyprodukovaného KO ako u občanov alebo u pracovníkov samosprávy s bydliskom v inej obci.

Hoci je podiel všetkých, ktorí sú pri minimalizovaní množstva vyprodukovaného komunálneho odpadu potešujúco vysoký (z testu predpokladu 5), keď sme chceli spresnenie odpovedí uvedením miery, do akej respondentom na minimalizácii záleží analyzovali sme otázku: „Do akej miery Vám záleží na tom, aby ste minimalizovali množstvo vyprodukovaného komunálneho odpadu?“ s krajnými možnosťami: 1: Áno, maximálne mi záleží na tom, aby som v domácnosti neprodukoval/a takmer žiaden komunálny odpad a 6: Nie, vôbec mi nezáleží na tom, koľko komunálneho odpadu vyprodukujem. Hoci v predchádzajúcej otázke traja respondenti uviedli „Áno“, robia niečo preto, aby KO minimalizovali, v tejto otázke označili krajnú 6. možnosť, ktorá prezrádza to, že aj keď niečo v prospech minimalizácie KO urobili, nebolo to preto, že by im na tom záležalo. Získali sme odpovede, ako sú uvedené v tabuľke 5.

Tabuľka 5: Do akej miery Vám záleží na tom, aby ste minimalizovali množstvo vyprodukovaného komunálneho odpadu? (samospráva/občania)

Aktivita/ Súbor respondentov (počet, podiel)	**Kompetentní pracovníci samosprávy**		**Pracovisko samosprávy v obci s trvalým bydliskom**		**Pracovisko samosprávy je v inej obci ako je obec trvalého bydliska**		**Občania bez znalosti problematiky KO**	
Vysoká miera (úroveň 1 a 2)	757	0,7985	676	0,8115	81	0,7043	82	0,7082
Nižšia miera (3-6)	163	0,1719	135	0,1621	28	0,2435	28	0,2444
Žiadna aktivita	28	0,0295	22	0,0264	6	0,0522	6	0,0474
Spolu	948	1	833	1	115	1	116	1

Nulové hypotézy: podiely v populáciách (a: kompetentní pracovníci, b: kompetentní pracovníci s bydliskom a pracoviskom v jednej obci) sú rovnaké.

Pri testoch sme za vyššiu mieru vôle minimalizovať KO kategorizovali prvé dve najvyššie úrovne poskytnutej škály od 1-6. Kompetentní pracovníci uvádzajú túto vysokú mieru v takmer 80-tich percentách, občania bez znalosti problematiky KO túto vysokú mieru uvádzajú v cca 71 percentách. V rámci samosprávneho úradu pracovníci s trvalým bydliskom v obci, kde sa úrad nachádza, mieru záujmu o minimalizáciu odpadu majú vyššiu (81,15%) na úkor miery záujmu medzi dochádzajúcimi zamestnancami samosprávy z iných obcí (70,43%). Miera, do akej respondentom záleží na tom, aby minimalizovali množstvo vyprodukovaného KO, je porovnávaním kompetentných pracovníkov samospráv s občanmi (p-hodnota jednostranného testu zhody podielov je 0,01227) a pracovníkov samospráv v mieste bydliska verzus pracovníkov samospráv s bydliskom v inej obci (p-hodnota jednostranného testu = 0,003603) je štatisticky významne odlišná, t. j potvrdzujeme vyššiu motiváciu pracovníkov pred občanmi a miestnych pracovníkov samospráv pred dochádzajúcimi z iných obcí.

Tieto výsledky preukazujú, že dochádzajúci pracovníci do úradu samosprávy sú menej motivovaní pre vyššiu mieru záujmu o minimalizáciu produkcie komunálneho odpadu. Môžu byť dôvodom nevýhody dochádzania na vzdialenejšie pracovisko, alebo že vo vlastnej obci nepoznajú dopady svojej činnosti v produkcii komunálneho odpadu, či to, že ich pracovné úsilie v rámci samosprávy v inej obci sa neprejaví v obci, kde žijú? Tieto otázky sme v rámci nášho prieskumu nepokrývali, odpovede na nich si môžu obce zistiť sami.

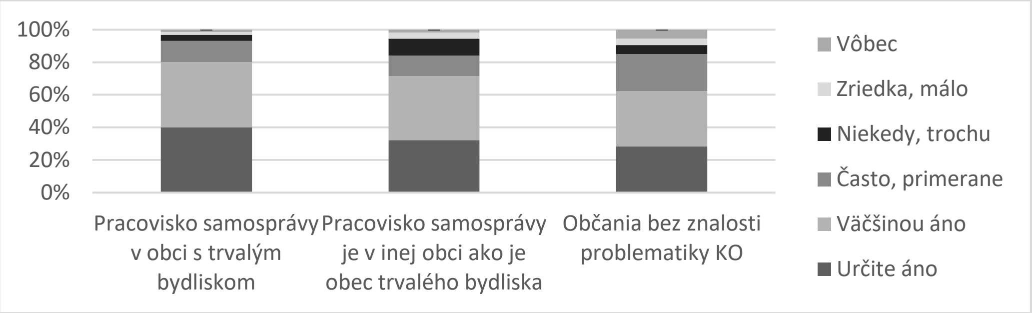
Predpoklad 6: Ste dostatočne motivovaní k triedeniu odpadu?

Názory na úroveň motivácie ľudí na separáciu a iné aktivity znižujúce zaťaženie životného prostredia sa rôznia. Túto úroveň nám pomôžu zistiť odpovede na otázku: „Ste dostatočne motivovaní k triedeniu odpadu?“ s odstupňovanou škálou možných odpovedí: „1. Určite áno“, 2. Väčšinou áno, „3. Často, primerane“, „4. „Niekedy, trochu“, 5. „Zriedka, málo“, 6. Vôbec“. V tabuľke 6 sú odpovede zoskupené po dve do kategórií Áno, som „dostatočne motivovaný/á“, „stredne motivovaný/á“ a „málo motivovaný/á“. Rozdelenie zoskupených odpovedí sa nachádza v tabuľke 6 a v grafe 3 ja znázornenie rozdelenia nezoskupovanej škály odpovedí podľa súborov respondentov.

Tabuľka 6: Ste dostatočne motivovaní k triedeniu odpadu? (samospráva/občania)

Kvalita/Súbor respondentov (počet, podiel)	**Kompetentní pracovníci samosprávy**		**Pracovisko respondentov v rámci samosprávy v obci s trvalým bydliskom**		**Pracovisko respondenta v rámci samosprávy je v inej obci ako je obec trvalého bydliska**		**Občania bez znalosti problematiky nakladania s komunálnym odpadom**	
Áno	748	0,7902	666	0,8007	82	0,7141	72	0,6224
Stredne	166	0,1756	140	0,1680	27	0,2308	33	0,2828
Málo	32	0,0341	26	0,0312	6	0,0552	11	0,0948
Celkový súčet	947	1,0000	832	1,0000	115	1,0000	116	1,0000

Graf 3: Ste dostatočne motivovaní k triedeniu odpadu?



Z grafu aj tabuľky je vidieť tendenciu rozdelenia odpovedí, pričom opäť pracovníci samosprávy s kompetenciami ohľadom KO vykazujú štatisticky významne častejšie vyššie úrovne motivácie ako bežní občania. Podiel odpovedí hodnotiacich úroveň motivácie zhrnutých do kategórie „Áno“ (motivovaní respondenti) z celého súboru respondentov v rámci samosprávy je rovný 0,7902 z n_1 = 947 odpovedí a podiel „Áno“ v súbore občanov je 0,6224 z n_2 = 116.

Testujeme nulovú hypotézu, že podiely odpovedí kategórie „Áno“ v prvom súbore (respondenti samosprávy) a druhom súbore (respondenti občania) sú zhodné oproti alternatívnemu tvrdeniu, že podiel v prvom súbore (respondenti samosprávy) je reálne vyšší na hladine významnosti $\alpha = 0,5$.

Testovacia štatistika: $z = (0,79 - 0,622) / 0,0412916 = 4,06862$

Jednostrannému testu prislúcha p-hodnota 2,365e-005 $\ll \alpha = 0,05$, preto nulovú hypotézu zamietame a prijímame alternatívnu hypotézu, že podiel v najväčšej miere motivovaných zamestnancov v prvom súbore je vyšší ako podiel v najväčšej miere motivovaných občanov.

Zároveň v rámci samosprávy sú štatisticky významne častejšie viac motivovaní zamestnanci, ktorí sú zamestnaní v samospráve v mieste svojho bydliska:

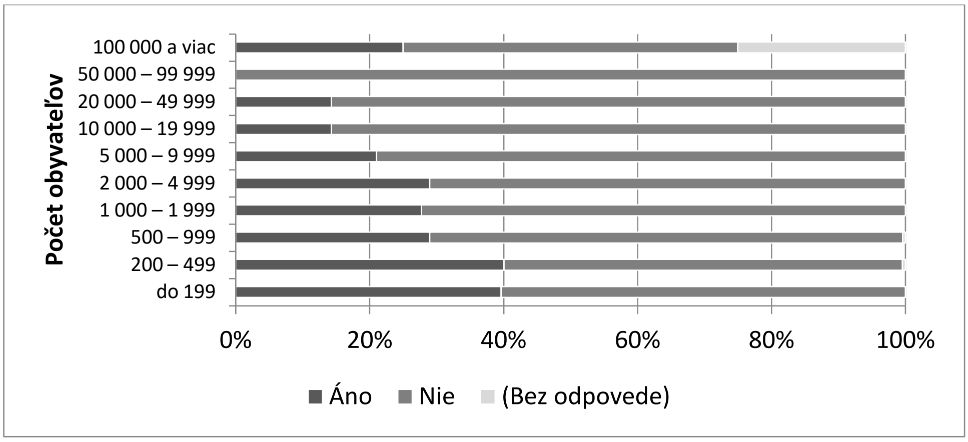
Testovacia štatistika: $z = (0,801 - 0,714) / 0,0404908 = 2,14863$; jednostranná p-hodnota = 0,01583, zamietame H_0 o zhode podielov.

Predpoklad 7: Menšie obce do 1000 obyvateľov sa častejšie spájajú s inými samosprávami alebo organizáciami pri jednaní o cenách a iných otázkach ako väčšie obce.

Mnohé výskumy venujú pozornosť otázke verejného a súkromného poskytovania verejných služieb, vrátane odpadového hospodárstva, ktoré sú zamerané na analýzu poskytovateľov odpadového hospodárstva, efektívnosti zmeny poskytovateľa odpadového hospodárstva. Struk, M. porovnaním výdavkov za nakladanie s komunálnym odpadom vo viac ako 60 obciach v ČR, ktoré zmenili poskytovateľa, poukazuje na znižovanie výdavkov obcí pri zmene dodávateľa bez ohľadu na to, či novým poskytovateľom je verejná alebo súkromná spoločnosť, namiesto neustáleho predlžovania zmlúv so súčasným poskytovateľom[17]. Iné výskumy v oblasti odpadového hospodárstva sú zamerané na možnosti a následne efektívnosti spájania sa obcí pri nakladaní s komunálnym odpadom. Stručný prehľad o tom poskytuje Soukopová[18]. Na príklade ČR poukazuje na spoluprácu medzi mestami a prezentuje hodnotenie nákladovej efektívnosti nakladania s komunálnym odpadom.

V podmienkach SR sme zisťovali, aký podiel obcí využíva komunikáciu a spoluprácu s inými obcami či organizáciami s cieľom zefektívniť svoje výsledky, pričom sme si všimli, že častejšie takúto spoluprácu využívajú obce s menším počtom obyvateľstva.

Graf 4: Spájate sa pri organizácii a jednaní o cenách za nakladanie s odpadom s inou samosprávou/organizáciou?



Predpoklad sme otestovali testom zhody dvoch podielov súhlasných odpovedí na otázku: „Spájate sa pri organizácii a jednaní o cenách za nakladanie s odpadom s inou samosprávou/organizáciou?“

Výsledky nášho prieskumu (Tabuľka 7) poukazujú na to, že cca 36% obcí do 999 obyvateľov a len 26% obcí s počtom obyvateľov 1000 a viac sa spája pri riešení otázok nakladania s komunálnym odpadom. Nenáhodnosť výsledku potvrdíme zamietnutím nulovej hypotézy, že podiely spolupracujúcich obcí v populáciách obcí s menej ako 1000 obyvateľmi a s 1000 alebo viac obyvateľmi sú rovnaké a prijatím alternatívnej hypotéza vyjadrujúcej predpoklad vyššieho podielu kooperujúcich obcí v prvom súbore tvorenom menšími obcami.

Súbor 1: Počet takýchto obcí je v našej databáze n_1 = 585, podiel_1 spolupracujúcich z nich 0,3556.

Súbor 2 je tvorený obcami s počtom obyvateľov 1000 alebo viac obyvateľov väčším alebo rovným 1000. Počet týchto obcí je n_2 = 359, podiel_2 spolupracujúcich z nich je 0,2563.

Testovacia štatistika: z = (0,3556 - 0,2563) / 0,0312181 = 3,18084.

Jednostranná p-hodnota = 0,0007342.

Častejšie spoluprácu pri organizácii a iných aspektoch nakladania s komunálnym odpadom podľa očakávania uplatňujú menšie obce, ktoré si takýmto partnerstvom zefektívňujú organizáciu riadenia záležitostí ohľadom komunálneho odpadu, ale stále je to relatívne nízka početnosť. Rozdiel považujeme za štatisticky významný na základe testu hypotézy rovnosti podielov v oboch súboroch na hladine významnosti α =0,05, keďže jednostranná p-hodnota je < α, môžeme nulovú hypotézu zamietnuť a konštatovať, že rozdiel v podieloch spolupracujúcich obcí v súboroch s menšími a väčšími obcami je štatisticky významný potvrdzujúci prevahu viac spolupracujúcich menších obcí.

Tabuľka 7: Spájate sa pri organizácii a jednaní o cenách za nakladanie s odpadom s inou samosprávou/organizáciou? (obce do 999 obyvateľov vrátane/obce s 1000 obyvateľmi alebo viac)

Spájanie/Súbor respondentov (počet, podiel)	**Obce s počtom obyvateľom <1000**		**Obce s počtom obyvateľom ≥ 1000**	
Áno	208	0,3556	92	0,2563
Nie/neviem	377	0,6444	267	0,7437
Celkový súčet	585	1	359	1

„Čo by ste navrhli pre zlepšenie situácie v odpadovom hospodárstve?“

Otázkou v dotazníku sme očakávali získanie nie konečných riešení problémov v odpadovom hospodárstve, ale podnety pre úvahy a podklady pre ďalšie projekty, odborné štúdie a analýzy. Mnoho odpovedí bolo laických, ale nemôžeme očakávať, že názory individuálnych respondentov, aj keď reprezentujú v otázke administratívy komunálnych odpadov kompetentných zástupcov obce, že budú vysoko odborné, analytické či inovatívne u všetkých administratívne kompetentných zástupcov obcí viac-menej len aplikujúcich existujúcu legislatívu v predmetnej oblasti do praxe obce.

S týmito očakávaniami sme odpovede na uvedenú otázku rozdelili do siedmych skupín, pričom niektoré odpovede sme zaradili aj do viacerých skupín z dôvodu, že niektoré rozsiahlejšie odpovede smerovali do viacerých oblastí.

Prvú skupinu odpovedí sme vytvorili v súlade s hierarchiou odpadového hospodárstva. Do tejto skupiny sme zaradili odpovede respondentov súvisiacich s jednotlivými prioritami. Respondenti na zlepšenie situácie v odpadovom hospodárstve odporúčali predchádzať vzniku komunálneho odpadu už priamo pri výrobe, respektíve pri balení a následne pri distribúcii produktov a to tak, aby sa používalo menej obalového materiálu, v rámci distribúcie odporúčali zálohovanie obalov (PET fliaš, sklenených fliaš, plechoviek). Prípravu na opätovné použitie a recykláciu zahrnuli do odpovedí, v ktorých zamerali na potrebu rozšírenia počtu triedených zložiek komunálneho odpadu, zriadenie zberných dvorov v obciach, zabezpečenie farebných kontajnerov do jednotlivých obcí, či farebné nádoby, ktoré by boli zabezpečené za účelom triedenia komunálnych odpadov do domácností. Medzi odpoveďami boli uvedené aj podnety na dobudovanie spaľovní, či doriešenie koncovky využívania vytriedeného odpadu. Vo viacerých odpovediach bol kladený dôraz na nastavenie systému, aby ten kto triedi odpad platil nižší poplatok. Do tejto skupiny odpovedí bolo zaradených viac ako jedna tretina odpovedí respondentov.

Druhú skupinu odpovedí tvorili odpovede, ktoré súviseli s financovaním nakladania s komunálnym odpadom. Respondenti odporúčajú upraviť finančné vzťahy, viac finančných prostriedkov pre samosprávy zo štátnych zdrojov, Eurofondov, Envirofondu, či OZV za účelom nákupu techniky, kontajnerov a predovšetkým motivovať tých, ktorí triedia komunálny odpad (takmer 9 % respondentov).

Tretiu skupinu odpovedí tvorili odpovede, v ktorých respondenti poukazujú na potrebu legislatívnych zmien, potrebu zvýšenia poplatkov a dodržiavania platnej legislatívy s uplatňovaním postihov pre tých, ktorí ju nedodržiavajú, netriedia komunálny odpad, znečisťujú životné prostredie a tvoria čierne skládky (viac ako 9 % respondentov). Do tejto skupiny sme zaradili aj odpovede, v ktorých respondenti očakávajú pomoc od štátu pri likvidácii čiernych skládok.

Štvrtá skupina odporúčaní respondentov bola zameraná na Nevyhnutnosť kontroly v systéme nakladania a triedenia komunálneho odpadu s dôrazom prenesenia zodpovednosti za kontrolu na obvodný úrad životného prostredia, políciu, prípadne vytvorenie samostatnej kontrolnej inštitúcie (viac ako 4 % respondentov).

Takmer štvrtinu odpovedí tvorila piata skupina odporúčaní smerujúcich k propagácii triedenia odpadu medzi obyvateľstvom na rôznych úrovniach ako územných, tak aj ku všetkým vekovým kategóriám obyvateľstva.

Na piatu skupinu odpovedí logicky nadväzovali odporúčania požadujúce zvyšovať mieru vytriedeného odpadu apelovaním na vyššiu zodpovednosť občanov a zvyšovaním ich motivácie (šiesta skupina).

Poslednú siedmu skupinu tvorili odpovede respondentov, ktorí uvádzali „nič“, „neviem“, neuviedli žiadnu odpoveď na túto otázku, teda nedali konkrétny návrh na zlepšenie v danej oblasti, prípadne sú spokojní s daným stavom nakladania s odpadom v ich obci. Do tejto skupiny sme zaradili aj odpovede typu: „dohliadnuť na to, aby sa zabezpečilo, aby do našej krajiny neprivážali na skládky odpadov odpad z iných štátov“ alebo „vrátiť sa do čias z rokov 1980“, alebo „zlepšiť vymožiteľnosť pohľadávok za neplatičov komunálneho odpadu (t. z., siahnuť aj na dávky)“.

Záver

Veľké množstvo odpadu, nakladanie a hospodárenie s odpadom predstavuje vážny environmentálny, ekonomický a sociálny problém, nakoľko odpady ohrozujú všetky zložky životného prostredia. Európska únia určuje pre členské štáty jednoznačnú hierarchiu nakladania s odpadom, ktorú sa však nedarí dodržiavať.

Závery experimentálnej časti tohto príspevku sú založené na subjektívnych názoroch zástupcov samospráv a bežných občanov. Každý človek je zdrojom škály rôznorodých názorov, postojov a činov, čo predstavuje náhodnú zložku štatistického javu, ovplyvnených okolnosťami prostredia, vedomosťami skúsenosťami a samotnou situáciou. Testovanie štatistických hypotéz napomáha odhaliť tendenciu vnímania, postojov a správania sa ľudí za špecifikovaných okolností pomáhajúc rozhodnúť sa, či je testovaný jav výsledkom pôsobenia len náhodných prirodzených odchýlok alebo vplyvom objektívnych špecifík, čo následne môžeme spoľahlivejšie využiť v manažmente procesov odpadového hospodárstva a snahách o dosahovanie vytýčených cieľov.

Jedným z takýchto cieľov pre Slovenskú republiku je do roku 2020 zvýšiť recykláciu odpadu z domácností a z iných zdrojov, ktoré obsahujú podobný odpad ako domácnosti, najmenej na 50 % podľa hmotnosti. Aby bol tento cieľ splnený, je potrebné zvýšiť úroveň triedeného zberu recyklovateľných časti komunálnych odpadov. Týmito časťami rozumieme najmä papier, lepenku, plast, kov, sklo a biologicky rozložiteľný odpad. Nakoľko jednotlivé vytriedené zložky komunálnych odpadov nie sú plne recyklovateľné, ciele pre mieru triedeného zberu komunálnych odpadov prevyšuje samotný cieľ recyklácie a v roku 2020 má triedenie komunálneho odpadu dosiahnuť 60 %, ako predpoklad 50 % recyklácie, nakoľko nie všetok vytriedený odpad je možné aj reálne recyklovať. Takto stanovené ciele sa zatiaľ na Slovensku, ale aj v mnohých ďalších krajinách Európskej únie nedarí dodržiavať, čo vytvára tlak na potrebu prijatia účinných opatrení. Efektívnosť opatrení je vo veľkej miere závislá od realizovaných legislatívnych zmien, ako aj systému nakladania s odpadom, tak ako sa to darí v najvyspelejších krajinách v tejto oblasti.

Na základe dotazníkového prieskumu a zistených výsledkov si dovoľujeme navrhnúť nasledujúce opatrenia, ktoré by mali napomôcť k zvýšeniu záujmu o triedenie komunálneho odpadu:

1. Upraviť poplatok za vývoz KO tak, aby tí, čo triedia, platili menej, alebo mali iné výhody z triedenia. Túto kompetenciu v súlade s platnou legislatívou majú obce, ktoré zodpovedajú za nakladanie s komunálnymi odpadmi, ktoré vznikli na území obce, a s drobnými stavebnými odpadmi, ktoré vznikli na území obce. Za zber, prepravu a zneškodňovanie komunálnych odpadov a drobných stavebných odpadov sa platí obci miestny poplatok. Okruh platiteľov poplatkov, výšku a sadzbu poplatkov, vznik a zánik povinnosti platenia poplatkov a ďalšie náležitosti poplatkov upravuje všeobecne záväzné nariadenie o miestnych daniach a o miestnom poplatku za komunálne odpady a drobné stavebné odpady pre územie obce. Obec pri ustanovení výšky miestneho poplatku za komunálny odpad a drobný stavebný odpad vychádza zo skutočných nákladov obce na nakladanie s komunálnym odpadom a drobným staveným odpadom. Pritom obec do miestneho poplatku nemôže zahrnúť náklady triedeného zberu oddelene zbieranej zložky komunálneho odpadu, ktoré znášajú výrobcovia vyhradených výrobkov, tretie osoby alebo organizácie zodpovednosti výrobcov, ktorí zodpovedajú za nakladanie s vyhradeným prúdom odpadu v danej obci. Výnos miestneho poplatku za komunálne odpady a drobné stavebné odpady použije obec výlučne na zber, prepravu, zhodnocovanie a zneškodňovanie komunálnych odpadov a drobných stavebných odpadov. Od polovice roka 2016 obce neuhrádzajú náklady na triedený zber. Finančnú zodpovednosť za triedený zber komunálneho odpadu v obciach prevzali organizácie zodpovednosti výrobcu. Z výsledkov ankety medzi samosprávami vyplýva, že v dôsledku prechodu finančnej zodpovednosti za triedený zber komunálneho odpadu na organizácie zodpovednosti výrobcu, ktorý povodne bol zahrnutý do poplatku za komunálny odpad, ani jedna z 33 anketovaných obcí neznížila poplatky za komunálny odpad. Obce to zdôvodňujú tým, že náklady na komunálny odpad dotovali z rozpočtu obce (21 obcí), vzrástli náklady na biologicky rozložiteľný odpad (7 obcí), vznikli nové náklady na prevádzku zberného dvora (2 obce)[19].

Napriek uvedeným faktom a existencii rozporu, kedy respondenti (obce) na jednej strane ako jednu z reálnych možností zvyšovania podielu triedeného komunálneho odpadu odporúčajú ako jeden z faktorov motivácie ku triedeniu odpadu aj finančnú motiváciu tých, čo odpad triedia vo forme znižovania poplatku za komunálny odpad a na druhej strane, keď obce sú oslobodené od nákladov na financovanie nakladania s triedeným odpadom, poplatky za komunálny odpad neznižujú, lebo uvedenými úsporami financujú novovzniknuté náklady, odporúčame znižovať poplatky za komunálny odpad pre tých, čo triedia. Obce by mali hľadať aj iné možnosti znižovania celkových, ako aj novovznikajúcich nákladov.

2. Zlepšiť organizáciu nakladania s odpadom tak, aby občania mali dostatok vriec na vyseparované zložky odpadu v rodinných domoch a pri obytných blokoch dostatok kontajnerov. Zabezpečiť pravidelný zvoz týchto vyseparovaných zložiek, aby nedochádzalo k preplňaniu zberných nádob.

3. Zaviesť separáciu KO v tých mestách a obciach, kde tento zber zatiaľ nebol zavedený, alebo nebol zavedený primerane.

4. Zvýšiť osvetu a propagáciu medzi občanmi ohľadom dôležitosti triedenia komunálneho odpadu.

Náš výskum sa zameriava na analýzu a riešenia podporujúce plnenie cieľov EÚ ohľadom triedenia komunálnych odpadov, ktoré reprezentujú variant aktuálneho stále len čiastkového riešenia globálnych problémov s odpadmi. Pre udržateľnosť stavu životného prostredia je však nevyhnutné zabezpečiť zároveň spoľahlivé a stabilné riešenie odbytu a spracovávania vyseparovaných zložiek.

Potreba zvyšovania miery triedenia a zhodnocovania KO je nesporná. Dosiahnuť sa to dá hlavne zvýšenou aktivitou v oblasti triedeného zberu priamo u pôvodcov jednotlivých zložiek odpadu. Aj napriek jasným environmentálnym, ekonomickým a sociálnym prínosom sú na Slovensku kvalitné a účinné systémy triedeného zberu zatiaľ len málo rozšírené. Z toho dôvodu je potrebné vykonať zmeny, ktoré sú v súlade s cieľmi a legislatívou Slovenskej republiky a Európskej únie. Potreba týchto zmien, hlavne v oblasti motivácie občanov, vyplynula aj z nášho prieskumu.

Poďakovanie

Príspevok je čiastočným výstupom projektu VEGA č. 1/0582/2017 "Modelovanie ekonomickej efektívnosti materiálovo energetického zhodnocovania komunálnych odpadov" riešenom na Podnikovohospodárskej fakulte Ekonomickej univerzity v Bratislave so sídlom v Košiciach vďaka podpore Vedeckej grantovej agentúry Ministerstva školstva, vedy, výskumu a športu Slovenskej republiky, začo jej vyjadrujeme svoje poďakovanie.

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Views of municipalities on selected municipal waste management issues

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Summary

The European Union in its development strategy has set the goal in circular economy to achieve maximum of material and energy recovery of waste with minimization of its disposal. The Slovak Republic has been failing to meet these goals for a long time and, in comparison with the European Union countries, it is in the last places in the field of waste recovery, including municipal waste. In this context, the contribution helps to identify the opportunities and barriers to the effective recovery of municipal waste, based on a questionnaire survey focused on self-government in the Slovak Republic. The outcome of the evaluation of the survey is to identify the attitude of the representatives of municipalities towards the environment as well as to propose measures, whose implementation would contribute to increasing the level of municipal waste sorting in Slovak towns and municipalities.

***Keywords**: municipal waste, recovery of waste, waste disposal, landfilling, municipal, questionnaire survey*

Výzkum možností zpracování komunálních odpadů s ohledem na platnou a nově plánovanou legislativu na území statutárního města Opavy

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Souhrn

Cílem výzkumných aktivit bylo zhodnocení současného stavu nakládání s komunálním odpadem na území statutárního města Opavy a ideový návrh případného nového systému, který umožní nakládání s komunálním odpadem v souladu s novými trendy, které budou zakotveny v připravované legislativě platné v členských státech Evropské unie. Město Opava, situované v Moravskoslezském kraji, ukládá na skládky ročně přibližně 17000 tun směsného komunálního odpadu. V rámci výzkumných aktivit byl vytvořen technologicko – ekonomický model, který umožňuje srovnat náklady na případné zavedení nového systému nakládání se směsným komunálním odpadem (SKO) v různých variantách. V rámci výzkumu byly analyzovány technické varianty zpracování SKO, jako je třídicí linka, komunální bioplynová stanice, kompostárna, zařízení pro energetické využití odpadů, překládací stanice a předání odpadů k externímu zpracování. Jednotlivé varianty a jejich kombinace byly ekonomicky zhodnoceny.

Klíčová slova: *směsný komunální odpad, variantní zpracování odpadů, třídicí linka, energetické využití, bioplynová stanice, kompostárna*

Úvod

Pro řešení problematiky nakládání s odpady v rámci Statutárního města Opava je vhodné zařazení do kontextu v rámci Evropské unie, České republiky a regionální úrovně. Klíčový pro trend v nakládání s komunálním odpadem je ale legislativní rámec, zejména příprava nového zákona o odpadech.

V současné době je v České republice v platnosti zákon č. 185/2001 Sb., o odpadech[1]. Tento zákon zapracovává příslušné předpisy Evropské unie a upravuje pravidla pro předcházení vzniku odpadů a pro nakládání s nimi při dodržování ochrany životního prostředí, ochrany lidského zdraví a trvale udržitelného rozvoje a při omezování nepříznivých dopadů využívání přírodních zdrojů a zlepšování účinnosti tohoto využívání.

V rámci výzkumu byl brán ohled zejména na povinnosti při nakládání s komunálním odpadem, se směsným komunálním odpadem a biologicky rozložitelnou složkou komunálního odpadu.

Zákon[1] stanovuje, že v rámci odpadového hospodářství musí být dodržována následující hierarchie způsobů nakládání s odpady:

a) předcházení vzniku odpadů,

b) příprava k opětovnému použití,

c) recyklace odpadů,

d) jiné využití odpadů, například energetické využití,

e) odstranění odpadů.

Zákon[1] dále stanovuje povinnosti a oprávnění obce a fyzických osob při nakládání s komunálním odpadem. Obec ve své samostatné působnosti stanoví obecně závaznou vyhláškou obce systém shromažďování, sběru, přepravy, třídění, využívání a odstraňování komunálních odpadů vznikajících na jejím katastrálním území. Obec může vybírat úhradu za shromažďování, sběru, přepravy, třídění, využívání a odstraňování komunálních odpadů od fyzických osob na základě smlouvy. Vybírá-li obec tuto úhradu, nemůže stanovit poplatek za komunální odpad ani místní poplatek za provoz systému shromažďování, sběru, přepravy, třídění, využívání a odstraňování komunálních odpadů podle zákona o místních poplatcích. Obec může obecně závaznou vyhláškou stanovit a vybírat poplatek za komunální odpad vznikající na jejím území.

Obcím je stanovena povinnost zajistit místa pro oddělené soustřeďování složek komunálního odpadu, minimálně nebezpečných odpadů, papíru, plastů, skla, kovů a biologicky rozložitelných odpadů. Na skládky je od roku 2024 zakázáno ukládat veškerý neupravený směsný komunální odpad a recyklovatelné a využitelné odpady[2].

Nakládání s biologicky rozložitelnými odpady se řídí zákonem o odpadech[1] a vyhláškou MŽP č. 341/2008 Sb., o podrobnostech nakládání s biologicky rozložitelnými odpady[3]. Dle platné legislativy lze biologicky rozložitelné odpady zpracovávat v zařízeních, jejichž technologie je založena na aerobním nebo anaerobním biologickém rozkladu.

V současnosti je návrh nového zákona o odpadech v režimu připomínkového řízení[4]. Nový zákon o odpadech měl být platný od 1. 1. 2018. Hierarchie nakládání s odpady je obdobná jako v současně platném zákoně o odpadech a vychází ze Směrnice EU 75/442/ES. Specifikace podmínek pro nakládání s odpady k dosažení této hierarchie je však konkrétnější. Návrh nového zákona o odpadech[4] specifikuje i nástroje, jak této hierarchie dosahovat. Nově je uvedeno, kdy odpad přestává být odpadem. Jedná se zejména odpad, který je určen k opětovnému použití (např. díly autovraků) a dále odpad v okamžiku zpracování do výrobku v zařízení, které odpad přijímá jako vstupní surovinu.

Na skládky bude od roku 2024 zakázáno ukládat odpady, jejichž výhřevnost v sušině je vyšší než 6,5 MJ/kg, odpady, které nesplní parametr biologické stability AT4 vymezený v příloze č. 9 zákona[4] (charakterizuje biologickou aktivitu odpadu), a odpady, které je za stávajícího stavu vědeckého a technického pokroku možné účelně recyklovat. Návrh zákona[4] dále upravuje poplatky za ukládání odpadů na skládky. Navrhované poplatky za uložení jednotlivých druhů odpadů na skládku jsou uvedeny v tabulce 1.

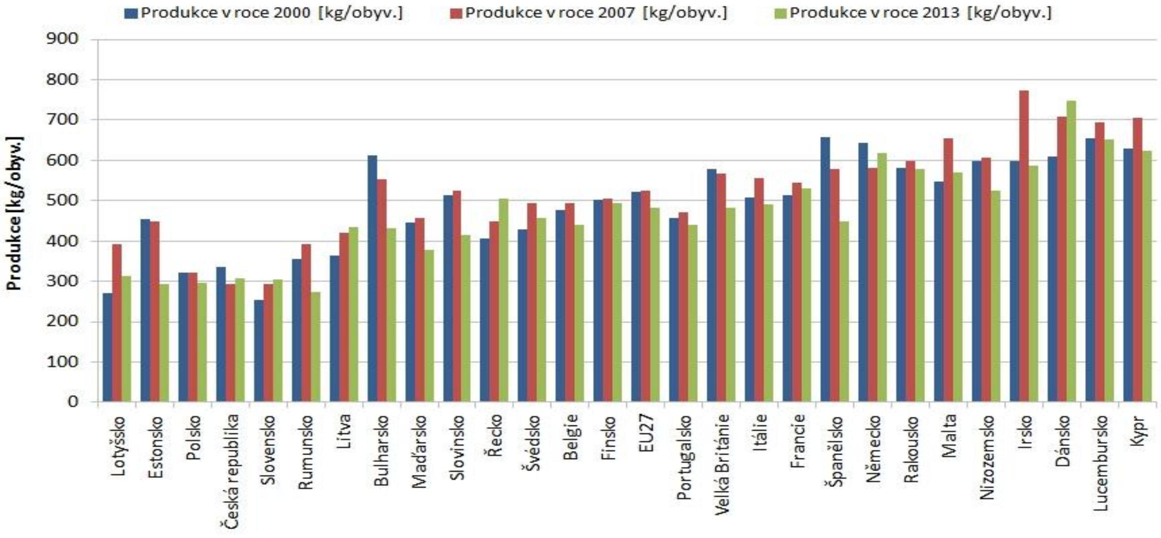
Tabulka 1: Sazba za ukládání odpadů na skládku (CZK/t)[4]

Dílčí základ poplatku za ukládání	**Poplatkové období v roce**												
	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030 a dále
využitelného odpadu	900	1150	1350	1550	1700	1850	2000	2000	2000	2000	2000	2000	2000
zbytkového odpadu	500	500	500	500	500	500	500	500	600	600	700	700	800
nebezpečného odpadu	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
vybraného technologického odpadu	45	45	45	45	45	45	45	45	45	45	45	45	45

Návrh nového zákona o odpadech[4] v obecné rovině rovněž řeší problematiku nakládání s **biologicky rozložitelným odpadem**, komunitního kompostování, používání kalů z ČOV i z potravinářských provozů na půdě a sedimentů vytěžených z vodních toků a nádrží.

Nakládání s komunálním odpadem ve vybraných zemích Evropy a v České republice

Základními zdroji dat o produkci a nakládání s odpady v Evropě jsou Evropská agentura pro životní prostředí, data zpracoval statistický úřad Evropské unie Eurostat a Organizace pro hospodářskou soutěž a rozvoj OECD. Mezinárodní srovnání produkce komunálních odpadů na obyvatele uvádí obrázek 1. Podíl energetického využití SKO ve vybraných zemích Evropy uvádí tabulka 2.



Obrázek 1: Mezinárodní srovnání produkce komunálních odpadů na obyvatele[5]

Tabulka 2: Energetické využití SKO ve vybraných zemích[5]

Země	Energetické využití [hm. %]
Rakousko	11
Belgie	33
ČR	13
Dánsko	53
Finsko	10
Francie	38
Německo	44
Maďarsko	8
Itálie	8
Nizozemsko	31
Norsko	15
Španělsko	6
Švédsko	38
Švýcarsko	48
Velká Británie	9

V roce 2017 bylo v České republice vyprodukováno 24,9 mil. tun odpadu, z toho 3,6 mil. tun komunálního odpadu. Směsný komunální odpad, představoval 2,1 mil. tun, tedy 58 % z celkové produkce komunálního odpadu[6]. Směsný komunální odpad je v České republice zpracováván ukládáním na skládky (cca 87 %) a energeticky využíván ve spalovnách odpadů (cca 13 %). Pro energetické využití směsného komunálního odpadu jsou v provozu 4 spalovny komunálních odpadů.

Možnosti nakládání s komunálním odpadem na katastrálním území města Opavy

Návrh možností nakládání s komunálním odpadem v Opavě reflektuje Plán odpadového hospodářství Moravskoslezského kraje pro období 2016-2026, který schválilo zastupitelstvo Moravskoslezského kraje dne 25. února 2016[7].

Stávající stav

Produkce komunálního odpadu samotného města Opavy ve výši cca 23 000 tun ročně je na úrovni 60 % okresu Opava. Podíl nevytříděného SKO činí 70 % z celkové produkce komunálního odpadu. Produkci komunálního odpadu a jeho složek uvádí tabulka 3[8]. Zpracování komunálních odpadů ve městě Opava provádí Technické služby Opava, s.r.o. (TSO).

Tabulka 3: Produkce komunálního odpadu v Opavě v letech 2014 a 2015

Druh odpadu	Celková produkce v tunách		kg/obyvatele
	2014	2015	
Papír a lepenka	2092,8	1519,3	26,3
Sklo	696,5	675,8	11,7
Nebezpečný odpad	20,5	15,9	0,3
Plasty	703,8	708,6	12,3
Kovy	3575,7	3664,9	63,5
Biologicky rozložitelný odpad	912,5	774,9	13,4
Směsný komunální odpad	13874,8	13 410	232,5
Objemný odpad	2618,5	2535,8	44,0
CELKEM	**24494,9**	**23305,0**	**404,1**

Část uvedené produkce je svážena TSO, s.r.o. jako tříděný odpad. Ten se dále dotřiďuje na ruční dotřiďovací lince a prodává jako surovina. Objemný odpad je po snížení objemu ukládán na skládku. Směsný komunální odpad je rovněž ukládán na skládku. Biologicky rozložitelný odpad spolu s odpadem z údržby zeleně je předáván ke kompostování externím subjektům. Zdrojem SKO je tedy svoz ze sběrných nádob a provoz sběrných dvorů, který zajišťují TSO, s.r.o. Biologicky rozložitelný odpad od občanů je v současnosti odebírán v rámci sběrných dvorů a jsou prováděny pokusné svozy sběrných nádob na biologicky rozložitelný komunální odpad (BRKO), aby bylo možno ověřit náklady na jeho svoz.

Návrhová část – technické zhodnocení

Podle stávající i připravované legislativy je SKO považován za využitelný a od roku 2024 jej nebude možno ukládat na skládky a bude potřeba jej upravit tak, aby jej bylo možno označit, dle nově připravované legislativy, odpadem „zbytkovým“. Po zhodnocení současných technických možností ve světě i v ČR byla vybrána dostupná technická zařízení pro možné zpracování SKO v Opavě se zahrnutím svozu z okolních obcí. Pak by bylo možno počítat s kapacitou alespoň 20000 t SKO za rok. To je obvyklá limitní minimální kapacita pro technologie na zpracování SKO. Základní technologie pro zpracování SKO s odlišnou filosofií jsou zařízení pro materiálové využití složek SKO a zařízení pro energetické využití SKO. Doplňkovými technologiemi jsou zařízení pro zpracování BRKO a případně linka pro hrubé předtřídění SKO na dvě základní složky. Ruční třídění SKO podle zkušeností z Evropy není vhodné, dochází k velké chybovosti, je nutný velký počet zaměstnanců, a vzhledem k jeho potenciální infekčnosti nastává problém s hygienou práce. Proto tato varianta nebude dále uvažována.

Pro uvažovanou kapacitu přicházejí v úvahu následující zařízení:
- linka pro třídění SKO
- zařízení pro hrubé předtřídění SKO
- zařízení pro anaerobní digesci BRKO
- zařízení pro aerobní digesci BRKO
- přímé energetické využití oxidačním procesem (spálení)
- překládací stanice a odvoz směsného komunálního odpadu k odstranění externí firmou.

Linka pro třídění SKO

Návrh technologie pro třídění SKO v zájmovém území vychází z moderních ověřených technologií, které fungují ve srovnatelných územích. Jedná se například o technologii třídicí linky směsného komunálního odpadu v polském městě Bielsko-Biała. Technologie uvedená do provozu v roce 2012 splňuje standardy BAT (Best available techniques - nejlepší dostupné techniky). Směsný komunální odpad je mechanicky tříděn na bubnových sítech na 3 frakce, a posléze ručně dotříděn na jednotlivé materiálově využitelné frakce, energeticky využitelný podíl a biologicky rozložitelnou frakci (lehká nadsítná frakce pro dotřídění na materiálově využitelné složky, střední frakce pro energetické využití, těžká podsítná frakce pro využití biologickými procesy). Na obdobném principu je navržena instalace linky pro dotřídění SKO v Karvinském regionu ve městě Havířov s kapacitou cca 40 000 t SKO/rok[9].

Linka pro hrubé předtřídění SKO

V případě použití jednoduššího zařízení na předtřídění SKO, budou výsledkem třídění dvě základní frakce:

- podsítná frakce, která obsahuje zejména BRKO a inertní odpad,
- nadsítná frakce, která obsahuje ostatní složky (materiálově a energeticky využitelné).

Výhřevnost podsítné frakce je zanedbatelná a výhřevnost nadsítné frakce je cca 18 Mg/kg. Předpokládá se, že podsítnou frakci bude pravděpodobně možné po stabilizaci biologicky rozložitelné složky uložit na skládku jako zbytkový odpad a nadsítnou frakci bude možno využít pro výrobu alternativního paliva. Navíc se předpokládá využití magneticky separovatelné složky – železa. Výše uvedené informace vyplývají z výsledků pilotních pokusů provedených ve společnosti OZO Ostrava, s.r.o.

Komunální bioplynová stanice (anaerobní digesce)

Podsítnou frakci získanou mechanickou separací tuhého komunálního odpadu lze zpracovat na rekultivační materiál pomocí procesu anaerobní digesce. Tímto procesem je možno rovněž zpracovat biologicky rozložitelný odpad z údržby městské zeleně i bioodpad separovaný u zdroje (obyvatel, živnostníků či firem) na energii a hnojivo. Produkován je bioplyn využitelný k výrobě elektrické energie aplikovatelné do sítě a tepelné energie (případně i chladu) v kogeneračních jednotkách. Odplyněnou biomasu je nejvhodnější ošetřit z hlediska obsahu závadných látek a navrátit ji do půdy, kde organická složka v dnešní době schází. Využít lze technologii bioplynové stanice (BPS) s „mokrým“, „polosuchým“ a „suchým“ procesem.

Kompostárna (aerobní digesce)

Pro účely kompostování jsou z technického hlediska k dispozici dvě základní technologie, a to kompostování na volných pásových hromadách a kompostování v biotabilizačních boxech. Kompostování na hromadách je vhodné pro zpracování velkých objemů biologicky rozložitelných odpadů za předpokladu zajištění vhodného složení vsázky, zajištění vhodných skladovacích prostor a dodržení správných procesních podmínek. Pro technické řešení lze uvažovat se dvěma variantami, a to podle způsobu provzdušňování. Jedná se o kompostování na pásových hromadách s použitím samochodného překopávače a kompostování na plošných hromadách s použitím překopávací frézy. Pro účely výroby certifikovaného kompostu lze využít BRKO z údržby veřejné zeleně respektive bioodpad separovaný u zdroje (obyvatel, živnostníků). Kompost vyrobený z podsítné frakce třídicí linky je méněhodnotný s ohledem na příměsi inertních materiálů a na možnou přítomnost toxických prvků a lze jej využít jako rekultivační materiál.

Zařízení pro energetické využití odpadů

Pro město Opava lze předpokládat návrh zařízení pro energetické využití SKO s jmenovitým výkonem 20 000 t SKO/rok. Instalaci takového zařízení v ČR provádí např. společnost EVECO Brno, s.r.o., která dodává jednotku s názvem EVELINE. Tato jednotka je schopna energeticky zpracovat až 30 000 tun SKO/rok. Jako stabilizační a přídavné palivo je použit zemní plyn. Energie spalin je využita pro výrobu páry o požadovaných parametrech. Vyrobená pára slouží pro generování elektrické energie turbínou pracující v Rankinově cyklu. Organický Rankinův cyklus (ORC) funguje na stejném fyzikálním principu jako tepelné oběhy v konvenčních elektrárnách a teplárnách. Zásadním rozdílem je použitá pracovní látka pro pohon turbín. U klasických bloků se využívá voda, ale ORC využívá organické látky (chladiva, silikonové oleje apod.). Organické látky mají výrazně nižší výparné teploty, proto se dají nasadit na recyklaci tepelné energie o nižších teplotách, která by se v tradičních zařízeních již nedala efektivně využít[10].

Předpokládaná průměrná výhřevnost komunálního odpadu je cca 8 až 10 MJ/kg. Toto tvrzení dokládá skutečnost, že v rámci prováděných výzkumných aktivit bylo provedeno roztřídění vzorku SKO (1 svozový vůz – cca 6 tun SKO) na vybrané frakce metodikou používanou ve společnosti SAKO Brno a.s., úprava těchto frakcí na analytický stav a stanovena hodnota výhřevnosti jednotlivých frakcí. Váženým průměrem byla určena hodnota výhřevnosti původního vzorku SKO, jak je uvedeno v tabulce 4.

Tabulka 4: Průměrná výhřevnost SKO v Opavě

Frakce SKO	% hm.	Hmotnost [t]	Výhřevnost složky [MJ/kg složky]	Podíl na výhřevnosti SKO [MJ/kg SKO]
Nevyužitelný zbytek	27,4	5452	1,50	0,41
Střední frakce	17,2	3429	18,50	3,19
Sklo	1,2	239	0,00	0,00
PET barevný	0,8	159	21,64	0,17
PET zelený	0,6	119	21,64	0,13
PET modrý	0,7	139	21,64	0,15
PE-folie	4,2	842	32,56	1,38
PEHD	0,7	131	29,14	0,19
PP	0,8	159	39,01	0,31
Nápojový karton	0,6	119	13,00	0,08
Papír, lepenka	15,4	3 066	13,00	2,00
Železo	1,1	215	0,00	0,00
Hliník	0,5	96	0,00	0,00
BRKO 0-80 mm	28,8	5 728	2,05	0,59
Celkem	**100**	**19 894**		**8,61**

Překládací stanice a odvoz SKO k externímu zpracování

Překládací stanice představují prostorově méně náročné vybavení pro překládání směsného komunálního odpadu ze svozových vozů do velkokapacitních kontejnerů. Předpokládá se denní naložení cca 4 – 6 kontejnerů o kapacitě 10 t. Toto množství přepraví ke zpracovateli cca 2 až 3 těžká nákladní vozidla denně. Překládací stanice musí být vybavena vhodnou manipulační plochou a nakladačem. V současnosti je možná varianta dodávky veškerého množství SKO z Opavy do třídicí linky OZO Ostrava s.r.o. Je závislá na dohodě Magistrátu města Opavy s OZO Ostrava s.r.o., tedy zejména na ceně za zpracování jedné tuny SKO. Vzhledem ke skutečnostem, že ještě není schválená nová legislativa, společnost OZO Ostrava s.r.o. není schopna stanovit přesnou cenu za odstranění odpadu. Po konzultacích s vedením OZO Ostrava s.r.o. byla odhadnuta cena za zpracování 1400,- až 1650,- Kč za 1 tunu směsného komunálního odpadu v místě odběru (areál OZO Ostrava a.s. v Ostravě – Kunčicích).

Návrhová část - ekonomické zhodnocení jednotlivých variant

Pro zpracování SKO v Opavě přichází v úvahu řada variant možných kombinací využití, přičemž jednotlivé varianty byly samostatně posouzeny. Jedná se o následující varianty:

1. Třídicí linka SKO a jeho materiálové využití
2. Třídicí linka a bioplynová stanice
3. Třídicí linka a kompostárna
4. Hrubé předtřídění SKO
5. Hrubé předtřídění SKO a kompostárna
6. Hrubé předtřídění SKO, kompostárna a separovaný sběr BRKO
7. Energetické využití SKO
8. Hrubé předtřídění a energetické využití SKO
9. Překládka a externí zpracování SKO v OZO Ostrava a.s.

Kromě uvedených variant byla uvažována varianta nulového stavu (nakládání dle současnosti) s přepokládanými požadavky připravované legislativy. Protože technologie a jejich výstupy i ekonomické využití spolu souvisí, byl vytvořen komplexní matematický model ekonomiky všech variant s řadou vstupů. Výstupem z modelu je cena za odstranění 1 t SKO a přepočet na jednoho obyvatele.

Vzhledem k značnému množství získaných a vypočítaných dat bude následně pro ukázku uvedena ekonomická bilance pro variantu 1 a variantu 7. Pro podrobnější informace o vytvořeném ekonomickém modelu popsaném v rozsáhlé výzkumné zprávě možno kdykoliv kontaktovat autory tohoto článku.

Varianta 1 - Ekonomická bilance třídicí linky SKO

Výše investičních nákladů v případě třídicí linky s kapacitou 20 000 t/rok je cca 240 mil. Kč. Cena zahrnuje veškeré strojní a technologické zařízení, stavební a montážní práce. Při stanovení ceny a provozních nákladů třídicí linky se vycházelo ze studie proveditelnosti Aquatest a.s.[8], z konzultací se zástupci ostravské pobočky firmy Aquatest a.s. a z konzultací s pracovníky společnosti Technické služby Havířov a.s. Cena může být ovlivněna technologickou skladbou třídící linky a stupněm automatizace. Při hodnocení příjmů a provozních nákladů hraje důležitou roli několik faktorů, jejichž hodnoty jsou nejisté. Jsou to zejména poplatky za zpracování různých druhů zbytkových odpadů a ceny za získané komodity. Dále hraje významnou roli cena dopravy včetně manipulace a složení SKO. Tyto údaje jsou stanoveny s podstatně menší nejistotou. Další údaje jsou exaktní a vycházejí z cen a z regionální ceny práce v roce 2015. Ekonomická bilance je uvedena souhrnně v tabulce 5.

Tabulka 5: Ekonomická bilance třídicí linky SKO

Celkové investiční náklady	Kč	240 000 000
s dotací	Kč	36 000 000
Celková životnost	roky	20
BILANCE ROČNÍCH NÁKLADŮ	**JEDNOTKA**	**NÁKLAD**
Náklady na třídění celkem	Kč	**-11 938 214**
náklady dle bilance odpadů a druhotných surovin v Kč na třídění 1 t	Kč/t	-600
Personální náklady celkem	Kč	**-6 311 803**
mzdy	Kč	-4 476 456
povinné pojistné	Kč	-1 566 760
sociální náklady	Kč	-268 587
Fixní náklady	Kč	**-1 850 000**
roční náklad z investice	Kč	-1 800 000
náklady na pojistné	Kč	-50 000
Proporcionální náklady	Kč	**-10 238 137**
energie a média - zpracování odpadu	Kč	-5 626 098
servis a údržba a reinvestice	Kč	-3 536 725
transport odpadů k lince	Kč	-1 075 315
CELKEM	Kč	**-30 338 154**
Měrné náklady na 1 t SKO	Kč	**-1 525**
Měrné náklady na 1 obyvatele	Kč	**-391**

Výše nákladů dle bilance odpadů a druhotných surovin je výsledkem ekonomické bilance využití případně odstranění složek směsného komunálního odpadu v cenách platných v roce 2016.

Varianta 7 – Energetické využití SKO

Cena jednotky na energetické využití směsného komunálního odpadu (EV SKO) byla stanovena na základě „know-how“ společnosti EVECO Brno, tedy na základě realizovaných (zejména zařízení na čištění spalin a spalovny průmyslových odpadů) a připravovaných (menší spalovny SKO) projektů. Z těchto zkušeností bylo vycházeno i v případě stanovení provozních nákladů jednotky na EV SKO.

Výše investičních nákladů v případě jednotky na EV SKO s kapacitou 20 000 t/rok je cca 250 mil. Kč. Cena zahrnuje veškeré strojní a technologické zařízení i stavební a montážní práce. Předpokládaná životnost této jednotky je 24 let. Životnost jednotky zcela zásadně ovlivňuje množství zpracovaného odpadu a tedy i ekonomiku provozu. V optimálním stavu je jednotka mezi 2. a 10. rokem. Výše investičních nákladů je ovlivněna konkrétní technologickou skladbou jednotky a může být tedy v určitém rozsahu upravena. Ekonomická bilance této varianty je uvedena v tabulce 6.

Tabulka 6: Ekonomická bilance jednotky EV SKO

Celkové investiční náklady	Kč	250 000 000
s dotací	Kč	250 000 000
Celková životnost	roky	24
BILANCE ROČNÍCH NÁKLADŮ	**JEDNOTKA**	**NÁKLAD**
Příjem za prodej komodit	Kč	**32 045 787**
prodej vyrobené elektrické energie	Kč/t	14 507 099
prodej vyrobeného tepla	Kč	17 538 688

Personální náklady celkem	Kč	**-6 223 311**
mzdy	Kč	-4 413 696
povinné pojistné	Kč	-1 544 794
sociální náklady	Kč	-264 822
Fixní náklady	Kč	**-10 416 667**
roční náklad z investice	Kč	-10 416 667
Proporcionální náklady	Kč	**-26 601 171**
energie, média - zpracování odpadu	Kč	-8 221 824
servis a údržba a reinvestice	Kč	-8 631 250
náklady spojené s rezidui (popel, škvára, odpadní voda)	Kč	-9 748 097
CELKEM	Kč	**-11 195 362**
Měrné náklady na 1 t SKO	Kč	**-563**
Měrné náklady na 1 obyvatele	Kč	**-144**

Vyhodnocení dosažených výsledků

Pro základní ekonomickou analýzu navrhovaných možností úpravy SKO byly vytvořeny modely ekonomických rozpočtů v rámci jednoho kalendářního roku. Pro možnost srovnání se stávajícím stavem byla použita vždy použita vstupní data z roku 2015. Cílovým rokem je rok 2024, kdy bude podle platného zákona o odpadech[2] zakázáno ukládání neupraveného SKO na skládky. K tomuto období jsou uvažovány odhady cen za odstraňování upravených složek odpadů, které budou souviset zejména s předpokládanou výší poplatků za ukládání na skládky.

Nakládání s SKO pro město Opava zajišťuje zejména podnikTSO, s.r.o. Tento podnik zajišťuje služby spojené s nakládáním s odpady také pro další obce na základě obchodních vztahů. Při ekonomickém hodnocení potenciálních zařízení se uvažuje, že i nadále budou zpracovány odpady z okolních obcí minimálně ve stejném rozsahu. Výsledky modelování - ekonomické analýzy jsou uvedeny v následující tabulce 7.

Tabulka 7: Přehled nákladů na odstranění SKO pro uvažované varianty

Varianta	**Zpracování 1 t SKO** [Kč/t]	**Zpracování SKO** [Kč/obyv.]	**Celkem za SKO** [Kč/obyv.]
stávající stav (současná legislativa)	**-1044**	-289	-585
stávající stav (návrh zákona)	**-2544**	-703	-1 000
třídící linka (TL)	**-1525**	-391	-688
TL + BPS	**-1081**	-277	-574
TL + kompostárna	**-1123**	-288	-585
předtřídění	**-2026**	-519	-816
předtřídění a kompostárna	**-1324**	-339	-636
předtřídění, svoz BRKO a kompostárna	**-1258**	-322	-619
jednotka EV SKO	**-563**	-144	-441
předtřídění a jednotka EV SKO	**-710**	-182	-479
externí zpracování v OZO	**-1917**	-491	-788

Tabulka 7 srovnává jednotkové náklady jednotlivých variant. V tabulce jsou zvlášť uvedeny náklady na zpracování 1 t SKO a na jednoho obyvatele pro každou technologii nebo jejich kombinaci a dále náklady na odstranění včetně stávajících nákladů na svoz a zpracování SKO ze sběrných dvorů.

Bilance zahrnuje ve svých modelech některé nejistoty ve vstupních datech. Jedná se zejména o možnost využití tepla z jednotky energetického využití SKO, konečné ceny investic jednotlivých staveb a technologií, poplatky za ukládání odpadu a povinná míra úpravy odpadu před uložením. Uvedené varianty jsou vybrány tak, aby reprezentovaly odlišné přístupy k řešení problematiky zpracování SKO. Je možné zahrnout i další kombinace různých technologií, které by kombinovaly úpravu SKO, materiálové využití některých složek a energetické využití jiných. To, jaký bude výsledný mix technologií, nebude záležet pouze na ekonomickém vyhodnocení, ale hlavně na dikci připravované legislativy. Rovněž bude záležet na časovém vývoji hodnoty peněz (inflaci).

Provedená ekonomická bilance ukazuje, že za uvedených předpokladů se jako nejvýhodnější ukazuje energetické využití SKO bez předchozí úpravy. Je pravděpodobné, že jako jediná varianta umožňuje ekonomickou návratnost investic v případě vyššího využití výroby tepla na úkor výroby elektrické energie. A to i bez dotací. Všechny ostatní varianty předpokládají pouze menší nebo větší zvýšení nákladů oproti současnému stavu. Z hodnocení automatické třídící linky je zřejmé, že v každém případě bude výhodné ji doplnit o další zařízení na zpracování vytříděné biologicky rozložitelné složky.

Závěry

1. Ze všech hodnocených variant vychází ekonomicky, prostorově a technicky nejvýhodněji varianta energetického využití SKO bez předchozí úpravy. Tuto variantu je možno realizovat za předpokladu dostatečného využití vyrobené tepelné energie. Energie je dostatečná na vytápění cca 1000 až 1500 bytů nebo objektu se spotřebou cca 50000 GJ za rok. Je možné uvažovat o vytápění ostrovního systému (například průmyslová zóna s okolní obytnou zástavbou) nebo o náhradě části energetických zdrojů společnosti Opatherm, a.s., která zajišťuje systém centrálního zásobování teplem v Opavě. Výhodou by byl přístup do celé opavské rozvodné sítě a spolu s ostatními zdroji Opathermu bezproblémové uplatnění celého tepelného výkonu zdroje.
2. Využití třídicí linky nebo hrubého předtřídění bez koncového zařízení na zpracování BRKO je ekonomicky nevýhodné.
3. Pokud bude volen způsob zpracování BRKO, je třeba brát v úvahu možnosti případného využití tepla a elektrické energie a hlavně to, že nakládání se znečištěným digestátem bude pravděpodobně vyžadovat další aerobní stupeň – kompostování. Znečištěný digestát totiž nebude pravděpodobně použitelný přímo jako hnojivo a jeho uložení na skládku bude vyžadovat další stabilizaci. U bioplynové stanice není možno zpracovávat odděleně znečištěný BRKO a čistý separovaný BRKO a je nevýhodné míchat tyto dvě složky dohromady. Proto je technicky i organizačně vhodnější přímo kompostování na hromadách, i když je ekonomicky mírně nevýhodnější, než bioplynová stanice. Kompostárna by kromě technického (znečištěného) kompostu mohla zároveň odděleně vyrábět prodejný kvalitní kompost ze zbytků z údržby zeleně a případného ze separovaného sběru BRKO.
4. Separovaný sběr BRKO je z ekonomického hlediska přibližně neutrální. Při určitých objemech může být ekonomicky výhodný, ale pokud by se uvažoval separovaný sběr i v zástavbě s hromadným bydlením, přinese s sebou i technické problémy a rizika. Například problém zápachu a případnou nutnost hygienizace.

V rámci výzkumných aktivit byl vytvořen technický a ekonomický model, který je možno modifikovat podle aktuálně schválené legislativy a použít pro hodnocení další řady variant pro nakládání s SKO nejen na katastrálním území města Opavy, ale rovněž může posloužit jako podpůrný materiál pro většinu měst, která budou v blízké budoucnosti problematiku nakládání s SKO řešit.

Poděkování

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Researech of New System of Municipal Waste Management with Regard to Valid and New Planned Legislation in Europenan Union Countries

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Summary

The aim of the research activities was to evaluate the current state of municipal waste management in the territory of Opava's statutory city and the real design of the new system with regard to the new trends that will be embedded in the forthcoming legislation on municipal waste management in the countries of the European Union. The city of Opava, located in the Moravian Silesian Region of Czech Republic, produces about 17,000 tonnes of mixed municipal waste per year. In the framework of the research, a technological and economic model has been created to compare the costs of introducing a new system of mixed municipal waste management in different variants. The research has analyzed technical variants of municipal waste treatment, such as the sorting line, the municipal biogas station, the composting plant, the waste energy utilization facility, the transfer station and the waste removal for external processing. These variants and their combinations were subsequently evaluated from an economic point of view. The results of these technological and economic analyzes will be of great benefit to many simillar cities across the Europe.

Keywords: *mixed municipal waste, options of waste treatment, separating unit, energy recovery, biogas station, composting plan*

FAKULTA STAVEBNÍ ústav technologie stavebních hmot a dílců

Ústav technologie stavebních hmot a dílců Fakulty stavební Vysokého učení technického v Brně zajišťuje výuku studentů **bakalářského i magisterského studijního oboru M** – Stavebně materiálové inženýrství, **doktorského studia** oboru Fyzikální a stavebně materiálové inženýrství a dále zajišťuje **specializované odborné kurzy, semináře a workshopy**.

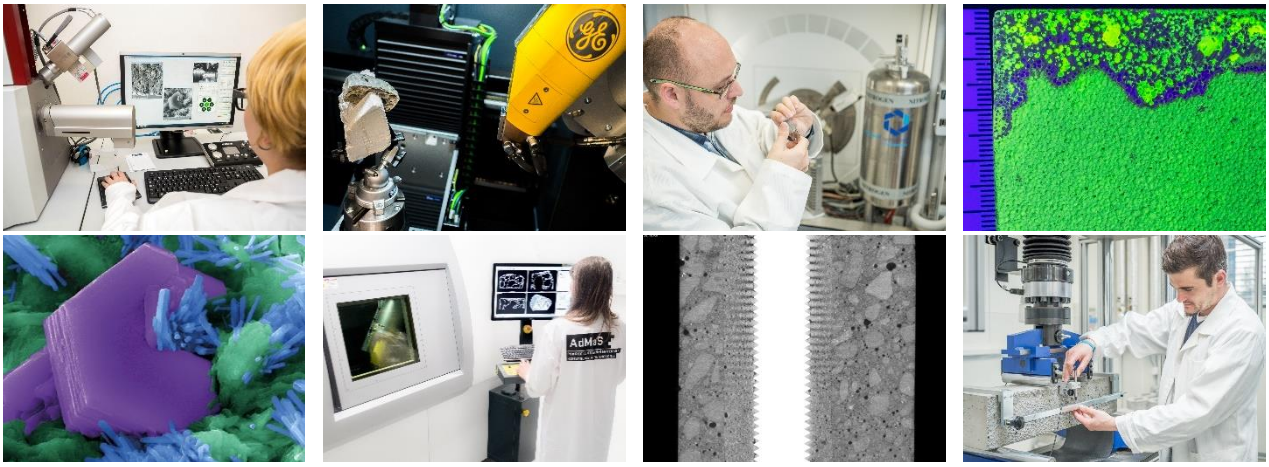
Výhodou studia na oboru M je prostor pro **individuální, až rodinný přístup** k jednotlivým studentům.

Absolventi oboru M disponují všemi patřičnými znalostmi profilujícími stavebního inženýra a získávají ucelený přehled o stavebních konstrukcích, klasických i nejnovějších stavebních materiálech a jejich aplikacích ve stavebnictví, získávají rovněž potřebné ekonomické vzdělání a díky univerzálním znalostem předpoklady uplatnit se v široké oblasti stavebních činností, ve velkých podnicích i při soukromém podnikání.

Vědeckovýzkumná činnost ústavu je zaměřena na technologii, užití stavebních hmot a výzkum stavebních dílců včetně jejich zkoušení.

Ústav technologie stavebních hmot a dílců nabízí služby, zaměřené na:

- vývoj a komplexní posouzení vlastností stavebních hmot a materiálů,
- zkušebnictví všech typů betonů, pojiv, kameniv, malt a keramických výrobků v akreditované zkušební laboratoři,
- analýzu mikrostruktury hmot včetně určení fázového složení a stanovení obsahu dílčích složek,
- 3D zobrazení mikro a makro struktury zkoumaných materiálů,
- testování reologických vlastností čerstvých kompozitů,
- detekci a lokalizaci poruch a vad materiálů, sledování rozvoje jejich deformace, rozvoje trhlin a koroze,
- simulace působení agresivních a klimatických vlivů pro ověření i prognózu trvanlivosti stavebních hmot,
- analýzy chování materiálů při různých teplotách až do výše 1 600 °C,
- stanovení objemových změn materiálů v různých teplotních a vlhkostních poměrech,
- diagnostika a posouzení (stavebně technické průzkumy, expertízy) stavebních hmot v konstrukcích,
- materiálové i technologické řešení sanací stávajících konstrukcí,
- testování tepelně izolačních, akustických, difúzních a jiných fyzikálních vlastností,
- návrh a ověření optimálního využití druhotných surovin jako náhrady surovin primárních,
- experimenty ve zkušebních pecích a aparaturách pro extrémní namáhání stavebních materiálů, prvků a konstrukcí (stanovení reakce na oheň, stanovení požární odolnosti).



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