# WASTE FORUM

ELECTRONIC PEER-REVIEWED JOURNAL ON ALL TOPICS
OF INDUSTRIAL AND MUNICIPAL ECOLOGY

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

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# Households as an important part of the circular economy

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## Summary

*Since the first industrial revolution, the economy has worked on a linear approach. Natural resources have been used to produce goods without considering how to handle them. In a linear economy, raw natural resources are transformed into products and disposed of in some countries without reuse. Currently, only 9% of world production operates on the circular economy principle, suggesting that only 9% of the 92.8 billion tonnes of minerals, metals, biomass and fossil fuels entering the economy are reused every year and the remaining 91% represents a "circular gap". The subject matter of the paper is a circular economy with an emphasis on the household sector, which will significantly contribute to the consumption of raw materials through the attitude towards meeting their needs. Monitoring the development of waste production or recycling rates is an assessment of past developments. In order to make the transition to the circular economy successful, it is necessary to change the behaviour of households to the consumption of resources, in the contribution we bring findings obtained from the questionnaire survey of the attitude of the inhabitants of the Slovak Republic on the selected sample. By evaluating the answers to the research questions, we can say that the inhabitants of the Slovak Republic are in favour of a greener way of life, which is an important prerequisite for the progress of the next generation in the area of waste management, but above all in waste prevention, which will have an impact on the conservation of natural resources. However, in addition to the positive results, we find that a large group of people do not prefer environmental behaviour and many also for financial reasons.*

**Keywords:** *circular economy, households, waste management, recycling*

## Introduction

The circular economy is characterized by a closed-loop of material and energy, taking into account natural and human resources, science and technology. The beginnings of the circular economy concept date back to 1960, when increased interest in environmental protection was noted. A number of ecologists, economists and other professionals have begun to address the issue of the circular economy [1, 2, 3, 4]. Based on their work, the circular economy strategy according to some is based on three[3], on four, six[5] or up to 9 principles[6, 7]. The principles are an economic code of conduct. For example, the framework of the four principles is used by the European Union (Principles of "4R" - Reduce - Reuse - Recycle - Recover). The Reduce principle is the orientation of the economy to scientific and technological progress and innovation to streamline resource use while minimizing raw material use and energy consumption. Reuse principle means requiring the manufacture of products and packaging materials with a reuse requirement. Manufacturers and constructors should prioritize the design of durable and reusable products, thus extending their life cycle. Recycle means to reuse these products as available resources at the end of the life of products and products. The necessity to build and support the development of the recycling industry, which will return waste and scrap (generated intermediates, raw materials and other materials) to the production process or other uses. The Principle of Recovering Natural Systems.

Each of these circulation strategies places different demands on socio-institutional changes and innovations in core or supportive technologies, product design and revenue. In order to make a successful transition to the circular economy a new product chain is needed, from the extraction and processing of raw materials, the production of materials through the production of products and the use of products to the collection and processing of discarded products. There is currently no systematic method in place to measure the progress of the transformation processes into the circular economy. The

European Environment Agency (EEA, 2016b) measures the transitional processes of the circular economy only to a limited extent, focusing on addressing the problems of reducing primary material consumption, material re-use, reducing the proportion of hazardous substances in products, extending product lifespan as well as activities related to high-value recycling.

In the following sections, we will focus on the need for material reuse, which is currently possible in the linear economy process through waste management and recycling because it is one of the principles of circular economy and society is not. As households are an important subject in the circular economy, we also examined attitudes to consumption and resource conservation.

## The need for efficient use of resources

The priority of the circular economy is the saving and efficient use of limited natural resources, streamlining the production of products with high efficiency and low resource consumption and low (or even zero) emission production. This includes preventing and reducing the production of waste and, consequently sources of pollutants, up to recycling, when the resources are returned to the business cycle, which is of increasing practical importance. This is mainly related to critical raw materials, which are found in limited quantities throughout Europe.

Natural resources are a prerequisite for the functioning of the global economy and the foundation of the quality of our lives. The price of natural resources used in industry has doubled over the past 10 years, a historical shift compared to the 20th century, when resource prices fell. The intensive use of global natural resources over the past decades has exerted pressure to replace them with other materials. In the future, it will no longer be possible to use natural resources in the same way as they do today. If current trends continue and the population by 2050 is in line with forecasts (by 30% worldwide, to some 9 billion people), the pressure on natural resources will increase as a result of meeting the basic needs of the population and producing more products. A key instrument for relieving pressure on natural resources is the transition to a circular economy to make efficient use of natural resources, manufactured products, streamline waste management and recycling.

Before 1980, the recycling rate was negligible. However, since then recycling and incineration rates have been increasing slowly. Based on available data, the highest recycling rates are in Europe (30%) and China (25%). Based on waste management information for 52 other countries, they indicate that in 2014, the rest of the world had a recycling and incineration rate similar to that in the United States. Regarding the recycling of plastics in the United States since 2012, it is 9%. The incineration rate gradually increased to 40 and 30% in Europe and China during 2014. In the United States, the fibre-free combustion of plastics was 21% in 1995 and then fell to 16% in 2014, with a recycling rate of 75% during this period. So far, end-of-life (fibrous) textiles do not show significant recycling rates and are therefore incinerated or disposed of with other solid waste. The potential for recycling waste, especially plastic waste, is largely untapped in the EU. End-of-life reuse and recycling of plastics is very low, especially when compared to other materials such as paper, glass or metals.

The European Union is keen to deepen cooperation with international partners in resource efficiency. Encouraging us to move towards a cleaner way of producing and transferring energy. The solution to this problem is the adoption of several secondary legal acts. Green Paper - A European strategy for tackling plastic waste in the environment (7. 3. 2013). In December 2008, the European Council endorsed the European Economic Recovery Plan. In the context of plastic disposal, the European Commission adopted an EU Circular Economy Action Plan in December 2015. It identified plastics as a key priority and committed to "develop a strategy to address the challenges posed by plastics throughout the value chain and their entire life cycle".

By 2025, the proportion of recycled plastic waste should reach 50%, by 2030 it should increase to 55%, the proportion of recycled glass by 2025 will be 70% and by 2030 75%, and by 2025 65% and by 2030 70%. The Directive also introduces mandatory reporting on the negative effects of street discarding of cigarette sticks with plastic filters, plastic cups or moistened wipes on the environment. The warning should be on the packaging of these products. In addition, stricter rules for calculating recycling rates will help to better monitor actual progress towards a circular economy.

The reason for the new activities of the European Union is above-average waste production. Based on Eurostat data, the highest waste production in 2017 was in kg / person in the Netherlands (513 kg), Norway (748 kg), Denmark (781 kg), and Cyprus (637 kg). With these countries, relatively less waste is produced in Poland (315 kg), Romania (272 kg), the Czech Republic (344 kg), the Slovak Republic (378 kg). Although waste production in the Nordic countries is high, it is higher compared to post-socialist countries. Recycling is one of the important preconditions for the proper functioning of waste management and the circular economy. In 2016, 55% of all waste was recycled across the EU. Compared to the 2010 level (53%), this is a slight increase. Regarding recycling by waste type, recycling rates vary. Significant increases in recycling have been reported by Member States for mixed municipal waste, where recycling rates have increased from 35% in 2007 to 46% in 2017. The recovery rate for construction and demolition waste reached 89% in 2017 and the recycling of packaging waste exceeded 67% and plastic packaging recycling was 42%. In the case of waste electrical and electronic equipment (computers, televisions, refrigerators, mobile phones), 41% of the total volume was recycled in 2017, while in 2010 it was approximately 28%. Despite the increasing share of recycling, however, recycled materials are still low in the EU. Only about 12% of raw material resources come from recycled products and materials. Thus, the vast majority of the raw materials we use remain primary natural resources. Waste production is also associated with higher living standards in the country. In Figure 1 we can see the amount of waste production in kg / person and the GDP index.

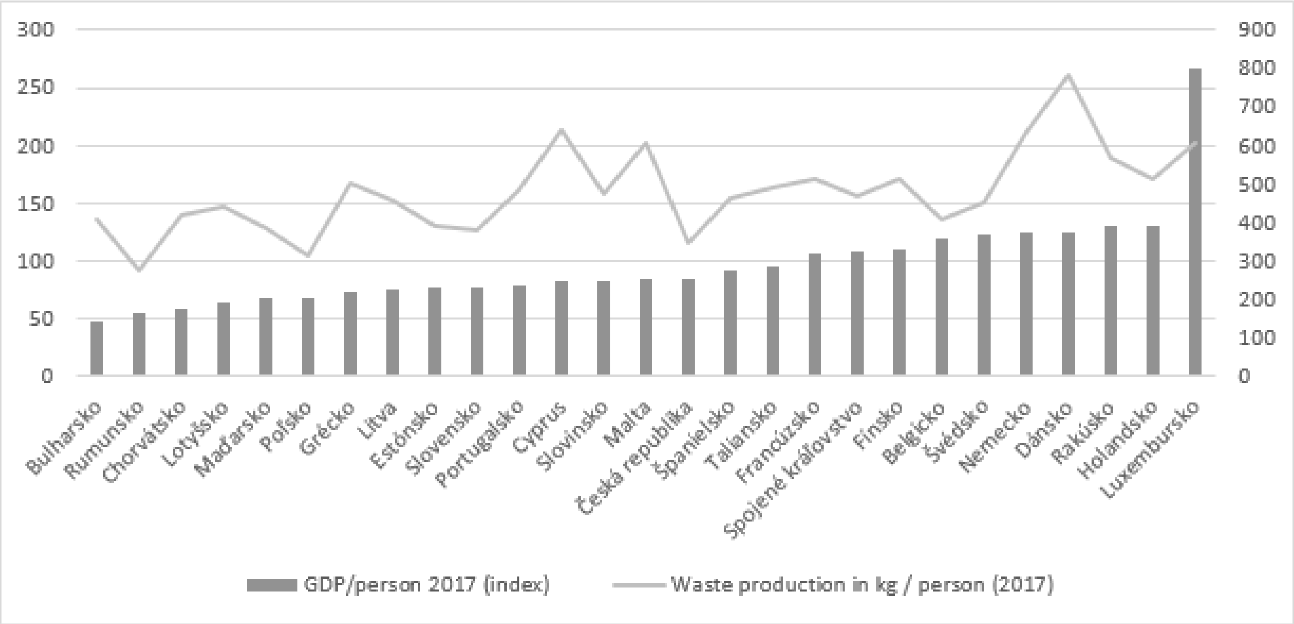


***Figure 1: Waste production (in kg /person) and GDP development (%) in EU countries***

*Source: graph based on Eurostat data*

As far as waste production in the Slovak Republic is concerned, the production of municipal waste is increasing, the production of hazardous waste has decreased and the production of other waste is increasing. However, the recycling rate of waste is very low and the number of landfills that pollute the environment is growing. Most of the waste produced (62%) was landfilled. However, in recent years, the reported rate of recycled packaging has declined in Slovakia. From a maximum level of 5 7% in 2012 to almost 52% in 2016. At the same time, Slovakia and some other countries are among those where recycling of this type of waste has tripled since 2005. Examples include countries such as Belgium, Denmark, the Netherlands, Germany, Austria and Sweden, where in 2014, for example, almost no municipal waste was landfilled. In 2017, the European Commission recommended Slovakia to improve waste management, in particular by increasing recycling, introducing separate collection and reducing landfill, improving air quality in critical regions of the country, especially in urban areas such as Bratislava and Košice, phasing out harmful brown coal subsidies, and improving water management and introducing more modern municipal waste water treatment systems.

Municipal waste charging is a necessary measure to ensure that waste is sorted. The average price for depositing one ton of waste in a landfill is € 25 in Slovakia. Compared to the surrounding countries, where the rate is 60 – 120 €, the fee in Slovakia is low. The Ministry of Environment of the Slovak Republic has already put forward a proposal for a decree, which includes an increase in landfill fees. Fees are based on a real survey of waste management needs. Municipalities that have landfills in their cadastre also welcome the increase in the landfill fee. They know that if the life of a landfill is extended by 10-15 years, the landfill contributions will be much longer than if the landfill had ended. In total, this will be an increase of just a few € per capita, since they no longer pay the collection fees. In EU countries, the waste fee is EUR 120 – 150 / person / year.  The higher the fee, the less landfills in the country (Figure 2)

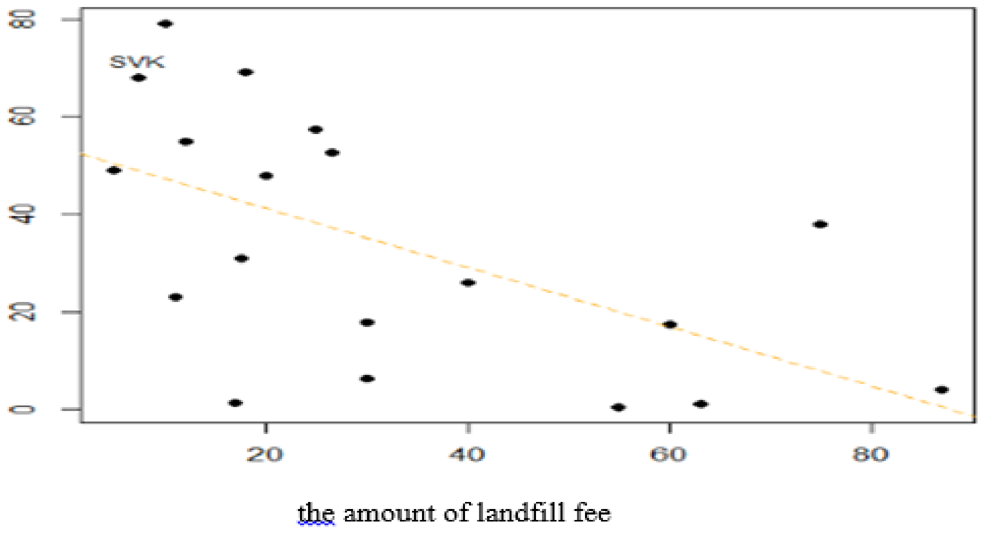


***Figure 2: Landfill rate (%) (Left axis) versus landfill charge***

A frequent counter-argument is the higher average wage in these countries. When recalculating costs per person per year compared to average wages, Slovaks only pay 0.22%. Other EU citizens, where the average wage is 2 – 3 times higher, pay up to 4.7% of the average wage. Few communities have well-defined waste targets and a plan to implement them over the years. Municipalities in Slovakia aim to fulfil certain obligations under the Waste Act. In the vast majority of cases, changes in self-government happen after legislation changes. However, it is good to make changes in advance. It is important to set the right motivation system, e.g. Pay as You Throw, where mixed municipal waste charges are set at such a high level that they are not liable to be irresponsible to their environment. They reward those residents by reducing the waste collection fee. A very important condition, which greatly affects the whole situation, is the level of awareness of the population as waste producers, the quality of the products they buy about the subsequent sorting of their waste, because the amount of landfilled waste develops depending on the price of landfilling. Based on the data on fees and landfill rates in different countries, we have found, using linear regression, that countries with higher fees have lower landfill rates.

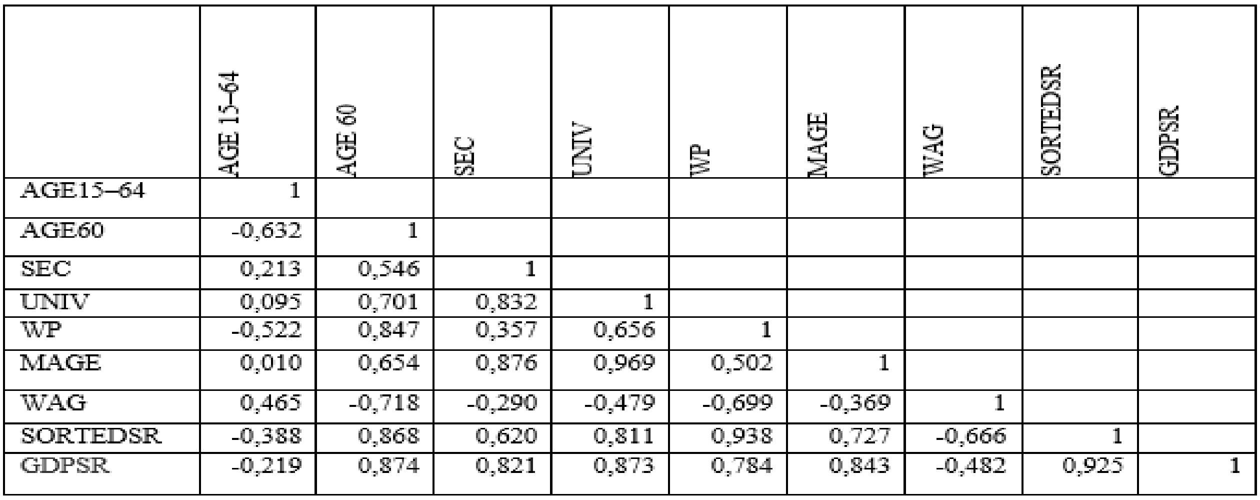
## Results and discussions

In addition to businesses, households make a significant contribution to the production of municipal waste, which was also documented by statistical data. Many factors influence the behaviour of households in relation to waste production. This behaviour has been investigated by several authors who have focused on monitoring the relationship between socio-economic characteristics of households (age, gender, household members, education, etc.) and waste management. According to Jenkins et al. [8], D'Elia [9], Bandara et al.[10], Benitez et al.[11] household size. Abbott et al.[12] found a positive relationship between the size of households and the recycling rate of bio-waste, the relationship was statistically insignificant when examining the relationship between the size of households and the recycling rate of other waste. The authors also investigated the relationship between recycling rates and Sidique et al. [13], Kipperberg[14] found a positive relationship between recycling rates and age.

Terry [15] found a positive relationship between recycling rates and the population aged 25 – 44. No influence of age on recycling behaviour has been confirmed in the works of D'Elia [9], Hage and Söderholm[16]. The impact of education on recycling rates was studied by Sidique et al.[13] and found that the higher the proportion of residents studying at university for at least 4 years, the higher the recycling rate for municipal waste. This fact was also confirmed in research by Miller et al. [17] and Jenkins et al.[8]. As far as waste production is concerned, in their work the authors dealt with the impact of the age on waste production[9, 16]. However, they did not confirm the impact of gender on the amount of municipal waste produced. In her research, Rybová[18] explored the impact of 13 socio-demographic variables on waste production and found that statistically significant are 6 variables (average household size, share of university graduates, share of family houses, purchasing power parity, share of employed persons) socio-economic factors also measure economic well-being and quality of life: quality of life is higher with rising income levels [19], GDP[20] and purchasing power index[21], which positively affects waste production.

In the following section, we present the results of the socio-economic analysis, for which we were inspired by the work of several authors and ascertained whether the findings we have obtained are identical, resp. differ from the development in the Slovak Republic. For the analysis we used data from the Statistical Office of the Slovak Republic, Eurostat and the Human Development Index. We followed the relationships between socio-economic characteristics of households and also selected macroeconomic variables and waste management (AGE15-64 - Percentage of population aged 15 – 64 age 15/64, AGE 60 Percentage of population aged 60 years, SEC - Percentage of population with secondary education UNIV - Percentage of university graduates, WP - Waste production kg / person MAGE - Median age, WAG Percentage of population working in agriculture, SORTEDSR - Development of the Sorted Impact in the Slovak Republic in % SR, GDPSR - GDP/person in €). From the found values we created a correlation matrix. Based on the findings, we can say that in the Slovak Republic there is a positive impact between university-educated and waste sorting, between the population over the age of 60 and waste sorting. Also, college and residents over 60 produce more waste. Weak dependence between people with secondary education and waste production.

***Table 1: Correlation matrix***



| | AGE 15–64 | AGE 60 | SEC | UNIV | WP | MAGE | WAG | SORTEDSR | GDPSR |
|---|---|---|---|---|---|---|---|---|---|
| AGE15–64 | 1 | | | | | | | | |
| AGE60 | -0,632 | 1 | | | | | | | |
| SEC | 0,213 | 0,546 | 1 | | | | | | |
| UNIV | 0,095 | 0,701 | 0,832 | 1 | | | | | |
| WP | -0,522 | 0,847 | 0,357 | 0,656 | 1 | | | | |
| MAGE | 0,010 | 0,654 | 0,876 | 0,969 | 0,502 | 1 | | | |
| WAG | 0,465 | -0,718 | -0,290 | -0,479 | -0,699 | -0,369 | 1 | | |
| SORTEDSR | -0,388 | 0,868 | 0,620 | 0,811 | 0,938 | 0,727 | -0,666 | 1 | |
| GDPSR | -0,219 | 0,874 | 0,821 | 0,873 | 0,784 | 0,843 | -0,482 | 0,925 | 1 |

## Analysis of questionnaire survey of household attitudes towards circular economy

Circular economy, also called a green economy, is a new economic model, which is the opposite of the current model - a linear economy, based on high consumption of non-renewable raw materials, which is an unsustainable state in the long term. The introduction of a circular economy requires the cooperation of consumers, business, development workplaces, academia and politics. An important subject in the circular economy is just households, which at the same time have a positive tendency to consume and increase pressure on the production of goods. In the following section we present the results of the questionnaire research carried out by us to find out the attitudes of the population or the households in the Slovak Republic to the circular economy and waste prevention.

The research was carried out in the months of March and April 2019, attended by 482 respondents, divided into six age ranges (under 18 in 20 respondents, 159 respondents in the age range 18 – 26, 27 – 35 in the age range 147 respondents, 53 respondents in the age range of 36 – 50 years, 47 respondents in the age range of 51 – 62 years, and 56 respondents in the age range of 62 and more years). Depending on the level of education attained, the highest number of respondents with secondary education (%), first-level university education (%), with second level university education (%). Most respondents were from the Bratislava region (%). Almost equal numbers were from other regions. 259 respondents come from the city and 223 live in the village. A large group of respondents are employed and self-employed. The largest group according to the income level is respondents with the income of 501 – 1000 EUR. The surveys themselves concerned the survey of respondents' attitudes to waste management.

The circular economy model is supposed to contribute to stable economic growth and a healthy environment. As the respondents perceive this model through the research question 1: Do they know the circular economy model and what is its advantage? Respondents had the opportunity to choose 3 variants (I know, I know little, I don't know). 58% of respondents said they knew little, 26.7% did not know and 15.3% knew what the circular economy was. At the same time, respondents who said they knew the circular economy model said they were solving waste problems, protecting the rye environment.

Respondents' answers to Research Question 2: How often do you get rid of waste? We find that the highest number of respondents throws out garbage as needed 46.5%, of which the most in the age category 18-26, employment and household income of 501 – 1000 EUR per month. Most people throw rubbish as needed in the Bratislava region. The second research question 3: Do you have the possibility of separate collection in your town / municipality? We have investigated whether respondents have the opportunity to sort waste at their place of residence. Almost all respondents have the option of separate waste collection (93.4% of respondents). Only two replied that they were unable to sort waste at their place of residence.

Consumer behaviour is an important factor in preventing waste production. From the answers to the research question 4: Do you think when buying goods ecologically? We found that up to 56.8% of respondents responded negatively, 6.6% of respondents do not care and only 36.6% deal with this problem. Respondents with completed secondary education had the most negative answers, but we have to mention that people with a tertiary level of tertiary education and a tertiary level of tertiary education responded in equal numbers and are not very different from those in secondary education. Young people in the 18 – 26 age group were the largest group on the one hand in the answer "yes", but on the other hand in the answer "no". So it may be noted that a group of young people are interested in whether they are buying products without further waste production. The respondents in the 501 – 1500 € income group are also thinking about the environment when purchasing.

In research, we also looked for answers to research question 5: What shopping bags do you use? The answers clearly show that most of the respondents carry their own bag with them (76%). The second most common answer was the option "depending on the trade offered to me". In most stores we have a choice of several kinds of bags and so the consumer himself can decide what kind of bag he chooses. In general, paper bags are more expensive and so the price for a bag can affect consumer behaviour. However, even in the case of plastic bags, shops are introducing more environmentally friendly bags with reduced lifetime. In connection with plastic waste, we also investigated through research question 6: Would you agree to return used plastic bottles back to the store? Where as in many countries this method of reducing the production of plastic waste is put into practice. In Germany and Sweden, recycling rates of up to 98% have been achieved through bottle backup. Up to 85% of respondents agree to return plastic bottles back to the store, with only 1% disagreeing with bottle backups. The implementation of this system in Slovakia has been accompanied for many years by fighting between traders who claim that this system is too expensive.

Since Slovakia is one of the countries with a low recycling rate (28%) and a large number of legal and illegal landfills, we have researched question 7: Would you agree to increase the fees for municipal waste? Almost 97.3% of university graduates welcome the increase in these fees. At the same time, they propose to increase fines for illegal landfill. Only 23.6% of respondents with primary education living in the village disagree with raising fees. From answers to research question 8: What is your attitude towards a shared economy? We have found that 25.8% of respondents with primary education over the age of 62 do not recognize the concept, 56.7% of respondents in the 36 – 50 age range have heard about the shared economy, but do not use the services offered, 87.4% of those with secondary education and 88.7% of respondents with a university degree in the 18 – 26 age group living in cities use the opportunities offered by the shared economy model.

## Conclusions

In recent years, the possibility of replacing the current production and consumption model, which is based on continuous growth and increasing resource consumption, has been increasingly appealing. The reason for encouraging change to a new production model within the economic system is to increase resource efficiency, with particular emphasis on urban and industrial waste, in order to achieve a better balance and consistency between the economy, the environment and society. The intensive use of the world's natural resources over the past decades has exerted pressure on their substitution by other materials, and in particular plastics of various kinds. When they started to be used more than a century ago, no one thought that they would be the enemy of our planet and would endanger the lives of its people.

Building a circular economy will require a coherent change in the interconnection of activities of multinational, national, regional and non-governmental entities in the Slovak Republic and other countries of the world. Such a transition will be very complex and requires changes, which is already being implemented slowly in the European Union through many measures (energy union, greener transport, organic farming, new industrial policy) to change people's attitudes (efficient heating, waste separation) , enterprises (supporting research and innovation activities) to respond to changes in energy, logistics or financial subsystems. It is also necessary to steer the education system towards education and understanding these changes and to introduce effective changes, as the transition to the circular economy is not necessarily “better” than linear systems. Inefficient circular systems can create many social, economic and environmental damages (eg due to overexploitation of transport and energy when production has moved to countries with cheap labour, mineral resources) quality in the production process, the organization of smart logistics, investment in training processes to acquire the necessary technical skills, shortening delivery times, maintenance and environmental protection requires a change in production and business models

It will be very important to change consumer behaviour, as the growth of the world population places increasing demands on the natural resources, which put more pressure on the environment. Only in the twentieth century, global population growth combined with welfare growth resulted in increased material consumption 34 times, mineral more than 27times, and 12times higher fossil fuel consumption. Demand for consumer products is projected to increase material consumption in 2050 compared to 2000, three times. Of course, consumers will influence manufacturers and they will be forced to respond to their needs. The transition to a circular economy from linear can be considered as an innovation. However, innovation must be accepted by the society. However, this also applies to all other process changes related to the further functioning of our life on the planet and to the understanding that the beginning of the circular economy is not just a waste management, as many have presented.

The transition to a circular economy can be seen as innovation. However, this innovation must be accepted by the entire society. All procedural changes related to the further functioning of our life on the planet require an understanding that the beginning of the circular economy is not just waste management as it is often presented.

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## Literature

1. Allwood, J.M., et al.: Material efficiency: a white paper resources. (2011). Conserv. Recycling 55 (3), 362 – 381.
2. Beek, M. van, et al.: From Rhetoric to Reality: The Circular Economy Index of Dutch Businesses. (2016).
3. Ghisellini, P.: Cialani, C.: Ulgiati, S.: A review on circular economy: the expected transition to a balanced interplay of environmental and economic systems. (2016). J. Clean. Prod. 114, 11 – 32.
4 Gladek, E.: The Seven Pillars of the Circular Economy. (2017).
5. Sihvonen, S.: Ritola, T. V.: Conceptualizing ReX for aggregating end-of-life strategies in product development. Proc. CIRP 29, 639 – 644. (2015).
6. van Buren, N., et al.: 2016. Towards a circular economy: the role of dutch logistics industries and governments. Sustainability 647.
7. Potting, J., et al.: Circular Economy: Measuring Innovation in the Product Chain. (2017). Planbureau voor de Leefomgeving, No. 2544. https://www.pbl.nl/sites/default/files/cms/publicaties/pbl-2016-circular-economy-measuring-innovation-in-product-chains-2544.pdf
8. Jenkins, R. R., et al.: The determinants of household recycling: a material-specific analysis of recycling program features and unit pricing. (2003). Journal of environmental economics and management, vol. 45, issue 2, p. 294 – 318. ISSN 0095-0696.
9. D'Elia, J. L. I.: Determinants of Household Waste Recycling in Northern Ireland. (2008). Economic Research Institute of Northern Ireland. 2008.
10. Bandara, N. J. G. J., et al.: Relation of waste generation and composition to socio-economic factors: A case study. (2007). Environ. Monit. Assess. 135, 31 – 9.
11. Benitez, S. O. et al.: Mathematical modeling to predict residential solid waste generation. (2008). Waste Management, vol. 28, supplement 1, p. 7 – 13. ISSN 0956-053X
12. Abbott, A.: Nandeibam, S.: O'Shea, L.: Explaining the variation in household recycling rates across the UK. Ecological Economics. (2011) vol. 70, issue 11, s. 2214 – 2223. ISSN 0921-8009.
13. Sidique, S. F.: Joshi, S. V.: Lupi, F.: Factors influencing the rate of recycling: An analysis of Minnesota counties. (2010). Resources, Conservation and Recycling. 2010, vol. 54, issue 4, s. 242 – 249. ISSN 0921-3449.
14. Kipperberg, G.: A comparison of household recycling behaviors in Norway and the United States. (2007). Environmental and Resource Economics. 2007, vol. 36, issue 2, s. 215 – 235. ISSN 1573-1502.
15. Terry, N.: The determinants of municipal recycling: a time series approach. (2002).Southwestern Economic Review. 2002, vol. 29, issue 1, p. 53 – 62. ISSN 1941-7683.
16. Hage, O.: Söderholm, P.: An econometric analysis of regional differences in household waste collection: the case of plastic packaging waste in Sweden. (2008). Waste management. vol. 28, issue 10, p. 1720–1731. ISSN 0956-053X.

17. Miller, I., et al.: Determinants of Municipal Solid Waste Generation and Recycling in Western New York Communities. (2009). The Journal of Solid Waste Technology and Management, Number 4. November 2009, 209 – 236(28). ISSN 1088-1697. DOI: https://doi.org/10.5276/JSWTM.2009.209
18. Rybová, K.: Jak ovlivňují socio-demografické proměnné produkci tříděného sběru komunálního odpadu? Případová studie České republiky. WASTE FORUM. 2017, číslo 2, ISSN: 1804-0195.
19. Monavari, S.M.: Omrani, G.A.: Karbassi, A.: Raof, F.F.: The effects of socioeconomic parameters on household solid-waste generation and composition in developing countries (a case study: Ahvaz, Iran). (2012). Environ. Monit. Assess. 184, 1841 – 1846.
20. Beigl, P.: Wassermann, G.: Schneider, F.: Salhofer, S.: Forecasting municipal solid waste generation in major European cities. 2004. International Congress: Complexity and Integrated Resources Management. Osnabrueck, Germany.
21. Bach, H.: Mild, A.: Natter, M., Weber, A.: Combining socio-demographic and logistic factors to explain the generation and collection of waste paper. Resour. Conserv. Recycl. 41, 65 – 73. (2004). https://doi.org/10.1016/j.resconrec.2003.08.004.

# Domácnosti ako dôležitá súčasť cirkulárnej ekonomiky

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## *Súhrn*

*Od prvej priemyselnej revolúcie fungovala ekonomika na lineárnom prístupe. Prírodné zdroje sa využívali vo výrobe tovarov bez úvahy o tom, ako sa s nimi bude nakladať. V lineárnej ekonomike sa surové prírodné zdroje transformujú na produkty a likvidujú sa v niektorých krajinách bez opätovného využitia. V súčasnosti iba 9 % svetovej výroby funguje na princípe cirkulárnej ekonomiky, čo vypovedá o tom, že iba 9 % z 92,8 miliárd ton nerastov, kovov, biomasy a fosílnych palív, ktoré vstupujú do ekonomiky, sa každý rok opätovne používa a zvyšných 91 % predstavuje „kruhovú medzeru“. Predmetom skúmania v príspevku je cirkulárna ekonomika s dôrazom na sektor domácností, ktoré postojom k uspokojovaniu svojich potrieb výrazne prispievajú k spotrebe surovín. Sledovanie vývoja produkcie odpadov, či miery recyklácie je hodnotenie minulého vývoja. K tomu, aby bol prechod na cirkulárnu ekonomiku úspešný, je potrebné predovšetkým zmeniť správanie sa domácností k spotrebe zdrojov, V príspevku prinášame zistenia získané z dotazníkového prieskumu postoja obyvateľov Slovenskej republiky na vybranej vzorke. Vyhodnotením odpovedí na výskumné otázky môžeme konštatovať, že obyvatelia Slovenskej republiky sú naklonení ekologickejšiemu spôsobu života, čoho dôležitým predpokladom k pokroku je výchova ďalších generácií v oblasti odpadového hospodárstva, no predovšetkým k výchove o predchádzaní vzniku odpadov, čo bude mať vplyv na šetrenie prírodných zdrojov. Okrem pozitívnych výsledkov, však zisťujeme, že značná skupina obyvateľov nepreferuje ekologické správanie a mnohí aj z dôvodov finančnej náročnosti.*

***Keywords:*** *Cirkulárna ekonomika, domácnosti, odpadové hospodárstvo, recyklácia*

# Changes of chemical and biological parameters during vermicomposting of kitchen biowaste with an emphasis on pathogens

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## *Summary*

*Food and kitchen biowaste can be an environmental and economic problem if not managed properly. The aim of this study was to uncover the effect of an outdoor vertical-flow vermicomposting system with continuous feeding by kitchen biowaste on pathogens in relation to the biological and chemical properties. After one year of outdoor vermicomposting the chemical and biological stability of vermicompost was found. Pathogens were reduced by 66%, while Salmonella spp. was not present at all. With the increasing age of the vermicompost, the total microbial biomass and its components (fungi, actinobacteria, G+ and G- bacteria) as well as enzymatic activity declined. The average activity of enzymes such as β-D-glucosidase, phosphatase, sulfatase, lipase, chitinase, cellobiohydrolase, in the bottom layer was less by 53% compared to the top layer. The moisture and EC decreased to 48% and 722 $\mu S \cdot cm^{-1}$, respectively. On the other hand, the pH increased up to 8.0. The decreasing trends of $C_{tot}$ and $N_{tot}$ correlated positively with their available forms such as DOC, $N\text{-}NO_3^-$, and $N\text{-}NH_4^+$, with their proportions of the total content at 1.1%, 0.9%, and 0.3%, respectively. Among other nutrients, $Ca_{tot}$, $K_{tot}$, and $Fe_{tot}$ exhibited the greatest contents (identically 1.3%) followed by $Mg_{tot}$ (0.35%) and $P_{tot}$ (0.3%). The proportion of the available contents of K, Fe, Mg, and P constituted on average in all of the three layers 39%, 2%, 12%, and 16%, respectively, of the total content.*

***Keywords:*** *vermicomposting, earthworms, kitchen biowaste, layers, pathogens, chemical and biological properties*

## Introduction

Only 2/3 of the food products produced each year are utilized, which equates to 1.3 billion tons of food which is unnecessarily wasted[1]. In the countries of the European Union, food losses amount to 88 million tons per year, which has a negative impact on the use of primary resources, individual segments of the environment, and ultimately, the economy[2]. Food waste contains a wide range of chemical substances. The chemical composition is affected by the proportion of individual foods. On average, it contains 60% starch, 30% lipids, and 10% proteins[3,4].

Besides the avoidance of food loss or waste, a proper re-utilization seems to be the only responsible way of dealing with wasted food today and in the future[5]. Food and kitchen biowaste can be an environmental and economic problem if not managed properly[6]. The food waste produced from restaurants and canteens form a major component of the putrefying organic waste that ends up in landfill sites. High moisture, the requirement for a bulking substrate, and low pH are the main problems encountered with food or kitchen biowaste composting or vermicomposting[7,8]. Therefore, especially, constant care with moisture management and a suitable ratio of carbon and nitrogen is required for successful processing[9].

The earthworms are involved in the vermicomposting process of biowaste by creating small corridors through which the air can flow. Using microorganisms and their enzymes, they digest organic substances, creating vermicompost with a high agronomic value[10]. From the operational point of view, vermicomposting unlike classical composting is a mesophilic process. With the use of temperatures above 35 °C the earthworms will leave the processed biowaste or die. The elevated temperature maintained for some time is a key factor in classical composting for reduction of human pathogens such as *E. coli, Salmonella* spp., helminths, and various human viruses. However, elevated temperatures of 70 °C have adverse effects on the rate of decomposition because the activity of microorganisms decreases[11]. The sensitivity of the earthworms to high temperature can be solved by the initial thermophilic pre-composting without the presence of earthworms and subsequent vermicomposting[12]. However, this combination may not be possible for technical, spatial, or economic reasons. Previously, there was a view that vermicomposting itself was capable of reducing or completely eliminating the number of pathogenic microorganisms[13,14]. The mechanisms by which this occurred are not fully known. These are direct influences (mechanical disruption using ingestion and grinding, microbial assimilation, enzymatic digestion, effect of microbial antagonists and antimicrobial substances produced by the earthworms) and indirect influences (phagocytic activity with the participation or absence of earthworms, production of antimicrobial substances such as humic acids, the stimulation of endemic or other microbial species leading to competition). The most likely mechanism is probably a combination of these effects[15]. It was reported that the inactivation of the pathogenic load largely depends on the earthworm species involved in vermicomposting, because individual species have different abilities to eliminate pathogens[16].

The aim and at the same time novelty of this study was to uncover the effect of an outdoor vertical-flow vermicomposting system with continuous feeding by kitchen biowaste on pathogens in relation to the biological and chemical properties.

## Experimental part

### *Experimental setup*

The experiment was conducted in three concrete boxes each with a ground plan 2 m x 2 m placed in outdoor conditions at the Research Institute of Agricultural Engineering, Prague, Czech Republic (50°5'11.327"N, 14°18'7.522"E).

The bedding of grape marc with earthworms (*Eisenia andrei*) was placed first. Next 10 cm layers of kitchen biowaste were added every 3 weeks. Adding a thin layer prevents the warming which the earthworms are sensitive to. To reduce evaporation, the surface was covered with special fabrics which allowed for air exchange while retaining water. If necessary, the vermicomposted material was irrigated to maintain 80 – 85% moisture content which is optimal for earthworms[17]. After one and half years from the beginning of the experiment, samples were taken up from the cross profiles of different depths, and the average ages above the bedding from each of the 3 boxes in the three replications was as follows:

A: 0 – 20 cm, 1 – 6 months
B: 20 – 40 cm, 6 – 12 months
C: 40 – 60 cm, 12 – 18 months

The weight of each primary sample was about 5 kg. The resulting vermicompost sample without earthworms was divided into 3 parts, each of 1 kg, and treated as required for laboratory analyses. One part of the vermicompost sample was stored for a brief period at 4 °C, the second part was dried at 35 °C to a constant weight, the third part of the vermicompost sample was frozen at -20 °C and then lyophilized.

### *Biological and chemical analyses*

Pathogenic microorganisms were determined in the fresh sample by cultivation on selective diagnostic media and confirmed by biochemical tests[18]. The contents of the containers with the tested substrates were first weighted, diluted, and homogenized. Ten-fold diluted suspensions of samples were used for cultivation of microorganisms. Dehydrated complete preparations (HiMedia) were used for the initial suspensions, dilutions, and culture media. Thermotolerant total coliform bacteria were determined by capturing on the surface of the solid soil with lactose. M-FC agar (Membrane Fecal Coliform Agar) was used as the culture medium. This agar is selective for thermotolerant coliform microorganisms and contains lactose, bile salts and aniline blue. After culturing for 24 hours at 43 ± 1.0 °C, characteristic blue colonies were counted. At least 5 characteristic colonies were inoculated onto nutrient agar for subculture for 24 hours at 36 ± 1.0 °C for oxidase testing. Subsequent confirmation was performed by a negative oxidase assay. To determine the number of *Escherichia coli* (*E. coli*), selected colonies from M-FC agar were inoculated onto 4-methylumbelliferyl β-D-glucuronide-saturated medium (MUG) and cultured for 4 hours at 37 ± 1.0 °C. *E. coli* showed a light blue fluorescence under a UV light emitting radiation of 360 nm wavelength. Enterococci were cultured on solid medium with sodium azide and 2,3,5-triphenyltetrazolium chloride, which reduced the bacteria to red formazan, causing the characteristic colony staining. Incubation was carried out for 4 hours at 36 ± 1.0°C and then 24 hours at 43 ± 1.0 °C. Colonies were confirmed on bile-esculin-azide agar by culturing for 4 hours at 43 ± 1.0 °C. For positive or negative finding of *Salmonella* spp. non-selective cultivation in peptone water was performed for 20 hours at 36 ± 2.0 °C, selective growth in Rappaport-Vassiliadis medium for 24 hours at 41 ± 1.0°C, and growth in soil with selenite and cystine for 24 hours at 36 ± 1.0 °C, followed by cultivation on solid selective soil - phenol red and brilliant green agar and xylosol-lysine-deoxycholate agar. After incubation of the cultures for 24 hours at 36 ± 1.0 °C, growing colonies were subjected to confirmation by biochemical assays.

Samples for the phospholipid fatty acid (PLFA) analysis were extracted in triplicate using a mixture of chloroform-methanol-phosphate buffer (1:2:0.8; v/v/v) from the lyophilized samples. Analyses were done by the Institute of Microbiology of the Czech Academy of Sciences, Prague, Czech Republic. The extracts were analyzed by tandem gas chromatography-mass spectrometry (GC-MS; 450-GC, 240-MS Varian, Walnut Creek, CA, USA). Methylated fatty acids were identified according to their mass spectra using a mixture of chemical standards obtained from Sigma-Aldrich, Prague, Czech Republic and Matreya LLC, USA. The gram positive (G+) bacteria biomass were quantified as the sum of i14:0, i15:0, a15:0, i16:0, i17:0, and a17:0. The gram negative (G-) bacteria were determined by sum of 16:1ω7, 18:1ω7, cy17:0, cy19:0, 16:1ω5. The 10Me-17:0, 10Me-18:0, and 10Me-16:0 were used for actinobacteria biomass. For the total biomass of the bacteria, the acids for G+, G-, actinobacteria, and also 16:1 ω 9, 17:0, 10Me-18:0, cy19:0 were used. The 18:2ω6,9 was used to determine the fungal biomass. The total biomass was quantified as the sum of all of the markers together with 16:0 and 18:1ω9[19].

The enzymatic activity of β-D-glucosidase, acid phosphatase, arylsulphatase, lipase, chitinase, cellobiohydrolase, alanine aminopeptidase, and leucine aminopeptidase were measured in 96-well microplates. 0.2 g of lyophilized vermicompost was extracted with 20 mL of acetate buffer (pH 5.0, c = 50 $\text{mmol}\cdot\text{L}^{-1}$) in an Erlenmeyer flask. The mixture was homogenized using the Ultra-Turrax (IKA Labortechnik, Germany) for 30 s at 8,000 rev/min. Individual enzyme activities were measured in four replications. 200 µL of the homogenized sample was pipetted into appropriate wells in the microplate and then 40 µL of substrate was added. The microplate was placed in an incubator heated to 40 °C for 5 min, and after the fluorescence was measured using the Tecan Infinite® M200 (Austria). The microplate was again placed in the incubator for 2 h and the fluorescence was measured again[20]. For the calibration curve 1.0 $\text{mmol}\cdot\text{L}^{-1}$, 0.1 $\text{mmol}\cdot\text{L}^{-1}$, 0.01 $\text{mmol}\cdot\text{L}^{-1}$ methylumbellyferol, and 0.1 $\text{mmol}\cdot\text{L}^{-1}$, 0.01 $\text{mmol}\cdot\text{L}^{-1}$ 7-aminomethyl-4-coumarin were used.

The pH, oxidation-reduction potential (ORP), and electrical conductivity (EC) were measured in the fresh samples. Measurements were conducted on samples mixed with deionized water (1:5 w/v wet basis) using a WTW pH 340 i (pH and ORP) and WTW cond 730, respectively according to BSI EN 13037[21]. The CHNS Vario MACRO cube analyzer (Elementar Analysensysteme GmbH, Germany) was used for the determination of total carbon ($C_{tot}$) and nitrogen ($N_{tot}$) in the dried samples. The total contents of P, K, and Mg were determined by decomposition utilizing digests obtained by pressurized wet-ashing ($HNO_3 + H_2O_2$) of dried sample in a closed system with microwave heating (Ethos 1, MLS GmbH, Leutkirch im Allgäu, Germany). The contents of ammonium nitrogen ($N\text{-}NH_4^+$), nitrate nitrogen

($N\text{-}NO_3^-$), dissolved organic carbon (DOC), and the available portions of P, K, and Mg were determined in CAT solution (0.01 mol·$L^{-1}$ $CaCl_2$ and 0.002 mol·$L^{-1}$ diethylene triamine pentaacetic acid (DTPA)) at the rate of 1:10 (w/v), according to the International BSI EN 13651[22]. The $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, and DOC contents in the extracts were measured using the SKALAR SANPLUS SYSTEM® (the Netherlands). The total and available element concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN VistaPro, Varian, Australia).

### Statistical analysis

The results are presented as the mean values of three replicates. Nonparametric Kruskal-Wallis ANOVA ($P \leq 0.05$), including testing for normality and homogeneity of data, were performed using STATISTICA 12 software (StatSoft, Tulsa, USA).

## Results and discussion

Total coliforms, enterococci, and *E. coli* were the most represented pathogens. *E. coli* is generally found in animal waste[23] and food waste[24]. *Salmonella* spp. was absent during vermicomposting (Figure 1).

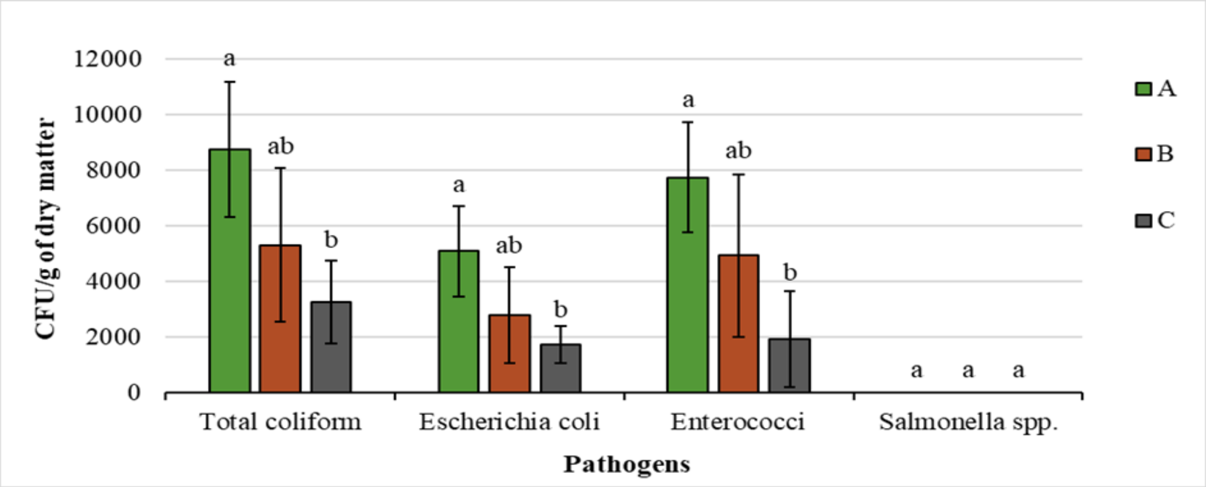

**Figure 1: Distribution of bacterial pathogens in layers A, B, and C during vertical-flow vermicomposting. The values are the means ± SD (n=3). Different letters indicate significant differences within a group (Kruskal-Wallis test, P≤0.05)**

**A: 0 – 20 cm, 1 – 6 months; B: 20 – 40 cm, 6 – 12 months; C: 40 – 60 cm, 12 – 18 months**

All pathogens showed the greatest values in layer A (total coliform bacteria: 8,733 CFU/g of dry matter; *E. coli*: 5,100 CFU/g of dry matter; enterococci 7,733 CFU/g of dry matter) and the least values were in layer C (total coliform bacteria: 3,267 CFU/g of dry matter; *E. coli*: 1,733 CFU/g of dry matter; enterococci 1,913CFU/g of dry matter). The oldest layer C contained the least amount of total coliforms, *E. coli*, and enterococci by 63%, 66%, and 75%, respectively, compared the young layer A. Statistically significant differences were found between these two layers (A and C) for all pathogens (except Salmonella spp., which was not present in all layers). In another experiment, apple pomace substrate was artificially inoculated with *E. coli*, *Salmonella* spp., thermotolerant coliform bacteria, and enterococci to assess the contribution of earthworms *Eisenia andrei* during the selective reduction of the pathogens. The inner side of the intestinal tract of earthworms was changed by the artificial bacterial load. On the contrary, intestinal activity, reproduction, and earthworm weight were not affected by the addition of pathogens. The earthworms reduced the amount of *E. coli* significantly more (63-fold, 77-fold, and 840-fold) than enterococci (6-fold, 36-fold, and 7-fold) after 2, 4, and 6 weeks, respectively[25]. The authors explain the rapid reduction of *Salmonella* spp. by the upregulated expression of two pattern recognition receptors, which bind lipopolysaccharide-binding protein, lipopolysaccharide, and coelomic cytolytic factor. Similarly, other authors found a reduction of pathogens during the vermicomposting of the organic fraction of municipal solid waste using *Eudrilus eugeniae*, even greater than during in-vessel composting[26]. In the case of total coliforms and *E. coli* a 3.12 log and 6.14 log reduction, respectively, was found for food waste after 10 weeks of vermicomposting. Both composting and vermicomposting generated Salmonella-free products. They speculated that the absence of *Salmonella* spp. in vermicompost might be caused by the stimulation of an endemic microflora that reduces the pathogens. In another study, *Salmonella spp*. decreased by 97.8% to 99.9% compared to the control without earthworms[27]. Khwairakpam and Bhargava[28] exhibited a reduction of 99% in total coliforms using *Eisenia fetida*, *Eudrilus eugeniae*, and *Perionyx excavatus* after 6 weeks of vermicomposting of sewage sludge. Yadav et al.[29] reported 100% removal of both total and fecal coliforms during 60 days of vermicomposting of source-separated human feces using *Eisenia fetida*. Complete sanitization of *E.coli*, *Salmonella* spp., and *Shigella* spp. during 60 days of vermistabilization of various agricultural wastes, such as rice straw, sugar cane, and vegetable wastes amended with cow dung was reported by Kumar and Shweta[30]. Swati and Hait[31] summed up the results of 15 experiments with different feedstock and concluded that reduction varied from 85 to 100% for total coliforms, 93 to 100% for fecal coliforms, 99.7% for fecal enterococci, 97.66 to 100% for *E. coli*, and 85.7 to 100% for *Salmonella* spp. In contrast to previous studies, Cao et al.[32] found that the *E. coli* levels decreased slightly during the first 75 days, while increased levels were observed after 90 days of both lab and field experiments with mixtures of vegetables, fruits, and paper. At the end of the experiments, *E. coli* levels were in the same orders of magnitude as in the initial samples. The results of their study showed that the pathogen reduction in vermicomposting is uncertain, probably due to low temperature and the insufficient air circulation. The mechanism for pathogen inactivation might vary with different feedstock and experimental conditions, which requires improved understanding to consolidate the pathogen inactivation mechanisms in the vermicomposting process.

During vermicomposting, the pathogens enter the food chain of earthworms and the predator-prey relationship is established, resulting in the rapid sanitization of wastes. The major sources of nutrients in the diet of earthworms include fungi and protozoa, whereas bacteria are of the least importance[23]. It is known that actinobacteria and fungi metabolize products that have antibacterial effects on the composting process[33]. In the current study, the proportion of the sum of fungi and actinobacteria in the total microbial biomass among the layers (10.7% ±1.3) was similar (Figure 2).

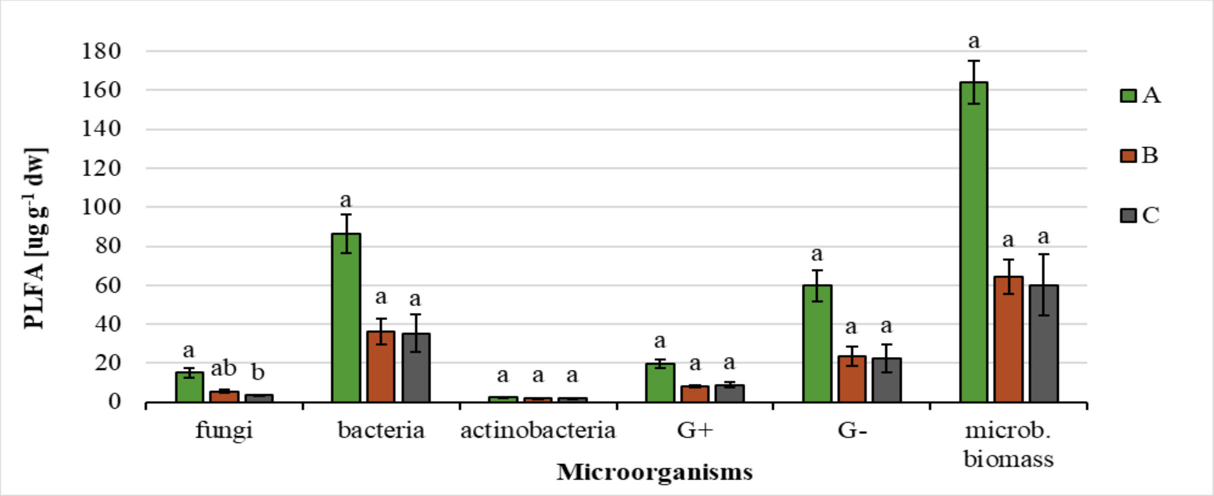

***Figure 2: Changes in fungal PLFAs, bacterial PLFAs, and total microbial PLFAs biomass in the layers of the vertical flow vermicomposting system. The values are the means ± SD. Different letters within a group indicate significant differences (Kruskal-Wallis test, P≤0.05)***
***A: 0 – 20 cm, 1 – 6 months; B: 20 – 40 cm, 6 – 12 months; C: 40 – 60 cm, 12 – 18 months***

However, with the increasing age of the vermicompost, the total microbial biomass and its determined components (fungi, actinobacteria, G+ and G- bacteria) declined. The bacteria, especially G- bacteria were the most represented in vermicompost. The greatest content of G- bacteria (59.8 $\mu g \cdot g^{-1}$ dw) was found in the youngest layer A as well as the total microbial biomass. The least total microbial biomass and its components were found in the oldest layer C, with the exception of the G+ bacteria which had the lowest value (8.3 $\mu g \cdot g^{-1}$ dw) in layer B. No statistically significant differences between the layers were found in microbial biomass, except the fungi PLFAs, where a statistically significant difference between layer A and layer C was found. The bacterial/fungal ratio increased with the age of the layers (layer A: 5.7; layer B: 6.4; layer C: 9.9). The greatest microbial biomass content was in layer A (164.2 $\mu g \cdot g^{-1}$ dw) and it was more than two times greater than the least content of microbial biomass (60.1 $\mu g \cdot g^{-1}$ dw, which was found in layer C), but no statistical difference was found. Swati and Hait[31] compared five vermicomposted wastes from the point of view of total bacterial, fungal, and actinomycetes population[31]. The greatest content of all the populations was found in the case of herbal pharmaceutical waste (initial total bacterial population: 9,500 x $10^7$ CFU/g, final total bacterial population: 15,000 x $10^7$ CFU/g, initial total fungal population: 120 x $10^4$ CFU/g, final total fungal population: 400 x $10^4$ CFU/g, initial total actinomycetes population: 10,000 x $10^4$ CFU/g, final total actinomycetes population: 20,000 x $10^7$ CFU/g). The total bacterial population was found during the vermicomposting of paper mill sludge, and the fungal and actinomycetes populations were found in the case of toxic weeds. Since the above results were determined by another procedure, they cannot be compared with the results of this study. Aira et al.[23] found 70-fold, 9-fold, and 1.5-fold total, bacterial, and fungal PLFA during the vermicomposting of cow manure compared food waste in this study.

The greatest values of all enzymatic activities were measured in the youngest layer A (Table 1) and the least values were for ß-D-glucosidase (448.3 µmol MUFG$\cdot h^{-1} \cdot g^{-1}$), acid phosphatase (587.4 µmol MUFP$\cdot h^{-1} \cdot g^{-1}$), arylsulphatase (15.0 µmol MUFS$\cdot h^{-1} \cdot g^{-1}$), lipase (2,233.7 µmol MUFY$\cdot h^{-1} \cdot g^{-1}$) in the oldest layer C, and for chitinase (16.4 µmol MUFN$\cdot h^{-1} \cdot g^{-1}$) and cellobiohydrolase (8.6 µmol MUFG$\cdot h^{-1} \cdot g^{-1}$) in layer B.

***Table 1: Enzymatic activity of different layers (A-C) in the vertical-flow windrow vermicomposting system***

| **Layer** | **A** | **B** | **C** |
|---|---|---|---|
| β-D-glucosidase [µmol MUFG$\cdot h^{-1} \cdot g^{-1}$] | 775.9 ± 252.3 $^{a}$ | 683.4 ± 224.4 $^{a}$ | 448.3 ± 256.3 $^{a}$ |
| Acid phosphatase [µmol MUFP$\cdot h^{-1} \cdot g^{-1}$] | 1707.5 ± 309.6 $^{a}$ | 884.1 ± 154.1 $^{ab}$ | 587.4 ± 57.7 $^{b}$ |
| Arylsulphatase [µmol MUFS$\cdot h^{-1} \cdot g^{-1}$] | 36.9 ± 16.7 $^{a}$ | 28.8 ± 10.5 $^{a}$ | 15.0 ± 4.3 $^{a}$ |
| Lipase [µmol MUFY$\cdot h^{-1} \cdot g^{-1}$] | 2977.3 ± 804.4 $^{a}$ | 2452.4 ± 325.1 $^{a}$ | 2233.7 ± 166.2 $^{a}$ |
| Chitinase [µmol MUFN$\cdot h^{-1} \cdot g^{-1}$] | 66.1 ± 65.1 $^{a}$ | 16.4 ± 8.6 $^{a}$ | 26.8 ± 14.6 $^{a}$ |
| Cellobiohydrolase [µmol MUFC$\cdot h^{-1} \cdot g^{-1}$] | 43.1 ± 24.2 $^{a}$ | 8.6 ± 7.1 $^{a}$ | 14.6 ± 8.6 $^{a}$ |
| Alanine aminopeptidase [µmol AMCA$\cdot h^{-1} \cdot g^{-1}$] | n. d. | n. d. | n. d. |
| Leucine aminopeptidase [µmol MUFG$\cdot h^{-1} \cdot g^{-1}$] | n. d. | n. d. | n. d. |

*Values are the means ± SD (n=3). Different letters in a superscript indicate significant differences (Kruskal-Wallis test, P≤0.05). n. d. = no detection*
*A: 0 – 20 cm, 1 – 6 months; B: 20 – 40 cm, 6 – 12 months; C: 40 – 60 cm, 12 – 18 months*

The most active enzymes were lipase and acid phosphatase, which exhibited multiple times greater activity than the least active enzymes (arylsulphatase, cellobiohydrolase, and chitinase). The activity of ß-glucosidase in the experiment done by Fernández-Gómez et al.[34], who vermicomposted sheep manure for 210 days using *E. fetida*, increased (from 1000 µg PNP$\cdot g^{-1} \cdot h^{-1}$ to 6000 µg PNP$\cdot g^{-1} \cdot h^{-1}$) initially, but after 90 days of vermicomposting decreased (to 500 µg PNP$\cdot g^{-1} \cdot h^{-1}$). They also measured the activity of acid phosphatase, which decreased from 4000 µg PNP$\cdot g^{-1} \cdot h^{-1}$ to 1000 µg PNP$\cdot g^{-1} \cdot h^{-1}$ as in our study. The same trend was also observed in a vermicomposting study of winery waste (vinasse biosolids mixed with vine shoots) in laboratory conditions[35]. The activity of ß-glucosidase increased from 10,000 µg PNP$\cdot g^{-1} \cdot h^{-1}$ to 20,000 µg PNP$\cdot g^{-1} h^{-1}$ after 8 weeks of vermicomposting, and then decreased to 5000 µg PNP$\cdot g^{-1} \cdot h^{-1}$. The activity of phosphatase only decreased with the time of vermicomposting (from 80,000 µg PNP$\cdot g^{-1} \cdot h^{-1}$ to 10,000 µg PNP$\cdot g^{-1} \cdot h^{-1}$). The activities of alanine and leucine aminopeptidase were below the detection limit. Only one enzymatic activity, in which a statistically significant difference (between layer A and C) was found, was acid phosphatase activity.

The greatest moisture content (Table 2) was found in the youngest layer (layer A), and it was similar in the vermicompost from grass clipping, shredded paper, and kitchen waste done by Nair et al[9] using *Lumbricus rubellus* and *Eisenia fetida* earthworms[9].

***Table 2: Select parameters of different layers (A-C) in the vertical-flow windrow vermicomposting system***

| Layer | A | B | C |
|---|---|---|---|
| Moisture [%] | 52.4 ± 3.9 $^a$ | 51.3 ± 1.3 $^a$ | 50.5 ± 3.2 $^a$ |
| pH/$H_2O$ | 7.6 ± 0.2 $^a$ | 7.8 ± 0.2 $^a$ | 7.9 ± 0.1 $^a$ |
| EC [$\mu S \cdot cm^{-1}$] | 999 ± 231 $^a$ | 813 ± 125 $^a$ | 783 ± 54 $^a$ |
| ORP [mV] | 254 ± 5.8 $^a$ | 260 ± 2.4 $^a$ | 257 ± 4.9 $^a$ |
| $C_{tot}$ [%] | 21.3 ± 2.6 $^a$ | 21.1 ± 2.7 $^a$ | 17.9 ± 1.3 $^a$ |
| C/N | 13.7 ± 1.2 $^a$ | 14.8 ± 1.8 $^a$ | 13.0 ± 1.2 $^a$ |
| $N\text{-}NH_4^+$ [$mg\ N \cdot kg^{-1}$] | 94.3 ± 38.2 $^a$ | 52.5 ± 32.6 $^a$ | 38.3 ± 11.0 $^a$ |
| $N\text{-}NH_4^+/N\text{-}NO_3^-$ | 0.7 ± 0.4 $^a$ | 0.3 ± 0.2 $^a$ | 0.4 ± 0.1 $^a$ |
| DOC [$mg\ C \cdot kg^{-1}$] | 2530 ± 417 $^a$ | 2184 ± 105 $^a$ | 2118 ± 102 $^a$ |

*Values are the means ± SD (n=3). Different letters in a superscript indicate significant differences within a parameter (Kruskal-Wallis test, P≤0.05).*
*A: 0 – 20 cm, 1 – 6 months; B: 20 – 40 cm, 6 – 12 months; C: 40 – 60 cm, 12 – 18 months*

In this experiment, the moisture decreased with the age of the layers, but was not statistically significant. The pH value ranged from 7.6 (layer A) to 7.9 (layer C), which is slightly less than in experiments done by Hanc and Pliva[7], and Nair et al.[9], where the pH values were about 8.5. The EC decreased with the age of the layers, which is also confirmed by Majlessi et al.[36], who vermicomposted pre-composted food waste for 7 weeks in plastic bags using *Eisenia fetida*. The ORP fluctuated between 248 mV (layer A) to 262 mV (layer B). The $C_{tot}$ was the greatest in layer A (on average 21.3%), but the greatest C/N ratio (on average 14.8) was found in layer B. The $C_{tot}$ value decreased with the age of the vermicompost, as well as in the vermicompost from food waste in a study by Arancon et al.[37], where the C*tot* value of the mature vermicompost was 19.5%. The reduction of the C/N ratio can be influenced by the enzymatic activity[9], which was the greatest in layer A (see above). The decreasing trends of $C_{tot}$ and $N_{tot}$ correlated positively with their available forms such as DOC, $N\text{-}NO_3^-$, and $N\text{-}NH_4^+$. The greatest

$N\text{-}NH_4^+$ and $N\text{-}NH_4^+/N\text{-}NO_3^-$ ratio were found in layer A, and these values decreased with the age of the layers (Table 1). The $N\text{-}NH_4^+$ value in the experiment done by Hanc and Pliva[7], who vermicomposted kitchen waste with wood chips for 5 months using *Eisenia*, first dropped from 160 mg N·kg$^{-1}$ to 40 mg N·kg$^{-1}$. However, after 3 months of vermicomposting this value increased slightly (to about 50 mg N·kg$^{-1}$). The least DOC (2118 mg C·kg$^{-1}$) value was observed for layer C, and the greatest DOC value (2530 mg C·kg$^{-1}$) was seen in layer A. With respect to the total contents of elements, K and Fe were the most represented (Figure 3).

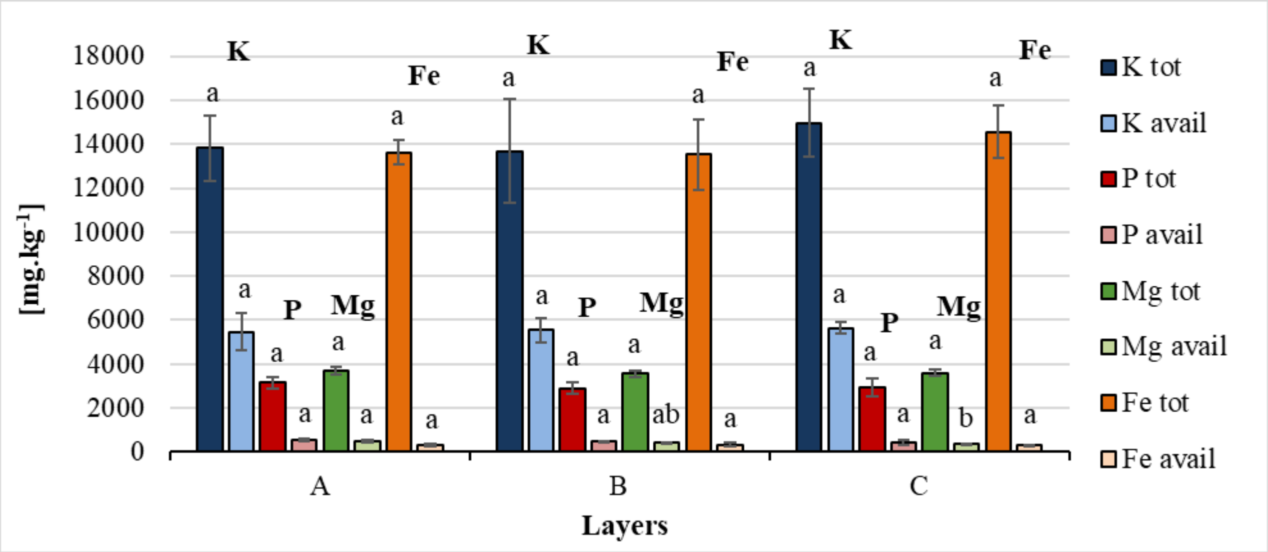

***Figure 3: Changes in total and available K, P, Mg, and Fe contents [mg·kg$^{-1}$] in layers A, B, and C of the vertical-flow vermicomposting system. The values are the means ± SD (n=3). Different letters indicate significant differences within a nutrient (Kruskal-Wallis test, P≤0.05). A: 0 – 20 cm, 1 – 6 months; B: 20 – 40 cm, 6 – 12 months; C: 40 – 60 cm, 12 – 18 months***

The greatest total contents of these two elements (K: 14,971 mg·kg$^{-1}$; Fe: 14,563 mg·kg$^{-1}$) were measured in the oldest layer (layer C). On the other hand, the total contents of P (3,150 mg·kg$^{-1}$) and Mg (3,692 mg·kg$^{-1}$) were the greatest in the youngest layer (layer A) (Figure 3). The total contents of these nutrients were greater in the vermicompost from food waste in the experiment by Arancon et al.[38] (P: 27,000 mg·kg$^{-1}$; K: 92,000 mg·kg$^{-1}$; Mg: 4,364 mg·kg$^{-1}$; Fe: 23,264 mg·kg$^{-1}$). The proportion of the available contents of K, P, Mg, and Fe constituted on average in all three layers 39%, 16%, 12%, and 2%, respectively, of the total content. The greatest percentage of the available P and Mg were in layer A (P: 17.1% of the total content; Mg: 12.8% of the total content), and of the available K and Fe were in layer B (K: 40.6% of the total content; Fe: 2.4% of the total content). The least percentage of available nutrients were in the oldest layer (layer C), but there were not statistically significant differences between the layers, except layers A and C in the available content of magnesium. Compared to the study done by Hanc and Pliva[7], our study contained a lesser percentage of available phosphorus by 54% and magnesium by 17%. The percentage of available potassium was greater in our experiment by 22%, which could be due to the addition of wood chips in the case of the experiment by Hanc and Pliva[7].

## Conclusions

Although select chemical parameters did not differ significantly in individual layers, the stability of vermicompost from kitchen biowaste was found after one year of outdoor vermicomposting. This was evident from the assessment of the biological parameters. The average activity of enzymes such as β-D-glucosidase, phosphatase, sulfatase, lipase, chitinase, cellobiohydrolase, in the bottom layer was less by 53% compared to the top layer, and the pathogens were reduced by 66%, while *Salmonella* spp. was not present at all.

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## References

1. Revilla B. P., Salet W.: J. Cleaner Prod. *198*, 320 (2018).
2. Scherhaufer S., Moates G., Hartikainen H., Waldron K., Obersteiner G.: Waste Manage. *77*, 98 (2018).
3. Pleissner D., Kwan T. H., Lin C. S. K.: Bioresour. Technol. *158*, *48* (2014).
4. Edjabou M. E., Petersen C., Scheutz C., Astrup T. F.: Waste Manage. *52*, 256 (2016).
5. Pleissner D.: Curr. Opin. Green Sustain. Chem. *13*, 39 (2018).
6. Salihoglu G., Saligohlu N. K., Ucaroglu S., Banar M.: Bioresour. Technol. *248*, 88 (2018).
7. Hanc A., Pliva P.: J Mat Cycl and Waste Manage. *15*, 431 (2013).
8. Sundberg C.., Jönsson H.: Waste Manage. *28*, 518 (2008).
9. Nair J., Sekiozoic V., Anda M.: Bioresour. Technol. *97*, 2091 (2006).
10. Maboeta M. S., van Rensburg L.: Ecotoxicol. Environ. Saf. *56*, 265 (2003).
11. Sánchez-Monedero M. A., Roig A., Paredes C., Bernal M. P.: Bioresour. Technol. *78*, 301 (2001).
12. Hanc A., Chadimova Z.: Bioresour. Technol. *168*, 240 (2014).
13. Hartenstein R., In: *Utilization of Soil Organisms in Sludge Management* (Hartenstein R., ed.), pp. 2. The National Technology Information Service. PB286932, Springfield, Virginia 1978.
14. Eastman B. R., Kane P. N., Edwards C. A., Trytek L., Gunadi B.: Compost Sci. Util. *9*, 38 (2001).
15. Edwards C.A., Subler S., In: *Vermiculture Technology: Earthworms, Organic Wastes and Environmental Management* (Edwards C. A., Arancon N. Q., Sherman R., ed.), pp. 249. CRC Press, Boca Raton 2011.
16. Soobhany N., Mohee R., Garg V. K.: Waste Manage. *64*, 51 (2017).
17. Dominguez J., Edwards C..A., In: *Vermiculture technology: Earthworms, Organic Wastes and Environmental Management* (Edwards C.A., Arancon N.Q., Sherman R., (ed), pp. 11. CRC Press, Boca Raton 2011.
18. Mateju L.: *Methodological guide for determination of indicator organisms in bio-waste, treated bio-waste, sludge from sewage treatment plants wastewaters, digestates, substrates, composts, auxiliary growth media and similar matrices*. The National Institute of Public Health, Prague 2009.
19. Šnajdr J., Cajthaml T., Valaskova V., Merhautova V., Petrankova M., Spetz P., Leppanen K., Baldrian P.: FEMS Microbiol Ecol *75*, 291 (2011).
20. Štursová M., Baldrian P.: Plant Soil *338*, 99 (2011).
21. EN 13037: *Soils improvers and growing media - Determination of pH* (1999).
22. EN 13651: *Soil improvers and growing media - Extraction of calcium chloride/DTPA (CAT) soluble nutrients* (2001).
23. Aira M., Gomez-Brandon M., Gonzalez-Porto, Domínguez J.: Bioresour. Technol. *102*, 9633 (2011).
24. Mainoo N. O. K., Barrington S., Whalen J. K.., Sampedro L.: Bioresour. Technol. *100*, 5872 (2009).
25. Procházková P., Hanč A., Dvořák J., Roubalová R., Drešlová M., Částková T., Šustr V., Škanta F., Pacheco N. I. N., Bilej M.: Environ. Sci. Pollut. Res. *25,* 26267 (2018).
26. Soobhany N.: J. Environ. Manage. *206*, 763 (2018).
27. Brown B. A., Mitchell M. J.: Pedobiologia *22*, 434 (1981).
28. Kwairakpam M., Bhargava R.: J. Hazard. Mater. *161,* 948 (2009).

29. Yadav K. D., Tare V., Ahammed M. M.: Ecol. Eng. *47*, 24 (2012).
30. Kumar R., Shweta: J. Environ. Sci. Technol. *4*, 621 (2011).
31. Swati A., Hait S.: J. Environ. Qual. *47*,16 (2018).
32. Cao W., Vaddella V., Biswas S., Perkins K., Clay C., Wu T., Zheng Y., Ndegwa P., Pandey P.: Environ. Sci. Pollut. Res. *23*, 23195 (2016).
33. Dincer S., Güvenmez H., Colak Ö.: Ann. Microbiol. *53*, 267 (2003).
34. Fernández-Gómez M. J., Nogales R., Insam H., Romero E., Goberna M.: Waste Manage. *30*, 2461 (2010).
35. Nogales R., Cifuentes C., Benítez E.: J. Environ. Sci. Health B *40*, 659 (2005).
36. Majlessi M., Eslami A., Saleh H. N., Mirshafieean S., Babaii S.: Iran. J Environ. Health Sci. Eng. *9*, 1 (2012).
37. Arancon N. Q., Edwards C. A., Atiyeh R., Metzger J. D.: Bioresour. Technol. *93*, 139 (2004).
38. Arancon N. Q., Edwards C. A., Bierman P., Metzger J. D., Lucht C.: Pedobiologia *49*, 297 (2005).

# Změny chemických a biologických parametrů během vermikompostování kuchyňského bioodpadu, s důrazem na patogeny

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## *Souhrn*

*Gastroodpad a kuchyňský bioodpad se mohou stát environmentálním a ekonomickým problémem, pokud s nimi nebude řádně nakládáno. Cílem této studie bylo zjistit vliv venkovního vermikompostování v systému průběžného krmení žížal kuchyňským bioodpadem na patogeny ve vztahu k biologickým a chemickým vlastnostem. Po jednom roce venkovního vermikompostování byla zjištěna chemická a biologická stabilita vermikompostu. Obsah patogenů byl snížen o 66 %, zatímco Salmonella spp. nebyla vůbec přítomna. S přibývajícím stářím vermikompostu klesala celková mikrobiální biomasa a její složky (houby, aktinobakterie, bakterie G+ a G-) a také enzymatická aktivita. Průměrná aktivita enzymů, jako je β-D-glukosidáza, fosfatáza, sulfatáza, lipáza, chitináza, cellobiohydrolasa, byla ve spodní vrstvě o 53 % menší než ve vrchní vrstvě. Vlhkost poklesla na 48 % a měrná vodivost na 722 $\mu S \cdot cm^{-1}$. Hodnota pH se zvýšila na 8,0. Klesající trendy $C_{tot}$ a $N_{tot}$ korelovaly pozitivně s jejich dostupnými formami, jako jsou DOC, $N\text{-}NO_3^-$ a $N\text{-}NH_4^+$, přičemž jejich podíl na celkovém obsahu činil 1,1 %, 0,9 % a 0,3 %. Nejvyšší obsahy byly zjištěny u $Ca_{tot}$, $K_{tot}$ a $Fe_{tot}$ (shodně 1,3 %) následované $Mg_{tot}$ (0,35 %) a $P_{tot}$ (0,3 %). Podíl dostupného obsahu K, Fe, Mg a P představoval v průměru ve všech třech vrstvách 39 %, 2 %, 12 % a 16 % z jejich celkového obsahu.*

***Keywords**: vermikompostování, žížaly, kuchyňský bioodpad, vrstvy, patogeny, chemické a biologické vlastnosti*

# Biochar – výroba, vlastnosti, certifikace, použití

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## *Souhrn*

*V přehledném článku jsou shrnuty základní znalosti o biocharu, který patří dle české legislativy mezi pomocné půdní látky. Díky jeho vlastnostem je biocharu v dnešní době věnována velká pozornost – může totiž pozitivně ovlivnit kvalitu půdy a změny klimatu. V druhé kapitole článku jsou představeny přední evropské firmy vyrábějící technologické linky na výrobu biocharu. V článku jsou též shrnuty relevantní fyzikálně-chemické a texturní vlastnosti biocharu s důrazem na „praktické“ kvalitativní parametry, mezi které patří stabilita biocharu, vodní kapacita, respektive nasákavost, a schopnost reverzibilní retence živin. Pátá kapitola článku se věnuje certifikaci biocharu, představuje jak českou legislativu, tak i dobrovolné iniciativy, které vydávají certifikáty kvality biocharu – European Biochar Certificate (EBC) a International Biochar Initiative (IBI). V práci jsou též popsány metody a způsoby využití biocharu v zemědělství.*

***Klíčová slova:*** *biochar, biouhlí, biomasa, termochemická konverze, karbonizace, pyrolýza, zplyňování*

## Úvod

Biochar (biouhlí) je pevný materiál získaný termochemickou přeměnou biomasy v prostředí s omezeným obsahem kyslíku. Proces výroby biocharu je u tradičních (jednodušších) technologií podobný výrobě dřevěného uhlí, což je možná nejstarší průmyslová technologie vyvinutá lidstvem[1]. Biochar je možné považovat za dřevěné uhlí, tj. porézní látku bohatou na uhlík.

Vlastnosti biocharu vyrobeného z biomasy v pyrolýzních či zplyňovacích reaktorech jsou shrnuty v níže uvedených bodech:

- Biochar obsahuje cca 10 – 30 % hmotnosti sušiny biomasy.
- Hlavní stavební složkou biocharu je chemicky stabilní uhlík (50 – 95 hm. %), který nepodléhá dalšímu rozkladu a oxidaci (v půdě). Jedná se o jednu z metod ukládání (sekvestrace) uhlíku.
- Biochar je porézní. Specifický povrch je 150 – 1200 $m^2/g$. Biochar zvyšuje zádrž vody a výživových látek v půdě.

Největší vliv na kvalitu biocharu má kromě samotného zařízení teplota v pyrolýzní zóně generátoru, rychlost ohřevu vstupního materiálu, čas zdržení v aktivní zóně reaktoru a typ použité biomasy. S rostoucí teplotou pyrolýzy se snižuje výtěžek (produkce). Schopnost zadržování vody a živin v půdě se zvětšuje do kritické teploty pyrolýzy v závislosti na typu zařízení. Zvyšování teploty pyrolýzy má též silný vliv na rozklad a volatilitu (těkavost) organických látek vzniklých procesem pyrolýzy a organických látek přítomných v biomase. Prodlužovaní doby zdržení biomasy/biocharu v pyrolýzní, případně v sekundární redukční zóně reaktoru, a pomalá rychlost ohřevu biomasy má celkově pozitivní vliv na kvalitu biocharu.

Díky jeho vlastnostem je biocharu v dnešní době věnována velká pozornost – může totiž pozitivně ovlivnit kvalitu půdy a mírnit nepříznivé změny klimatu. V nadcházejících, čím dál delších obdobích sucha pomáhá jako porézní látka v zemi zadržovat vláhu i živiny a také uzamyká (sekvestruje) v půdě velké množství uhlíku, které se pak dále neuvolňuje do atmosféry. Každá zmiňovaná vlastnost biocharu převažuje za jiných výrobních podmínek, a proto je nutné určit jejich optimální kombinaci.

## Výroba biocharu

Pyrolýza a/či zplyňování biomasy za cílem produkce biocharu využitelného v zemědělství se dá provádět pomocí mnoha technologií. Biochar tak vzniká v zařízeních založených na využití fluidní vrstvy, nehybné či pomalu se sunoucí vrstvy částic biomasy, ve vertikálních etážových pecích s prohrabováním etáží, ve vyhřívaných zařízeních s jedním či dvěma šneky ve žlabu, ve žlabu s dutým šnekem (spirálou), s vyhřívaným žlabem i vyhřívanou vnitřní trubkou, dále v rotační peci, v centrifugálně fungujícím pyrolyzéru, vícestupňovém generátoru a v dalších typech pyrolyzních a zplyňovacích zařízení různých velikostí a způsobů provozu[2-4].

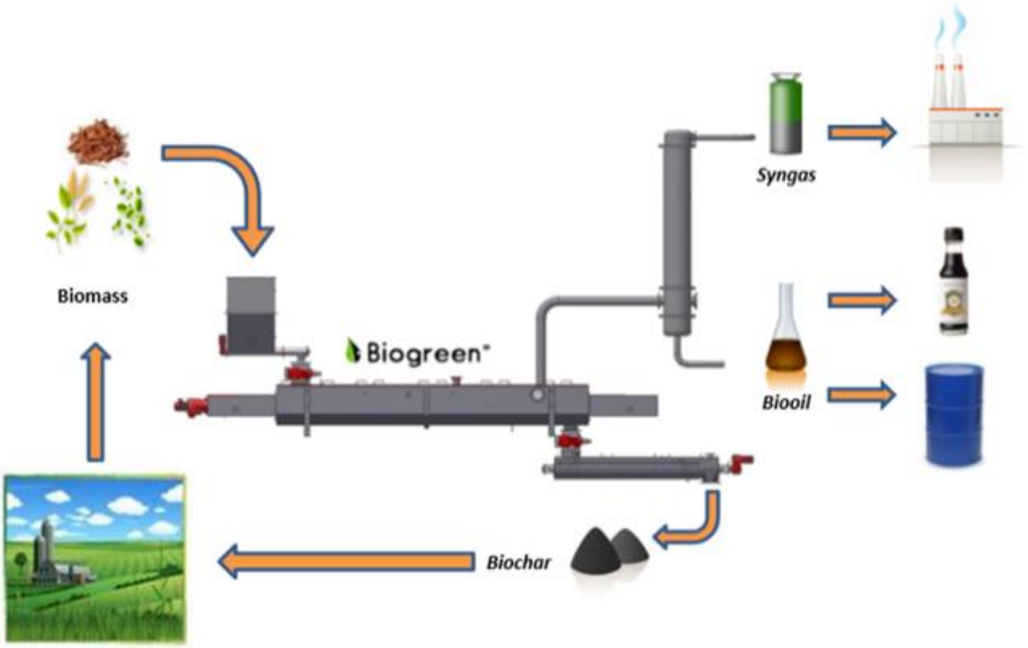
Výběr vhodného pyrolyzéru, respektive zplyňovače, a jeho uspořádání závisí do značné míry na povaze vstupní suroviny, na potřebné teplotě pyrolýzy (nízko-teplotní, středně-teplotní, nebo vysoko-teplotní pyrolýza), na rychlosti ohřevu, na čase zdržení a pracovním tlaku (podtlak, normální tlak nebo přetlak). Pro pyrolýzu velmi vlhké biomasy je často potřeba předsušit vstupní biomasu (upravenou na vhodnou velikost) v prvním stupni technologické linky (např. nízkoteplotní sušárnou).

Pro pyrolýzu biomasy za účelem výroby biocharu využívají zahraniční evropské firmy obvykle pyrolyzér s jedním nebo dvěma šneky. Jeděmi z lídrů na evropském trhu jsou firmy PYREG[5] a ETIA s produkty řady BIOGREEN[6] využívající dutých šneků ve žlabu pro pyrolýzu i chlazení vyrobeného biocharu. Popis technologie firmy PYREG v českém jazyce, včetně technologického schématu, je v naší předcházející publikaci[7] a na stránkách českého zástupce firmy PYREG[8].

Hlavní výhodou produktů firmy PYREG je alotermní ohřev pyrolyzéru spalinami vzniklými spálením primárního pyrolýzního plynu, oproti pyrolyzéru firmy ETIA, který je ohřívaný elektricky. Výhodou pyrolyzéru od firmy ETIA je možnost nastavení optimální karbonizační teploty a vhodného teplotního gradientu pro výrobu vysoce kvalitního biocharu.

Finálním produktem pyrolýzy je v případě pyrolyzéru od firmy PYREG biochar a užitné teplo, v případě pyrolyzéru od firmy ETIA biochar, pyrolýzní olej, užitné teplo a případně i elektrická energie. Pyrolýzní olej z pyrolyzéru BIOGREEN je podle firemních prezentací využitelný v potravinářském průmyslu pro výrobu potravinářských aromat, dřevního octa a dalších produktů (biomolekul).

Referenčním vstupním materiálem největšího komerčního zařízení (BGR750) jsou dřevěné piliny o velikosti částic do 3 mm, sypné hmotnosti cca 250 kg/m$^3$ a vstupní vlhkosti do 10 hm. %. Jmenovitý hmotnostní tok paliva je 1 t/h a vhodná pracovní teplota je 550 °C. Výtěžek biocharu je cca 25 hm. %, kondenzujícího podílu (organická i vodní fáze) 35 hm. % a pyrolýzního plynu 40 hm. %. Schéma technologické linky Biogreen na výrobu biocharu je na obrázku 1.



***Obrázek 1: Schéma technologické linky Biogreen na výrobu biocharu[6] (biomass – biomasa, syngas – plynný produkt pyrolýzy, biooil – kondenzující produkt pyrolýzy)***

## Typy biocharu podle pyrolýzní teploty

Biochary můžeme pro zjednodušení rozdělit do tří kategorií podle pyrolýzní teploty použité při jejich výrobě. Každá kategorie má své specifické vlastnosti, svoje výhody a nevýhody. Jedná se o nízko-teplotní, středně-teplotní a vysoko-teplotní biochary.

Nízko-teplotní biochar je vyráběn při teplotách do 400 °C. Vyznačuje se malou stálostí v půdě, nízkým povrchem, vysokým KVK (kationtová výměnná kapacita), nižším pH, vyšším výtěžkem a silnou hydrofobicitou. Ta je způsobena vysokým podílem (alifatických) funkčních skupin. Póry bývají zaneseny primárními dehty, které se za těchto nižších teplot ještě netransformují na terciární a kvarterní dehty. Dehty tvoří tzv. dostupný (rozpustný) uhlík, který podporuje růst mikroorganismů v půdě[9].

Středně-teplotní biochar býval v minulé dekádě diskutován jako kompromisní varianta. V současné době lze však konstatovat, že tzv. středně-teplotní biochar v sobě nenese žádnou zásadní výhodu nízkoteplotního biocharu (jednoduchá výroba, velká KVK a dostupný (rozpustný) uhlík pro bakterie), ani vysokoteplotního biocharu (dlouhodobá stálost, velký povrch, tj. velká vodní kapacita).

Vysoko-teplotní biochar je vyráběn při teplotách nad 600 °C. Má dlouhodobou stálost v půdě, velký specifický povrch s otevřenými póry, vyšší pH a nižší hydrofobicitu. Na jeho povrchu se vyskytuje méně funkčních skupin.

## Fyzikálně-chemické vlastnosti biocharu

Fyzikálně-chemickými vlastnostmi je míněn souhrn vlastností plynoucích z technického (základního, hrubého) rozboru, prvkového (elementárního) rozboru, texturní analýzy a dalších specifických analýz. Jak je zdůrazněno v úvodu článku, hlavní vliv na výtěžek a kvalitu biocharu má, kromě samotného zařízení, teplota v pyrolýzní zóně generátoru, rychlost ohřevu vstupního materiálu, čas zdržení v aktivní zóně reaktoru a typ použité biomasy.

S rostoucí teplotou a časem zdržení biomasy/biocharu v aktivní zóně reaktoru do teploty 700 °C[10]:

- klesá hmotnostní i energetický výtěžek biocharu[11-14],
- v pyrolýzním zbytku klesá obsah přednostně v pořadí celulózy, hemicelulózy a ligninu[15-16],
- stoupá obsah popela[11-14, 17-24],
- stoupá obsah fixního uhlíku[12, 14, 17-19, 21, 23-25],
- klesá obsah prchavé hořlaviny[11-12, 14, 17-19, 21-25],
- stoupá výhřevnost i spalné teplo do teploty 500 – 600 °C[12, 14],
- stoupá obsah uhlíku[11-12, 14, 17, 19-20, 23-27],
- klesá obsah kyslíku[11, 14, 17, 23-25, 27],
- klesá obsah vodíku[11-12, 14, 17, 19-20, 23-25, 27],
- je přibližně konstantní obsah dusíku[11, 14, 17, 19-20, 23-25, 27],
- klesají molární poměry $H/C_{org}$ (H/C) a O/C – obrázek 2[11-12, 14, 17, 19-20, 23-25, 27],
- stoupá aromaticita[28],
- stoupá hydrofobicita do kritické teploty a pak slabě klesá[29],
- je přibližně konstantní sypná hmotnost (váha, hustota)[29-30],
- klesá zdánlivá (objemová, rtuťová) hustota[31-32],
- stoupá skutečná (skeletární, heliová) hustota[31-32],
- stoupá porozita částice[31-33],
- stoupá specifický povrch (BET povrch) – obrázek 3 a obrázek 4[11-14, 20-22, 24, 28, 31, 34-35, 45-46],
- stoupá celkový objem pórů[14, 31, 35],
- stoupá celkový objem mikropórů[14],
- stoupá vodní kapacita (WHC)/nasákavost do kritické teploty[24, 36],
- stoupá pH vodního výluhu – obrázek 5[10-13, 20-21, 25-26, 35],
- od kritické teploty klesá kationtová výměnná kapacita (KVK) i aniontová výměnná kapacita (AVK) – obrázek 6 [10, 13, 20-21, 25-26].

Od 700 °C výše je vliv teploty na většinu uvedených parametrů obvykle nevýznamný.

Jednou z nejdůležitějších vlastností biocharu je, že zvyšuje při vhodné aplikaci jakost půdy. Aby bylo možné uvedeného efektu dosáhnout, je nutné aplikovat příslušné množství kvalitního biocharu. Mezi nejdůležitější „praktické“ kvalitativní parametry patří:

- stabilita,
- vodní kapacita/nasákavost,
- reverzibilní retence (zádrž) živin (měřenými veličinami jsou KVK/AVK).

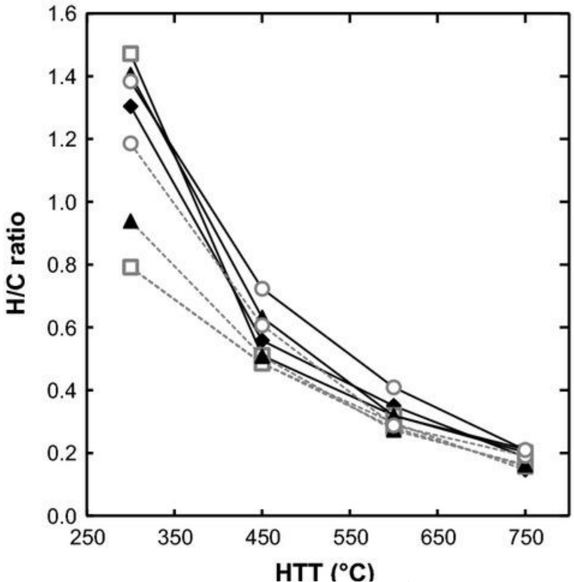
## Stabilita biocharu

Stabilita biocharu má zásadní význam při jeho použití do půdy ze dvou hlavních důvodů: za prvé, stabilita určuje, jak dlouho uhlík obsažený v biocharu zůstane sekvestrovaný v půdě, čímž pomáhá zmírnit změnu klimatu, a za druhé, pomocí stability můžeme stanovit, jak dlouho bude biochar přispívat kvalitě půdy, rostlin a vody[37].

S rostoucí teplotou pyrolýzy a časem zdržení v aktivní zóně generátoru se stabilita biocharu zvyšuje z důvodu zvyšující se aromaticity.

Podle IBI se rozdělují testy stanovující stabilitu biocharu do tří skupin[38]: (1) alfa metody – nízkonákladové rutinní odhady stability; (2) beta metody, které přímo kvantifikují stabilitu biocharu a mohou být použity pro kalibraci alfa metod; (3) gama metody, které mohou poskytovat teoretické fyzikálně-chemické základy pro metody alfa a beta.

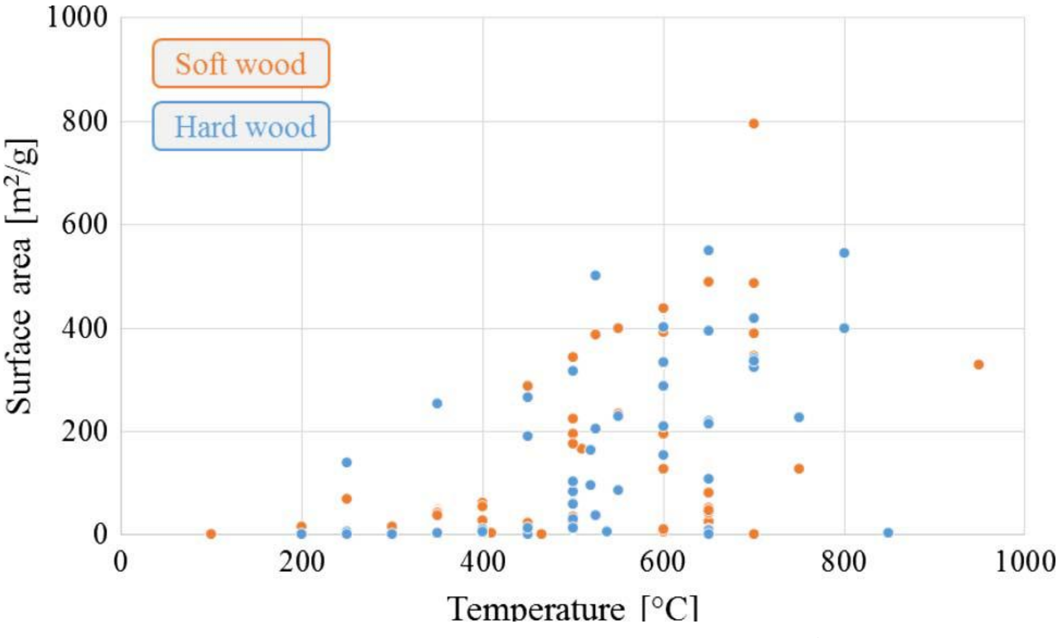
Alfa metody jsou definovány jako metody umožňující jednoduchá a spolehlivá měření relativní stability uhlíku v biocharu, která jsou snadno dostupná za cenu nižší než 100 USD a proveditelná v časovém rámci minut nebo hodin, maximálně několika dní. Mezi alfa metody patří stanovení molárního poměru vodíku k organickému uhlíku ($H:C_{org}$)[25, 39] a molárního poměru kyslíku k uhlíku (O:C)[40]. Oba poměry odrážejí fyzikálně-chemické vlastnosti biocharu spjaté s jeho stabilitou – čím nižší poměr, tím je biochar stálejší (viz obrázek 3)[41].



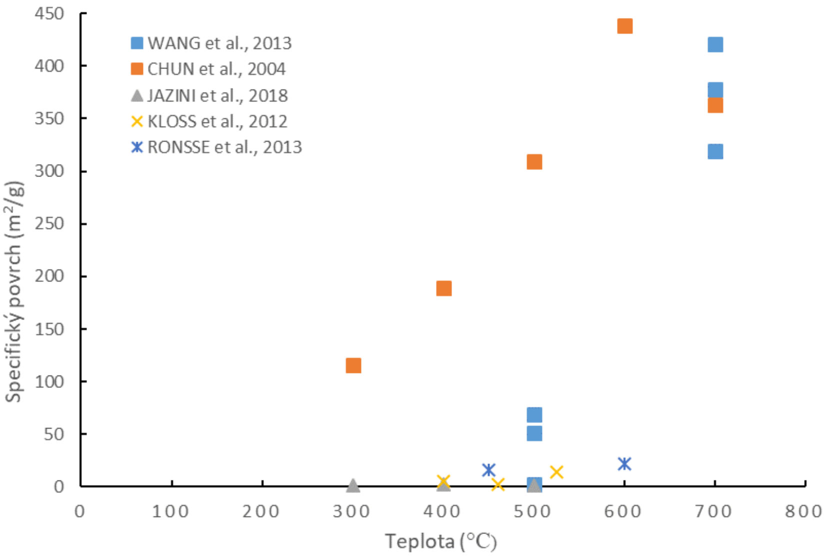
***Obrázek 2: Závislost H/C poměru na pyrolýzní teplotě[12] (H/C ratio – H/C poměr; HTT – nejvyšší dosažená pyrolýzní teplota)***

### *Vodní kapacita biocharu*

Vodní kapacita, respektive schopnost zadržovat vodu, se dá měřit buď přímo, nebo nepřímo. Přímé měření je popsáno v normě ČSN EN ISO 14238 a probíhá následovně: určené množství biocharu namočíme na předem určenou dobu do vody a zvážíme, kolik vody do sebe nasákl[24, 42]. Tato metoda je sice jednoduchá, ale má nízké vypovídací vlastnosti. Proto se vodní kapacita určuje i nepřímo, a to měřením objemu pórů a specifického povrchu. Celkový objem pórů, porozita a specifický povrch biocharu pozitivně ovlivňují afinitu biocharu k vodě. Hydrofobicita (na kterou mají vliv hlavně alifatické skupiny na povrchu biocharu) také hraje roli při určování vodní kapacity [24, 29, 43-44].



***Obrázek 3: Závislost specifického povrchu dřevní biomasy na teplotě[10] (surface area – specifický povrch; temperature – pyrolýzní teplota; soft wood – měkké dřevo; hard wood – tvrdé dřevo)***



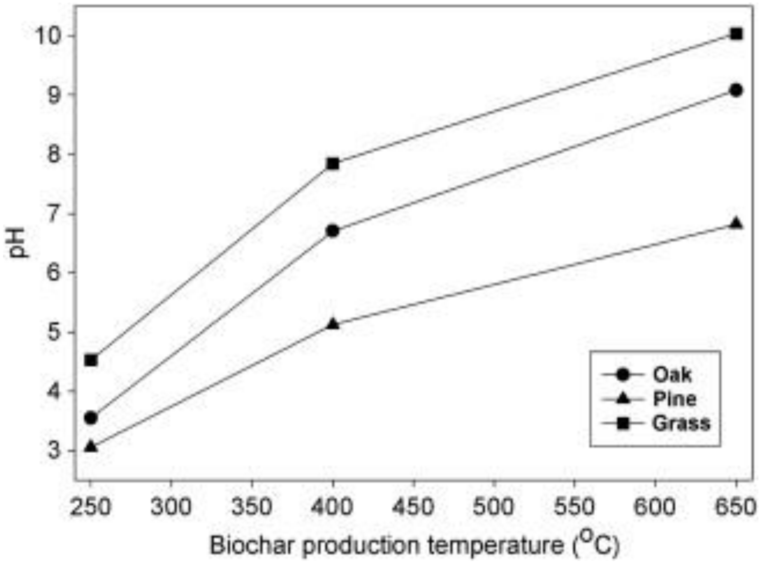
**Obrázek 4: Závislost specifického povrchu agrobiomasy (pšeničné a ječmenné slámy) na pyrolýzní teplotě[12-13, 20, 45-46]**

### Reverzibilní retence (zádrž) živin

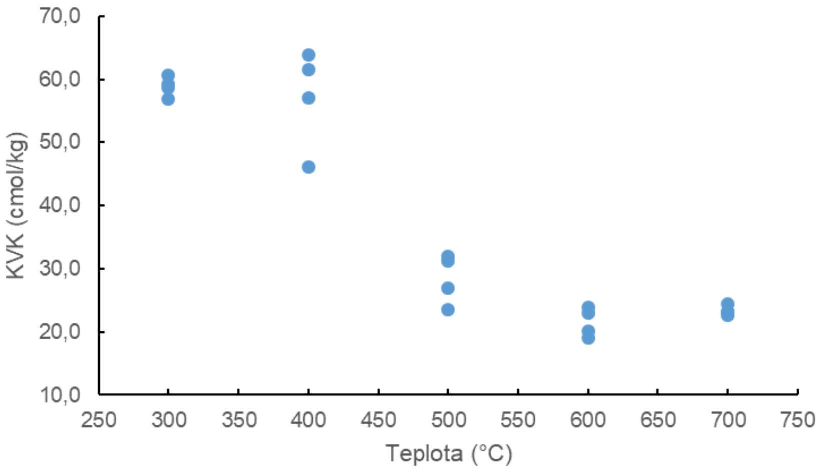
Zádrž živin se určuje podle schopnosti (kapacity) vázat kationty a anionty hlavních makronutrientů rostlin. K tomu slouží veličiny nazvané kationtová výměnná kapacita (KVK) a aniontová výměnná kapacita (AVK). V podstatě jde o počet záporně, resp. kladně nabitých míst na povrchu biocharu, která fungují jako příjemce a zároveň donor kationtů, resp. aniontů. Tím biochar rostlinám usnadňuje zachycování živin a současně je schopen živiny z půdy/hnojiva déle udržet v blízkosti kořenů[22].

S rostoucí teplotou se zvyšuje hodnota pH výluhu biocharu z důvodu většího podílu popelotvorných látek vůči látkám těkavým[10]. Se zvyšujícím se pH výluhu biocharu stoupá KVK a AVK, tudíž i zádrž živin v půdě[47-48].

S rostoucí teplotou a časem zdržení biomasy/biocharu v aktivní zóně reaktoru však klesá KVK z důvodu stoupající aromaticity, respektive klesajícího podílu alifatických skupin[10, 20-21, 25].



**Obrázek 5: Závislost pH na pyrolýzní teplotě[22] (Biochar production temperature – pyrolýzní teplota, oak – dub, pine – borovice, grass – tráva)**



***Obrázek 6: Závislost KVK na pyrolýzní teplotě[49]***

Na závěr kapitoly o fyzikálně-chemických vlastnostech biocharu si autoři dovolují popsat jeden praktický test jak poznat „špatný“ biochar, tj. biochar obsahující dehet. Do litrové zavařovačky dejte přibližně 100 ml biocharu a 500 ml teplé vody, protřepejte a nechte cca půl hodiny stát. Otevřete víčko sklenice a čichněte si. Pokud vzorek nezapáchá, mohl by být biochar pro Vaší zahrádku/pole užitečný, za předpokladu, že ho budete řádně aplikovat, že je dlouhodobě stabilní a má reálnou schopnost retence vody či/a živin.

## Certifikace biocharu

Kvalitu biocharu, který se používá jako půdní aditivum, sleduje mnoho národních i nadnárodních institucí. V České republice registruje biochar Ústřední kontrolní a zkušební ústav zemědělský (ÚKZÚZ). Dále existují organizace, od kterých může výrobce biocharu po splnění určitých podmínek získat certifikát. Tyto certifikáty bývají dobrovolné a náročnější na splnění, protože kontrolují více oblastí než národní legislativy (tabulka 1). Na našem území jde například o European Biochar Certificate (EBC) nebo International Biochar Initiative (IBI). Cílem těchto iniciativ je zajistit bezpečný produkt pro životní prostředí a vytvořit jednotný a spolehlivý znak pro spotřebitele.

### *Ústřední kontrolní a zkušební ústav zemědělský (ÚKZÚZ)*

Tento český úřad v dnešní době kontroluje pouze nezávadnost biocharu, nikoli jeho kvalitu. Zaměřuje se tedy na obsah toxických látek a těžkých kovů, ale nijak nezaručuje, že vyrobený biochar bude opravdu zlepšovat kvalitu půdy. Certifikace je platná v celé EU.

### *European Biochar Certificate (EBC)*

EBC je, jak už napovídá název, evropská iniciativa, která zavádí kontrolní mechanismus založený na nejnovějším výzkumu a praxi. Pravidla EBC se aktualizují každý rok a poskytují podklady pro tvorbu legislativy. Tento certifikát cílí na umožnění a garantování udržitelné produkce biocharu. Je určen zákazníkům, kterým dává záruku kvality, ale i výrobcům, kterým dává možnost dokázat, že jejich výrobek splňuje definovaná kritéria. Iniciativa si dává za cíl předcházet nebezpečí a zabraňovat zneužití výroby biocharu od samého počátku.

Organizace je nezávislá, a tudíž neupřednostňuje žádné partikulární zájmy. Díky této nezaujatosti a transparentnosti z něj mají prospěch jak výrobci, tak spotřebitelé. Pro stanovení chemických a fyzikálních vlastností biocharu se používá již platných ISO a DIN norem[50].

### *International Biochar Initiative (IBI)*

Jediná organizace, která se snaží uplatnit po celém světě, je IBI. IBI poskytuje platformu, kde se mohou navazovat nové spolupráce mezi zainteresovanými subjekty, vyvíjet kvalitní průmyslové technologie a nastavovat environmentální a etická měřítka tak, aby vznikal bezpečný a udržitelný biochar. Její vizí je zvýšit výrobu biocharu na 1 miliardu tun ročně do 50 let, což se snaží splnit následujícími způsoby:

- podporou mezinárodní spolupráce mezi vědou, průmyslem, zemědělstvím, vládními a nevládními organizacemi tak, aby se propagovalo a demonstrovalo použití biocharu a aby se vyvíjely snahy o zavedení kontrol kvality,
- spoluprací s průmyslem, aby se nalézala ekonomicky výhodná použití pro biochar,
- podporou výzkumu,
- poskytováním jasných, nezaujatých a spolehlivých informací o vlastnostech biocharu,
- tvorbou standardů a metod práce tak, aby veřejnost důvěřovala organizacím zabývajícími se biocharem, a aby byla přesvědčena, že biochar vyvinutý těmito organizacemi je bezpečný a vhodný pro doporučené použití.

IBI je organizace založená v USA a používá mezinárodně známé ASTM normy[1].

## Použití biocharu

Hlavním smyslem výroby biocharu je jeho aplikace do zemědělské půdy. Před vpravením do zeminy může biochar projít řadou jiných úprav, při kterých se mění jeho vlastnosti.

Biochar lze využít následujícími způsoby:

- přímé využití aktivovaného (navlhčeného) biocharu do zemědělské půdy,
- aditivum pro výrobu kompostu,
- krmná surovina,
- podestýlka pod zvířata,
- katalyzátor pro výrobu bioplynu.

### *Přímé použití biocharu na zemědělskou půdu*

Pro využití biocharu do půdy je nutné získat certifikaci od ÚKZÚZ. Biochar vyrobený z chemicky neošetřené biomasy je zařazen do skupiny pomocná půdní látka.

Aplikaci biocharu do zemědělské půdy lze zabezpečit standardními zemědělskými stroji, např. rozmetadlem – navlhčený biochar či secím strojem – granulovaný biochar. Množství dávkovaného biocharu do zemědělské půdy se pohybuje v širokém rozmezí: 1 – 50 t/ha (obvykle 5 – 10 t/ha), v závislosti zejména na sorpčních vlastnostech biocharu, vlastnostech půdy, pěstované plodině a obsahu Ca. Využívá se jak sypaného biocharu (po/bez odstranění prachové frakce v závislosti na způsobu předúpravy), tak i granulovaného biocharu o velikosti granulí (pelet) obdobných, jako má komerční kombinované hnojivo. Nejčastěji se jedná o pelety průměru 2, 3, či 4 mm. Do půdy se pak aplikuje biochar přímo po jeho navlhčení (aktivaci), která též snižuje jeho prašnost nebo ve směsi s kompostem, hnojem, či podestýlkou s hnojem a s digestátem, či fugátem apod, což je jiná metoda aktivace. Po aplikaci biocharu do zemědělské půdy zůstává biochar v půdě několik desítek/stovek let a plní níže uvedené funkce.

Hlavním důvodem aplikace biocharu do zemědělské půdy je, že **zvyšuje kvalitu půdy**. Přítomnost biocharu vyvolává níže uvedené procesy:

- zvyšuje zádrž vody v půdě,
- zlepšuje využití biogenních prvků z hnojiv – zadržuje je a pomalu uvolňuje,
- snižuje průnik výživových látek do podzemních vod,
- kypří (zlehčuje) půdu,
- v prvních měsících po aplikaci upravuje pH půdy z důvodu vyšších koncentrací Ca, vhodné pro kyselé půdy[41, 51].

**Tabulka 1: Seznam sledovaných parametrů biocharu dle ÚKZÚZ, EBC a IBI (r – původní vzorek)**

| Parametr | Veličina | Kritérium ÚKZÚZ | Kritérium EBC | | Kritérium IBI |
|---|---|---|---|---|---|
| | | | Základní | Prémium | |
| **Základní** | | | | | |
| Sypná hmotnost | kg/m$^3$ | - | deklarace | | - |
| Popel, $A^d$ | % hm. v sušině | - | deklarace | | deklarace |
| Vlhkost, W | % hm. v sušině | - | deklarace | | deklarace |
| Prchavá hořlavina, $V^d$ | % hm. v sušině | - | deklarace | | volitelná deklarace |
| pH | | - | deklarace | | deklarace |
| Distribuce velikosti částic | % < 0,5 mm;<br>% 0,5 – 1 mm;<br>% 1 – 2 mm;<br>% 2 – 4 mm;<br>% 4 – 8 mm;<br>% 8 – 16 mm;<br>% 16 – 25 mm;<br>% 25 – 50 mm;<br>% > 50 mm | - | - | | deklarace |
| **Elementární** | | | | | |
| Obsah uhlíku, $C^d$ | % hm. v sušině | - | > 50% | | pro výpočet $C_{org}$ |
| Obsah organického uhlíku, $C_{org}{}^d$ | % hm. v sušině | - | výpočtem | | 10% minimum<br>třída 1: ≥60%<br>třída 2: ≥30% a <60%<br>třída 3: ≥10% a <30% |
| Obsah vodíku, $H^d$ | % hm. v sušině | - | pro výpočet $H/C_{org}$ | | pro výpočet $H/C_{org}$ |
| Obsah dusíku, $N^d$ | % hm. v sušině | - | deklarace | | deklarace |
| Obsah kyslíku, $O^d$ | % hm. v sušině | - | výpočtem | | - |
| Molární poměr $H/C_{org}$ | - | - | < 0,7 | | < 0,7 |
| Molární poměr O/C | - | - | < 0,4 | | - |
| Obsah síry, S | mg/kg sušiny | - | - | | volitelná deklarace |
| Obsah fosforu, P | g/kg sušiny | - | deklarace | | volitelná deklarace |
| Obsah draslíku, K | g/kg sušiny | - | deklarace | | volitelná deklarace |
| Obsah vápníku, Ca | g/kg sušiny | - | deklarace | | volitelná deklarace |
| Obsah hořčíku, Mg | g/kg sušiny | - | deklarace | | volitelná deklarace |
| **Toxické látky, těžké kovy** | | | | | |
| Ekotoxicita - inhibice klíčivosti | - | - | - | | splnil |
| Obsah arsenu, As | mg/kg sušiny | 20 | 13$^r$ | 13$^r$ | 13 – 100 |
| Obsah kadmia, Cd | mg/kg sušiny | 1 | 1,5 | 1 | 1,4 – 39 |
| Obsah chromu, Cr | mg/kg sušiny | 50 | 90 | 80 | 93 – 1200 |
| Obsah kobaltu, Co | mg/kg sušiny | - | - | - | 34 – 100 |
| Obsah mědi, Cu | mg/kg sušiny | 100 | 100 | 100 | 143 – 6000 |
| Obsah rturi, Hg | mg/kg sušiny | 1 | 1 | 1 | 1 – 17 |
| Obsah molybdenu, Mo | mg/kg sušiny | - | - | - | 5 – 75 |
| Obsah niklu, Ni | mg/kg sušiny | 50 | 50 | 30 | 47 – 420 |
| Obsah olova, Pb | mg/kg sušiny | 150 | 150 | 120 | 121 – 300 |
| Obsah selenu, Se | mg/kg sušiny | - | - | - | 2 – 200 |
| Obsah zinku, Zn | mg/kg sušiny | 400 | 400 | 400 | 416 – 7400 |
| Obsah boru, B | mg/kg sušiny | - | - | - | deklarace |
| Obsah chlóru, Cl | mg/kg sušiny | - | - | - | deklarace |
| Obsah sodíku, Na | mg/kg sušiny | - | - | - | deklarace |
| Suma 12 PAH | mg/kg sušiny | 20 | - | - | - |
| Suma 16 PAH | mg/kg sušiny | - | 12 | 4 | 6 – 300 |
| Obsah dioxinů/furanů, PCDD/Fs | ng/kg sušiny | - | 20 (I-TEQ OMS) | | 17 (WHO-TEQ) |
| Obsah bifenylů, PCBs | mg/kg sušiny | - | 0,2 | | 0,2 – 1 |
| **Funkční** | | | | | |
| Specifický povrch | m$^2$/g | - | deklarace, nejlépe > 150 m$^2$/g | | volitelná deklarace |
| Elektrická vodivost | µS/cm | - | deklarace | | deklarace |
| Vápnový ekvivalent | % $CaCO_3$ | - | - | | deklarace, pokud je pH > 7 |
| Vodní kapacita | | - | volitelná deklarace | | - |

Biochar mohou jako půdní kondicionér používat i zahrádkáři, stačí ho navlhčený (aktivovaný) přidat ke kořenům rostlin při přesazování, nebo ho zapravit do vrchní vrstvy zeminy záhonu a dobře promíchat.

Biochar se může aplikovat i ke stromům, a to různými způsoby. Ideální je aplikace okolo kmenu v průměru koruny dospělého stromu. Biochar se může zapravit povrchově do půdy v okolí stromu, nebo lokálně vsypáváním do sazebních jamek a zákopů postupně vzdalujících se od kmene stromu nebo tzv. svislým mulčováním (vsypáváním biocharu do děr vyhloubených v různých vzdálenostech od kmene stromu). Lokální aplikace zlepšuje rovnoměrný růst kořenů a tím i stabilitu stromu[41, 51].

### *Aditivum pro výrobu kompostu*

Důvodem přídavku biocharu k biologicky rozložitelnému odpadu (BRO) pro výrobu kompostu je:

- zkrácení doby kompostování,
- snížení zápachu,
- zvýšení záchytu nutričních prvků v kompostu,
- zvýšení pH kompostu.

Při kompostování se střídavě vrství bioodpad a biochar, přičemž se musí dbát, aby byla vrchní vrstva biocharu dobře zakryta bioodpadem, popř. směsí zeminy a bioodpadu, a aby se zamezilo ztrátám prášením. Přidanou hodnotou je aktivace (navlhčení) biocharu během procesu kompostování a sorpce dusičnanů. Této nezbytné aktivace je dosaženo tím, že neaktivovaný (suchý) biochar, který má vysokou nasákavost, sorbuje velké množství vody (uvolňované z kompostované biomasy), která je bohatá na různé živiny[52-54].

### *Krmná surovina*

V případě, že biochar dosahuje vysoké kvality a vykazuje konstantní vlastnosti, lze biochar certifikovat jako krmnou surovinu u ÚKZÚZ. Biochar může být podáván zvířatům samostatně, nebo může být neoddělitelnou součástí krmiva.

Již mnoho studií ukázalo[1, 55-60], že přídavek biocharu do krmiva hospodářských zvířat má pozitivní (v některých případech pouze neutrální) účinky:

- zvýšení příjmu krmiva,
- zvýšení hmotnosti zvířat,
- zvýšení účinnosti krmiv,
- zvýšení produkce a kvality vajec u drůbeže,
- posílení imunitního systému zvířat,
- zlepšení kvality masa a mléka,
- snížení zápachu,
- snížení veterinárních nákladů,
- snížení úmrtnosti,
- stabilizace poporodního stavu u dobytka,
- celkové zlepšení zdraví a vzhledu.

Na proces trávení krmiva ve zvířeti lze pohlížet jako na elektrochemickou reakci, kterou biochar svou elektrickou vodivostí ulehčuje, a proto může zvyšovat účinek (zvláště vysokoenergetických) krmiv a tím i hmotnostní růst zvířete. V ideálním případě, kdy má biochar vhodné vlastnosti, může úplně nahradit antibiotika. Prasata z korejské studie[60] měla stejný přírůstek hmotnosti jako ta krmená antibiotiky, ale bez jejich negativních vedlejších účinků. Různé studie také potvrzovaly vyšší obsah proteinů v mase či více kolagenu ve vejcích[61-62].

V bachoru skotu se potrava může rozkládat na dál nerozložitelný metan, čímž nejenže vzniká energetická ztráta, ale i jeden z nejaktivnějších skleníkových plynů. Přídavek samotného biocharu produkci metanu snižuje jen minimálně, výzkum však ukazuje, že pokud se do krmiva přidají i dusičnany, emise metanu mohou být sníženy až o 40 – 49 %[55, 59].

Diskutovaný postup použití biocharu je přirozený způsob jeho aktivace (navlhčení) s inkorporací živin. Je tudíž environmentálně i agronomicky výhodnější, než prosté vlhčení biocharu, nebo jeho míchání s hnojem, podestýlkou, či jiným nutričně bohatým materiálem před jeho aplikací na půdu.

### *Podestýlka pod zvířata*

Biochar je jako porézní materiál schopen nasáknout velké množství vody a s ním i další látky. Pokud se přidá do podestýlky, snižuje její vlhkost a obsah amoniaku. Právě voda a amoniak jsou jedny z příčin zánětu kopyt/pařátů u hospodářských zvířat. Biochar tedy nejen předchází vzniku těchto nemocí, ale i napomáhá léčit již postižená zvířata. Použití biocharu také umožňuje snížit množství vápna ve stelivu, čímž se sníží pH a emise amoniaku. U drůbeže mohou tyto nemoci a záněty způsobovat úbytek hmotnosti, kanibalismus, sníženou kvalitu masa a dokonce smrt zvířat.

Do podestýlky by se mělo přidávat 5 – 10 obj. % biocharu v závislosti na typu. Biochar může být předem navlhčen, aby se zabránilo prášení. Biochar se také může přidávat do siláže[63].

### *Katalyzátor pro výrobu bioplynu*

Přidání biocharu do vstupní směsné suroviny pro výrobu bioplynu může zvýšit výtěžek metanu, pokud se dodrží doporučené provozní podmínky[63]. Detailní chemizmus není zcela objasněn. Při aplikaci digestátu i fugátu na zemědělskou půdu jsou živiny vázány i na biochar, což zvyšuje jejich využití[64-68].

## Závěr

Biochar je pevný materiál získaný termochemickou přeměnou biomasy v prostředí s omezeným obsahem kyslíku plnící zákonné a kvalitativní parametry. V České republice registruje biochar Ústřední kontrolní a zkušební ústav zemědělský (ÚKZÚZ). V mezinárodním kontextu jsou nejdůležitější dvě dobrovolné iniciativy vydávající certifikáty kvality biocharu: European Biochar Certificate (EBC) a International Biochar Initiative (IBI).

Největší vliv na kvalitu biocharu má, vedle samotného zařízení, teplota v pyrolýzní zóně generátoru, rychlost ohřevu vstupního materiálu, čas zdržení v aktivní zóně reaktoru a typ použité biomasy. Z rešerše vyplynulo, že mezi nejdůležitější „praktické“ kvalitativní parametry patří stabilita biocharu, vodní kapacita biocharu, respektive nasákavost a reverzibilní retence (zádrž) živin (měřená signifikantní veličina je kationtová výměnná kapacita – KVK a aniontová výměnná kapacita – AVK).

Hlavním smyslem výroby biocharu je jeho aplikace do zemědělské půdy. Před použitím biocharu do zemědělské půdy je biochar nutné aktivovat (navlhčit). Před vpravením do zeminy může biochar projít řadou jiných aplikací, při kterých se mění jeho vlastnosti – aditivum pro výrobu kompostu, krmná surovina, podestýlka pro zvířata, či katalyzátor pro výrobu bioplynu.

Důvodem aplikace biocharu do zemědělské půdy je, že zvyšuje kvalitu půdy. Zvyšování kvality půdy je způsobeno zejména zvyšováním zádrže vody v půdě a zvýšeným stupněm využití biogenních prvků z hnojiva. Mezi lídry na evropském trhu vyrábějící technologické linky na výrobu biocharu jsou firmy PYREG a ETIA s produkty řady BIOGREEN.

## Seznam symbolů

AVK – aniontová výměnná kapacita
EBC – European Biochar Certificate
KVK – kationtová výměnná kapacita
IBI – International Biochar Initiative
ÚKZÚZ – Ústřední kontrolní a zkušební ústav zemědělský

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## Literatura

1. International Biochar Initiative: https://biochar-international.org, staženo 3.6.2019.
2. Jahirul M., Rasul M., Chowdhury A., Ashwath N.: Energies *5*, 4952 (2012). doi: 10.3390/en5124952.
3. Nsamba H. K., Hale S. E., Cornelissen G., Bachmann R. T.: J. Sustainable Bioenergy Syst. *05*, 10 (2015). doi: 10.4236/jsbs.2015.51002.
4. Garcia-Perez M., Lewis T., Kruger C. E.: Methods for Producing Biochar and advanced bio-fuels in Washington state – Literature Review of Pyrolysis Reactors, Washington State University (2010).
5. Pyreg GmbH: www.pyreg.de, staženo 3.6.2019.
6. E.T.I.A.: http://www.biogreen-energy.com/, staženo 3.6.2019.
7. Pohořelý M. a 13 spoluatorů: Waste Forum 2017 *2*, 42 (2017).
8. HST Hydrosystémy s.r.o.: http://www.hydrosystemy.cz/, staženo 3.6.2019.
9. Feng Z., Sheng Y., Cai F., Wang W., Zhu L.: Sci. Total. Environ. *645*, 887 (2018). doi: 10.1016/j.scitotenv.2018.07.224.
10. Weber K., Quicker P.: Fuel *217*, 240 (2018). doi: 10.1016/j.fuel.2017.12.054.
11. Jindo K., Mizumoto H., Sawada Y., Sanchez-Monedero M. A., Sonoki T.: Biogeosciences *11*, 6613 (2014). doi: 10.5194/bg-11-6613-2014.
12. Ronsse F., van Hecke S., Dickinson D., Prins W.: GCB Bioenergy *5*, 104 (2013). doi: 10.1111/gcbb.12018.
13. Wang Y., Hu Y., Zhao X., Wang S., Xing G.: Energy Fuels *27*, 5890 (2013). doi: 10.1021/ef400972z.
14. Angin D.: Bioresour. Technol. *128*, 593 (2013). doi: 10.1016/j.biortech.2012.10.150.
15. Burhenne L., Messmer J., Aicher T., Laborie M.-P.: J. Anal. Appl. Pyrolysis *101*, 177 (2013). doi: 10.1016/j.jaap.2013.01.012.
16. Gani A., Naruse I.: Renewable Energy *32*, 649 (2007). doi: 10.1016/j.renene.2006.02.017.
17. Crombie K., Mašek O., Sohi S. P., Brownsort P., Cross A.: GCB Bioenergy *5*, 122 (2013). doi: 10.1111/gcbb.12030.
18. Fisher E. M., Dupont C., Darvell L. I., Commandre J. M., Saddawi A., Jones J. M., Grateau M., Nocquet T., Salvador S.: Bioresour. Technol. *119*, 157 (2012). doi: 10.1016/j.biortech.2012.05.109.
19. Cheah S., Malone S. C., Feik C. J.: Environ. Sci. Technol. *48*, 8474 (2014). doi: 10.1021/es500073r.
20. Kloss S., Zehetner F., Dellantonio A., Hamid R., Ottner F., Liedtke V., Schwanninger M., Gerzabek M. H., Soja G.: J. Environ. Qual. *41*, 990 (2012). doi: 10.2134/jeq2011.0070.
21. Lehmann J., Rillig M. C., Thies J., Masiello C. A., Hockaday W. C., Crowley D.: Soil Biol. Biochem. *43*, 1812 (2011). doi: 10.1016/j.soilbio.2011.04.022.
22. Mukherjee A., Zimmerman A. R., Harris W.: Geoderma *163*, 247 (2011). doi: 10.1016/j.geoderma.2011.04.021.
23. Park S.-W., Jang C.-H., Baek K.-R., Yang J.-K.: Energy *45*, 676 (2012). doi: 10.1016/j.energy.2012.07.024.
24. Zhang J., You C.: Energy Fuels *27*, 2643 (2013). doi: 10.1021/ef4000769.
25. Enders A., Hanley K., Whitman T., Joseph S., Lehmann J.: Bioresour. Technol. *114*, 644 (2012). doi: 10.1016/j.biortech.2012.03.022.

26. Gaskin J. W., Steiner C., Harris K., Das K. C., Bibens B.: Transactions of the ASABE *51*, 2061 (2008). doi: 10.13031/2013.25409.
27. Klupfel L., Keiluweit M., Kleber M., Sander M.: Environ. Sci. Technol. *48*, 5601 (2014). doi: 10.1021/es500906d.
28. Ahmad M., Lee S. S., Dou X., Mohan D., Sung J. K., Yang J. E., Ok Y. S.: Bioresour. Technol. *118*, 536 (2012). doi: 10.1016/j.biortech.2012.05.042.
29. Gray M., Johnson M. G., Dragila M. I., Kleber M.: Biomass Bioenergy *61*, 196 (2014). doi: 10.1016/j.biombioe.2013.12.010.
30. Abdullah H., Wu H.: Energy Fuels *23*, 4174 (2009). doi: 10.1021/ef900494t.
31. Brewer C. E., Chuang V. J., Masiello C. A., Gonnermann H., Gao X., Dugan B., Driver L. E., Panzacchi P., Zygourakis K., Davies C. A.: Biomass Bioenergy *66*, 176 (2014). doi: 10.1016/j.biombioe.2014.03.059.
32. Somerville M., Jahanshahi S.: Renewable Energy *80*, 471 (2015). doi: 10.1016/j.renene.2015.02.013.
33. Plötze M., Niemz P.: Eur. J. Wood Wood Prod. *69*, 649 (2010). doi: 10.1007/s00107-010-0504-0.
34. Kasozi G. N., Zimmerman A. R., Nkedi-Kizza P., Gao B.: Environ. Sci. Technol. *44*, 6189 (2010). doi: 10.1021/es1014423.
35. Suliman W., Harsh J. B., Abu-Lail N. I., Fortuna A.-M., Dallmeyer I., Garcia-Perez M.: Biomass Bioenergy *84*, 37 (2016). doi: 10.1016/j.biombioe.2015.11.010.
36. Song W., Guo M.: J. Anal. Appl. Pyrolysis *94*, 138 (2012). doi: 10.1016/j.jaap.2011.11.018.
37. Lehmann J., Gaunt J., Rondon M.: Mitig Adapt Strat Glob Change *11*, 403 (2006). doi: 10.1007/s11027-005-9006-5.
38. Budai A. a 13 spoluatorů: *Biochar Carbon Stability Test Method: An assessment of methods to determine biochar carbon stability*; International Biochar Initiative, 2013.
39. IBI: *Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil 2012. https://biochar-international.org/characterizationstandard/, staženo* 3.6.2019
40. Spokas K. A.: Carbon Manage. *1*, 289 (2014). doi: 10.4155/cmt.10.32.
41. Major J.: *Guidelines on Practical Aspects of Biochar Application to Field Soil in Various Soil Management Systems*; IBI, 2010.
42. Weil R., Brady N., *The Nature and Properties of Soils*. Pearson Education, 2016.
43. Batista E., Shultz J., Matos T. T. S., Fornari M. R., Ferreira T. M., Szpoganicz B., de Freitas R. A., Mangrich A. S.: Sci. Rep. *8*, 10677 (2018). doi: 10.1038/s41598-018-28794-z.
44. Das O., Sarmah A. K.: Sci. Total. Environ. *512-513*, 682 (2015). doi: 10.1016/j.scitotenv.2015.01.061.
45. Chun Y., Sheng G., Chiou C. T., Xing B.: Environ. Sci. Technol. *38*, 4649 (2004). doi: 10.1021/es035034w.
46. Jazini R., Soleimani M., Mirghaffari N.: Water and Environment Journal *32*, 125 (2018). doi: 10.1111/wej.12307.
47. Cha J. S., Park S. H., Jung S.-C., Ryu C., Jeon J.-K., Shin M.-C., Park Y.-K.: J. Ind. Eng. Chem. *40*, 1 (2016). doi: 10.1016/j.jiec.2016.06.002.
48. Lee J. W., Kidder M., Evans B. R., Paik S., Buchanan A. C., 3rd, Garten C. T., Brown R. C.: Environ. Sci. Technol. *44*, 7970 (2010). doi: 10.1021/es101337x.
49. Wu W., Yang M., Feng Q., McGrouther K., Wang H., Lu H., Chen Y.: Biomass Bioenergy *47*, 268 (2012). doi: 10.1016/j.biombioe.2012.09.034.
50. European Biochar Certificate: http://www.european-biochar.org/en/objectives, staženo 3.6.2019.
51. Yarrow D.: Acres U.S.A. magazine, May 2013.
52. Hagemann N., Kammann C. I., Schmidt H. P., Kappler A., Behrens S.: Plos One *12*, (2017). doi: 10.1371/journal.pone.0171214.

53. Kammann C. I., Schmidt H. P., Messerschmidt N., Linsel S., Steffens D., Muller C., Koyro H. W., Conte P., Joseph S.: Sci. Rep. *5*, 11080 (2015). doi: 10.1038/srep11080.
54. Agegnehu G., Bass A. M., Nelson P. N., Bird M. I.: Sci. Total. Environ. *543*, 295 (2016). doi: http://dx.doi.org/10.1016/j.scitotenv.2015.11.054.
55. Gerlach A., Schmidt H.-P.: Journal for terrior-wine and biodiversity, (2008).
56. Leng R., Preston T., Inthapanya S.: Livestock Research for Rural Development *24*, (2012).
57. McHenry M. P.: Journal of the Science of Food and Agriculture *90*, 183 (2010). doi: 10.1002/jsfa.3818.
58. Van D. T. T., Mui N. T., Ledin I.: Anim. Feed Sci. Technol. *130*, 242 (2006). doi: 10.1016/j.anifeedsci.2006.01.008.
59. Schmidt H.-P., Kammann C., Gerlach A., Gerlach H.: Ithaka-Journal, 364 (2016).
60. Chu G. M. a 11 spoluatorů: Anim. Sci. J. *84*, 113 (2013). doi: 10.1111/j.1740-0929.2012.01045.x.
61. Yamauchi K., Manabe N., Matsumoto Y., Yamauchi K.-e.: Connect. Tissue Res. *54*, 416 (2013). doi: 10.3109/03008207.2013.834895.
62. Lee J.-J., Park S.-H., Jung D.-S., Choi Y.-I., Choi J.-S.: Korean J. Food Sci. Anim. Resour. *31*, 296 (2011). doi: 10.5851/kosfa.2011.31.2.296.
63. Gerlach H., Schmidt H.-P.: Ithaka-Journal *1*, 262 (2012).
64. Meyer-Kohlstock D., Haupt T., Heldt E., Heldt N., Kraft E.: Energies *9*, (2016). doi: 10.3390/en9040247.
65. Kumar S., Jain M. C., Chhonkar P. K.: Biol. Wastes *20*, 209 (1987). doi: 10.1016/0269-7483(87)90155-8.
66. Inthapanya S., Preston T. R., Leng R. A.: Livestock Research for Rural Development *24*, (2012).
67. Rodger J.-M., Ganagin W., Krieg A., Roth C., Loewen A.: Müll und Abfall *9*, 476 (2013).
68. Mumme J., Srocke F., Heeg K., Werner M.: Bioresour. Technol. *164*, 189 (2014). doi: 10.1016/j.biortech.2014.05.008.

## Biochar – production, properties, certification, and utilization

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### *Summary*

*This review article summarizes fundamental knowledge about biochar. Biochar is getting paid a lot of attention recently for its ability to enhance crop yield and mitigate climate change. Main European furnace producers for generating biochar are introduced. Relevant physicochemical and textural properties are reviewed with emphasis on a stability of biochar, pH, water holding, and nutrient retention capacity. Czech legislation, where biochar is classified as a supplementary soil substance and voluntary certification initiatives such as European Biochar Certificate (EBC) and International Biochar Initiative (IBI) are discussed. The methods of application of biochar in agriculture are described as well.*

**Keywords:** *Biochar, Biomass, Thermochemical conversion, Carbonization, Pyrolysis, Gasification*

# The processes of accumulation and transport of automobile waste in the city of Tashkent

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## Abstract

*The state of the problem of automotive waste in the Republic of Uzbekistan is discussed in the paper. In spite of a high growth rate of motorization, the issue of automotive waste disposal is solved very slowly. To know the fate of automotive waste, a survey of car owners was conducted. It revealed that no more than 32% of the waste is directly passed to recycling by car owners; but such hazardous waste as antifreeze is almost completely discharged into water or on the ground. The lack of knowledge among car owners is the reason of the destruction of catalysts, which leads to a sharp increase in exhaust emissions. State programs for recycling are not sufficiently advertised, as a result, the car owners are not aware of the possibility of waste disposal for recycling. It is necessary to increase the interest of citizens in the delivery of waste for recycling and the development of infrastructure for the collection, transportation and disposal of automobile waste.*

***Keywords:*** *end of life cars, waste, recycling, social survey*

## Introduction

The problem of recycling automotive waste is a priority in many countries around the world. Car waste is a valuable secondary raw material, recycling of which allows not only to ensure the rational use of resources, but also to create workplaces [1, 2, 3, 4]. End of life vehicles (ELV) include various materials (mercury, cadmium, antifreeze, etc.) that have a negative impact on the environment - the portion of such waste is about 25% [1].

In the EU, old cars already in the early 1990s were considered as a priority waste flow [1, 5]. Recycling and reuse of parts and components of old cars, as well as the extraction of metals and other materials were very important for governments and manufacturers. The organization of the disposal of the ELV highly depends on the country's attitude to environmental issues, and it is now one of the main areas of scientific research in the field of environmental protection. Management of the process of recycling car waste is a challenging one and it requires a multifaceted approach for the restoration, reuse and recycling of materials.

At present many countries offer and use the measures for solid waste management. For the elimination and minimization of waste, the most appropriate measures are the restoration, reprocessing and recycling, which allow saving money on the production of parts and operational materials from primary raw materials [1, 6].

A very important aspect is the state regulation of the recycling process. For example, in China, due to a sharp increase in the number of vehicles (and their waste), the Regulations on Mandatory Standard of Scrapping Vehicles were introduced in 2013, limiting the possibility of operating private cars to 600,000 km mileage [7].

Solving the problem of waste cars are researchers in various countries. The number of publications on this issue is growing every year [8], including:

- research in the field of development of methodological approaches for modeling and forecasting of complex ELV utilization systems [9, 10];
- research in the field of production and operation management, assessment of the impact of legislation on the choice of the ELV disposal strategy [11, 12, 13, 14];
- the study of the possibilities of the new application of components and parts of the car [15, 16, 17].

However, in many countries the problem of automobile waste has not yet found a solution [1, 2, 4, 8, 9].

The aim of this paper is to assess the state of the problem of automobile waste in the Republic of Uzbekistan on the example of the city of Tashkent. The economy of Uzbekistan is developing steadily and one of its main pillars is the automotive industry; its volume of output growing rapidly.

The growth of motorization leads to a sharp increase in the amount of automobile waste. The fate of this waste has not been sufficiently studied, since most of the cars are in personal possession by citizens. In Tashkent, the number of personal vehicles is 431398 units. Since at present there is no well-established system for collecting and processing waste, and no legislative basis for the rules of car owners' behavior during waste disposal, the car owners eliminate waste at their discretion: burn tires, waste oil, pour antifreeze on the ground or down the drain, throw end of life cars in parking lots or keep them in the courtyards of residential houses, etc. All this causes significant damage to the environment, in particular to soil and water [6, 18, 19]. Only metal parts of cars and car batteries (accumulators) are disposed of in official way.

In recent years in the Republic of Uzbekistan, a special attention has been paid to waste recycling; regulatory documents and programs for their management are being created. Nevertheless, the problem of automobile waste has not yet attracted appropriate attention.

To take some measures to regulate the waste management system, it is necessary first of all to study the state of the spontaneously developing process of waste transportation from the car owner to the place of disposal or recycling. Since there are no statistics of this nature in Uzbekistan, it was decided to obtain the necessary information by interviewing car owners.

## Experimental part

### Research method

Car owners of large cities, in particular, the city of Tashkent, present a kind of social communities and can be the object of sociological research. Thus, a sociological survey method has been adopted as a research method. Considering the comparative analysis of the types of opinion polls carried out in [20, 21, 22], we chose the method of direct questioning using questionnaires. This method allows us to involve a large number of people and get results in a short time.

To obtain data on the formation and transportation of waste from car owners to the places of waste elimination or recycling, car owners were asked a questionnaire in which the questions were divided into three groups: 1) information about the car owned by the respondent; 2) car owner's handling of vehicle waste; 3) the awareness of car owner of the programs of recycling of automobile waste.

In the course of the survey, car owners were selected among students and teachers of the Tashkent Institute of Design, Construction and Maintenance of Automotive Roads and the Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, among employees of various enterprises and retirees. The age of the respondents ranged from 18 to 82.

Completed questionnaires were pre-checked, some of them were eliminated due to erroneous data and incorrectly filled positions. For the statistical analysis of the questionnaires two men were involved in order to reduce statistical errors.

### Determining the sample size

As a rule, sociological studies of such communities are selective, since economic and time constraints do not allow for a complete survey. Certain difficulties are connected with selective research. The sample should reflect the common characteristics of the studied population, i.e. have a representativeness.

The sample representativeness is characterized by two interrelated parameters - the level of error and the probability. It is usually assumed that the error of the representativeness of a given sample with a confidence probability $p$ does not exceed $\Delta$ [23].

When planning a sociological research, a certain level of accuracy of the result is set in admissible error and confidence probability; a required sample size for these parameters is determined. In particular, the sample size to determine the portion of some characteristic $X$ in the general population of more than 5000 units is determined by formula [24]:

$$n = \frac{1}{\Delta^2} \qquad (1)$$

where Δ is the value of the permissible error, assumed as 5% (0.05) with a probability of 0.954.

When planning the sample size, it should be borne in mind that the specified accuracy, when analyzing the sample as a whole, could not be obtained, so we should divide it on terms. Let us clarify it on an example: it is necessary to determine the portion of car owners on whose cars a catalyst is installed. After questioning $n$ randomly selected people, determine the sought for portion with an error not exceeding 5% (with a probability of 0.95). But if the task is to determine the portion of car owners who are hampered by the catalyst, i.e. not for the entire array, but only for the part of car owners with installed catalyst, this means that it is necessary to have $n$ cars with an installed catalyst.

Planning the sample size to determine numerical characteristics of the population (for example, the averages) is done in the following way.

Firstly, a test survey is conducted (30 or more respondents). Then, based on the results of this survey, the sample size is determined by formula [23, 25]:

$$\mathrm{N} = \frac{\sigma^2 \cdot \mathrm{t}^2}{\mathrm{d}^2} \qquad (2)$$

where $N$ is the sought for sample size; $\sigma$ is the dispersion of the characteristic, the expected average deviation of the results obtained from the expected average value; $t$ is the value of the Student criterion corresponding to the confidence probability level (for 0.954 $t = 2$, for 0.99 $t = 2.7$); $d$ is the level of accuracy for this factor (absolute error of measurements).

The error of representativeness is determined by the formula:

$$M = \frac{\sigma}{\sqrt{n_i - 1}} \qquad (3)$$

Where $\sigma = \sqrt{\sigma^2}$ is the standard deviation.

The limit error of sampling is determined by the formula [25]:

$$\Delta = t \cdot M \qquad (4)$$

The required sample size was determined in the following order:

The required sample size to determine the portion of characteristics $X$ in a general population (for example, the portion of car owners throwing waste into landfills, etc.) was obtained by formula (1).

The required sample size to determine numerical characteristics of the general population (annual car mileage, age of cars, gas mileage) was obtained by formula (2).

The absolute error of measurements $d$ was set as follows:

- for the annual mileage of the car $d_{annual} = 2$ thousand km (8.4%);
- for gas mileage $d_{gas} = 0.1$ liters per 100 km (1.1%);
- for the age of cars $d_{age} = 0.8$ years (9.9%).

Results of calculations based on the preliminary survey, are given in Table 1.

***Table 1: Results of the preliminary survey to determine the sample size***

| | **The number of pre-interviewed people, persons** | **Arithmetic average X** | **Disper-sion $\sigma^2$** | **Standard deviation $\sigma$** | **Repre-sentative error M** | **Limit error of samp-ling $\Delta$** | **Required sample size n, persons** |
|---|---|---|---|---|---|---|---|
| Annual mileage | 86 | 23.93 thousand km per year | 248.98 | 15.7794 | 1.7115 | 3.423 | 497.96≈498 |
| Gas mileage | 78 | 9.12 liters per 100 km | 6.5726 | 2.5637 | 0.2921 | 0.5843 | 262.8≈263 |
| Car age | 92 | 8.02 year | 73.946 | 8.5992 | 0.9014 | 1.8028 | 462.12≈ 462 |

From the above calculations it is seen that the largest sample (498 people) is required to determine numerical characteristics in the general population. For the convenience of conducting a survey of car owners, a sample size of 500 people was adopted.

## Results and discussion

The survey showed that the average gas mileage is very high, since a significant number of powerful cars are in the property of citizens. This, in turn, leads to the emission of a large amount of exhaust gases (for example, the CO emission is 12179.6 tons/year from gas running cars, 101.4 tons/year from methane running cars, 50.4 tons/year from propane running cars. The total is 12331.4 ton/year. If the cars with low-powered engines were used, emissions could be 12 – 15% less).

The amount of emissions increases due to the inexpert use of catalysts: many owners do not know whether they have a catalyst and why they need it. About 3% of car owners destroy dead catalyst, contributing to an increase in emission.

The survey results are given in Tables 2 – 4.

***Table 2: Automobile waste management in Tashkent***

| **Waste management method** | **Type of waste** | | | | | |
|---|---|---|---|---|---|---|
| | **Storage battery** | **Antifreeze** | **Oil** | **Glass** | **Tires** | **Metal** |
| Dispatch solid waste to landfills, discharge into drains or on the ground, incineration, % | 20.6 | 54.2 | 32 | 58.1 | 26.1 | 28 |
| Storage in the garage (cluttering), % | 4.4 | 17 | 4.8 | 2 | 7.3 | 5.1 |
| Sending for recycling, % | 31.8 | 2 | 2.8 | 4.8 | 20.3 | 30.8 |
| Leaving in the car service centers *, % | 17 | 38.6 | 48.8 | 27.1 | 15.9 | 21.5 |
| Sale on the car markets, % | 25.8 | 2.1 | 7.8 | 3,5 | 28.1 | 13.2 |
| Use for other purposes, % | 0.4 | 1.4 | 3.8 | 4,5 (repair) | 2.3 | 1.4 |
| Number of respondents, persons | 519 | 515 | 537 | 399 | 521 | 493 |

* *the workers of car service centers give information reluctantly, therefore, further transport of waste left in services centers can be judged only approximately: some of the waste is managed under contracts (the firms are unknown); some parts are destroyed (for example, part of the tires is burned due to the complexity of the delivery to the collection points); part of liquid waste (oil, antifreeze) is poured into cars of a lower class.*

**Table 3: Distribution of passenger car fleet by consumed fuel, %**

| Type of fuel | Number of cars |
|---|---|
| Petrol | 75.2 |
| Gas/petrol | 2.3 |
| Gas | 14.3 |
| Diesel fuel | 1 |

**Table 4: Average numerical characteristics of the car park in Tashkent according to the survey results**

| Name of the index | Value of the index |
|---|---|
| Age of the car, years | 8.3 |
| Mileage, thousand km | 148 |
| Annual mileage, thousand km/year | 26 |
| Gas mileage, liters per 100 km | 9.3 |

From the presented data it is seen that the most disastrous is the situation with antifreeze, waste oil and glass; their percentage of processing being very low. It should be borne in mind that if the thrown glass simply leads to cluttering the area, then the antifreeze and oil poured into the water or to the ground leads to serious environmental pollution.

Assessing environmental damage according to the method [25] and taking into account price coefficients operating in the Republic of Uzbekistan, it can be revealed that the damage from an unapproved draining to the ground and to the water is:

- for electrolyte 1863.4 thousand USD/year;
- for antifreeze 4670 thousand USD/year;
- for used oil 38237 USD/year.

A comparison of the results obtained by the authors with the publications of other researchers shows that the situation with car waste in Uzbekistan is typical for developing countries.

For example, in Ghana the most of the old parts are immediately reused, or are thrown away or burned [18]. Citizens are dissatisfied with this situation, but do not have the experience and means to organize the recycling process.

In India [4] polls show that 54% of car owners exchange or sell their old cars. Only heavily damaged vehicles that cannot be further exploited are disposed of. 65% of car owners in India operate their cars from 3 to 8 years, while in Uzbekistan cars are used for 10-15 years. The situation with engine and transmission oils in Uzbekistan is also analogous to that of India: oils are burned, sent to informal processing enterprises, modified to obtain grease, or simply poured out to the ground. The situation with the acid from the accumulator and rubber parts is the same.

It is clear that a poorly organized process of recycling automobile waste is characteristic of states in which state support for environmental protection is weak and there are no mechanisms for controlling waste sources (car owners and car services centers).

## Conclusions

Based on the processing of survey results, we can draw the following conclusions:

- average fuel consumption is very high, because the citizens own a significant number of cars with powerful engines used to drive in the city. This, in turn, leads to the emission of large amounts of exhaust gases. For example, the specific CO emission for cars with an engine capacity of less than 1.4 liters is 10-12% less than for cars with an engine capacity of more than 2 liters.
- the amount of emissions increases due to inexpert use of catalysts: many owners do not know whether they have a catalyst and why they need it. 8.1% of car owners who have cars with a catalyst (358 people were polled) destroy it or replace it with an exhaust pipe without a catalyst, thereby contributing to an increase in emissions. If a car of the Euro-4 class is not equipped with a catalyst, this moves it from the Euro-4 category to the Euro-1; and leads to a sharp increase in CO emission — an annual emission increases by 2.74 times (with a specific CO emission of 2.7 g/km for Euro-4 class and 7.4 g/km for Euro-1 class);
- currently, half of the waste (from 25% for batteries to 60% for glass) falls into the water, soil, is burned in organized or unorganized landfills, clogging the environment. Part of the waste just clutters the area;
- the age of the vehicle fleet is quite old, which leads to a noticeable increase in the amount of emissions at the vehicle motion (for example, emission of vehicles with a mileage of 300 or more thousand km is approximately 1.39 times greater than emission from vehicles with a mileage of up to 100 thousand km). The state makes the attempts to "rejuvenate" the car park. The program “Let's give a chance to nature”, designed to increase the interest of citizens in the delivery of old cars for recycling, has been developed. However, the survey shows that only 3.2% of the respondents heard about this program, which indicates poorly organized advertising and insufficient explanatory work.

Using data from a sociological survey, as well as other initial data obtained using developed and tested regulatory and statistical methods for recording operational and construction materials consumed during the operation of the car fleet, data on the content of these materials in abandoned and written-off cars, end of life vehicles which are out of service and are subject to disposal, will help to assess the mass formation of certain types of waste from the transport operation for the conditions of the city of Tashkent.

In conclusion, it can be said that the current situation with car waste is unacceptable. The following measures can be proposed to solve the identified problems:

- introduction of regulatory and legislative documents prohibiting car owners and car service centers to drain liquid toxic waste (oil, antifreeze, electrolyte) into the sewage system, watercourse and into the soil and establishing appropriate penalties for such actions;
- organization of monitoring and inventory of liquid and solid wastes accumulation in car service centers;
- organization of delivery points for used antifreeze, electrolyte and oils in areas of maximum accumulation of service stations (Mirabad, Yashnabad, Mirzo-Ulugbek, Sergeli, Chilonzar and Yunusabad districts);
- the establishment of a fee to car owners for the delivery of waste, and wide advertising of waste delivery points among the population;
- introduction of antifreeze processing technologies (for example, in distillation columns) and the creation of appropriate small enterprises.

## Reference

1. Sharma P., Sharma A., Sharma A., Srivastava P.: Automobile Waste and Its Management. Research Journal of Chemical and Environmental Sciences Vol . 4 [2] 2016, 1
2. Nwachukwu M.A., Feng H., Achilike K.: Integrated Study for Automobile Wastes Management and Environmentally Friendly Mechanic Villages in the Imo River Basin, Nigeria. African Journal of Environmental Science and Technology Vol. 4(4),2010. 234.
3. Sivakumar G.D., Barnabas G.S., Anatharam S.: Indian Automobile Material Recycling Management. International Journal of Innovative Research in Science, Engineering and Technology. Vol. 3, Special Issue 3, 2014. pp. 2754 – 2758
4. Chaturvedi A., Arora R., Chaturvedi B, Short A.: *The Story of a Dying Car in India. Understanding the Economic and Materials Flow of End-of-Life vehicles.* Chintan Environmental Research and Action Group. 2012.
5. Nicolli F., Johnstone N., Soderholm P.: Resolving failures in recycling markets: The role of technological innovation. Environmental Economics and Policy Studies. 14, 3 (2012), 261.
6. Ashaa M.N., Chandanb K.S. et al.: Recycling Of Waste Water Collected From Automobile Service Station. Procedia Environmental Sciences 35. 2016, 289
7. Jinhui Li,  Keli Yu, Peng Gao: Recycling and Pollution Control of the End of Life Vehicles in China. Mater Cycles Waste Manag. (2014) 16:31 – 38
8. Simic V.: End-of-life Vehicle Recycling - a Review of the State-of-the-Art. Technical Gazette 20, 2(2013), 371.
9. Papadogiannis A., Chondros T., Dentsoras A.: A Proposal for End of Life Vehicles Recycling in Greece. Izvestiya vysshikh uchebnykh zavedeniy. 2013, 7
10. Blume T., Walther M.: The end-of-life vehicle ordinance in the German automotive industry – corporate sense making illustrated. Journal of Cleaner Production. (2012), doi: 10.1016/j.jclepro.2012.05.020.
11. Joung H., Cho S., Seo Y., Kim W. H.: Status of recycling end-of-life vehicles and efforts to reduce automobile shredder residues in Korea. Journal of Material Cycles and Waste Management. 9, 2(2007), 159.
12. Chen M., Zhang F.: End-of-life vehicle recovery in China: Consideration and innovation following the EU ELV directive. JOM. 61, 3 (2009), pp. 45 – 52.
13. Chen K.-c., Huang S.-h., Lian I-w.: The development and prospects of the end-of-life vehicle recycling system in Taiwan. // Waste Management. 30, (2010), 1661.
14. Ptashkina MG, Idrisova V.V.: Application of recycling collection in relation to wheeled vehicles in the Russian Federation. Russian Foreign Economic Bulletin 1. 2013, 10
15. Tarasov Yu., Molodan A.: Evaluation of recycling efficiency of vehicles released from operation. Vestnik KHNADU, 72. 2016, 7
16. Ignatov V.I.: Recycling fee: the path to the development of the industry in Russia or its further degradation? Nauchnyy zhurnal KubGAU, 121 (07), 2016. http://ej.kubagro.ru/2016/07/pdf/75.pdf. Downloaded May 11, 2018.
17. Ignatov V.I.: Organizational-technological complex of works on utilization of agricultural machinery. Nauchnyy zhurnal KubGAU. 128 (04), 2017. http://ej.kubagro.ru/2017/04/pdf/63.pdf. Downloaded March 11, 2019
18. Nyamekye P. *Degree thesis.* Arcada University Of Applied Sciences, Helsinki. 2012.
19. Ogundapo Tayo, Tobinson A. Briggs: Assessment of the Impact of Automobile Waste on the Environment. International Journal of Engineering Inventions. Volume 7, Issue 7. 2018, 1
20. Kelley K., Clark B., Brown V., Sitzia J.: Good Practice in the Conduct and Reporting of Survey Research. International Journal for Quality in Health Care. Vol. 15, No. 3. 2003, 261
21. Karim M. A.: Learning of Environmental Engineering - On-line, Hybrid, or Face-to-Face: A Case Study. Electronic Source. Available at

https://www.researchgate.net/publication/298630417_Learning_of_Environmental_Engineering_-_On-line_Hybrid_or_Face-to-face_A_Case_Study. downloaded June 1, 2018.

22. Xi Meng, Weijie Liang et al.: Survey Research on Living Environment and Energy Consumption in the West Rural Areas of China. Procedia Engineering 121 ( 2015 ), 1044
23. Paniotto V.I., Maksimenko V.S.: *Quantitative Methods in Sociological Research.* Naukova Dumka, Kiev. 1982.
24. Berezin I.S.: Practical Ways to Build a Sampling in Studies and Surveys. E-resource. URL: http://www.elitarium.ru/issledovanie-vyborka-reprezentativnost-dostovernost-doveritelnyj-interval-formuly. downloaded June 2, 2018.
25. Gorodilin S.K.: *Applied Case Studies in the Field of Physical Education and Sports*. Publishing by the Grodno State University named after Yanka Kupala, Grodno, 2006.
26. Trofimenko Yu.V., Vorontsov Yu.M., Trofimenko K.Yu.: *Disposal of cars*. AKRPESS, Moscow. 2011.

# Proces akumulace a pohybu odpadních vozidel ve městě Taškent

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## *Souhrn*

*Článek pojednává o problematice nakládání s vyřazenými automobily v Uzbekistánu. Navzdory vysoké míře rozvoje motorizace se problém recyklace vyřazených vozidel řeší velmi pomalu. Pro zjištění dalšího osudu vyřazených automobilů byl proveden průzkum u majitelů automobilů. Ukázalo se, že ne více než 32 % jich je přímo předáno k recyklaci; ale nebezpečné složky, jako je například nemrznoucí kapalina, je téměř výhradně vypuštěn do vody nebo na zem. Nedostatek informací mezi vlastníky automobilů je příčinou zničení katalyzátorů během provozu, což vede k prudkému nárůstu emisí výfukových plynů. Vládní program recyklace vyřazených vozidel nejsou dostatečně propagovány, takže majitelé automobilů nejsou informováni o této možnosti. Je nutné zvýšit zájem občanů o předávání vyřazených automobilů k recyklaci a rozvíjet infrastrukturu pro sběr, přepravu a likvidaci automobilového odpadu.*

***Klíčová slova:*** *vyřazená vozidla, autovrak, odpad, recyklace, sociální průzkum*

# Vliv vybraných podmínek na opakovatelnost potenciálové odezvy stříbrné amalgámové elektrody v průmyslových vodách

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## Souhrn

*Použití popsaného způsobu vyhodnocení potenciometrických měření s pevnými stříbrnými amalgámovými elektrodami (AgSAE) umožnilo využít tyto elektrody i při nižších požadavcích na mechanické obnovení jejich povrchů. Opakovatelnost závislostí zobrazujících kvaziustálené hodnoty potenciálů $E_i$ vs. Vzi (označujících sledované vzorky vody odebrané v pořadí od Vz1 do Vz5 její postupné úpravy a po přídavku* $1 \cdot 10^{-2}$ M $AgNO_3$) *týkajících se AgSAE větších průměrů d než 1 mm byla lepší než u menších AgSAE. Výsledky potvrdily, že při $d > 1$ mm byl charakter získaných závislostí $E_i$ vs. Vzi v pořadí od i = 1 do i = 5 přibližně neměnný a potenciálně využitelný.*

***Klíčová slova:*** potenciometrie, stříbrná amalgámová elektroda, úprava vod, iontoměniče

## Úvod

Mezi nejrozšířenější metody sledování kvality upravovaných vod za běžných podmínek patří konduktometrie pro charakterizaci celkové čistoty vody a potenciometrie zejména pro zjišťování jejího pH nebo obsahu vybraných iontů[1-3]. Již dříve byly navrženy[4-7] způsoby použití potenciometrie se speciálně připravenými stříbrnými pevnými amalgámovými elektrodami AgSAE, poskytující doplňkové nebo alternativní ukazatele pro indikaci změn celkové čistoty vzorků vody. Speciální příprava AgSAE a jejich využití se opíraly o dlouhodobé zkušenosti z voltametrie jak se rtuťovými[8], tak s podobnými AgSAE[8-15]. Příkladem takové nové potenciometrické aplikace AgSAE v oblasti sledování obsahu nanostříbra v roztoku byla práce[16]. V návaznosti na zájem Jaderné elektrárny JE Dukovany (ČEZ a.s.) i v rámci souvisejícího předběžného výzkumu byl obdobný princip sledování změn nernstovského potenciometrického chování zinkové nebo stříbrné amalgámové elektrody během procesu čištění vod využit v cit.[17,18]. Avšak aby mohla být v budoucnu potenciometrická měření na takových amalgámových elektrodách využita v praxi, je třeba pro každou elektrodu i typ aplikace postupně zjistit, jak se tyto elektrody chovají při různých experimentálních podmínkách a jaké podmínky jsou pro jejich využití optimálními. Cílem tohoto sdělení bylo rozšířit dosud shromážděné poznatky o podmínkách zmíněné nedávno navržené[4,18] potenciální aplikace potenciometrie na AgSAE, například pro alternativní způsob kontroly dodržování technologických kroků uvedené výroby čisté vody.

## Experimentální část

Potenciometrická měření probíhala s pracovní stříbrnou amalgámovou elektrodou AgSAE, s referentní merkurosulfátovou elektrodou $Hg/Hg_2SO_4$ (1M $K_2SO_4$) se solným můstkem 0,5M $KNO_3$ (Elektrochemické detektory, s.r.o., Česká republika) a s voltmetrem BM 551 (Laboratorní přístroje, Praha, Česká republika) v režimu přesnosti ±1 mV s připojeným potenciometrickým modulem. Měření byla prováděna při laboratorní teplotě 298 ± 0,5 K v lázni termostatu VWR 210 (VWR International, s.r.o., Stříbrná Skalice, Česká republika). Všechny chemikálie, vč. $AgNO_3$ (Merck, SRN), byly čistoty p.a. a zásobní roztoky byly připravovány s použitím demineralizované vody o vodivosti $< 0{,}1\ \mu S \cdot cm^{-1}$.

Pro vybrané podmínky testování byla použita řada pěti vzorků vod Vi (i = 1 až 5) dodaných pracovištěm výroby demineralizované vody Jaderné elektrárny JE Dukovany (ČEZ, a.s., ČR). Pocházely z odběrových míst pěti technologických kroků poskytujících konkrétně tyto zmíněné vzorky: V1 – vstupní voda po dekantaci; V2 – voda V1 po čiření a filtraci, V3 – voda V2 po aplikaci katexu Lewatit S 100 (Lanxess, Kolín nad Rýnem, Německo) o střední velikosti částic cca 650 $\mu$m, V4 – voda V3 po aplikaci anexu Lewatit MonoPlus MP 64 (Lanxess, Kolín nad Rýnem, Německo) o střední velikosti částic cca 600 $\mu$m; V5 – výstupní voda ze sběrného zásobníku.

Výrobce jednak analyticky kontroloval kvalitu vstupní vody V1, jednak konduktometricky kontroloval[4,17] přísné dodržování postupu operací pomocí měření změn vodivostí vod V1 až V5. Proto pracoviště JE Dukovanydodalo údaje o složení vstupní vody V1 a o specifických elektrických vodivostech $\kappa$1 až $\kappa$5 vod V1 až V5. Voda V1 tedy obsahovala: cca 40 $mg \cdot l^{-1}$ Ca, 14 $mg \cdot l^{-1}$ Mg, 5 $\mu g \cdot l^{-1}$ Cu, 40 $mg \cdot l^{-1}$ $Cl^-$, 8 $mg \cdot l^{-1}$ $NO_3^-$, 57 $mg \cdot l^{-1}$ $SO_4^{2-}$, 2 $\mu g \cdot l^{-1}$ Cd, 10 $mg \cdot l^{-1}$ $SiO_2$, 75 $\mu g \cdot l^{-1}$ AOX, pH ~7,4, 0,1 $mg \cdot l^{-1}$ C10-C40. Při postupu od V1 do V5 byl přitom registrován charakteristický průběh změn vodivostí vyplývající z následujících změřených hodnot $\kappa i$ ($\mu S \cdot cm^{-1}$) od $i = 1$ do $i = 5$: *$\kappa 1 \sim 460$; $\kappa 2 \sim 430$; $\kappa 3 \sim 1440$; $\kappa 4 \sim 0{,}02$; $\kappa 5 \sim 0{,}02$.* Extrémně nízkou vodivostí $\kappa$ demineralizovaných vod V4 a V5 o hodnotách $\kappa < 0{,}05$ $\mu S \cdot cm^{-1}$ dokladoval tak výrobce (bez dalších analýz) jejich čistotu, při objemu průběžné výroby víc než 600 000 $m^3$ za rok. Jak bylo uvedeno, z věcných i ekonomických důvodů používal konduktometrii současně i pro orientační sledování změn kvality vod V2 a V3 (rovněž bez jejich chemického rozboru).

V tomto sdělení jsou dále popsána měření prováděná ve vzorcích Vz1 až Vz5 připravených tak, že do všech vzorků vod V1 až V5 byl přidán $AgNO_3$ o výsledné koncentraci $1 \cdot 10^{-2}$M $AgNO_3$.

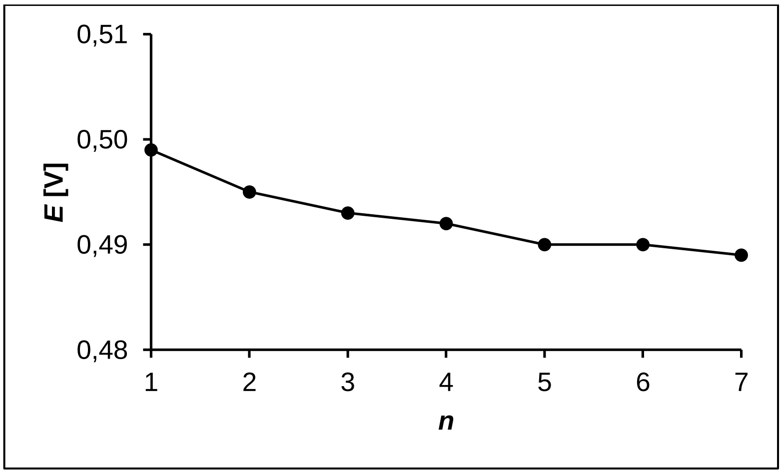
Stříbrná amalgámová elektroda byla vytvořena z prášku o velikosti částic 2 $\mu$m, po jeho napěchování do plastové špičky typu „plastic typ“[6,19] (dále uvedeného průměru) a po zasunutí špičky do rtuti na cca 8 hod.[6,7,8,14,17]. Aktivní diskovou amalgámovou elektrodu vytvořenou tak na čele plastové špičky bylo možno vyleštit pomocí 0,3 $\mu$m-emulze aluminy (Elektrochemické detektory, s.r.o., Česká republika). Vyleštěná AgSAE byla aktivována provedením série měření *Ei* vs. Vzi od i = 1 do 5, poté byl její povrch otřen o polyethylenovou podložku a pomocí střičky krátce opláchnut demineralizovanou vodou. Otření povrchu elektrody bylo provedeno vždy před dále popsanou sérií pěti měření ve vzorcích Vzi (i = 1 až 5), přičemž byl navíc povrch AgSAE před každým jednotlivým měřením Vzi též opláchnut demineralizovanou vodou. Průměry použitých elektrod označených postupně EL1, EL2, EL3, EL5 a EL6 činily postupně 0,4; 0,7; 1,1; 1,5; 2,2 a 2,7 mm.

## Výsledky a diskuse

Z podnětu uvedeného výrobce demineralizované vody o výsledné vodivosti $\kappa < 0{,}05$ $\mu S.cm^{-1}$, zaměřeného na otázku možného doplnění konduktometrické kontroly další v principu nezávislou kontrolou dodržování sekvence operací od V1 do V5, bylo při popsaném pokračování předběžného výzkumu v tomto směru postupováno v souladu se zmíněným účelovým zadáním uvedené aplikované výrobní praxe.

Jak bylo naznačeno v předchozích sděleních[4,16-18], ukázala se potenciometrie s AgSAE potenciálně nadějnou doplňkovou metodou například pro již uvedené potvrzení dodržování sekvence čisticích kroků při čištění sledovaných typů průmyslových vod. Při měření potenciálu *E* AgSAE za použití dané sekvence typů vod od V1, přes V2, V3, V4 do V5, do nichž byl přidán $AgNO_3$ vždy o stejné koncentraci, byl – jak citované práce[4,18] uvádějí – získán vždy stejný typ diagramu $E_i$ vs. Vi ($i$ = 1 až 5). Ve zmíněných případech měl vždy náběžnou část (V1 až V3) s vrcholem uprostřed při V3, následovaným sestupnou částí (V3 až V5). Tento průběh byl poměrně typický pro danou posloupnost a podmínky měření, málo závislý na jejich citlivosti nebo opakovatelnosti. Podmínkou však bývalo použití elektrod AgSAE, které byly před prováděným měřením obnoveny důkladným přeleštěním jejich povrchu pomocí již zmíněné 0,3 $\mu$m – emulze aluminy.

Pozornost byla proto zaměřena na ověření takového dříve navrženého[4,18] postupu měření, který mohl poskytnout zmíněný charakteristický průběh $E_i$ vs. Vzi i jen při otření měrné AgSAE o polyethylenovou podložku před každou sérií měření a při občasném přeleštění jejího povrchu, například jedenkrát za dva až čtyři pracovní týdny – v závislosti na frekvenci měření. Uvedený postup byl založen na určování těch hodnot potenciálů $E_i$, kterých bylo (v rámci potřebné opakovatelnosti měření, např. ±1 až 2 mV) dosaženo při opakování měření v daném vzorku roztoku Vzi při daném konstantním přídavku $AgNO_3$. Cílem opakovaných měření bylo tedy získání hodnoty *Ei* pro daný vzorek Vzi. Bylo očekáváno, že zejména anionty (halogenidy, sírany, $OH^-$ aj., i jejich nerozpustné produkty s $Ag^+$, $Hg_2^{2+}$) vyvolají na povrchu AgSAE po jejím zasunutí vždy do daného Vzi změny spějící do kvaziustáleného stavu, navíc jiného než u jiných Vzi (zcela odlišného složení a mj. významně záměrně ovlivněných vždy stejným přídavkem $AgNO_3$). Po označení čísla opakovaného měření písmenem *n* s AgSAE daného průměru *d* ve vzorku Vzi bylo možno vynést změřené hodnoty *E* proti *n*. Ukázalo se, že z průběhu *E* vs. *n* bylo tak možno určit průměrnou kvaziustálenou hodnotu $E_i$ mezi *n* = 5 až 7 pro danou AgSAE o průměru *d* a ve Vzi. Popsaný postup ilustruje pro vzorek Vz1 obrázek 1, znázorňující průběh *E* proti *n* pro AgSAE o průměru *d* cca 1 mm. Potřebná doba kvaziustálení potenciálu činila 150 s. Odečtená průměrná hodnota $E_1$ mezi *n* = 5 až 7 činila 491 mV.



***Obrázek 1: Změřené hodnoty potenciálu E při n opakovaných měřeních s využitím AgSAE průměru cca 1 mm, ve vzorku Vz1 obsahujícím $0{,}9\cdot10^{-3}$ M $AgNO_3$***

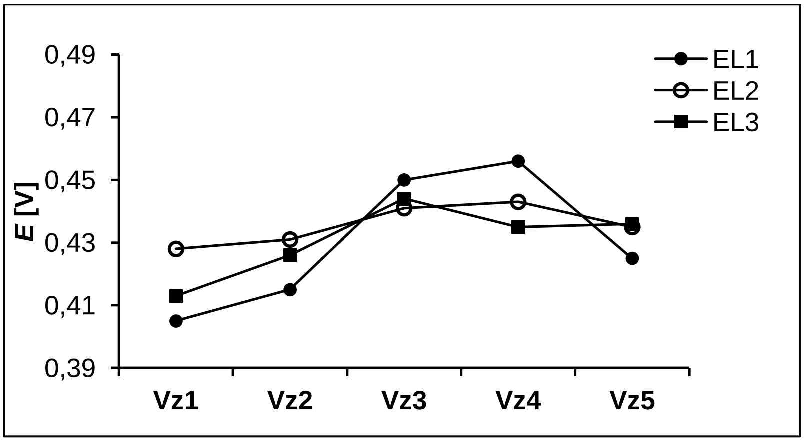
Popsaný postup určování $E_i$ byl pak aplikován pro potenciometrická měření ve vzorcích označených Vz1, Vz2, Vz3, Vz4 a Vz5, a to postupně s elektrodami EL1 až EL6 o různých průměrech. Každý vzorek Vzi (i = 1 až 5) přitom obsahoval příslušnou vodu Vi s přídavkem $1\cdot10^{-2}$ M $AgNO_3$. Tato zvolená koncentrace $AgNO_3$ umožňovala jak rychlé ustavování potenciometrické rovnováhy na AgSAE vůči aktivitám iontů $Ag^+$ v čistých vodných roztocích, tak potenciometrickou detekci výrazných změn těchto aktivit v roztocích obsahujících složky tvořící s $Ag^+$ produkty s nízkými součiny rozpustnosti. Na obrázcích 2 a 3 jsou pro elektrody EL1 až EL3 s $d < 1$ mm zobrazeny průběhy *Ei* vs. Vzi, a to pro měření provedená jak od Vz1 do Vz5 (obrázek 2), tak pro informaci i naopak od Vz5 do Vz1 (obrázek 3).

Z výše uvedených principů popisovaného studia vyplývá, že série pěti měření v pořadí vzorků od i = 1 do i = 5 by měla poskytnout jiný průběh *E*i vs. Vzi než v případě pořadí od i = 5 do i = 1 a dále, že (i za optimální velikosti elektrod a v kombinaci s popsaným obnovením jejich povrchu otěrem po každé sérii měření od i = 1 do i = 5 následované opačným postupem od i = 5 do i = 1) by měl průběh *Ei* vs. Vzi pro i = 1 až 5 a 5 až 1 vykazovat rozdíly.

Tento předpoklad se opíral zejména o dva důvody: 1) Jak již bylo uvedeno, přídavky $AgNO_3$ významným, komplexním a pro každý vzorek Vzi specifickým způsobem ovlivnily většinou již tak velmi rozdílná složení sledovaných roztoků Vzi (v důsledku uplatnění součinů rozpustnosti vůči $Ag^+$, $Hg_2^{2+}$ atd.). 2) Změny iontové skladby a skladby vzniklých (nerozpustných) produktů na povrchu AgSAE (i vlivem jejich adsorpce až chemisorpce), by měly do určité míry záviset na experimentálních podmínkách, na použitém pracovním postupu (vč. pořadí) od vzorku jednoho složení ke vzorku jiného složení, na s tím spojeným přenášením chemisorbovaných zbytkových produktů z předchozích vzorků (specifických pro danou posloupnost) na povrchu AgSAE – i po jeho opláchnutí čistou vodou apod. Právě tato citlivost ve výsledku umožnila experimentální hledání postupů umožňujících (za popsaného obnovování AgSAE otěrem) získat diagramy *Ei* vs. Vzi, jejichž kvaziustálený charakter (nehledě na absolutní hodnoty *Ei*) by vykazoval rovněž vyhovující opakovatelnost, byl by málo závislý například na velikosti AgSAE a bylo by ho – vedle již zmíněné konduktometrie – možné rovněž využít.

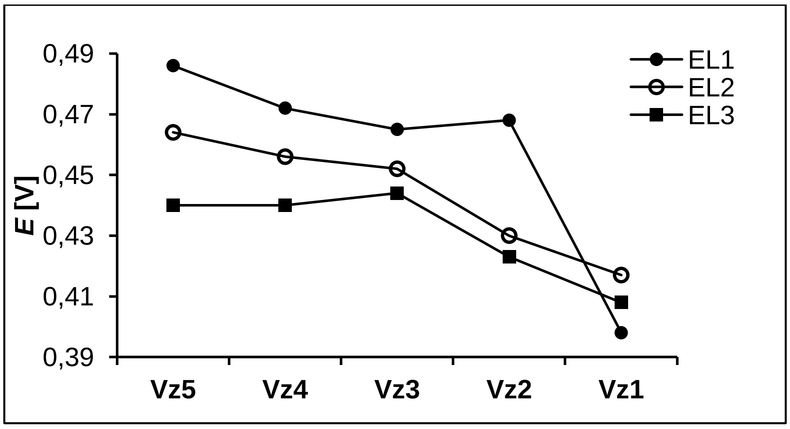
Z analogických důvodů bylo též očekáváno, že se charakter diagramů *Ei* vs. Vzi (opět bez ohledu na absolutní hodnoty *Ei*) – byť i jen za jiných sekvencí stejných vzorků – mohou vzájemně více či méně lišit. Dále uvedené výsledky tyto předpoklady plně potvrdily. Z nich byly v této práci vybrány ty, které ilustrovaly vliv velikosti průměru *d* AgSAE a zvoleného pořadí vzorků na charakter *Ei* vs. Vzi. Pro informaci byly porovnány průběhy *Ei* vs. Vzi pro i = 1 až 5 a i = 5 až 1.

Dále prezentované poznatky rozšiřují nedávno publikované výsledky[4,18] v tomto směru. Obrázek 2 ukazuje, že u AgSAE menších průměrů *d* < 1 mm, obnovovaných (po jejich aktivaci) vždy před danou sérií měření pouze otěrem s následným opláchnutím čistou vodou, nebyly při sledování postupu od Vz1 do Vz5 získány charakteristické *Ei* vs. Vzi s očekávaným[4,18] maximem u Vz3, které by byly málo závislé na hodnotách *d*.



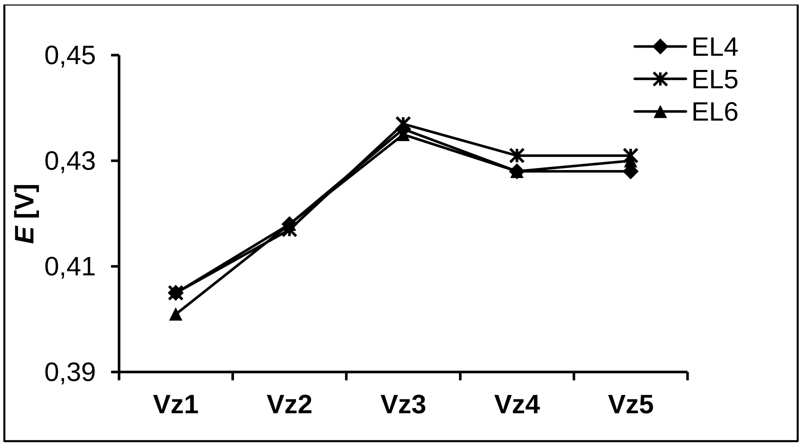
**Obrázek 2: Změřené potenciály $E_i$ pro sledované vzorky Vzi v posloupnosti od Vz1 do Vz5 a při použití elektrod EL1, EL2 a EL3**

Obdobné diagramy na obrázku 3 změřené stejným postupem v opačném pořadí vzorků od Vz5 do Vz1 vykázaly sice v jednom ze tří případů u Vz3 očekávané maximum, avšak jejich opakovatelnost pro různé hodnoty *d* byla rovněž nevyhovující.



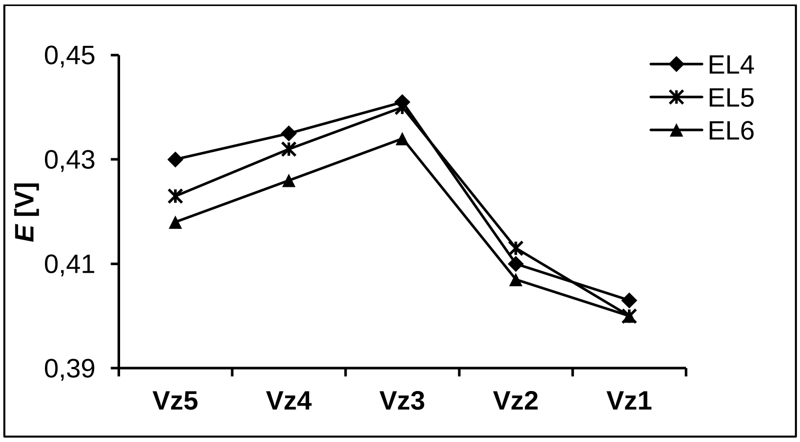
**Obrázek 3: Změřené potenciály $E_i$ pro sledované vzorky Vzi v posloupnosti od Vz5 do Vz1 a při použití elektrod EL1, EL2 a EL3**

Jak ukazuje obrázek 4, v případě elektrod AgSAE, u nichž činila velikost průměrů *d* > 1 mm, byly za jinak stejných podmínek získány závislosti *Ei* vs. Vzi s maximem u Vz3, které pro posloupnost od Vz1 do Vz5 vykázaly jak dostatečně charakteristický (očekávaný) průběh, tak vyhovující opakovatelnost, málo závislou na hodnotách *d*.



***Obrázek 4: Změřené potenciály $E_i$ pro sledované vzorky Vzi v posloupnosti od Vz1 do Vz5 a při použití elektrod EL4, EL5 a EL6***

O něco horší kvalitu těchto parametrů poskytly (ačkoliv jiné co do průběhu) případně rovněž využitelné obdobné závislosti na obrázku 5 pro pořadí od Vz5 do Vz1.



***Obrázek 5: Změřené potenciály $E_i$ pro sledované vzorky Vzi v posloupnosti od Vz5 do Vz1 a při použití elektrod EL4, EL5 a EL6***

Další aspekty popisovaných experimentálních podmínek a vlivů na měřené nernstovské směsné potenciály *Ei* byly již dříve diskutovány například v cit.[18,4].

## Závěry

Získané výsledky potvrdily, že použití hodnot potenciálů *Ei,* získaných popsaným postupem vyhodnocení opakovaných měření, umožňuje aplikaci AgSAE při obnovování jejího povrchu otřením o polyethylenovou podložku před každou sérií měření, s následným opakovaným oplachováním jejího povrchu čistou vodou po měření v každém vzorku. Současně bylo potvrzeno, že za těchto podmínek a při využití AgSAE průměrů *d* > 1 mm vykazovaly změřené *Ei* vs. Vzi charakteristický průběh, málo závislý na hodnotách *d*. Uvedené výsledky obohatily výše zmíněné nedávno publikované poznatky v diskutovaném směru.

## *Poděkování*

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## Literatura

1. Pitter P.: *Hydrochemie.* VŠCHT, Praha 1999.
2. Scholz F.: Electroanalytical Methods, Springer-Verlag, Berlin 2002.
3. Moretto L. M., Kalcher K.: Environmental Analysis by Electrochemical Sensors and Biosensors, Springer Science+Business Media New York, New York 2014.
4. Novotný L.: Úřad průmyslového vlastnictví Praha, UV 2014-30527 (2014).
5. Novotný L.: Úřad průmyslového vlastnictví Praha, PV 2006-600 (2006).
6. Novotný L.: Úřad průmyslového vlastnictví Praha, UV 2007-19501 (2007).
7. Novotný L.: Úřad průmyslového vlastnictví Praha, PV 2001-1 (2001).
8. Novotný L.: *DrSc. Disertační práce*. AV ČR, Praha 1998.
9. Novotný L., Yosypchuk B: Chem. Listy *94*, 1118 (2000).
10. Yosypchuk B., Novotný L.: Crit. Rev. Anal. Chem. *32*, 141 (2002).
11. Barek J., Fischer, Navrátil T., Pecková K., Yosypchuk B., Zima J.: Electroanalysis *19*, 2003 (2007).
12. Yosypchuk B., Barek J.: Crit. Rev. Anal. Chem. *39*, 189 (2009).
13. Danhel A., Yosypchuk B., Vyskočil V., Zima J., Barek J.: J. Electroanal. Chem. *656*, 218 (2011).
14. Novotný L.: *XXIX. Moderní elektrochemické metody, Jetřichovice, 25. 5. – 29. 5. 2009,* Sborník přednášek (Barek J., Navrátil J., eds.), str. 82.
15. Šelešovská R.: *Habilitační práce*. Univerzita Pardubice, Pardubice 2015.
16. Novotný L., Petráňková R.: Anal Lett *49*, 161 (2016).
17. Novotný L., Kočanová V., Kabutey A., Karásková A., Dušek L., Petráňková R., Mikulášek R.: WASTE FORUM *2*, 117 (2018).
18. Novotný L., Kabutey A., Petráňková R., Langášek P.: WASTE FORUM *2*, 209 (2018).
19. Novotný L.: Electroanalysis, *12*, 1240 (2000).

# Influence of selected conditions on repeatability of potential response of the silver amalgam electrode in industrial waters

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## *Summary*

*The use of the described evaluation of potentiometric measurements using silver solid amalgam electrodes (AgSAE) enabled to apply these electrodes even with lesser requirements on mechanical renewing of its surfaces. Dependences Ei vs. Vzi based on quasi-steady values of electrochemical potentials Ei of AgSAE in the set of aqueous samples (containing added $1 \cdot 10^{-2}$M $AgNO_3$) Vzi, i = 1 to 5 and corresponding to the purification steps of the technical waters were registered. Repeatability of diagrams Ei vs. Vzi concerning AgSAE of diameters more than 1 mm was better than that of lower diameters. Certain influence of the tested sequences of aqueous solutions on the profile of Ei vs. Vzi has been observed, as well.*

***Keywords**: potentiometry, silver amalgam electrode, water treatment, ion-exchange*

# Estimation of Emissions in the Wastewater Treatment Plant Operation

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## *Abstract*

*Municipal wastewater treatment plants serve to minimize the negative environmental impacts of discharged water. Processes and products of wastewater treatment may adversely affect the environment. The purpose of the submitted case study is to determine the emissions ($CH_4$, $N_2O$) generated in the ordinary operation of WWTP. In the calculation of individual emissions, we proceeded according to several authors. In the first part, the direct and indirect emissions of the produced methane determined during the operation of the WWTP. Furthermore, the potential volume of $N_2O$ was calculated using emission factors. The last part of the case study aimed at determining the potential quantity of greenhouse gases generated by the final sludge disposal. In that case, the final sludge disposal is composting. The assessment of the WWTP operation based on the calculation of emission dependencies. These based on defined relation with the addition of emission factor values occurring in each relation according to literature retrieval.*

***Keywords:** emissions, wastewater treatment, greenhouse gas, emission factors.*

## Introduction

Municipal wastewater treatment plants (MWWTPs) serve to minimize the negative environmental impacts of discharged water. Processes and end products of wastewater treatment may adversely affect the environment. The implementation of the Water Framework Directive and Directive 91/271/ECC concerning Urban WasteWater Treatment increases the volume of sewage sludge produced on a pan-European scale [1, 2]. Based on Hospodito et al. and Yoshida et al. studies in the wastewater treatment and processes in the sludge management, several environmental pollutants generated (e.g. greenhouse gases) [3, 4]. Therefore, the optimization of processes in the sludge management is among the priorities of research tasks. A significant impact on the environment also has a way of disposing of sewage sludge. The most common methods of disposing of sludge in Slovakia include incineration, composting, and landfilling. All methods of sludge disposal have a different negative impact on the environment.

Diversion and purification of wastewater represent an environmental load in the form of greenhouse gases. Direct emissions from WWTPs during sewage treatment as well as sludge treatment and disposal are methane ($CH_4$) and nitrous oxide ($N_2O$). Indirect greenhouse gas emissions formed by electricity, the burning of fossil fuels during transport, the use of chemicals, and the use of sludge. The emissions produced on the model WWTP split according to the following Table 1.

It can conclude that the highest volume of $CH_4$ emissions arises in the treatment and storage of sludge, and these also flow in the receiving water. $N_2O$ emissions predominantly generated during the sewage treatment by activated sludge, and we can also monitor their occurrence at the outflow from the WWTP.

***Table 1: Distribution of emissions from model WWTP*** [5, 6]

| **Direct emissions** | **Indirect emissions** |
|---|---|
| • wastewater discharge,<br>• WWTP operation,<br>• discharge of treated waste water into the receiving water body. | • electricity supply,<br>• transportation,<br>• application of chemicals,<br>• sludge disposal. |

The content of pollutants in incoming wastewater, wastewater treatment, electricity generation, and sludge treatment are processed using emission factors typical of the Central European region.

The purpose of the submitted case study is to determine the volume of emissions ($CH_4$, $N_2O$, and greenhouse gases) generated in the ordinary operation of WWTP. In the calculation of individual emissions, we proceeded according to several authors. In the first part, the direct and indirect emissions of the produced methane determined during the operation of the WWTP. Furthermore, the potential volume of $N_2O$ was calculated using emission factors. The last part of the case study aimed at determining the potential quantity of greenhouse gases generated by the final sludge disposal. In that case, the final sludge disposal is composting. The assessment of the WWTP operation based on the calculation of emission dependencies. These based on defined relation with the addition of emission factor values occurring in each relation according to literature retrieval.

## Material and methods

### Description of the model wastewater treatment plant

The calculation of direct and indirect emissions performed for a MWWTP which parameters correspond to the parameters of MWWTPs with a treatment capacity for an equivalent population of 25 000 inhabitants in Slovakia.

The WWTP under study is a mechanically-biological treatment plant with anaerobic sludge stabilization and with gas management. This MWWTP was designed for a population equivalent (PE) of 50 000 inhabitants, but currently, it works just about half capacity (22 300 inhabitants). The sludge management consists of a sludge pumping station, thickening tank, digestion tank, storage tanks, sludge fields.

The water company performed the long-term field measurements, and they provided information about the influent wastewater flow rate, effluent flow rate, and pollutant load. Specification of the influent and effluent pollutant load summarized in Table 2 and Table 3. The following processes did not include in the estimation of direct and indirect emissions:

- Greenhouse gas emissions from the sewage system [7],
- Greenhouse gas emissions produced during the construction/reconstruction of WWTPs [6],
- Greenhouse gas emissions produced during long-term sludge storage [6,8].

***Table 2: Average annual pollutant load of the influent wastewater***

| **Influent** | **2012** | **2013** | **2014** | **2015** | **2016** | **Average 2012-2016** | **Content in g/PE/day** |
|---|---|---|---|---|---|---|---|
| BOD5 [kg/d] | 1827 | 1726 | 1862 | 2219 | 5537 | 1862 | 31033.3 |
| COD [kg/d] | 5143 | 4459 | 4690 | 5432 | 21910 | 5142 | 85715 |
| Ptotal [kg/d] | 75.6 | 65.8 | 82.6 | 91 | 421.4 | 82.6 | 1376.7 |
| Ntotal [kg/d] | 382 | 324.1 | 377.3 | 413.7 | 287 | 377.3 | 6288.3 |

***Table 3: Average annual pollutant load of the wastewater outflow***

| Discharge | 2012 | 2013 | 2014 | 2015 | 2016 | Average 2012-2016 | Content in g/PE/day |
|---|---|---|---|---|---|---|---|
| $BOD_5$ [kg/d] | 7.7 | 9.1 | 14 | 11.9 | 12.6 | 11.9 | 198.3 |
| COD [kg/d] | 133 | 155.4 | 161.7 | 146.3 | 168.7 | 155.4 | 2590 |
| $P_{total}$ [kg/d] | 9.8 | 6.3 | 9.1 | 1.89 | 1.33 | 6.3 | 105 |
| $N_{total}$ [kg/d] | 85.4 | 34.3 | 20.3 | 36.19 | 51.3 | 36.19 | 603.16 |

## Estimation of methane production from WWTP

Wastewater and the sludge components can produce $CH_4$ mainly in anaerobic processes. The production of methane emissions depends on the volume of degradable organic material in the wastewater, the temperature and the type of treatment [9]. Methane production can be quantified based on the following relation. This relation was defined in WSAA 2007 [10]:

$$CH_{4\ production} = (BOD_{5\ influent\ WW} - BOD_{5\ WW\ outflow}) * EF \qquad (1)$$

$$CH_{4\ in\ receiving\ water\ body} = BOD_{5\ WW\ outflow} * EF \qquad (2)$$

where $BOD_{5\ influent\ WW}$ - $BOD_5$ in influent wastewater [kg/d]
$BOD_{5\ WW}$ outflow - $BOD_5$ in wastewater outflow [kg/d]
EF – the used emission factor.

The emission factor used in the calculation can be divided into several groups as shown in Table 4.

***Table 4: Emission factors used to determine GWP related to methane emissions***

| Direct emissions from WWT | |
|---|---|
| Direct methane emissions | 0.0025 $CH_4$/kg $BOD_5$ [11] |
| $CH_4$ emissions in receiving water body | max. 0.025 kg $CH_4/BOD_5$ in discharge [12] |
| Methane emissions from combustion | 0.003 kg $CH_4$/kg burned $CH_4$ [13] |

## Calculation of nitrous oxide production from WWTP

Nitrous oxide production is related to the degradation of nitrogenous components in wastewater in the nitrification and denitrification process. $N_2O$ emissions occur in both processes, more frequently and in larger quantities during the denitrification process [9]. The production of nitrous oxide emissions can be quantified based on the following relation:

$$N_2O\ emissions = N_{influent\ WW} * EF_{WW\ discharge} * 44/28 \qquad (3)$$

where $N_{influent\ WW}$ – total nitrogen in incoming wastewater [kg $N_{tot}$/year],
$EF_{WW\ discharge}$ – emission factor for $N_2O$ emission from wastewater [kg $N_2O$ – N/kg N]
*44/28 - correction of molecular weight $N_2O$/ molecular weight N.

The emission factor is expressed based on emission constants in Table 5:

***Table 5: Emission factors used to determine GWP related to methane emissions***

| **Direct emissions from WWT** | |
|---|---|
| Nitrogen oxides emissions from sludge | 0.05 kg $N_2O$/kg $NH_4$ [14] |
| Emissions of nitrogen oxides direct | 0.0157 kg $N_2O$/kg $N_{denitrif.}$ [15] |
| $N_2O$ emissions in receiving water | 0.0005 kg $N_2O$/kg N in inflow [15] |

### Calculation of greenhouse gas emissions production from sludge composting

Sewage sludge treatment and disposal are one of the most significant aspects of wastewater purification in terms of emissions formation. Sludge represents 1 to 2% of the volume of purified water in which 50 to 80% of the original pollution concentrated [16]. Currently, two main directions of end-use and sludge disposal observed in the form of sludge utilization in agriculture and various methods of thermal treatment. Calculating greenhouse gas emissions from sludge composting is defined by the relation:

$$E_i = M * EF_i \qquad (4)$$

where $E_i$ – $CH_4$ or $N_2O$ emissions from composting [kg $CH_4$ or $N_2O$],
M – the volume of composted organic matter [kg],
$EF_i$ – emission factor valid for composting,
i - set values $CH_4$ or $N_2O$.

The emission factors used in the calculation were defined based on the Intergovernmental Panel on Climate Change (IPCC) documented in Table 6.

***Table 6: Emission factors used to determine GWP related to the production of sludge composting emissions***

| **Direct emissions from composting** | |
|---|---|
| Nitrogen oxides emissions from sludge | 0.3 g $N_2O$ /1 kg sludge dry residue [17] |
| Methane emissions from sludge | 4 g $CH_4$ /1 kg sludge dry residue [17] |

## Results

### Methane production from WWTP

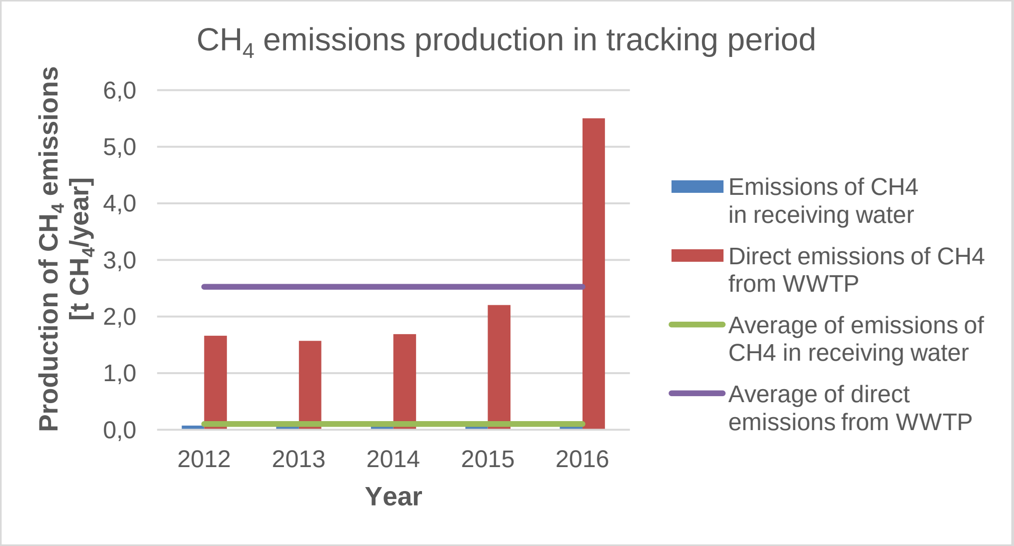
Based on a defined relationship (1,2) for methane emissions, we obtain $CH_4$ values in t $CH_4$ for individual years of the tracking period produced as direct emissions from WWTPs and gas emissions in the receiving water body. In calculating $CH_4$ emissions in the receiving water body, the above relationship (2) with EF was valid for methane emissions in the receiving water (0.025 kg $CH_4$ / $BOD_5$ in wastewater discharge). The calculation of direct emissions was made in with accordance EF for methane emissions (1), namely 0.0025 $CH_4$ / kg COD (Table 7).

***Table 7: Emissions $CH_4$ of for the tracking period***

| **Year** | **Emissions of $CH_4$ in receiving water [t $CH_4$/year]** | **Direct emissions of $CH_4$ from WWTP [t $CH_4$/year]** |
|---|---|---|
| **2012** | 0.070 | 1.66 |
| **2013** | 0.083 | 1.57 |
| **2014** | 0.128 | 1.69 |
| **2015** | 0.109 | 2.02 |
| **2016** | 0.115 | 5.05 |

The highest annual production of $CH_4$ emissions in the receiving water was recorded in 2014 when they represented 0.128 t $CH_4$ per year, which we expect was caused by the high share of $BOD_5$ at the inlet to the WWTP (Graph 1). The average emission production in the receiving water during the tracking period was 0.101 t $CH_4$ per year.

Direct methane emissions from WWTPs were lower than the methane emissions in the receiving water. The average emissions produced during the monitored period were 2.43 t $CH_4$ per year. As in the previous case, the resulting average value was significantly affected by 2016, when methane emissions rose to 5.05 t $CH_4$ per year, which is almost four times higher than in previous years. Between 2012 and 2015, methane emissions moved steadily; from 1.57 to 2.02 t $CH_4$ per year.



***Graph 1: $CH_4$ emissions production in tracking period***

## Nitrous oxide production from WWTP

Based on the relation (3) applicable to the calculation of nitrous oxide emissions, we receive the values of the receiving water and direct emissions over the tracking period in t $N_2O$ per year (Table 8).

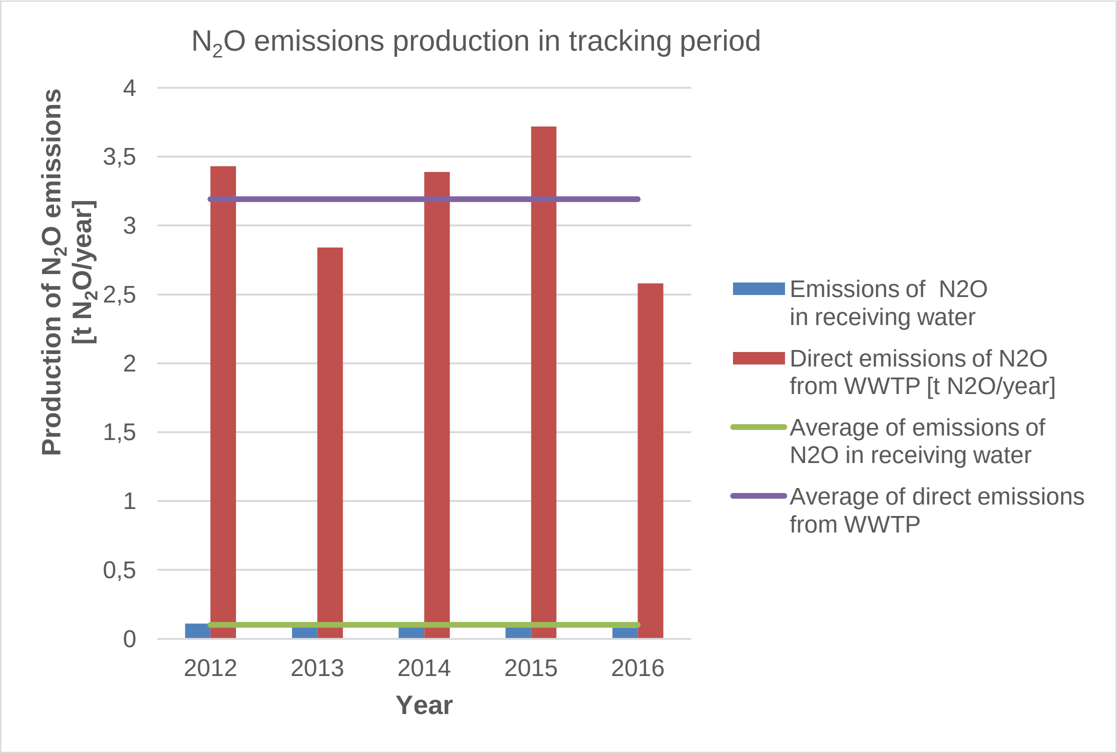
The emission factors used to calculate the quantity of nitrous oxide emissions have been mentioned in Table 5 above in relation to the available literature. Furthermore, the calculated emissions were converted to nitrous oxide emissions in t $N_2O$ per year by conversion equivalents.

***Table 8: Emissions of $N_2O$ for the tracking period***

| **Year** | **Emissions of $N_2O$ in receiving water [t $N_2O$/year]** | **Direct emissions of $N_2O$ from WWTP [t $N_2O$/year]** |
|---|---|---|
| **2012** | 0.11 | 3.43 |
| **2013** | 0.09 | 2.84 |
| **2014** | 0.11 | 3.39 |
| **2015** | 0.12 | 3.72 |
| **2016** | 0.08 | 2.58 |

Direct $N_2O$ emissions from wastewater treatment plants were higher than $N_2O$ emissions in the receiving water with minimal deviations in individual years.

From Graph 2 can be seen that the lowest direct $N_2O$ emissions record in 2016 (2.58 t $N_2O$ / year), the highest in 2015 (3.72 t $N_2O$ / year). The average value of $N_2O$ during the tracking period was 3.19 t $N_2O$ per year. The $N_2O$ emissions in the receiving water varied from 0.08 to 0.12 t $N_2O$ per year. The average value was 0.10 t $N_2O$ per year.



***Graph 2: $N_2O$ emissions production in tracking period***

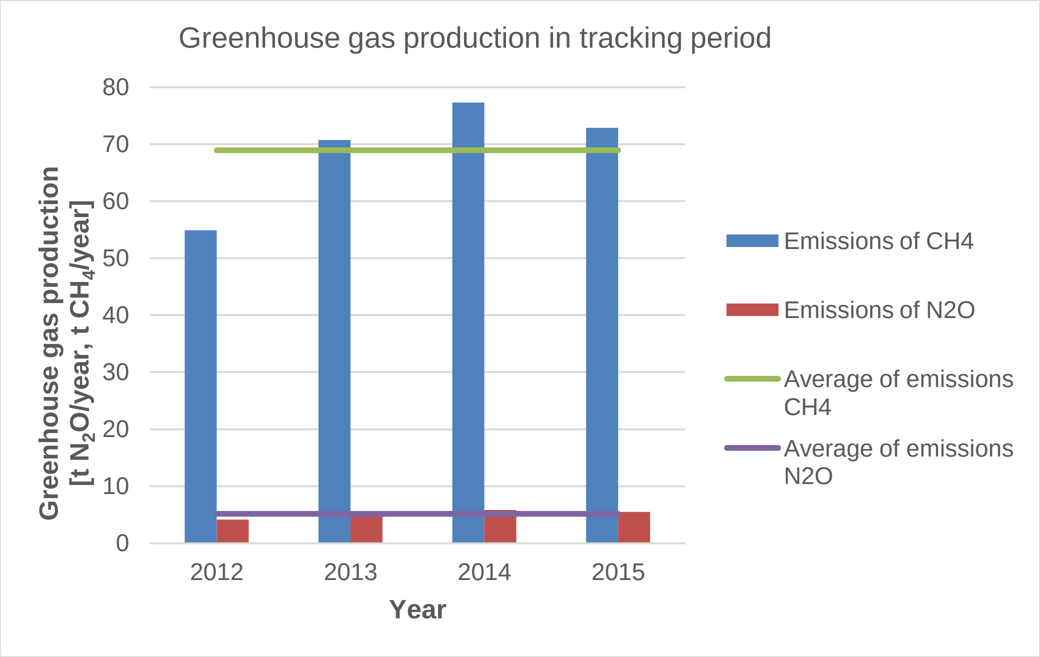
## Greenhouse gas emissions production from sludge composting

The calculation of greenhouse gas emissions based on the above relationship (4) in two variants, for $CH_4$ emissions and $N_2O$ emissions using defined emission factors based on GWP constants (Table 6).

***Table 9: Emissions of $N_2O$ for the tracking period***

| Year | Emissions of $CH_4$ [kg $CH_4$/year] | Emissions of $N_2O$ [kg $N_2O$/year] |
|---|---|---|
| **2013** | 54.90 | 4.12 |
| **2014** | 70.72 | 5.30 |
| **2015** | 77.32 | 5.80 |
| **2016** | 72.90 | 5.47 |

Two types of chief emissions arise in the context of sludge management and sludge composting; methane emissions and nitrous oxide emissions. Graphical representation (Graph 3) shows several times the higher share of methane emissions with an average value of 68.9 t $CH_4$ per year. The average value of nitrous oxide emissions in the reporting period was 5.17 t $N_2O$.



***Graph 3: Greenhouse gas emissions production in tracking period***

## Discussion

A research team at the Vienna Technical University deal with the issue of quantifying emissions from WWTP operations. Greenhouse Gas Emissions from WWTPs describes the process of calculating direct and indirect emissions by calculating the carbon footprint. Their estimations based on emission factors. They evaluated two different types of WWTP models: aerobic sludge stabilization model, and sludge anaerobic stabilization. Unlike this contribution, the volume of emissions expressed in $kgCO_{2e}$ [6].

Zeng, Chen, Dong, and Liu also deal with the number of greenhouse gases produced in the article: Efficiency assessment of urban wastewater treatment plants in China: Considering greenhouse gas emission [18].

Long-term research in this area also discussed by a group from the University of Delft in Denmark, who followed a dynamic change in methane emissions depending on the amount of wastewater flowing [19].

## Conclusions

The values of calculated emissions grew in proportion to increasing concentrations of monitored parameters at the inlet to WWTP. Emissions analysis showed a higher incidence of direct emissions of $CH_4$ compared to emissions in the receiving water body. Conversely, when quantifying $N_2O$ emissions, direct emissions were higher than those in the receiving water body. The sludge composting analysis showed that a relatively high amount of methane emissions to an environment with an average value of 68.9 t $CH_4$ per year produced in the storage of sludge on deposit. The average value of nitrous oxide emissions in the reporting period was 5.17 t $N_2O$. The analysis suggests that the composting is not a convenient way to dispose of sludge with respect to the environment.

## *Acknowledgment*

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## References

1. Regulation of the Slovak Government 269/2010 defining the requirements for achieving good status of waters, (in Slovak), 2010.
2. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment.
3. Hospido, A., Carballa, M., Moreira, M., Omil, F., Lema, J.M., Feijoo, G., 2010. Environmental assessment of anaerobically digested sludge reuse in agriculture: potential impacts of emerging micropollutants. *Water Res*. 44 (2010) 3225 – 3233.
4. Yoshida, H., Christensen, T.H., Guildal, T., Scheutz, C. A comprehensive substance flow analysis of a municipal wastewater and sludge treatment plant. *Chemosphere* 138 (2015), 874 – 882.
5. Genzowsky, K., Bolle F. W., $CO_2$ – Bilanzen und die Bedeutung für die WasserWirtschaft. *Wasser & Abfall* 6 (2014) 15 – 19.
6. Parravicini, V., Svardal, K., Krampe, J. Greenhouse Gas Emissions from Wastewater Treatment plants. *Energy Procedia* 97 (2016), 246 – 253.
7. Short, M.D., Daikeler, A., Peters, G.M., Mann, K., Ashbolt N.j., Stuetz, R.M., Peirson W.L., Municipal gravity sewers: an unrecognized source of nitrous oxide. *Sci Total Environ*. (2014) 468 – 469.
8. Lederer, J., Rechberger, H. Comparative goal – oriented assessment of conventional and alternative sewage sludge treatment options. *Waste management* 30 (2010), 1043 – 1056.
9. Forster, P., V., Ramaswamy, P., Artaxo, T., Berntsen, R., Betts, D.W., Fahey, J., Haywood, J., Lean, D.C., Lowe, G., Myhre, J., Nganga, R., Prinn, G., Raga, M., Schulz and R. Van Dorland, Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA
10. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.
11. Gustavsson D.J., Tumlin S., „Carbon footprints of Scandinavian wastewater treatment plants,“ *Water Science and Technology* 68 (2013) 887 – 889.

12. IPCC (2006a). Wastewater treatment and discharge. In: Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T. och Tanabe, K. (Eds.). 2006 IPCC Guidelines for National Greenhouse Gas Inventories, vol. 5, Waste. IGES, Japan (Chapter 6).
13. Brown, S., Beecher, N. och Carpenter, A., „Calculator tool for determining greenhouse gas emissions for biosolids processing and end use," *Environmental Science & Technology* vol. 44(24), (2010) 9509 – 9515.
14. Björlenius, B., „Lustgasutsläpp från kommunala reningsverk – Mätningar vid tolv svenska anläggningar. Utgiven i samarbete med NUTEK och Svenska Vatten- och Avloppsverksföreningen.," Skarvprojektet Rapport 4309. , 1944
15. Foley, J., de Haas D., Hartley, K. och Lant, P., „Comprehensive life cycle inventories of alternative wastewater treatment systems," *Water Research*, vol.44(5), pp. 1654 – 1666, 2010.
16. Gupta, D., Singh, S. K., „Greenhouse Gas Emissions from Wastewater Treatment Plants: A case Study of Noida," Journal of Water Sustainability 2 (2012), 131 – 139.
17. IPCC (2006b). N2O emissions from managed soils, and CO2 emissions from lime and urea application. In: Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.).2006 IPCC Guidelines for National Greenhouse Gas Inventories, vol. 5, Waste. IGES, Japan (Chapter 11).
18. Zeng, S., Chen, X., Dong, X., Liu, Y. Efficiency assessment of urban wastewater treatment plants in China: Considering greenhouse gas emission. Resources, *Conservation and Recycling* 120 (2017), 157 – 165.
19. Daelman, M.R.J., Van Voorthuizen, E.M., Van Dongen, U.G.J.M., Volcke, E. I.P., van Loosdrecht, M. C.M. Methane emission during municipal wastewater treatment. *Water Research* 46 (2012), 3657 – 3670.

## Vyčíslenie množstva emisií pri prevádzke čistiarne odpadových vôd

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### *Souhrn*

*Komunálne čistiarne odpadových vôd slúžia na minimalizáciu negatívnych dopadov vypúšťaných odpadových vôd na životné prostredie. Procesy a produkty čistenia odpadových vôd môžu nepriaznivo ovplyvniť životné prostredie. Účelom predloženej prípadovej štúdie je určiť potenciálne množstvo emisií ($CH_4$, $N_2O$), ktoré vznikajú pri bežnej prevádzke ČOV. Pri výpočte jednotlivých emisií sme postupovali podľa viacerých autorov. V prvej časti je množstvo priamych a nepriamych emisií vzniknutého metánu určené počas prevádzky ČOV. Následne sa potenciálne množstvo $N_2O$ vypočítalo pomocou emisných faktorov. Posledná časť prípadovej štúdie bola zameraná na stanovenie potenciálneho množstva skleníkových plynov vznikajúcich pri konečnej likvidácii kalov. V prípade modelovej čistiarne je konečnou likvidáciou kalu kompostovanie. Posúdenie prevádzky ČOV bola založená na výpočte podľa emisných faktorov.*

***Klíčová slova:*** *emisie, čistenie odpadovej vody, skleníkové plyny, emisné factory*

# Toxicity of the waste water from wildland fires suppression

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## *Abstract*

*The issue of contamination of environment caused by extinguishing water from wildland fires suppression is discussed in the paper. The wildland fire was simulated in the laboratory conditions. The cellulosic materials such as wood, straw and mixture of both were used. The samples were ignited and in the third stage of fire (full developed fire) extinguished with the hydrant water. The samples of extinguishing water were collected and tested using biological toxicity tests: the acute toxicity test on Daphnia magna, the test of the growth inhibition of the root of Sinapis alba, and the test of inhibition of the growth rate of Lemna minor L. The obtained results show, that the water from wildland fires extinguishing, which leaks after fire suppression into environment, has toxic effects on surface and subsurface waters. In the acute toxicity test all tested samples of extinguishing water were positive and caused immobilisation of tested organisms Daphnia magna. In the test of the root growth inhibition of Sinapis alba occurred root growth stimulation in the case of straw and mixed samples. In the test of the growth rate inhibition of Lemna minor L. all samples were positive, and necrosis and chlorosis were observed.*

***Key words:** wildland fires, fire suppression, water, ecotoxicity tests, Daphnia magna, Sinapis alba, Lemna minor*

## Introduction

In the context of global climate change, the issue of wildland fires is becoming higher importance. Due to extreme dry and hot periods, the number of wildland fires is increasing. Wildland fires are mainly encountered in countries around the Mediterranean (Spain, Portugal, Greece), selected areas of the US, Canada and Australia. But Slovakia is not exception. Depending on the region, the incidence of wildland fires ranges from 30 to 50% of all fires[1,2,3,4].

Wildland fires have a big impact on the environment, human life, and property. Not always negative. In some areas of North America, forest fires are a significant factor in the generating and functioning of some ecosystems. However, nowadays, in the anthropically influenced landscape the negative consequences of wildland fires are most evident[2,5,6].

Not only the fire devastates ecosystems, the fire suppression plays significant role too. Very important is selection of extinguishing agents and tactics of fire suppression[2,7]. Typically, is for extinction of wildland fires using of water, water with additives (mostly organic fluorine chemicals), progressive extinguishing substances (e.g. extinguishing gel Firesorb), exceptionally are used firefighting foams. Residues of used extinguishing agents remain in the fire place and leak into environment, mostly surface and subsurface water and soil (Figure 1)[2,9,10,11,12].

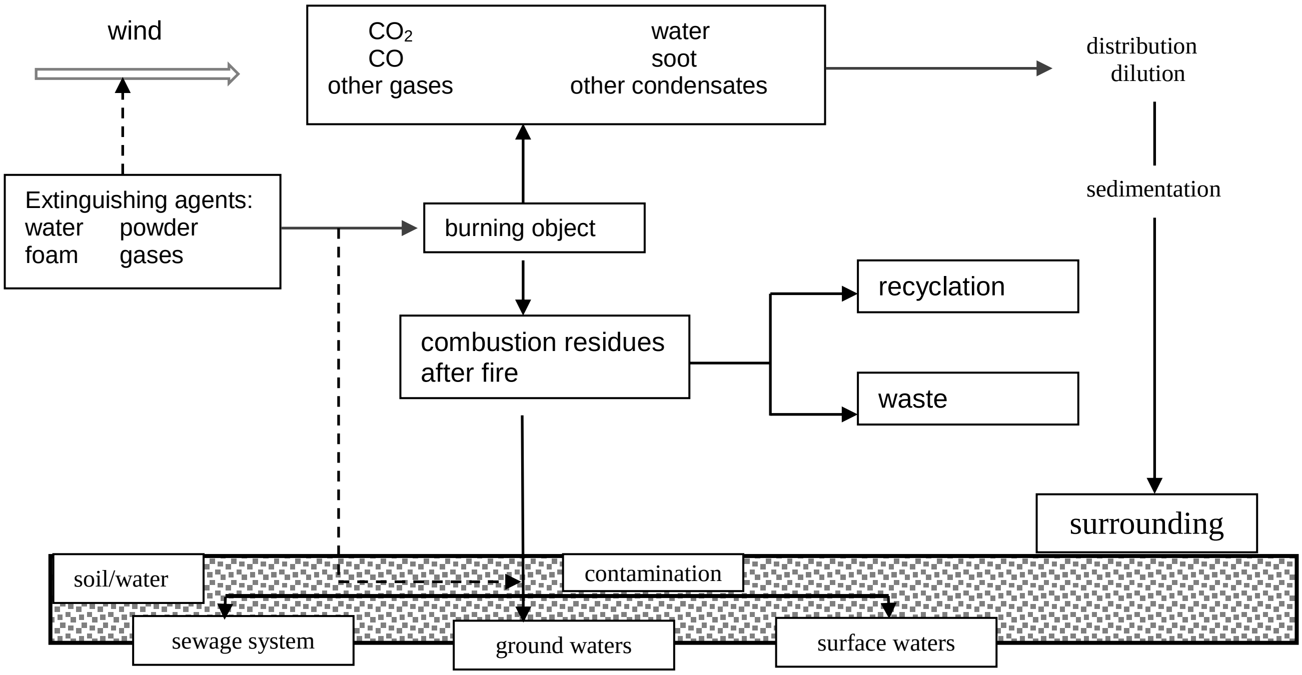

***Figure 1: Scheme of the soil and water contamination at the fire suppression[8]***

The environment contamination due to extinguishing agents is relatively new issue and is related mostly with the using of new progressive extinguishing agents (extinction gases, powders, firefighting foams) or additives to the water. The plain water is considered to be a safe extinguishing medium[8,9,12,13,14].

The commonly used extinguishing agent for wildland fire in Slovak republic is the plain water, in 2016 only about 2% of water used for wildland fire suppression in Prešov region was treated with fluoroalkyl additives[15].

The aim of the paper is to investigate the influence of the water after wildland fire extinguishing on the surface and subsurface waters using ecotoxicological tests with organisms *Daphnia magna*, *Sinapis alba* and *Lemna minor*.

## Experimental part

We used lignocellulosic material (wood and straw) to simulate wildland fire in laboratory conditions. We chose the wheat straw and spruce wood as representatives of lignocellulosic material in wildland fires. These materials were used separately and as a mixture of both. Samples were given into metal container with diameter 30 cm and 6 cm high and ignited. Samples were extinguished in the third stage of fire (full developed fire). The untreated hydrant water (drinking water quality) was used for extinguishing. The process is to see in the Figure 2.

After fire extinction the samples of water were taken into glass flasks. The solid fire residues were filtered from water.

### pH measurement

The pH value is one of the basic measured water quality indicators[16].

To measurement of pH value was used potentiometric method. The pH-meter WTW Level 3 with combined electrode and temperature compensation was used with three-point calibration.

***Figure 2: The process of sample preparing: sample of straw, simulated full developed fire, fire extinction (from the left to the right).***

## Ecotoxicological tests

Biological toxicity tests are used to assess the ecotoxicological properties of substances. Toxicity tests are used to determine the possible toxic effects of substances on the water and soil ecosystems, especially phytocenosis. They allow a rapid and enough recovery of wastes to assess the potential negative effects of these substances. The main aim of biotests is to determine the limit concentration at which the life of selected test organisms is possible[17].

## Acute toxicity test on *Daphnia magna*

Principle of the test is an assessment of percentage of immobilised individuals after 48 hours from the beginning of exposure of a tested sample to test organisms of *Daphnia magna*[18]. Conditions of the test, including control of meeting test conditions with a reference substance are shown in Table 1.

***Table 1: Preliminary test conditions for Daphnia magna*[16,19]**

| | |
|---|---|
| Test organism | *Daphnia magna* Straus (more than the third generation obtained by acyclic parthenogenesis under the conditions of healthy breeding), individuals younger than 24 hours since birth (no feeding) |
| Biotest conditions | 20°C ± 2°C; 7.8 ± 0.2; laboratory conditions |
| Control sample | Diluting water prepared from Table 2 |
| Reference substance | $K_2Cr_2O_7$, $EC_{50}$ = 1.02 mg.L$^{-1}$ (limit 0.3 – 1.5 mg L$^{-1}$) |
| Test duration | 48 hours |
| Preliminary test | 20 daphnia/undiluted sample (10 mL), same conditions for a control |
| Validity of the test | Immobilisation ≤ 10%, change of concentration of dissolved $O_2$ ≤ 2 mg L$^{-1}$ |
| Monitored response | % of immobilised individuals |

Results of preliminary test are:

- positive, if in the test occurred death or immobilization more than 50% daphnia compared with control sample, is necessary determine value of EC50 using orienting and basic test[16,20,20].

***Table 2: Stock solutions for reconstituted water[21]***

| Stock solution | Chemical substance | Concentration of stock solution [g $L^{-1}$] |
|---|---|---|
| 1 | $CaCl_2.2H_2O$, p.a. | 117.6 |
| 2 | $MgSO_4.7H_2O$, p.a. | 49.3 |
| 3 | $NaHCO_3$, p.a. | 25.9 |
| 4 | KCl, p.a. | 2.3 |

From stock solutions[21] (STN 83 8303:1999) a dose of 10 mL was added to a volumetric flask with a capacity of 1 litre and the solution was refilled with distilled (deionised) water up to the mark and used as a control. The pH of the diluent water should vary around 7.6 – 8.0.

## Test of the growth inhibition of the root of *Sinapis alba*

The test consists in the cultivation of seeds on pads soaked in solutions of the tested substance in comparison with seeds growing on a pad soaked in diluent water. Mustard is representative of cultural crops and higher plants in the toxicity tests. The test conditions are shown in Table 3.

***Table 3: Conditions of test of inhibition of growth of root of Sinapis alba[21]***

| | |
|---|---|
| Testing organism | *Sinapis alba,* germination > 90%, per 30 seeds of *Sinapis alba* L. in Petri dishes |
| Sample volume | 10 ml |
| Temperature | 20 °C ± 1 °C, thermostat TS 606 CZ/2-Var (WTW, Germany). |
| Control | Reconstituted water (Table 2) |
| Validity of the test | Germination in control sample = 99.6% (limit ≥ 90%) |
| Reference substance | $K_2Cr_2O_7$, $IC_{50}$, 72hours = 31.5 mg $L^{-1}$ (limit 4.1 – 85 mg $L^{-1}$) |
| Measuring root length | Steel calibrated measuring instrument |
| Exposure time | 72 hours |
| The response monitored | Inhibition/stimulation of growth of root of *Sinapis alba* compared with the control (IC), preliminary test |

Results of preliminary test are:

- negative, if the root growth inhibition is less than 30% or stimulation is less than 75% in comparison with the control sample. It will be recorded, and no further testing is performed.
- positive, if the root growth inhibition is more than 30% or stimulation is more than 75% in comparison with the control sample[21].

## Test of inhibition (stimulation) of the growth of *Lemna minor* L.

Test of phytotoxicity, based on inhibition (stimulation) of the growth of *Lemna minor* L. and quantification of toxic effects of the sample on its growth[16]. Conditions for the preliminary test are described in Table 4.

***Table 4: Conditions for the test of growth inhibition of common duckweed***[22]

| | |
|---|---|
| Test organism | *Lemna minor*; 12 –15 leaves at the beginning |
| Incubation temperature | 25°C ± 2°C – thermostatic cabinets ST FOT (Eko Pol Poland) with simulation of day and night; lighting continually, min. intensity of 6 500 lux |
| Control sample | Z-medium (was used as the nutrient solution and prepared in accordance with the instructions from its supplier - Culture Collection of Autotrophic Organisms - CCALA, Třeboň, the Czech Republic |
| Reference substance | 3,5-dichlorophenol, $EC_{50}$ = 2.80 mg $L^{-1}$ (limit 2.2 – 3.8 mg $L^{-1}$) |
| Exposure | 7 days |
| Preliminary test | 50 ml sample |
| Criterion of validity | average number of leaves in the control after the termination of the test > than octuple at the beginning of the test, pH at the end of the test < than 1.5 in comparison with initial pH |
| Biomass determination | whole plants of *Lemna minor*, including root, used for determination; biomass determined gravimetrically by drying into a constant weight at 105 °C (POL-EKO SL, Poland) |
| Monitored parameters | the number of leaves is counted, and the appearance of the leaves is evaluated (chlorosis, necrosis) at least three times during the test; growth inhibition (Iμ) in %; |

*Iμ - growth rate*

Results in graphs and tables are processed in the programme STATISTICA 12, ANOVA, one-factor analysis of variance (using 95% intervals of reliability for average values of individual samples).

# Results and discussion

## pH assessment

pH values were measured in the all water samples using pH-meter WTW Level 3. In the Table 5 there are shown the obtained values. All water samples were alkali and from the results point view we can say that the presence of wood in the combusted mixtures influenced increasing pH value.

If the soil is with extinguishing water contamined, it could possess increasing of soil alkalization. Such soils are poorly fertile, and only salt-loving plants grow on them[23].

**Table 5: Results of pH measurement of the water samples**

| | **Clean water** | **Extinguishing water** | | |
|---|---|---|---|---|
| | | **Wood** | **Straw** | **Wood + Straw** |
| pH | 7.99 | 9.01 | 8.84 | 9.34 |

## Ecotoxicological tests assessment

All the ecotoxicological tests were performed in accordance with STN and OECD standards The accuracy check was verified using reference solution $K_2Cr_2O_7$ in both of tests and the obtained values were within with defined limits.

## Acute toxicity test on *Daphnia magna*

The obtained results of acute aquatic toxicity test on *Daphnia magna* are shown in the Table 6 and in the Figure 3.

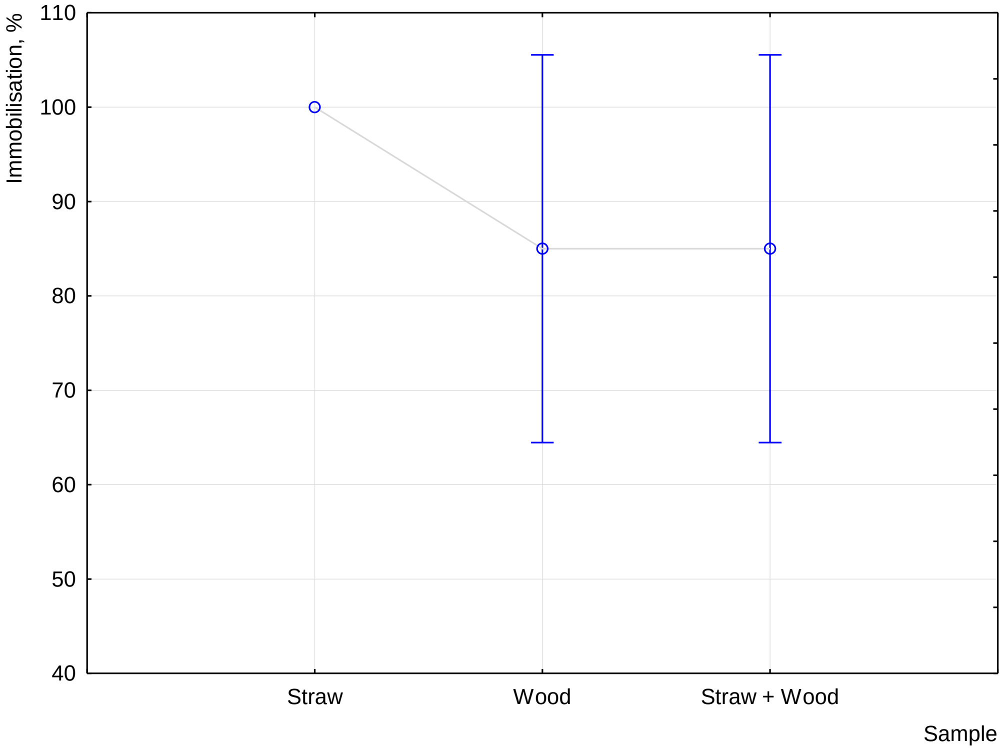

***Figure 3: Graphical statistics of immobilized Daphnia magna***

***Table 6: The basic statistical characteristics of immobilized Daphnia magna***

| **Sample** | **Immobilisation, %** | | | | **N** |
|---|---|---|---|---|---|
| | **Average** | **Standard Deviation** | **Minimum** | **Maximum** | |
| Straw | 100.00 | | | | 4 |
| Wood | 85.00 | 6.45 | 64.46 | 105.54 | 4 |
| Straw + Wood | 85.00 | 6.45 | 64.46 | 105.54 | 4 |

*N – number of repetitions*

All tested samples of extinguishing water were positive and caused immobilisation of tested organisms *Daphnia magna*. Immobilisation in control sample was less than 10%. This value corresponds with the test conditions in Table 1. Considering the values of the extinguishing water reaction we point out influence pH value on solubility of solid combustion residues in extinguishing water, what results in high immobilisation of *Daphnia magna*. At the end of test neither changes of pH values nor oxygen loss were recorded.

## Test of the growth inhibition of the root of *Sinapis alba*

By the terrestrial test of the growth inhibition of the root of *Sinapis alba* was observed impact of residual extinguishing water on the root's growth of vascular plants. The increments of white mustard roots were measured and obtained values were used for the calculation of the root growth inhibition in comparison with the control sample. Basic statistical characteristics are shown in the Table 7.

***Table 7: The basic statistical characteristics of the growth inhibition of the root of Sinapis alba***

| **Sample** | **Inhibition (IC), %** | | | | **N** |
|---|---|---|---|---|---|
| | **Average** | **Standard Deviation** | **Minimum** | **Maximum** | |
| Straw | -13.98 | 5.09 | -30.17 | 2.21 | 4 |
| Wood | 3.87 | 3.56 | -7.46 | 15.21 | 4 |
| Straw + Wood | -84.99 | 4.24 | -98.49 | -71.4 | 4 |

*N – number of repetitions*
*negative values – stimulation;*
*positive values – inhibition*

The results of this biotest show that the samples of waste water from extinguishing of straw and wood were negative. In the samples of waste water from extinguishing of mixture straw and wood is the strong stimulation to see, results were positive. Graphical are test results shown in the Figure 4. We assume that the dissolved solids in the extinguishing water acted as nutrients in the samples and promoted root growth compared to the control sample.

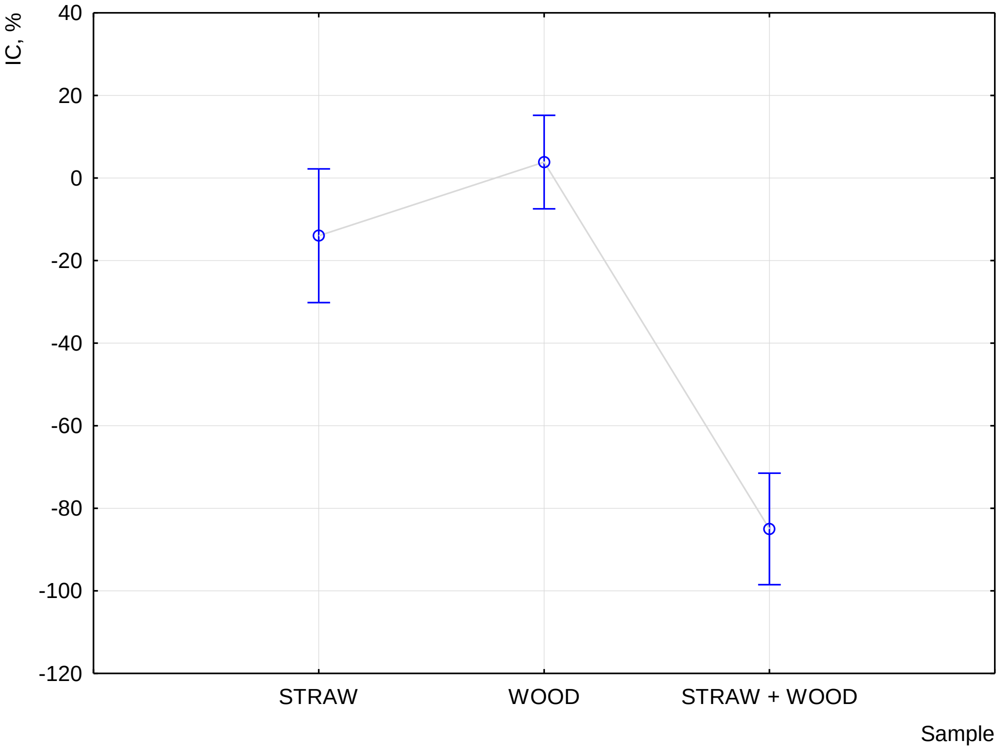

***Figure 4: Graphical statistics of the growth inhibition of the root Sinapis alba***

## Test of inhibition (stimulation) of the growth rate of *Lemna minor* L.

Test of growth of *Lemna minor* L., as a representative of freshwater vascular plants, allows simple studies of time dependence on toxicity of substances in the aquatic environment. *Lemna minor* L., together with other representatives of *Lemnaceae*, is an attractive test organism – not only due to its important ecological functions (source of food for birds and fish, stand for invertebrates), but also to its widespread occurrence[24].

The conditions for the aquatic test of growth rate inhibition of *Lemna minor* L. are in the Table 4. The required number of leaves at the end of the test was observed. Calculated growth rate inhibition (Iμ) is in the Figure 5 to see, and basic statistical characteristics are in Table 8 presented.

***Table 8: The basic statistical characteristics of the growth rate inhibition of Lemna minor* L.**

| **Sample** | **Inhibition of growth rate ($I_{\mu}$), %** | | | | **N** |
|---|---|---|---|---|---|
| | **Average** | **Standard Deviation** | **Minimum** | **Maximum** | |
| Straw | 68.90 | 1.90 | 60.72 | 77.08 | 4 |
| Wood | 45.57 | 2.08 | 36.64 | 54.50 | 4 |
| Straw + Wood | 50.17 | 0.45 | 48.24 | 52.09 | 4 |

*N – number of repetitions*

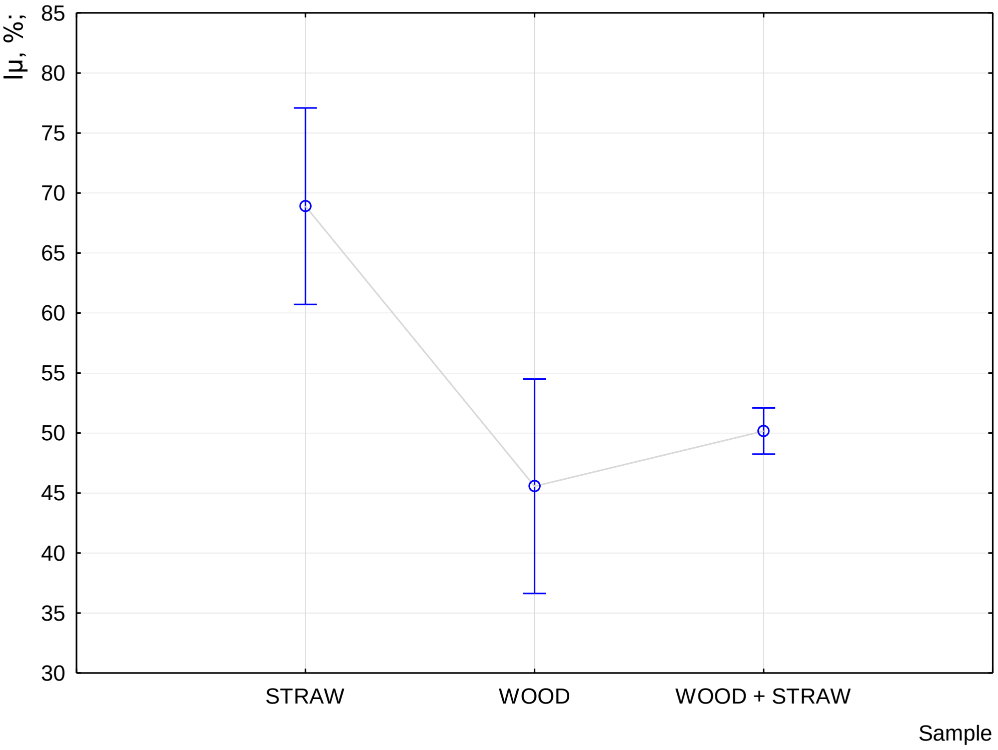

***Figure 5: Graphical statistics of the growth rate inhibition of Lemna minor L.***

STN EN ISO 20079[25] specifies, that the preliminary test is negative, if the growth rate inhibition is less than 30% in comparison to the control sample, and the test is positive, if growth rate inhibitions more than 30% in comparison with the control sample. According to this and the results in Table 8 can we ascertain, that all samples of extinguishing water were positive and are inhibiting on the growth of *Lemna minor* L. Visually were indicated necrosis and chlorosis during the test, too. We observed changes of chlorophyll loss from the fifth day in all water samples and leaf necrosis in the samples from straw extinguishing.

The samples of extinguishing water are inhibiting the growth of *Lemna minor* L. leafs although the same samples are stimulating onto root growth of *Sinapis alba*.

At the burning of wood, straw and its mixture, which are lignocellulosic materials, are formed gaseous, liquid and solid compounds. Content of volatiles is approx. 46%, ash content is usually 4 – 7% according to type of solid fuel (biomass), combustion conditions etc.[26, 27]. Part of combustion products is entrapped by extinguishing water and flow into surface or subsurface water and soil, and plants can use it as a natural fertilizer.

Dominant elements in the combustion products are carbon, hydrogen and oxygen, but also other macro- and microelements are present such as nitrogen, phosphorus, sulphur. Chemically, ash from biomass is mainly composed of a mixture of oxides $K_2O$, $Na_2O$, $CaO$, $MgO$, $Fe_2O_3$, $Al_2O_3$, $SiO_2$, $P_2O_5$[28,29].

Plants take up these salts in dissolved form through the root system. The results of the root growth inhibition test of *Sinapis alba* are in accordance (Figure 4). Lanzerstorfer[27] determined the high concentrations of potassium in the ash from straw combustion while in the ash from wood combustion the concentrations of Ca and Mg were higher. These elements are important for plants to build a healthy root system. The basic mark of the Ca and Mg deficiency is the acid reaction of soil. According the results of pH measurement of wood and straw extinguishing residual water (Table 5) we do not anticipate this deficiency and the root growth of *Sinapis alba* in the samples is proof, too.

Other part of biomass combustion products entrapped by extinguishing water represent volatile organic compounds such as benzene, toluene, xylenes, formaldehyde and polycyclic aromatic hydrocarbons[30]. We assume, that these organic compounds content, alkalinity and salinity of the extinguishing water could be more demonstrate in the test with *Lemna minor* (necrosis and chlorosis) in comparison with the nutrition effect in the test with *Sinapis alba*.

## Conclusions

There are results of toxicity testing of waste water from extinguishing wildland fires presented in the paper. For the simulation of wildland fires were used samples of lignocellulosic materials such as spruce wood, wheat straw and mixture of both.

Presented are results of the acute toxicity test on *Daphnia magna*, the *t*est of the growth inhibition of the root of *Sinapis alba,* and the test of inhibition of the growth rate of *Lemna minor* L. The obtained results show that the water from wildland fires extinguishing, which leaks after fire suppression into environment, can have toxic effects on surface and subsurface waters.

In the case of test of root growth inhibition of *Sinapis alba* the stimulating effect of the nutrients from the ash from lignocellulosic material combustion entrained by the extinguishing water was shown.

The only way to prevent contamination of environment caused by extinguishing water is to prevent the wildland fires.

## *Acknowledgement*

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## Literature

1. Majlingová A.: *Risk management of wildland fires (Manažment rizík požiarov v prírodnom prostredí)* (Majlingová A., Toman B. ed.), p. 18. Požiarnotechnický a expertízny ústav MV SR, Bratislava 2015.
2. Majlingová A.: Krízový manažment (Crisis Management) *2015*, 47.
3. Galla Š.: *Risk management of wildland fires (Manažment rizík požiarov v prírodnom prostredí)* (Majlingová A., Toman B. ed.), p. 6. Požiarnotechnický a expertízny ústav MV SR, Bratislava 2015.
4. MV SR https://www.minv.sk/?rozbory-a-statistiky-rok-2018 30. 06. 2019.
5. Simeoni A., in book: *SFPE Handbook of Fire Protection Engineering*, 5th edition (Hurley M. J. ed.), chapter 87, p. 3283. Springer, New York, US, 2016.
6. Collins B. M., Miller J. D., Thode A. E., Kelly M., van Wangtendonk J. W., Stephens S. L.: Ecosystems *12,* 114 (2009).
7. Monoši M., Kapusniak J.: Proceedings of International Conference Sustainability – Environment – Safety, December 3. 2012, Bratislava – Slovak Republic (Rusko P. ed.), p. 198, Bratislava 2012.
8. Mailair G., Simonson M., Gann R. G. https://www.nist.gov/publications/environmental-concerns-fires-facts-figures-questions-and-new-challenges-future 30. 05. 2019.

9. Rasbash D. J.: Fire Saf. Sci., Proc. Int. Symp. *1,* 1145 (1986).
10. Xiaomeng Z., Guangxuan L., Bo C.: Fire Saf. J. *41*, 39 (2006).
11. Štefanický B., Balog K.: *Risk management of wildland fires (Manažment rizík požiarov v prírodnom prostredí)* (Majlingová A., Toman B. ed.), p. 86. Požiarnotechnický a expertízny ústav MV SR, Bratislava 2015.
12. Särdqvist S., in book: *Water and other extinguishing agents* (Göransson A. L. ed.), chapter 2.13, p. 180. Swedish Rescue Services Agency, Karlstad, Sweden, 2002.
13. Mussabek D., Ahrens L., Persson K. M., Berndtsson R.: Chemosphere *227*, 624 (2019).
14. Dauchy X., Boiteux V., Colin A., Hémard J., Bach C., Rosin Ch., Munoz J. F.: Chemosphere *214*, 729 (2019).
15. https://www.minv.sk/?okresne-riaditelstva-hazz-v-presove 07. 05. 2017.
16. Hybská H., Samešová D.: *Ecotoxicology*. p. 78. Technical University in Zvolen, Zvolen, Slovakia, 2015.
17. Kijovská L.: *Ekotoxikológia vo vodnom hospodárstve Slovenska (Ecotoxicology in Water Management of Slovakia)*, p. 62. STU, Bratislava 2013.
18. Fargašová A.: *Ekotoxikologické biotesty (Ecotoxicological biotests)*, p. 75. Perspekt, Bratislava 2009.
19. OECD 202 I.: 2004: *Daphnia sp. Acute Immobilisation Test.*
20. STN EN ISO 6341: 2013. *Water quality. Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea). Acute toxicity test.*
21. STN 83 8303:1999. *Testing of dangerous properties of wastes. Ecotoxicity. Acute toxicity tests on aquatic organisms and growth inhibition tests of algae and higher cultivated plants*.
22. OECD 221: 2006. *Lemna sp. Growth Inhibition Test.*
23. Fiala P., Reininger D., Samek T., Němec P., Sušil A.: *Průzkum výživy lesa na území České republiky 1996-2011 (The Research of the Forest Nutrition in Czech Republic in 1996 – 2011), p. 43. Gill s. r. o., Brno 2013.*
24. Hybská H., Knapcová I., Fialová J., Veverková D.: Waste Forum *2018*, 190.
25. STN EN ISO 20079:2008-07. *Water quality. Determination of the toxic effect of water constituents and waste water on duckweed (Lemna minor). Duckweed growth inhibition test.*
26. Holubčik M., Jandačka J., Malcho M.: The Holistic Approach to Environment *5*, 119 (2014).
27. Lanzerstorfer Ch.: J. IES *30,* 191 (2015).
28. Werkelin j., Lindberg D., Boström D., Skrifvars B. J., Hupa M.: Biomass Bioenergy *35,* 725 (2011).
29. Vassilev S. V., Vassileva Ch. G., Song Y. C., Li W. Y., Feng J.: Fuel *208,* 377 (2017).
30. Reisen F., Bhujel M., Leonard J.: Fire Saf. J. *69*, 76 (2014).

# Stanovenie toxicity odpadovej vody z hasenia prírodných požiarov

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## Souhrn

*Článok sa zaoberá problematikou hodnotenia kontaminácie životného prostredia vplyvom vody z hasenia prírodných požiarov. V laboratórnych podmienkach bol simulovaný požiar prírodných materiálov s využitím slamy, dreva a ich zmesi ako paliva. Vo fáze plne rozvinutého požiaru bolo horenie ukončené hasením hydrantovou vodou. Boli odobraté vzorky hasiacej vody, ktoré boli testované biologickými testami toxicity: test akútnej toxicity na perloočke veľkej, test inhibície rastu koreňov horčice bielej, test inhibície rýchlosti rastu žaburinky menšej.*

*Získané výsledky ukazujú, že hasiaca voda, ktorá uniká do povrchových a podpovrchových vôd po hasení prírodných požiarov, má toxické účinky na životné prostredie. V teste akútnej toxicity boli všetky skúmané vzorky pozitívne a spôsobili imobilizáciu testovaných organizmov perloočky veľkej. V teste inhibície rastu koreňov horčice bielej preukázali vzorky z hasenia slamy a zmesná vzorka stimulačné účinky. V teste inhibície rýchlosti rastu žaburinky boli všetky sledované vzorky pozitívne, pričom vizuálne bola pozorovaná aj chloróza a nekróza testovaných organizmov.*

***Klíčová slova**: prírodné požiare, hasenie požiarov, voda, ekotoxikologické testy, Daphnia magna, Sinapis alba, Lemna minor*

# Environmental Properties of Wooden Shelter: A Comparison of Three Waste Management Scenarios

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## *Abstract*

*The main objective of this case study was to compare the environmental effectiveness of three different waste management scenarios for a selected construction – the wooden shelter. The effectiveness of the scenarios was evaluated in terms of environmental impacts based on Life Cycle Analysis, supported by SimaPro software. Each scenario included both often used technologies of waste management applied after the end of life of construction: (1) landfilling and (2) incineration. Differences among the scenarios consisted in the percentage distribution of single parts (wood and steel) of the wooden shelter. Various environmental impacts in mid-point categories (climate change, ozone depletion, human toxicity, etc.) and in end-point categories (human health, ecosystems and resources) were estimated by ReCiPe method. The waste management scenario with 30% landfilling and 70% incineration was identified to be the best in terms of the climate changes. The obtained analysis results differed in dependence on the used mid-point and end-point methodologies.*

***Keywords:*** *waste, LCA, environmental impacts, landfilling, incineration.*

## Introduction

Waste production rates are increasing worldwide. With rapid population growth and urbanization, annual waste production is expected to increase due to a continuous welfare improvement and changes in life style[1]. Waste management is a complex process and multidisciplinary problem which involves different processes and principles too. These include operations and technologies related to manufacturing, storage, operation, selection, transfer, freight, processing, and disposal of wastes[2]. The waste management should be considered from technical, economic and social aspects on a sustainability basis[3]. Different waste treatment options are available in the current time with different waste management capacities[4]. Integrated waste management system is commonly applied method in many developed countries. This integrated system offers the flexibility of waste treatment option based on different waste fraction e.g. construction waste, paper, plastic, glass, organic waste or combustible waste[5].

Life Cycle Assessment (LCA) is an internationally standardized methodology to access the environment, which is used to evaluate the environmental impact of a product or system within their whole life cycle including the end of life[6]. LCA consists of this four major steps: goal and scope definition, inventory analysis, impact assessment and interpretation[7]. The broad system perspective makes LCA a powerful tool for comparison of different options for waste management of a specific product, a material, or a complex waste flow[8]. LCA methodology can be widely used for simulation and modelling of various waste management scenarios to help find an optimal alternative of waste treatment for a particular construction.

The main objective of this paper is to evaluate the environmental impacts of construction waste treatment by using LCA SimaPro software based on life cycle methodology. In this study, two different waste management technologies at the end of life of a wooden shelter, landfilling and incineration, were analysed considering three LCA scenarios.

## Experimental part

### The analysed object

A real wood shelter, located in a private garden of family house in the village Valaliky near Kosice was selected to the examination. The wood shelter was made only of wood and some steel (for the nails and metal parts) materials. It was designed as just a very simply shelter, without doors, windows, heating or lighting.

### Waste management scenarios

Three different scenarios were under consideration. As mentioned above, all scenarios included both waste management options, landfilling and incineration. The scenarios differ from the percentage of the material treated in landfilling and incineration. The percentage distribution of the waste treated by the particular technology, based on the traditional approach in the Central European countries[9], is presented in Figure 1.

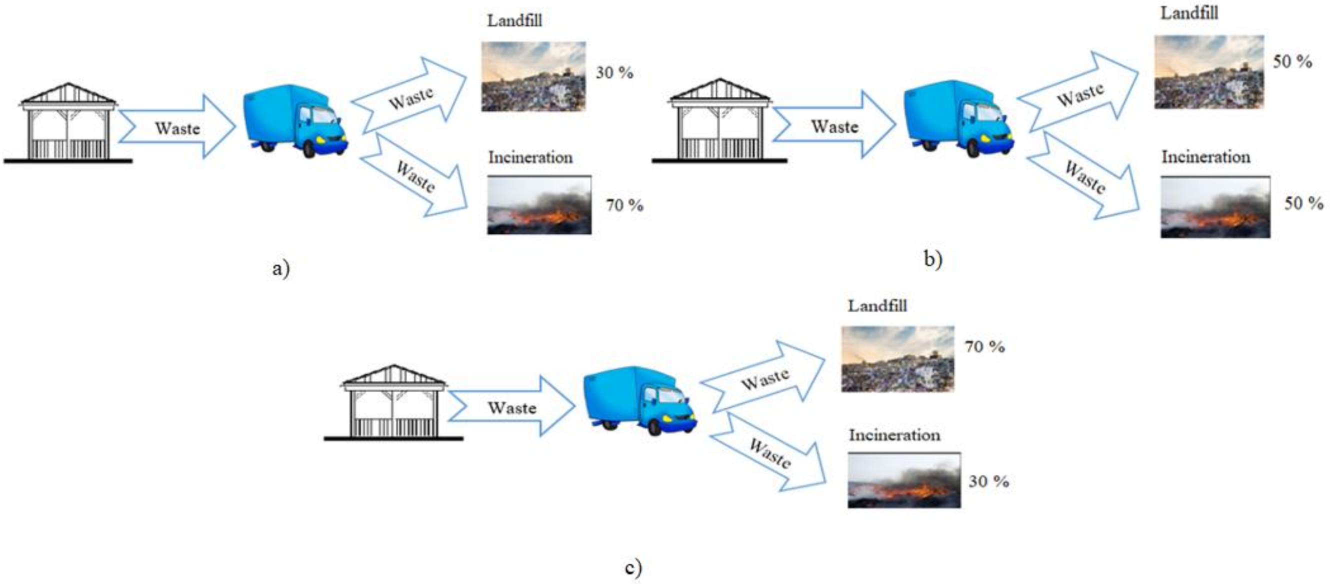

***Figure 1: Percentage distribution of the waste treated by landfilling and incineration: a) Scenario 1 (WS 1), b) Scenario 2 (WS 2), and Scenario 3 (WS 3)***

The first scenario (WS 1) was based on waste management as follows: 30% on landfill and 70% on incineration. In the second scenario (WS 2), the end-of-life of total waste of the wooden shelter was divided into equal parts, i.e. 50% landfilling and 50% incineration. The last scenarios (WS 3) as simulated in the same way as the first one, with percentages being exchanged by percentages of individual parts of waste management.

Landfill is the term to describe the physical facilities used for the disposal of solid wastes and solid waste residuals in the surface soils of the earth[10]. Landfilling is very old but still one of the extensively used technologies for waste management. Landfill has the option to collect landfill gas and to use as electricity production or biofuel. Landfill gas is generated directly from the landfill[11]. Landfill includes the dump infrastructure, the use of land and the effect of the landfilled waste. Construction wastes that are to be landfilled are special wastes disposed of in underground deposits or controlled landfills, inert wastes are disposed of in inert material landfills and non-special wastes are disposed of in landfills or sanitary landfills[12]. In this paper, parts of all the wastes are calculated to be disposed of in a landfill.

Raw waste can be used as a feed stock in the thermal incineration process[11]. In this scenario, incinerable wastes are disposed of at an incineration. This covers the plant infrastructure, the incineration process, the electricity generated and the disposal of ashes. Electrical energy recovery and the amount of residual ashes (which are disposed by landfill) are also considered[12].

## System boundaries

The study consisted of a from-cradle-to-grave LCA of a real case of wood including all the life cycle phases and end-of-life management with three different scenarios of waste management. The lifetime has been estimated at 30 years. Functional unit of the study has also been defined as amount of used wood and steel wastes in terms of kilograms. The amount of materials needed to build the shelter was determined on 1500 kg of wood and 450 kg of steel. Three distinct phases: pre-use, use and end-of-life were included in the LCA model as presented in Figure 2.

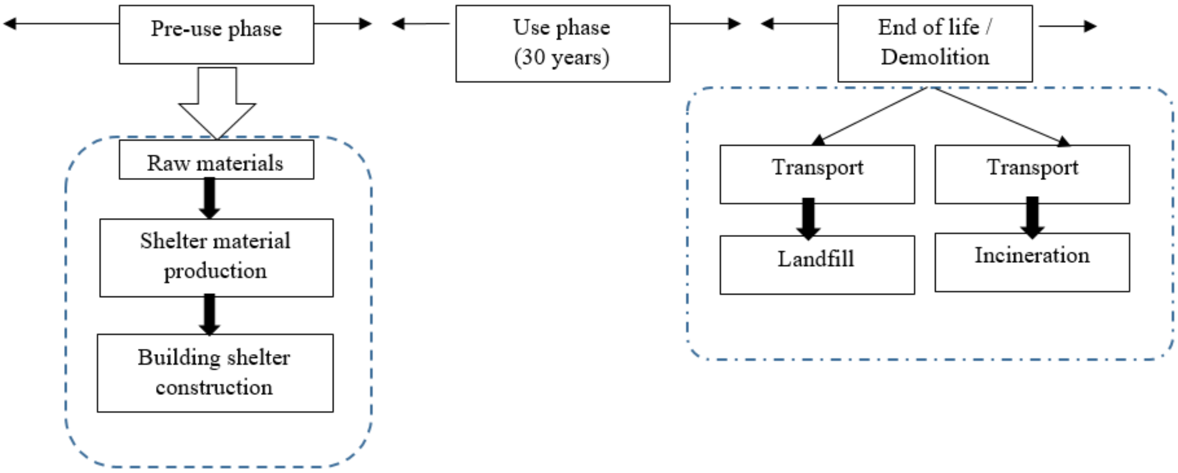

*Figure 2: LCA phases and processes included in modelling*

The pre-used phase in this study consists of (1) all the processes of the materials´ manufacturing (raw material extraction and processing, transport to the manufacturer, and proper manufacturing including provision of all materials, products and energy); (2) transport to the building site and (3) construction process - installation of the materials into the construction, including provision of all materials, products and energy. The transport in this phase covered the transportation of the finished wood material from the plant to the building site, Valaliky village (100 km) and steel (50 km).

The use phase of the shelter, within the lifespan of 30 years, included no maintenance, repair, replacement or refurbishment processes. No operational energy and no operational water were considered in the use phase, as the shelter was not heated and no lightening or water sources were installed in.

The end-of-life phase included the demolition processes, transport to waste processing and energy of the particular processes. Transport of the waste material from the demolition site (Valaliky village) to the nearest landfill in (V.O.D.S. - EKO a.s., Kosice-Myslava) (represented the distance of 12.8 km) whereas from to the nearest incineration plant (ZEVO Kosit, Kosice) (represented 7.5 km). Electricity included in all processes was selected from the database as Medium Voltage, Production SK.

## LCA method

Every stage of LCA methodology was supported by software SimaPro, version 9 [13]. SimaPro calculation were based on a commercial inventory, Ecoinvent, which is a validated database containing more than 2500 processes[14].

In this study, the environmental impacts were evaluated using the ReCiPe impact assessment method[15]. This method offers calculation of the impacts by using both mid-point and end-point indicators[16]. In the present study, both the problem-oriented methods (ReCiPe mid-point) and the damage oriented method (ReCiPe end-point) were used with application of the hierarchist approach.

Eighteen impact categories were addressed at the midpoint level (Figure 3):

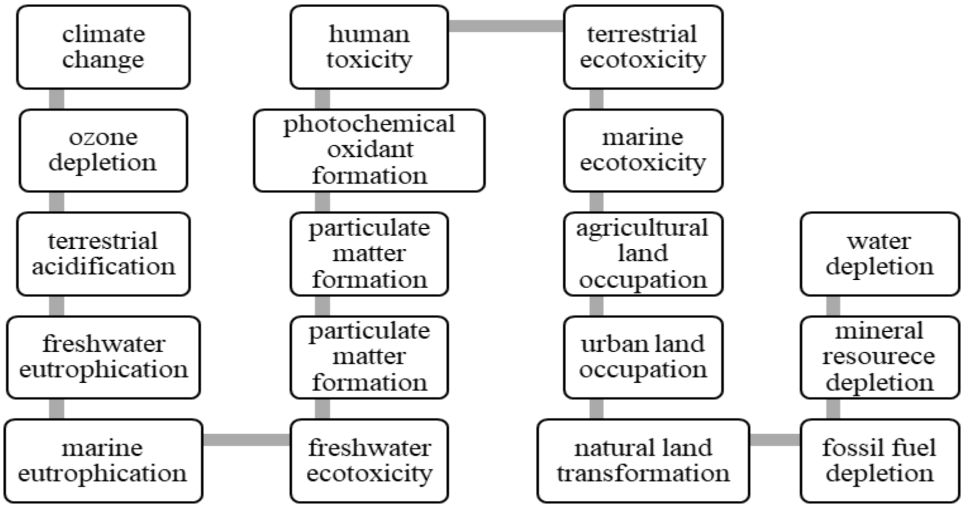

*Figure 3: Mid-point categories used in the study*

At the end-point level, most of these mid-point impact categories were further converted and aggregated into the following three end-point categories:

1) Damage to human health;
2) Damage to ecosystems and
3) Damage to resources availability[15].

## Results and discussion

In this paper, the environmental impacts of wood (1500 kg) and steel (450 kg) that were used as a building material for the wooden shelter were evaluated. The results of three waste management scenarios, calculated by the ReCiPe mid-point and end-point assessment methods, were used to compare the environmental impacts.

### Midpoint categories

By applying the characterisation factors proposed by ReCiPe to the mid-point impact categories, the results of the following environmental indicators were obtained: climate change (in kg $CO_2$ equivalent), ozone depletion (in kg CFC-11 equivalent), human toxicity (in kg 1,4-dichlorobenzene equivalent), photochemical oxidant formation (in kg of non-methane volatile organic compound - NMVOC), particulate matter formation (in kg $PM_{10}$ equivalent), ionising radiation (in kg $U^{235}$ equivalent), terrestrial acidification (in kg $SO_2$ equivalent), freshwater eutrophication (in kg P equivalent), marine eutrophication (in kg N equivalent), terrestrial and freshwater ecotoxicity (in kg 1.4 dichlorobenzene equivalent), agricultural and urban land occupation (in m$^2$), natural land transformation (in m$^2$), water depletion (in m$^3$), metal depletion (in kg Fe equivalent) and fossil depletion (in kg oil equivalent).

The calculated results for the individual waste scenarios are compared in Figure 4.

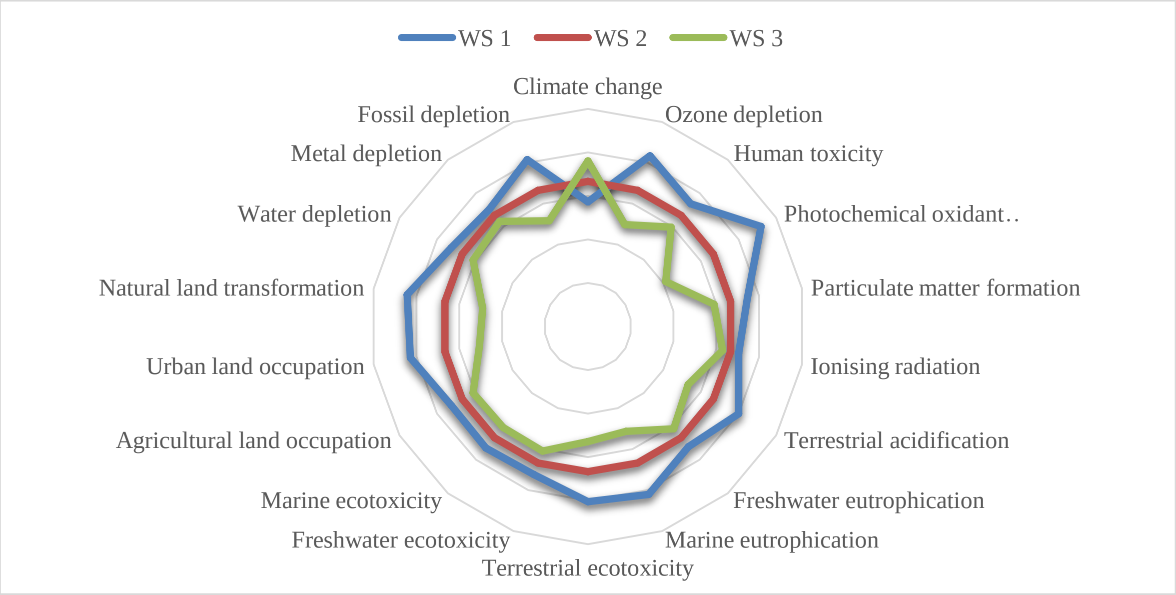

***Figure 4: Comparison of the results of waste management scenarios in the mid-point categories***

As it can be seen, the waste scenario WS 1 (30% landfilling and 70% incineration) was the worst alternative due to the highest score in all environmental impact categories, except for the climate change (Figure 4). This finding, regarding the climate change is surprising at first sight. However, considering that the global warming indicator is considering a 100-year horizon and taking into account the greenhouse gas emissions of the technologies analysed, this fact could be clarified by the different time period of releasing the greenhouse gases into the air. The is responsible for a greater immediate impact on climate change than landfilling in short-term period, since during the incineration process, there are intensively produced various harmful emissions: carbon dioxide and monoxide, hydrogen fluoride, sulphur dioxide, volatile organic carbon, dioxins and furans, heavy metals, etc.). On the other hand, landfilling is a long-term process. The landfill is designed for a longer period and the production of greenhouse gases is being continually during the whole lifetime of the landfill. In the first 150 years, the wood in a landfill slowly decomposes forming methane and carbon dioxide. Approximately 20% will not decompose and remain in the landfill as a stable material. Moreover, the release of 1 kg methane contributes over 20 times as much to climate change as the release of 1 kg carbon dioxide.

In the scenario 2 (WS 2), the waste on landfilling and incineration was divided into the equal percentage (50 / 50). Therefore, the impact category of climate change has higher impact WS 2 than in WS 1, because the total amount of waste has risen by 20%.

The waste scenario 3 (WS 3) with 70% on landfilling process was identified as the worst alternative in terms of the climate changes. In order to avoid or minimize the environmental impacts, a landfill needs to be monitored for centuries. However, comparing all other obtained environmental results, the waste scenario 3 (WS 3) was the best alternative in this study. The significant differences among the scenarios, up to 55%, were found in photochemical oxidant formation, terrestrial ecotoxicity, and natural land transformation. However, there is a need to note that these results do not include the energy recovery from the incineration process consideration of which could change the final results.

## Endpoint categories

The environmental performance of each scenario expressed damage categories are depicted in Table 1. The results in end-point damage categories achieved approximately the same values for all three waste management scenarios in human health and ecosystems (Table 1). Based on that, it is difficult to make a clear conclusion regarding the best and worst alternative because of the results with minimal differences. Therefore, the conclusion regarding the WS 3 alternative being identified as the best, cannot be definitely confirmed using the end-point-category results. A more significant difference among the scenarios was found in resources where the WS 3 reached the best score.

***Table 1: The results of waste management scenarios in the end-point categories***

| | **Damage category** | | |
|---|---|---|---|
| **Waste management scenario** | **Human health [DALLY]** | **Ecosystems [species×yr]** | **Resources [$]** |
| WS 1 | $21.4\times10^{-5}$ | $7.22\times10^{-7}$ | 273.66 |
| WS 2 | $22.4\times10^{-5}$ | $8.24\times10^{-7}$ | 223.72 |
| WS 3 | $23.4\times10^{-5}$ | $9.26\times10^{-7}$ | 173.15 |

The results in end-point damage categories achieved approximately the same values for all three waste management scenarios in human health and ecosystems (Table 1). Based on that, it is difficult to make a clear conclusion regarding the best and worst alternative because of the results with minimal differences. Therefore, the conclusion regarding the WS 3 alternative being identified as the best, cannot be definitely confirmed using the end-point-category results. A more significant difference among the scenarios was found in resources where the WS 3 reached the best score. The calculated values were converted to percentages for a better graphic expression (Figure 5).

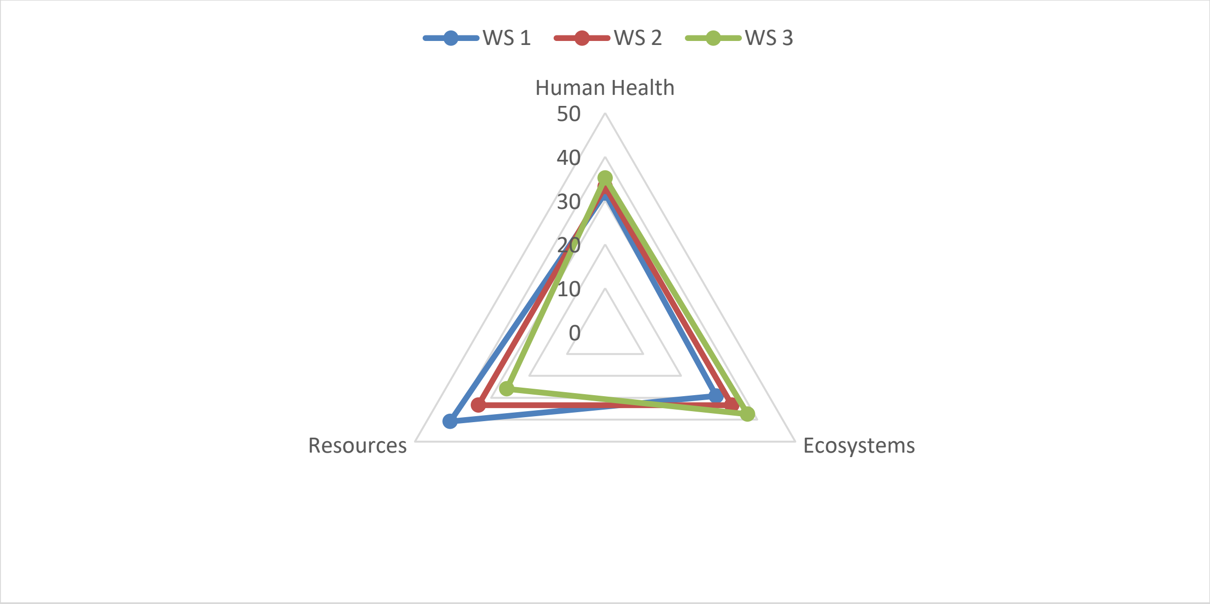

***Figure 5: Comparison of the percentage share of waste scenarios in end-point categories***

The difference in the obtained findings regarding the mid and end-point approach probably results from the assignment of the particular mid-point indicators into the end-point ones. For instance, the human health category includes: climate change, photochemical oxidant formation, human toxicity, particulate matter formation, ionizing radiation, and ozone depletion. Thus, in the overall value, the most negative contribution of the WS 1 in climate changes was compensated with the lowest one in ozone depletion. Findings revealed, that a mid-point calculation provided more precise impact of the evaluated waste management scenarios. On the other hand, the landfilling, which is preferable in the mid-point evaluation, could have more significant overall impacts to the ecosystem and human health in long-term perspective as shown in end-point approach.

## Conclusions

Three different waste management scenarios of the wooden shelter, including landfilling and incineration, were compared and evaluated by means of LCA. The analysis, focusing on comparison of a variation of the materials considered on incineration or landfilling, was performed using the assessment ReCiPe method. The present research showed that environmental results differed in dependence on the used mid-point or end-point methodology. Based on the more detailed results originated from the mid-point approach, the waste management scenario with 30% landfilling and 70% incineration was identified to be the best in terms of the climate changes which are currently one of the most important topic in environment protection and in sustainable development. Surprisingly, the scenario with domination of landfilling was found to be the best in all other environmental mid-point indicators. However, there is a need to note that these results do not include the energy recovery benefits from the incineration process consideration of which could change the final results.

## *Acknowledgment*

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## References

1. Ghinea C., Petraru M., Bressers H. T. A., Gavrilescu M.: Environ. Eng. Landsc. *20*, 76 (2012).
2. Nouri J., Nouri N., Moeeni M.: Int. J. Environ. Sci. Technol. *9*, 417 (2012).
3. Banar M., Cokaygil Z., Ozkan A.: Waste Manag. *29*, 54 (2009).
4. Zaman A. U.: Int. J. Environ. Sci. Technol. *7*, 225 (2010).
5. Finnveden G., Moberg A.: J. Clean Product. *13,* 1165 (2004).
6. ISO 14040:2006. Environmental management. Life cycle assessment. Principles and framework.
7. Esnouf A., Latrille É., Steyer J. P., Helias A.: Sci. Total. Environ. *621*, 1264 (2018).
8. Ekvall T., Assefa G., Björklund A., Eriksson O., Finnveden G.: Waste Manag. *27*, 989 (2007).
9. Castillo-Giménez, J., Montaᾓés, A.: Sci. Total Environ. *687*, 1305-1314. (2019).
10. Costa A. M., Alfaia R. G. D. S., Campos J. C.: J. Environ. Manag. *232*, 110 (2019).
11. Zaman A. U.: Int. J. Environ. Res. *3*, 155 (2009).
12. Ortiz O., Pasqualino J. C., Castells F.: Waste Manag *30*, 646 (2010).
13. Herrmann I. T., Moltesen A.: J. Clean. Prod. *86*, 163 (2018).
14. Turconi R., Butera S., Boldrin A., Grosso M., Rigamonti L., Astrup T.: Waste Manag. Res. *29*, 78-S90 (2010).
15. Goedkoop M., Heijungs R., Huijbregts M., De Schryver A. M., Struijs J., Van Zelm R.: ReCiPe: A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level. Report I: Characterisation (2009).
16. Hou D., Al-Tabbaa A., Guthrie P., Hellings J., Gu Q.: J. Clean. Product. *83*, 87 (2014).

# Environmentálne dopady dreveného prístrešku: Porovnanie troch scenárov nakladania s odpadom po skončení životnosti

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## *Souhrn*

*Problematika nakladania s odpadmi nie je v oblasti stavebníctva novinkou a v súčasnej dobe, kedy je tzv. obehová ekonomika predmetom širokého záujmu, je nevyhnutné zaoberať sa koncom životnosti stavieb a konštrukcií vo väzbe na podporu recyklácie alebo zhodnocovania stavebných odpadov. Posudzovanie životného cyklu (LCA) je medzinárodne štandardizovaná metodika prístupu k životnému prostrediu, ktorá sa používa na hodnotenie vplyvu výrobku alebo systému na životné prostredie počas ich celého životného cyklu vrátane poslednej fázy - ukončenia životnosti.*

*Hlavným cieľom tejto prípadovej štúdie bolo porovnať environmentálne dopady troch rôznych scenárov odpadového hospodárstva pre vybranú stavbu - drevený prístrešok. Pre porovnanie a hodnotenie environmentálnych dopadov boli vybraté dva spôsoby nakladania s odpadom, ktoré sa na Slovensku najčastejšie uplatňujú:(1) skládkovanie a (2) spaľovanie. Každý scenár zahŕňal tieto dve často používané technológie, a rozdiely medzi scenármi spočívali v percentuálnom pomere, akým sa jednotlivé technológie podieľali na záverečnom spracovaní použitých materiálov dreveného prístrešku.*

*Vplyvy na životné prostredie u jednotlivých alternatív, ktoré zahŕňali okrem poslednej fázy životného cyklu aj dopady počas výroby materiálov a konštrukcie prístrešku, boli hodnotené na základe analýzy životného cyklu LCA softvérom SimaPro. Dopady boli počítané metódou ReCiPe a výsledky boli prezentované pomocou tzv. stredových kategórií dopadov, ako sú zmena klímy, poškodzovanie ozónovej vrstvy, toxicita pre ľudí atď., ale aj pomocou tzv. koncových kategórií, ktoré sumarizujú celkové dopady a poškodenie v oblastiach ľudského zdravia, ekosystémov a vyčerpávania zdrojov.*

*Získané environmentálne výsledky sa mierne líšili v závislosti od použitej metodiky. Scenár nakladania s odpadom s 30% skládkovaním a 70% spaľovaním bol identifikovaný ako najlepší z hľadiska klimatických zmien. Prekvapujúce bolo zistenie, že scenár s dominanciou skládkovania (70 %) dosahoval najlepšie skóre vo všetkých ostatných stredových ukazovateľoch životného prostredia. Treba však poznamenať, že tieto výsledky nezahŕňajú prínosy z energetického zhodnotenia zo spaľovacieho procesu, ktoré by mohli zmeniť konečné výsledky. Výsledky stredových kategórií dopadov poskytli podrobnejšie hodnotenie dopadov uvažovaných scenárov odpadového hospodárstva. Na druhej strane skládkovanie má z dlhodobého hľadiska výraznejšie celkové dopady na ekosystém a ľudské zdravie, ako to vyplýva z hodnotenia pomocou tzv. koncových kategórií.*

***Klíčová slova:*** *odpad, LCA analýza, environmetálne dopady, skládkovanie, spaľovanie*

# Repair Mortars Containing Fly Ash and Crystalline Admixture

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## *Abstract*

*The paper discusses the utilisation of a by-product specifically a fly ash sourced from a landfill where it had been dumped over a period of several years. The fly ash had been produced from a coal burning power plant in Malta and landfilled in disused quarries in Bengħisa. The landfilled fly ash deposit dumped in the quarries is considered as an environmental hazard. The research addresses the potential use of the fly ash for recycling in the production of cement based materials particularly repair mortars. The paper presents the design and testing of repair mortars in which the fly ash is used as a partial replacement of cement. In order to improve the environmental resistance, the performance of the material with the addition of a crystalline admixture was assessed. The stabilisation of the fly ash in the mixture was verified through the assessment of physical-mechanical properties and through a microscopic examination of the microstructure of the mortar.*

***Keywords:*** *Fly ash, repair mortars, secondary crystallisation, stabilisation.*

## Introduction

Fly ash is currently the most common pozzolan used worldwide and it is widely accepted that using it as an ingredient in cement mortars and concrete provides benefits the properties of the final product. Improvement in the properties of the interfacial transition zone (ITZ) between particles of aggregate and the binder matrix can also be attributed to the addition of fly ash [1]. Research shows that fly ash with a low calcium content (class F according to ASTM) improves ITZ properties even though it is less reactive than e.g. silica fume [2].

For several years waste in Malta was landfilled in different waste disposal sites without separation. The landfill sites did not include measures for the collection of leachate and gases emitted from the waste, as in the case of engineered landfills. Fly ash produced at the coal-burning power plant in Marsa Malta had been landfilled in quarries at a cliff-edge in Bengħisa in Malta. The two quarries at the Bengħisa site, which were managed by Enemalta Corporation, did not have any environmental protective measures or leachate collection system [3,4]. Coal was last used in the Marsa power station in 1995, when it was modified to run on heavy fuel oil. Fly ash produced by the Marsa power station when it was still coal-fired and which was dumped on the cliff-edge in Bengħisa, had high levels of radioactivity [4,5,6]. The Bengħisa landfill, containing large quantities of fly ash deposit, presents an environmental hazard. The Marsa Power Plant has since been decommissioned and the Maltese Islands now rely on the Dellimara natural gas-fired power plant and an interconnector with Sicily, together with renewable energy sources, for its energy supply.

The environmentally-conscious course of action is to seek a solution that does not limit itself to mere stabilisation and landfilling, but utilizes the fly ash as a raw material. Civil engineering is one of the areas where the ash could be used, particularly in concrete as supplementary cementitious material for partial replacement of the cement [4]. The benefits of using fine fly ash in cement composites are for e.g.

improved strength, fewer shrinkage cracks, or better sulphate and other chemical resistance [7], as well as resistance to high temperatures. A marked improvement due to the addition of fly ash to cementitious mortars was observed in materials exposed to a high temperature of 900 °C [8].

The goal of the research described in this paper was to design repair mortars using the landfilled fly ash, which was produced at the coal-fired power plant in Malta. In order to deliver the required properties, the research referred also to the use of one of the emerging technologies for protecting cement-based composites against aggressive environments known as “secondary crystallization” or “crystalline technology” [9]. The mixtures also included components which are available in the Republic of Malta. The research was conducted through collaborative activity between the Brno University of Technology, Faculty of Civil Engineering and the University of Malta, Faculty for the Built Environment, addressing the use of secondary raw materials in polymer cement mortar and concrete.

## Experiments

The experiment examined the properties of polymer-modified repair mortars containing a crystalline admixture and varying amounts of fly ash (FA) at an age of 28, 60 and 90 days after casting. The mixtures contained the following raw materials: Portland cement, fly ash, dolomite sand, polymer admixture, cellulose ether, and crystalline admixture. The reference mixture is identified as F0X0 and contained no fly ash nor crystalline admixture.

The other mixtures differed in the amount of FA, which replaced up to 30% of cement. The composition of the mixtures is presented in the Table 1. The FA used had a high water-absorption and the mixes were developed with equal workability as the control reference mix, controlled using a flow table test. All tested mix formulations had a flow table result (diameter) of 130 mm.

***Table 1: Composition of the mortars per m$^3$***

| Raw materials [kg·m$^{-3}$] | Mixture ID | | | | |
|---|---|---|---|---|---|
| | **F0X0** | **F0X** | **F10X** | **F20X** | **F30X** |
| Cement CEM I 52.5 R | 601.5 | 601.5 | 533.3 | 473.2 | 413.0 |
| Fly ash (PFA) | 0.0 | 0.0 | 60.2 | 120.3 | 180.5 |
| Dolomite sand (0 – 2 mm) | 1310.3 | 1310.3 | 1310.3 | 1300.3 | 1292.3 |
| Water | 261.9 | 261.9 | 261.9 | 271.4 | 278.9 |
| Ethylene-vinyl acetate copolymer (EVA) | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| Cellulose ether | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Crystalline admixture | 0.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| Superplasticiser | 15.3 | 15.3 | 15.3 | 15.8 | 16.3 |
| W/C ratio | 0.4 | 0.5 | 0.5 | 0.6 | 0.7 |

## *A. Materials and Properties*

### A.1 Cement

Portland cement CEM I 52.5 N manufactured in Albania was used as the binder; its basic properties according to EN 196-1, EN 196-3 and EN 169-6 are presented in the Table 2. Cement is not produced in Malta and is imported from other countries.

***Table 2: Basic parameters of the cement CEM I 52.5 N manufactured in Albania***

| **Compressive strength [MPa]** | | **Flexural strength [MPa]** | | **Blaine fineness [cm$^2$·g$^{-1}$]** | **Initial setting time [min]** | **Final setting time [min]** | **Specific gravity [kg·m$^{-3}$]** |
|---|---|---|---|---|---|---|---|
| **7 days** | **28 days** | **7 days** | **28 days** | | | | |
| 46.9 | 53.5 | 7.9 | 9.1 | 5 109 | 150 | 190 | 3 140 |

### A.2 Fly ash

The Bengħisa fly ash (FA) used in the research was produced in the Marsa Power Station and subsequently landfilled in the Bengħisa quarries, on the island of Malta. The fly ash was extracted for the purpose of this research, directly from the quarry at a depth of 1m below the existing soil cover where the material was observed to be free from soil and any other contaminants. The sample was sealed in plastic bags and transported to the laboratory where it was oven dried for 24 hours at 105°C and sieved on a 250μm sieve prior to testing. The fly ash thus treated had a specific surface area of 4120 cm$^2$·g$^{-1}$ and specific gravity of 2380 kg·m$^{-3}$. Figure 1 shows the particle size distribution and Figures 2 – 4 Scanning Electron Microscopy SEM images of the fly ash after drying and sieving. Particle size measurement was performed using the laser diffraction method with the MALVERN Mastersizer 2000 instrument. The pre-treated fly ash was measured through the dry method. The particle size analysis through laser diffraction is based on the principle that larger particles reflect laser beams at a smaller angle and with greater laser intensity, and smaller particles have a greater reflection angle and lower reflected beam intensity. The chemical composition determination conducted according to EN ISO 11885, EN 15410: 2011, ČSN 72 0105-1 standards [10-12] carried out on the Bengħisa fy ash indicates that the fly ash contains mainly $SiO_2$, $Al_2O_3$, CaO and $Fe_2O_3$ (see Table 3). With regard of the mineralogical composition, the fly ash (FA) is made up primarily of β-quartz, mullite (3 $Al_2O_3$·2$SiO_2$) and hematite ($Fe_2O_3$).

***Table 3: Chemical composition of the Bengħisa fly ash [% wt. dry]***

| **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **CaO** | **MgO** | **$K_2O$** | **$Na_2O$** |
|---|---|---|---|---|---|---|
| 42.0 | 29.3 | 3.01 | 6.77 | 1.31 | 0.62 | 0.25 |

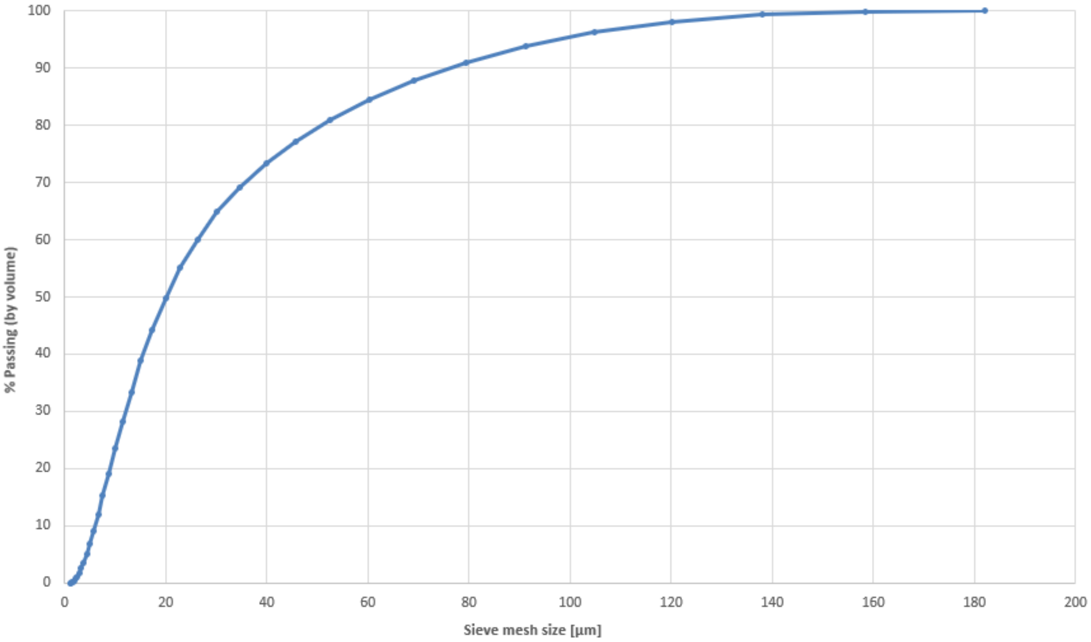

***Figure 1: Fly ash particle size distribution (Laser Diffraction)***

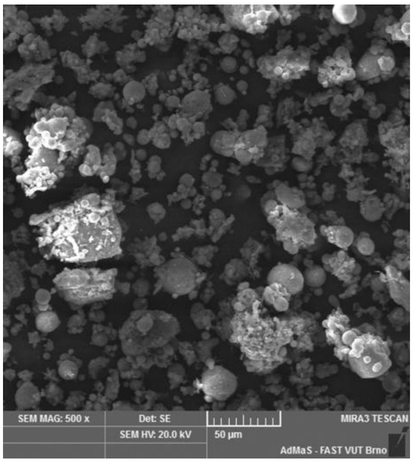

***Figure 2: SEM image of the fly ash***

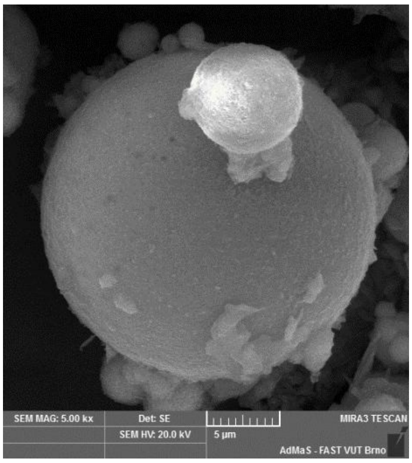

***Figure 3: SEM image: detail of a fly-ash cenosphere***

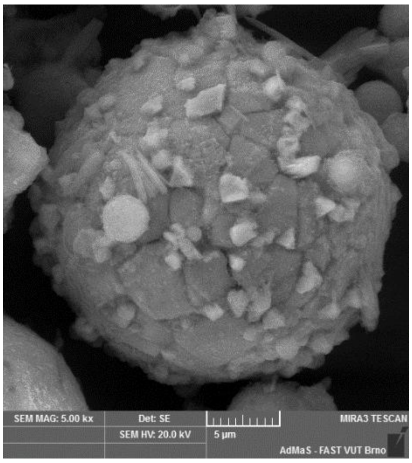

***Figure 4: SEM image: detail of a fly-ash cenosphere***

### A.3 Dolomite sand

Dolomite sand sourced in Italy was a major component of the polymer-cement mortar developed in this research. The dolomite sand was first oven dried and then sieved through a 2.0 mm sieve to achieve the required aggregate portion similar to a standard sand with a granulometry of 0 – 2 mm. Figure 5 shows the particle size distribution of the dolomite sand. The content of fine particles smaller than 300 µm was approximately 25% and the residue consisted of 0.3 – 2.3 mm grains. The dolomite sand sieve analysis was performed according to the standard EN 933-1:1997 [14].

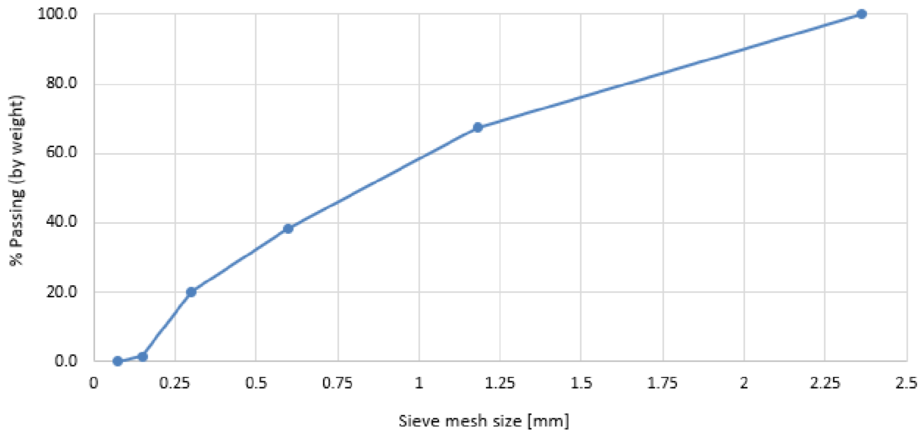

*Figure 5: Dolomite sand sieve analysis*

### A.4 Crystalline admixture

The chemical composition (according to EN ISO 11885, EN 15410: 2011, ČSN 72 0105-1 and ČSN 72 0117 [10-13]) of the Xypex crystalline admixture produced by Xypex Chemical Corporation is in the Table 4.

*Table 4: Chemical composition of the Xypex crystalline admixture*

| Chemical composition of CA [% wt.] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | $Cl^-$ | Organic Substances |
| 11.50 | 2.34 | 1.74 | 45.70 | 0.73 | 2.05 | 0.39 | 6.61 | 0.03 | 7.03 |

### A.5 Ethylene and vinylacetate copolymer (EVA)

The EVA copolymer is used to improve the properties of fresh and hardened mortars. Fresh mortars benefit through a lower water demand while retaining an extended workability. This is due to the surface-active compounds in the polymer emulsion, which allow cement particles in the mixture to disperse more easily. In hardened mortars EVA copolymer creates a polymer film that improves adhesion, flexural and compressive strength, and water absorption by sealing pores and preventing the ingress of moisture. The research described herein is based on a copolymer named VINNAPAS 4020N, produced by Wacker Chemie AG.

### A.6 Cellulose ether

Cellulose ether extends the workability of fresh cementitious mortars and, by increasing retention capacity, prevents the fresh mixture from releasing water into the substrate, which helps improve the final properties of the hardened mortar. The product used here was Culminal manufactured by Ashland.

### A.7 Superplasticiser

Superplasticisers have the ability to markedly reduce the amount of water in the mixture without reducing workability. The superplasticiser used here was MasterGlenium 51 produced by BASF.

### *B. Methods*

Six sets of mortar prism specimens with dimensions of 40×40×160 mm were prepared. The first set was stored for 28 days at a temperature of 23 °C and relative humidity of 95% (23 °C+95% RH), the second set was stored for 60 days at 23 °C+95% RH and the third set was stored for 60 days at 23 °C+95% RH and then placed for 62 days in a solution representing seawater. The concentration of the solution was 15%, and a fresh solution was prepared every 21 days. At the age of 28, 60 and 90 days the samples were tested for physical-mechanical properties and their microstructure was examined. The experiments were carried out through the collaboration between Brno University of Technology and University of Malta. The three-point flexural strength and the compressive strength were determined in accordance to EN 196-1 [15] and the dry bulk density of hardened mortar was determined in accordance to EN 1015-6 standard [16]. The study of the microstructure of selected specimens was conducted in order to gain a better understanding of the strength test results: DTA analysis was performed using a Mettler Toledo TGA/DSC 1 (heating rate 20 °C per minute; air atmosphere) and Scanning Electron Microscopy SEM imaging with a TESCAN MIRA3 XMU. Leaching behaviour of the fly ash and the mortar mixture, where 30% of cement was replaced with the fly ash was tested in compliance with Decree No. 294/2005 Coll., Annex No. 2, which defines leachability classes according to the maximum permissible values of indicators; i.e. concentration of pollutants in the eluate (mg·l$^{-1}$), according to ČSN EN 12457-4 standard [17].

## Results and discussion

The results of bulk density, compressive and flexural strength tests of the mortars performed after 28, 60 and 90 days are presented in Figures 6 – 8 below.

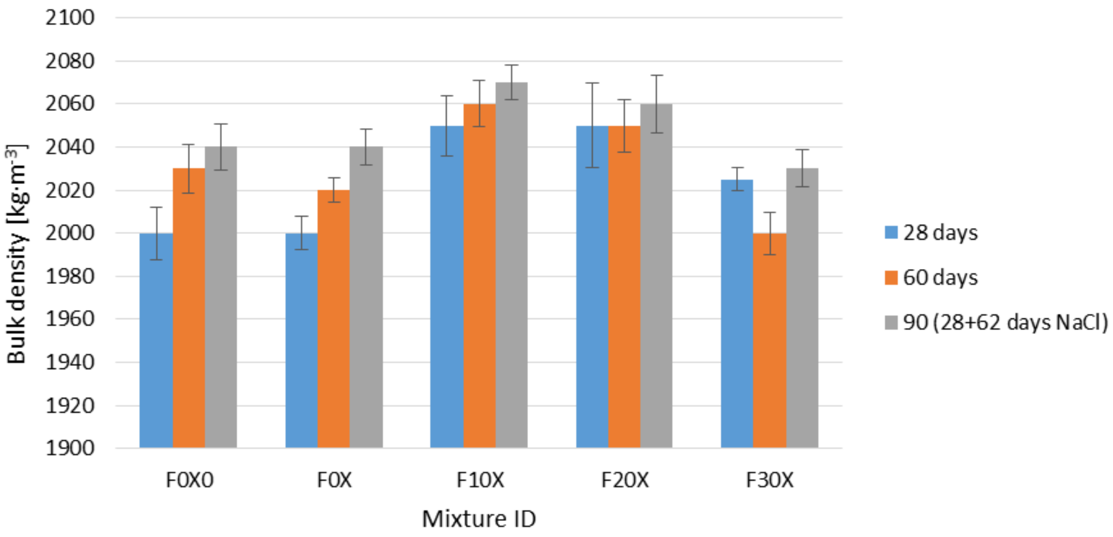

*Figure 6: Determination of the bulk density*

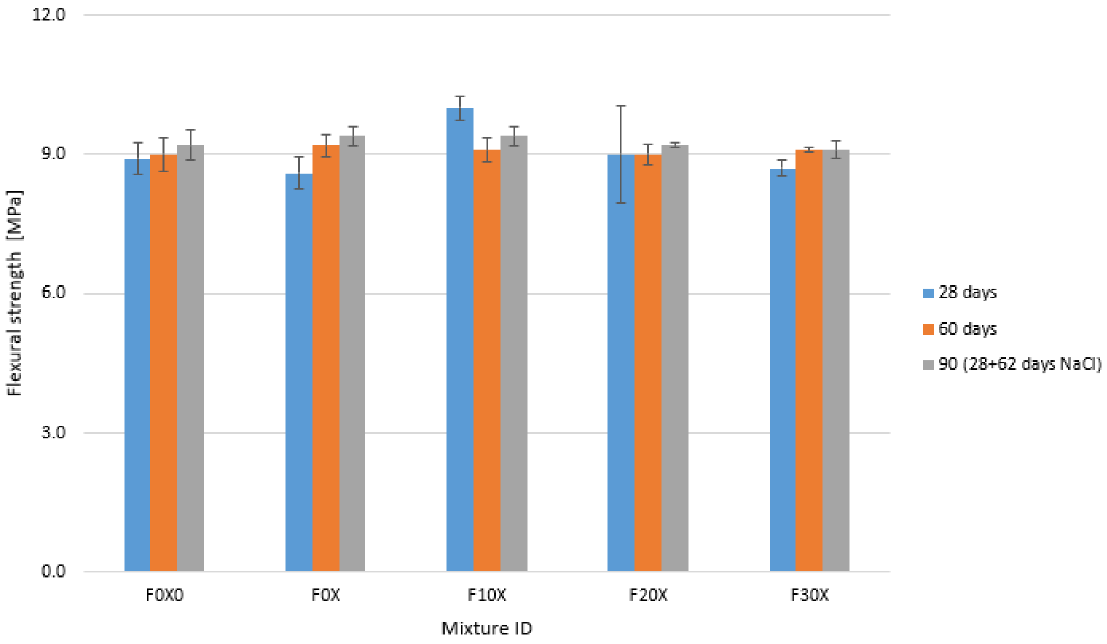

*Figure 7: Determination of the flexural strength*

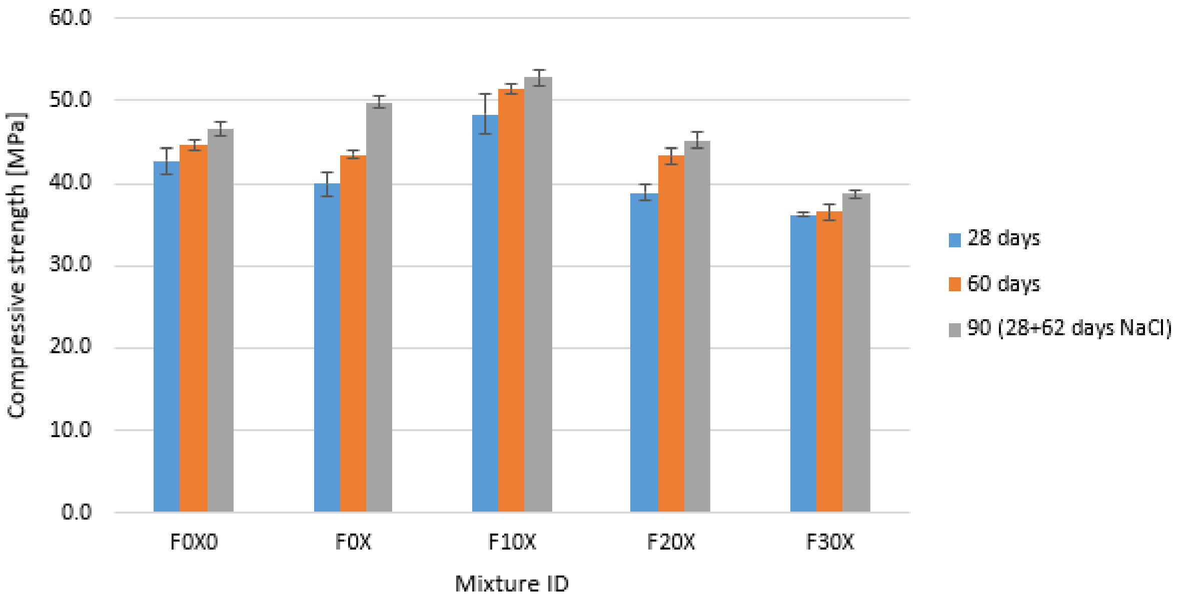

*Figure 8: Determination of the compressive strength*

As the figures above show, the highest values of bulk density, flexural strength, and compressive strength were reached in the mortar that contained the crystalline admixture and fly ash as a 10% cement replacement. Mixtures that contained more fly ash required additional water, which influenced both bulk density and strength.

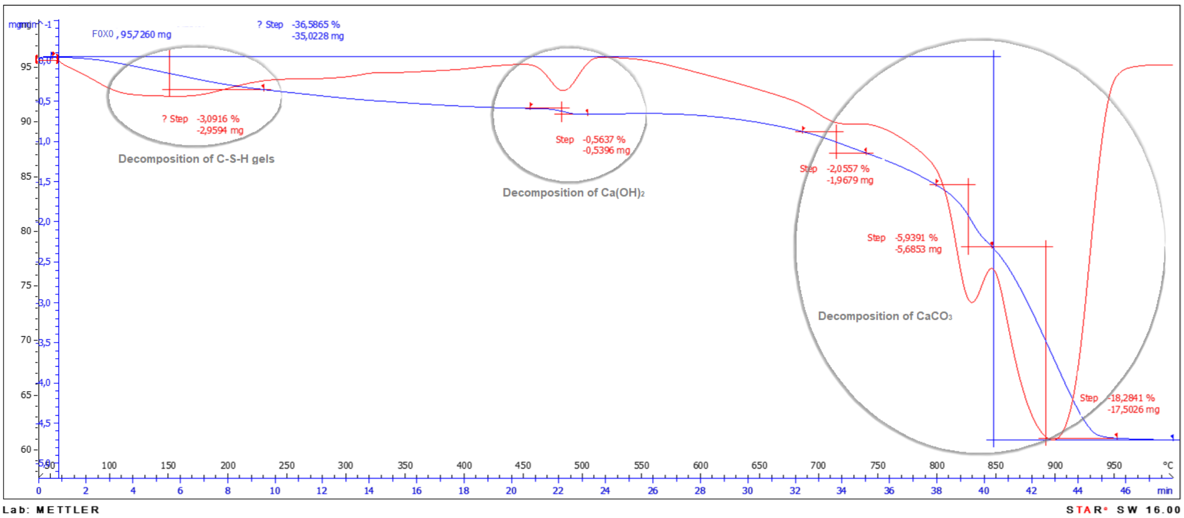

**Figure 9: DTA record of mixture F0X0 after 60 days**

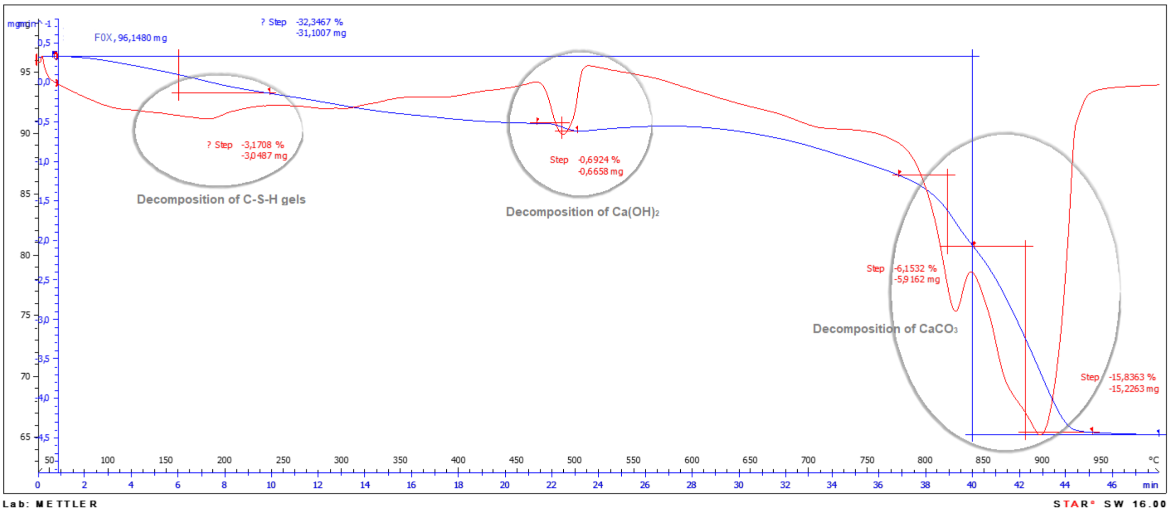

**Figure 10: DTA record of mixture F0X after 60 days**

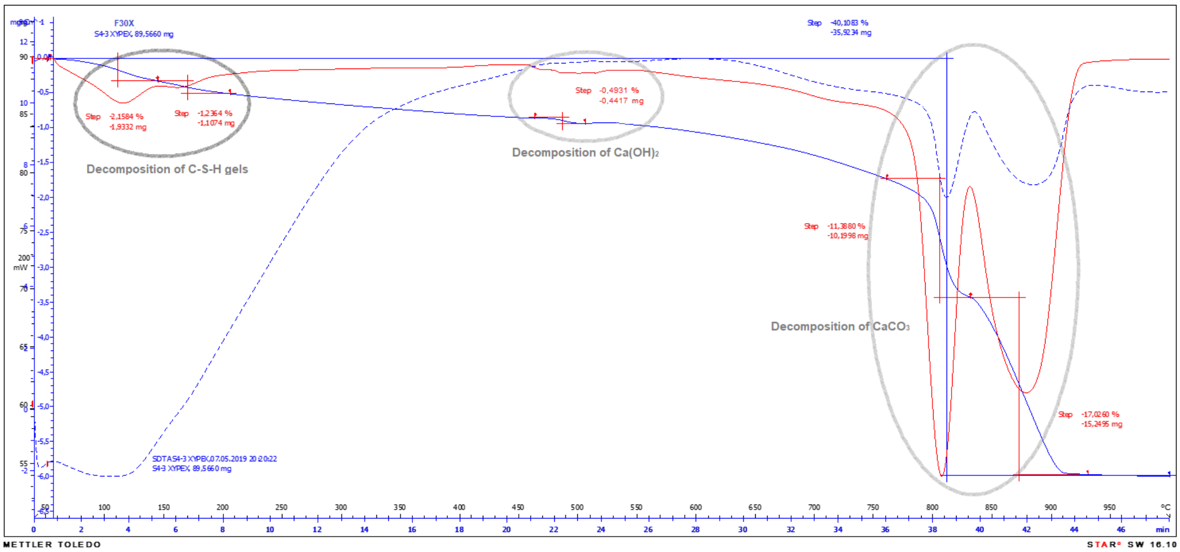

**Figure 11: DTA record of mixture F30X after 60 days**

Figures 9 – 11 show DTA records of mortars: F0X0 (reference), F0X (no FA but containing CA) and F30X (containing both FA and CA). All the mortars underwent three basic reactions: decomposition of C-S-H phase, $Ca(OH)_2$ and $CaCO_3$. Mass loss content and mass content are shown in the Table 5. The presence of portlandite ($Ca(OH)_2$) in the sample F30X was confirmed also by X-ray powder diffraction (XRD) analysis.

***Table 5. Results of DTA – mass loss and mass content***

| **Mixture ID** | **Mass loss corresponding to decomposition [%]** | | | **Mass content [%]** | |
|---|---|---|---|---|---|
| | **C-S-H** | **$Ca(OH)_2$** | **$CaCO_3$** | **$Ca(OH)_2$** | **$CaCO_3$** |
| F0X0 | 3.09 | 0.53 | 26.28 | 2.31 | 59.72 |
| F0X | 3.17 | 0.69 | 21.99 | 2.85 | 49.97 |
| F30X | 3.39 | 0.49 | 28.41 | 2.01 | 64.57 |

The crystalline admixture in combination with fly ash influences the increase in C-S-H phase content. The mixture containing FA registered an increase in the C-S-H phase and a decrease in $Ca(OH)_2$, which indicates that a pozzolanic reaction took place; i.e. a reaction between amorphous silicon dioxide and aluminosilicates with calcium hydroxide, producing compounds similar to those formed during Portland cement hydration. The chemical reaction between a pozzolan and calcium hydroxide results primarily in the formation of calcium silicate hydrates (C-S-H) which could vary in composition and structure [18]. The pozzolanic reaction can be presented as follows [19]:

$$x\,Ca(OH)_2 + y\,SiO_2 + z\,H_2O \rightarrow xCaO\cdot ySiO_2\cdot zH_2O \qquad (1)$$

The mixtures were also examined using the Scanning Electron Microscope SEM. Figures 12 – 17 show images of 60-day old mortars. Mortar F30X containing CA and FA showed crystals formed by the CA. Clearly visible are the fly ash particles undergoing pozzolanic reaction and being integrated into the cement matrix.

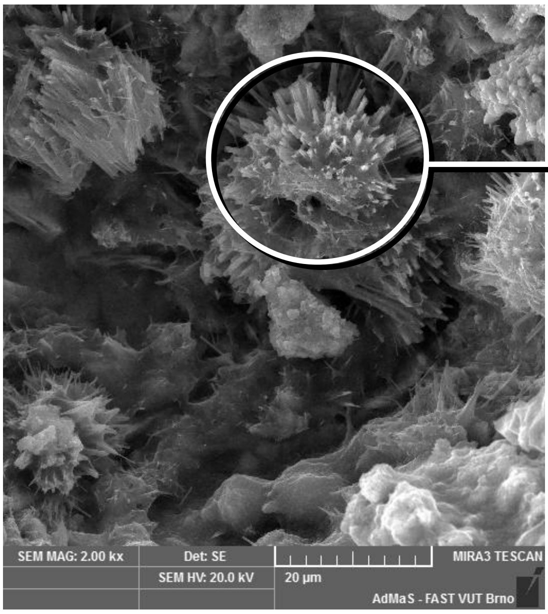

***Figure 12: SEM image of mixture F30X – pore***

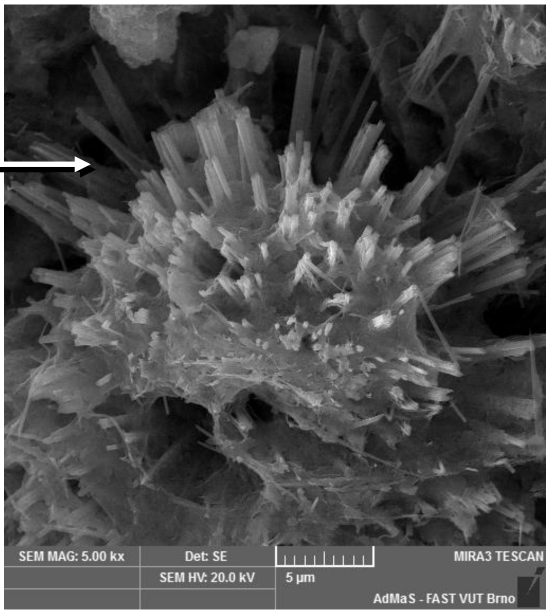

***Figure 13: SEM image of mixture F30X – detail of the crystalline formed inside of pores***

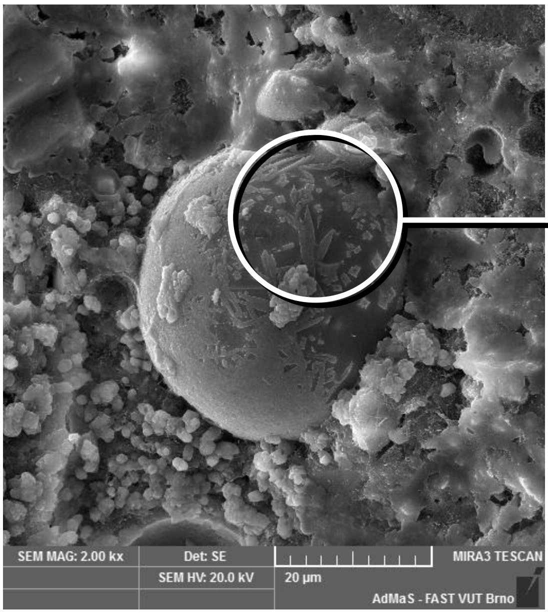

***Figure 14: SEM image of mixture F30X – detail of a fly ash particle undergoing pozzolanic reaction***

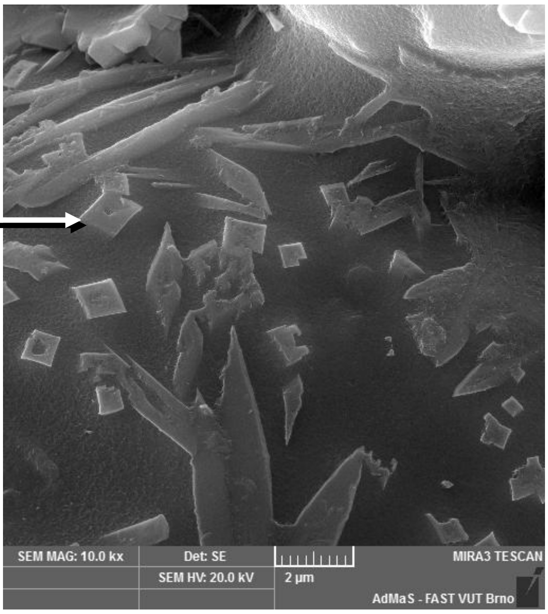

***Figure 15: SEM image of mixture F30X – detail of a C-S-H phase being formed***

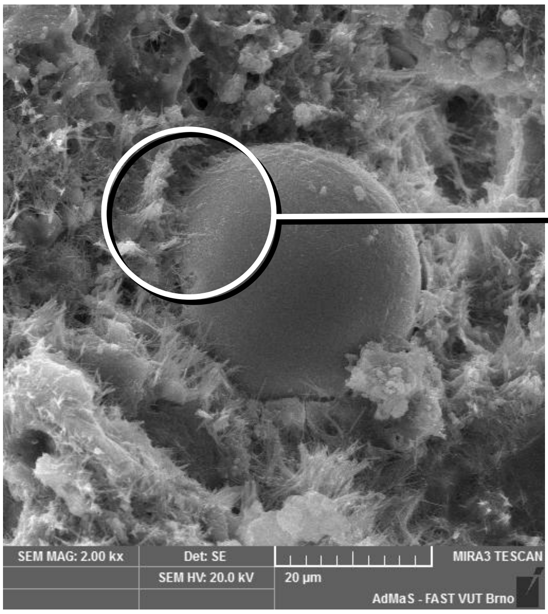

***Figure 16: SEM image of mixture F30X – detail of a fly ash particle integrated in the cement matrix***

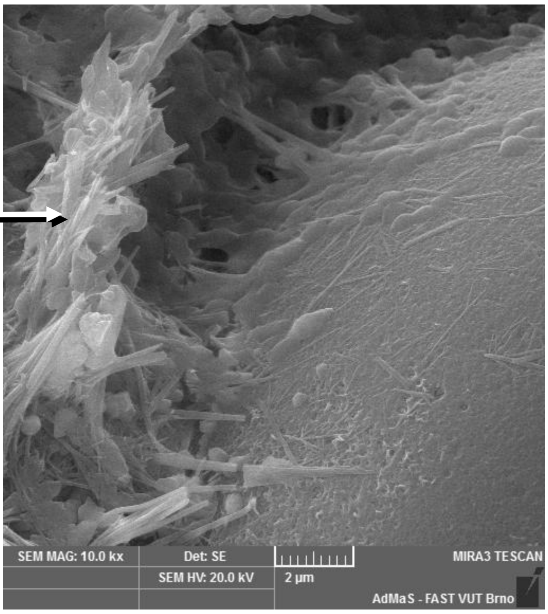

***Figure 17: SEM image of mixture F30X – detail of the fly-ash/cement matrix interface***

The effect of the chemical composition of the amorphous and crystalline phases of fly ash on the compressive strength of fly ash cement mortar has been assessed and reported in literature [20]. The fly ash cement mortars were made by replacing 25% of cement with 16 types of fly ash. It was found that the chemical parameters have a higher correlation with the 91-day strength than with the 28-day strength of fly ash cement mortars, as the pozzolanic reaction progressed further after 91 days. The results obtained in the present research confirmed that the incorporation of Bengħisa fly ash in the mortar positively influenced the compressive strength in the long term. However, the ongoing pozzolanic reaction was observed after 60 days. It is reported that it is possible to use 20% of optimized fly ash instead of 10% non-optimized by changing the particle size distributions of fly ash used [21]. The experiments in the present research confirmed that the mixture with 10% cement replaced with the Bengħisa fly ash (non-optimized) performed best in terms of strength, corresponding with literature [17]. One of the most effective ways to reduce the environmental burden associated with the production of cementitious materials is to intensify the wider use of supplementary cementitious materials in cement composition [22].

The leaching behaviour of the fly ash and mortar F30X (containing the highest amount of fly ash; i.e. 30%) was tested in compliance with ČSN EN 12457-4, and it was found that no dangerous pollutants were leached out of either material. Given the measured concentrations and limits defined by the standard, the material met the requirements for leachability class IIa, making it suitable for surface applications. Table 6 shows the values of pollutant concentrations in the eluate. The amount of each dissolved compound in the F30X eluate is influenced by the high amount of hardened cement paste.

***Table 6: Values of pollutant concentrations in the eluate***

| **Parameter** | **Bengħisa fly ash** | **Mixture F30X** | **Limit (IIa)** | **Unit** | **Verdict** |
|---|---|---|---|---|---|
| pH value | 7.75 | 12.5 | min. 6 | - | pass |
| Dissolved organic carbon | 23.8 | 52.0 | max. 80 | $mg \cdot l^{-1}$ | pass |
| Chlorides | 13.2 | 10.1 | max. 1500 | $mg \cdot l^{-1}$ | pass |
| Fluorides | < 0.200 | < 0.400 | max. 30 | $mg \cdot l^{-1}$ | pass |
| Sulphates e.g. $SO_4^{2-}$ | 8.20 | 7.96 | max. 3 000 | $mg \cdot l^{-1}$ | pass |
| Dissolved solids after drying (105°C) | 122 | 1 800 | max. 8 000 | $mg \cdot l^{-1}$ | pass |
| Hg | < 0.00100 | < 0.00100 | max. 0.2 | $mg \cdot l^{-1}$ | pass |
| As | < 0.0500 | < 0.0500 | max. 2.5 | $mg \cdot l^{-1}$ | pass |
| Ba | 0.0704 | 1.83 | max. 30 | $mg \cdot l^{-1}$ | pass |
| Cd | < 0.00500 | < 0.00500 | max. 0.5 | $mg \cdot l^{-1}$ | pass |
| Cr | 0.0193 | 0.0714 | max. 7 | $mg \cdot l^{-1}$ | pass |
| Cu | < 0.0100 | < 0.0100 | max. 10 | $mg \cdot l^{-1}$ | pass |
| Mo | < 0.0200 | < 0.0200 | max. 3 | $mg \cdot l^{-1}$ | pass |
| Ni | < 0.0200 | < 0.0200 | max. 4 | $mg \cdot l^{-1}$ | pass |
| Pb | < 0.0500 | < 0.0500 | max. 5 | $mg \cdot l^{-1}$ | pass |
| Sb | < 0.0500 | < 0.0500 | max. 0.5 | $mg \cdot l^{-1}$ | pass |
| Se | < 0.0250 | < 0.0250 | max. 0.7 | $mg \cdot l^{-1}$ | pass |
| Zn | 0.0261 | 0.0402 | max. 20 | $mg \cdot l^{-1}$ | pass |

## Conclusions

The Bengħisa fly ash produced at the Marsa power plant in Malta and sourced from the Bengħisa quarries disposal site was assessed for the potential partial replacement of cement in repair mortars. Previous studies had demonstrated the potential use of the fly ash as a supplementary cementitious material, for the production of cement based materials with improved performance [4]. All the mixtures tested in the present research possessed the required physical-mechanical properties, namely high compressive and flexural strength. The results show that the mixture with 10% of cement replaced by fly ash performed best in terms of strength. Incorporating the fly ash in the polymer-cement matrix with the crystalline admixture solidified the material, as evidenced by the results of tests of leaching behaviour. The crystalline admixture also improves the resistance of the mortar against the ingress of seawater. This research and analysis of the results were performed through cooperation between Brno University of Technology, Faculty of Civil Engineering and the University of Malta, Faculty for the Built Environment, addressing the recycling and the use of secondary raw materials in polymer cement mortars and concrete.

## *Acknowledgment*

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## References

1. Chindaprasirt P., Rukzon S.: Constr. Build. Mater. *22*, 1601 (2008).
2. Wong Y. L., Lam L., Poon C. S., Zhou F. P.: Cem. Concr. Res. *29*, 1905 (2008).
3. Government of Malta, *Malta National Waste Strategy* (1992).
4. Borg R.P.: 2014, Sustainable Concrete: Application of Waste Materials in Concrete and Self Compacting Concrete, PhD Thesis, Department of Civil and Structural Engineering, University of Sheffield, UK.
5. Sansone K.: https://timesofmalta.com/articles/view/Bengħisa-fly-ash-had-high-levels-of-radioactivity (cit. 25. 5. 2019).
6. Camilleri J., Sammut M., Montesin F. E.: Waste Management *26*, 853 (2006).
7. Chindaprasirt P., Homwuttiwong S., Sirivivatnanon S.: Cem. Concr. Res. *34*, 1087 (2004).
8. Ayidin S., Baradan B.: Cem. Concr. Res. 37, 988 (2007).
9. Drochytka R., Bohuš Š.: *Proceedings of 18th International Conference on Composite Materials*, *August 21.–26. 2011*, Korea (The Korean Society of Composite Materials), p. 92.
10. EN ISO 11885: *Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)* (2007).
11. EN 15410: *Solid recovered fuels. Methods for the determination of the content of major elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti)* (2011).
12. ČSN 72 0105-1: *Basic analysis of silicates – Determination of silicon oxide by gravimetric method* (2009).
13. ČSN 72 0117: *Basic analysis of silicates – Determination of sulphate sulfur by gravimetric method* (2009).
14. EN 933-1:1997: *Tests for geometrical properties of aggregates. Determination of particle size distribution. Sieving method* (1997).
15. EN 196-1: *Methods of testing cement – Part 1: Determination of strength* (2016).
16. EN 1015-6: *Methods of test for mortar for masonry – Part 6: Determination of dry bulk density of hardened mortar* (2017).
17. ČSN EN 12457-4: *Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges* (2003).
18. Mirzahosseini M., Riding K. A.: Cem. Concr. Compos. *56*, 95 (2015).
19. Šauman Z.: *Maltoviny I*, p. 198, VUT v Brně, 1993.
20. Young K. Ch., Sang H. J., Young Ch. Ch.: Constr. Build. Mater. *204*, 255 (2019).
21. Özer S., İlhami D.: Cem. Concr. Compos. *96*, 266 (2019).
22. Giergiczny Z.: Cem. Concr. Res. *124*, 124 (2019).

## Správková malta využívající vedlejší produkt a krystalizační přísadu

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### *Souhrn*

*Článek se zabývá možností využití druhotné suroviny, konkrétně popílku pocházejícího ze skládky, kde byl ukládán po dobu několika let. Tento popílek je vedlejším produktem uhelné elektrárny na Maltě a k jeho skládkování byly vyhrazeny nepoužívané lomy v místě Bengħisa. Popílek uložený v lomech je považován za nebezpečí pro životní prostředí. Výzkum se zaměřuje na potenciální využití popílku za účelem výroby materiálů na bázi cementu, a to zejména správkových malt.*

*V článku je představen návrh a testování správkových malt, ve kterých se popílek používá jako náhrada cementu. Pro zlepšení odolnosti vyvinuté správkové malty vůči povětrnostním podmínkám byl posuzován také vliv přídavku krystalizační přísady. Stabilizace popílku ve směsi byla ověřována posouzením fyzikálně-mechanických vlastností a sledováním mikrostruktury správkové malty pomocí elektronového mikroskopu.*

***Keywords:*** *Popílek, správkové malty, sekundární krystalizace, stabilizace.*

# Properties of Czech deposited high temperature fly ash

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## Abstract

*Fly ash, a by-product of coal combustion in coal-fired power plants, is a valuable raw material used in construction industry. At present, the combustion technology is gradually declining and the question arises as to whether it will be possible to use high temperature fly ash from stockpiles in the future. The aim of this work was to compare the properties of stockpiled high temperature fly ash (agglomerates) with fresh high temperature fly ash from the power plant Mělník (CZ). Laboratory tests were conducted to determine chemical and mineralogy composition, loss on ignition, changes in morphology, densities (particle, freely settled bulk and tapped), fineness, natural moisture content, standard consistency, setting times, soundness and strength activity index. Agglomerates from the surface layer of the stockpile Panský les (CZ) less than four months old had similar chemical properties as fresh high temperature fly ash. The behavior of agglomerates with cement slurries and mortars achieve the standard requirements for fly ash for concrete. Therefore, it would be possible to use the stockpiled high temperature fly ash for the same purposes as the fresh high temperature fly ash.*

**Keywords:** *High temperature fly ash, Stockpile, Deposited high temperature fly ash, agglomerates.*

## Introduction

Many countries use coal-fired power plants as a source of energy and heat. By-products of burning coal are fly ash, bottom ash and slag. The properties of these by-products depend mainly on the type and source of coal and type of burning process. The high variability of chemical-mineralogical properties, grain composition and the content of combustible carbon is the cause of their small use. However, the volume of these by-products produced all over the world is huge and large amounts are stored in stockpiles or lagoons[1, 2]. In 2016, the European (EU-15) power plants produced totals 40 million tons of coal combustion products. In the calculation for the European (EU-28) power plants produced totals more than 105 million tons[3]. They are several applications for fly ash (63.8% of total production of coal combustion products[3]) based on requirements in standard methods and national legislation (Table 1)[4–8]. At present, there is a gradual decline in combustion technology and the European Union is interested in recycling and reuse of stored by-products[1, 2]. Is a big question if it will be possible to use these deposit resources as fresh. Many researchers try to found ways how should deposited fly ash be used effectively[9–16]. Deposited fly ashes could be used in construction industry as part of the concrete[12–15], for road base course construction[13], controlled low strength material[14], lime-soil stabilization[15] and as part of the bricks[15, 16].

This work compare properties of deposited high temperature fly ash (agglomerates) with fresh high temperature fly ash from power plant Mělník (CEZ production facilities, Czech Republic). Power plant Mělník consists of three technological units built up gradually in the 1960s and 1970s as a complex of condensing power plants burning brown coal from North and West Bohemia mines. Only 10 – 15% of produced high temperature fly ash is sold. The remaining 80–90% of the high temperature fly ash is stored in the nearby stockpile Panský les[17] (CEZ production facilities, Czech Republic). Our goal was to find out if we have a valuable raw material for use in the construction industry from the stockpile Panský les.

***Table 1: Standards ČSN EN 450-1 specifications[6].***

| **Property** | **Limits** |
|---|---|
| loss on ignition | category A ≤ 5.0%; category B ≤ 7.0%; category C ≤ 9.0% |
| chloride $Cl^-$ content | ≤ 0.10% |
| sulphate content | ≤ 3.0% |
| free CaO | ≤ 1.5% |
| active CaO | ≤ 10.0% |
| active $SiO_2$ | ≥ 25.0% |
| total $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ content | ≥ 70.0% |
| total alkali content | ≤ 5.0% |
| MgO | ≤ 4.0% |
| activity index | ≥ 75.0% for 28 days, ≥ 85.0% for 90 days |
| soundness | ≤ 10 mm |
| particle density | ± 200 $kg/m^3$ |
| initial setting time | ≤ 200% of reference cement |

## Experimental

### *Materials*

We used tree fly ashes from the power plant Mělník (Czech Republic). One of them was freshly produced high temperature fly ash. The other two were agglomerates collected from the surface layer of the stockpile Panský les (Czech Republic), which were stored for four months or one day before sampling. The agglomerate is a mixture of freshly produced high temperature fly ash, Elbe water and a small fraction of slag. The compared freshly produced high temperature fly ash was not prepared as an agglomerate. Portland cement CEM I 42.5 R (Mokrá, Czech Republic)[18] was used as a reference cement.

### *Methods*

The chemical composition of fresh and stockpiled fly ashes were determined by X-ray fluorescence (XRF). A spectrometer ARL 9400 XP (Thermo ARL, Switzerland) was used for oxide analysis using software Uniquant 4. The mineral phases of fresh and stockpiled fly ashes were determined by X-ray diffraction (XRD). XRD data were collected using a PANanalytical X'Pert3 Powder diffractometer (PANanalytical, Holland) with parafocusing Bragg-Brentano geometry using Cu Kα radiation. An ultrafast PIXCEL detector was used to collect XRD data at an angular range of 5 to 90° (2θ) with a step size of 0.013° 2θ and a 180 s/step counting time. The definite amount of ZnO was used as an internal standard for the determination of amorphous content by the Rietveld method. The data were evaluated using the HighScore Plus V4.6 software package with the PDF4+ database. A representative sample (about 100 g) of material was taken for both X-ray measurement. The samples were subsequently homogenized in a laboratory vibration mill BVM – 2 (BRIO Hranice, s. r. o., Czech Republic).

The standard ČSN 72 0103[19] method was used to measure the loss on ignition, which was determined as constant weight loss at 1 100 °C.

The fly ashes morphology were studied using a scanning electron microscope EVO LS 10 (Zeiss, Germany). A laser-light scattering analyser Mastersizer 2000 MU (Malvern Instruments Ltd., UK) was used to determine the particle size distribution dispersed in isopropyl alcohol.

The standard ČSN 72 2071[4] method was used for the determination of particle density, freely settled bulk density, tapped density, fineness and natural moisture content in fly ashes. The particle density was based on the determination of the specific gravity of the samples by the pycnometric method. The freely settled bulk density was determined by pouring the material into a container with defined volume. Then, after tapping the container, the tapped density of the material was determined. The fineness was determined by the air permeability method, the Blaine method, which is measured as a specific surface. The natural moisture content was determined as constant weight loss during drying at 110 °C.

The standard ČSN EN 196-3[20] method was used for the determination of standard consistency, setting times and soundness of slurries. For the individual tests, different compositions of mixtures are specified according to the requirements of the standards[4, 6, 20]. The standard consistency and setting times were measured for slurries containing 25% of dry fly ash and 7 5% of reference cement. Both methods were tested immediately after mixing with a manual Vicat Apparatus – the plunger was used to measure standard consistency and the initial set needle with the final setting needle to determine the setting times. The soundness was measure for slurries containing 30% of dry fly ash and 70% of reference cement[6] according to the Le Chatelier method. The strength activity index was determined by measuring the compressive strength of mortars at ages of 28 and 90 days[4, 6, 21]. The mortars were prepared according to the standards ČSN 72 2071[4] and ČSN EN 196-1[21] by mixing powders (25% dry fly ash, 75% cement[4]) and silica sand with continuing grainsize [21] with binder-to-sand weight ratio 1 : 3 and water-to-binder ratio of 0.5[21]. Immediately after mixing were prepared specimen in size of 40×40×160 mm. The moulds were vibrated for 2 min. Mortars solidified and stored in a humidity chamber at 95% relative air humidity and 20 ± 2 °C. The compressive strength of mortars was determined on a compression-testing machine Werkstoffprüfmaschinen 267/56/17 (Leipzig GmbH, Germany) on a nominal area 40×40 mm.

## Results and discussion

### *Characterization of fly ashes*

Agglomerates from the surface layer of the stockpile less than four months old were a similar chemical composition as fresh high temperature fly ash (Table 2). All requirements for the chemical composition of fly ash have been achieved (Table 1)[6]. The differences between the oxide composition of the agglomerates and the fresh fly ash were negligible. The slag has a similar oxide composition to that of fly ash. Thus, the chemical differences were not detectable by XRF. The presence of slag in agglomerates shows the results from XRD. Cristobalite, a high-temperature form of silica, that does not commonly occurred in fly ash. In addition, the other mineral phases of the agglomerates from the surface layer of the stockpile were unchanged compared to the fresh high temperature fly ash (Table 3). All ashes were classified as category A[6] by loss on ignition (Table 2), the mass loss were below 5.0%.

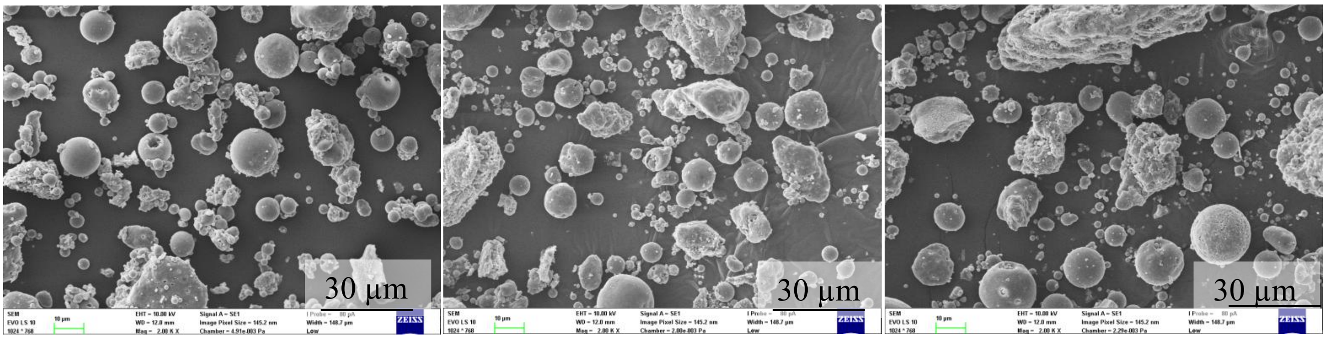
***Table 2: Selected results from XRF converted to oxides and loss on ignition of the high temperature fly ashes.***

| **Fly ash** | **$Al_2O_3$** | **$SiO_2$** | **$Fe_2O_3$** | **CaO** | **$TiO_2$** | **$SO_3$** | **$K_2O$** | **$Na_2O$** | **MgO** | **Loss on ignition [%]** |
|---|---|---|---|---|---|---|---|---|---|---|
| fresh | 34.5 | 47.5 | 7.6 | 1.9 | 3.1 | 0.5 | 1.2 | 0.5 | 1.0 | 1.5 ± 0.0 |
| 1 day | 34.5 | 47.1 | 7.5 | 1.8 | 2.8 | 0.6 | 1.2 | 0.4 | 0.9 | 2.5 ± 0.4 |
| 4 months | 35.3 | 47.6 | 7.0 | 1.6 | 3.3 | 0.3 | 1.1 | 0.4 | 0.9 | 1.9 ± 0.2 |

***Table 3: Results from XRD of the high temperature fly ashes. The symbol × indicates that the mineral phase has not been detected.***

| **Fly Ash** | **Amorphous** | **Mullite** | **Quartz** | **Cristobalite** | **Magnetite** | **Anatase** | **Rutile** | **Hematite** |
|---|---|---|---|---|---|---|---|---|
| fresh | 53.7 | 34.6 | 6.9 | × | 2.1 | 0.6 | 0.8 | 1.3 |
| 1 day | 54.7 | 34.8 | 5.6 | 0.9 | 1.8 | 0.5 | 0.5 | 1.1 |
| 4 months | 53.2 | 37.3 | 5.3 | 0.8 | 1.6 | 0.4 | 0.5 | 0.9 |

The four months storage of agglomerates does not change the morphology of the fly ash particles. Changes in surface morphology between fresh and deposited fly ash have been studied by Mahlaba et al.[9] and Eze et al.[11]. They reported that changes occurred by leaching or by the presence of secondary mineral phases. In our case, the chemical composition and the mineral phases of the stockpiled fly ash did not change during storage, so that the typical rounded shapes, cenospheres, can be seen in all three images (Figure 1). The fly ashes are mainly made up of spherical particles such as cenospheres, plerospheres and spheroids[1, 9, 22]. These spherical particles were sintered from the melted mineral constituents of coal. Small irregular shapes were unsintered parts of coal. Larger irregular porous shapes in agglomerates images were slag particles (Figure 1b – 1c).



***(a)*** ***(b)*** ***(c)***

***Figure 1: SEM images of (a) the fresh high temperature fly ash, (b) 1 day and (c) 4 months stockpiled high temperature fly ash in form of agglomerate.***

Three different types of densities were measured. The particle densities of the agglomerates measured by the pycnometers were only 1.5% lower than the fresh high temperature fly ash. The freely settled bulk densities of the agglomerates were slightly higher than 1 000 kg/m$^3$, which was 19.5% higher than the fresh high temperature fly ash. After mechanically tapping of the container containing the powder sample, the tapped density increased by 14% for aggregates and 17% for fresh high temperature fly ash (Table 4). The results of all three densities suggest that the fresh high temperature fly ash is slightly finer than the agglomerates. As expected, the presence of slag in the agglomerate increased the densities[22]. The specific surface of the fresh high temperature fly ash was 268 m$^2$/kg, which were 24 or 32 m$^2$/kg higher than the agglomerates 1 day or 4 months on stockpile. This is in agreement with the densities and particle size. The agglomerate particles were larger than the fresh high temperature fly ash (Table 4, Figure 2). Similar conclusions came from other authors[9, 11, 15, 16, 22]. The agglomerates were 3.3 times higher natural moisture than the fresh high temperature fly ash (Table 4). Both, the particles size and natural moisture content, were influenced by the addition of slag and water to the high temperature fly ash. The agglomerates from the surface layer of the stockpile less than four months old had similar input properties to the fresh high temperature fly ash.

***Table 4: Result from densities, specific surface, moisture and $d_{50}$ of the high temperature fly ashes.***

| **Fly ash** | **Particle density [kg/m$^3$]** | **Bulk density [kg/m$^3$]** | **Tapped density [kg/m$^3$]** | **Specific surface [m$^2$/kg]** | **Moisture [%]** | **$D_{50}$ [µm]** |
|---|---|---|---|---|---|---|
| fresh | 2 156 ± 7 | 860 ± 2 | 1 002 ± 3 | 268 ± 2 | 6.0 ± 0.1 | 39 |
| 1 day | 2 131 ± 7 | 1 020 ± 2 | 1 151 ± 2 | 244 ± 2 | 20.5 ± 0.2 | 58 |
| 4 months | 2 131 ± 4 | 1 035 ± 3 | 1 194 ± 1 | 236 ± 2 | 19.2 ± 1.0 | 70 |

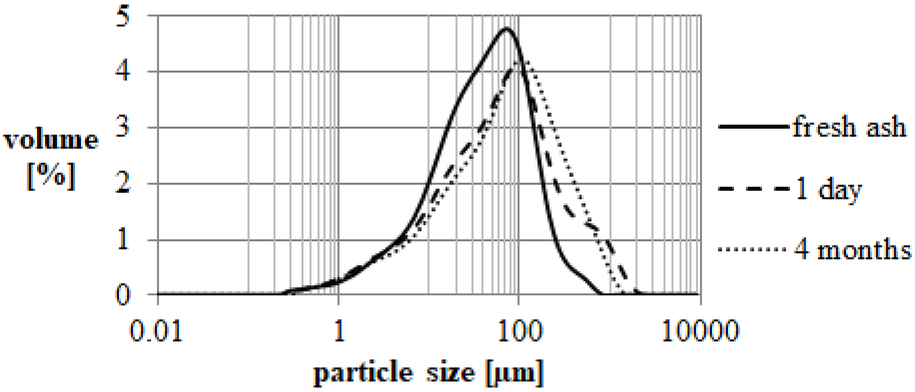


***Figure 2: Particle size distribution of the fresh high temperature fly ash (full line), 1 day (dashed line) and 4 months (dotted line) stockpiled high temperature fly ash in form of agglomerate.***

## *Physical properties*

For the standard consistency, where 25% of the cement was replaced by the high temperature fly ashes[6], the high temperature fly ashes required less water than agglomerated ones with stockpile time (Table 5). This can be due to the preparation of fly ash for stockpile and due to the effects of weathering during storage. The agglomerates have higher natural moisture than the fresh high temperature fly ash (Table 4). The soundness, where 30% of the cement was replaced by the high temperature fly ash[6], was worse with the stockpile time (Table 5) but still below the standard limit of 10 mm[6].

***Table 5: Standard consistency, soundness and the initial setting time of slurries where part of the cement was replaced by the high temperature fly ashes.***

| **slurry** | **standard consistency, w/b** | **soundness [mm]** | **initial setting time [min]** |
|---|---|---|---|
| CEM I 42.5 R | 0.30 | 0.05 | 170 |
| CEM I + fresh fly ash | 0.30 | 0.37 | 220 |
| CEM I + 1 day old fly ash | 0.29 | 0.67 | 210 |
| CEM I + 4 months old fly ash | 0.28 | 0.85 | 220 |

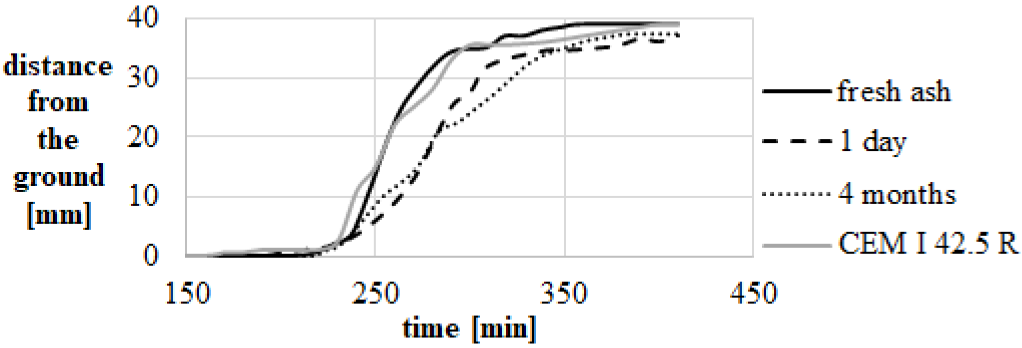


***Figure 3: The setting times of slurries where 25% of the cement was replaced by the high temperature fly ashes – fresh (black full line), 1 day (dashed line) and 4 months (dotted line) stockpiled high temperature fly ash in form of agglomerate and the reference cement CEM I 42.5 R (grey full line).***

The setting times of all three mixtures, where 25% of the cement was replaced by the high temperature fly ashes[4], were satisfactory (Table 5, Figure 3). The addition of the fly ashes prolong the initial setting times. The storage time does not play a significant role in the development of setting and hardening. An important parameter is the fineness of fly ash[23]. The initial setting times of the high temperature fly ashes were only about 130% of the reference cement. All setting times achieved the standard requirement that is no more than twice as long as for the reference cement.

The addition of the high temperature fly ash reduced the strength of the reference cement, where 25% of the cement was replaced by the high temperature fly ashes[6] (Table 6). The reduction was higher with stockpile time but the strength activity index of the hardened mortars were still sufficient[6].

***Table 6: Strengths and the strength activity index of hardened mortars where 25% of the cement was replaced by the high temperature fly ashes***.

| **Mortar** | **28 days** | | **90 days** | |
|---|---|---|---|---|
| | **compressive strength [MPa]** | **strength activity index [%]** | **compressive strength [MPa]** | **strength activity index [%]** |
| CEM I 42.5 R | 55.38 ± 1.79 | 100 | 60.50 ± 0.67 | 100 |
| CEM I + fresh fly ash | 46.88 ± 0.22 | 85 | 55.00 ± 0.88 | 91 |
| CEM I + 1 day old fly ash | 45.56 ± 0.18 | 82 | 54.04 ± 0.31 | 89 |
| CEM I + 4 months old fly ash | 45.12 ± 0.11 | 81 | 53.54 ± 0.33 | 88 |

## Conclusions

Less than four months old agglomerates from the stockpile Panský les had similar properties to the fresh high temperature fly ash. All measured properties of the agglomeretes achieved the standard requirements for the building industry purposes. Most of the difference was caused by preparation of the fly ash for storage. Thus, it would be possible to use the stockpiled agglomerates from the surface layers for the same purposes as the freshly produced high temperature fly ash.

This work serves as the basis for the subsequent study of the agglomerates from deeper layers of the stockpile Panský les.

## *Acknowledgment*

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## References

1. Robl T., Oberlink A., Jones R., Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation, 1st ed., Woodhead Publishing, 2017.
2. Fečko P., Popílky, Vysoká škola báňská-Technická univerzita, Ostrava, 2003.
3. ECOBA. CCPs Production <http://www.ecoba.com/ecobaccpprod.html> [accessed 13/03/19]
4. ČSN 72 2071 Fly ash for building industry purposes - Common provisions, requirements and test methods, Czech office for standards, metrology and testing, Prague (2011), 32 pp.
5. ČSN 72 2080 Fly ash and ash from fluidized bed combustion for building industry purposes - Common provisions, requirements and test methods, Czech office for standards, metrology and testing, Prague (2011), 36 pp.

6. ČSN EN 450-1 Fly ash for concrete - Part 1: Definition, specifications and conformity criteria, Czech office for standards, metrology and testing, Prague (2013), 28 pp.
7. ČSN 72 2072-1 Fly ash for building industry purposes – Part 1: Fly ash as an active component of binding materials, Czech office for standards, metrology and testing, Prague (2013), 12 pp.
8. ČSN EN 197-1 Cement – Part 1: Composition, specifications and conformity criteria for common cements, Czech office for standards, metrology and testing, Prague (2012), 36 pp.
9. Mahlaba J. S., Kearsley E. P., Kruger R. A., Physical, chemical and mineralogical characterisation of hydraulically disposed fine coal ash from SASOL Synfuels, Fuel 90 (2011) 2491 – 2500.
10. Akinyemi S. A. at all., Natural weathering in dry disposed ash dump Insight from chemical, mineralogical and geochemical analysis of fresh and unsaturated drilled cores, Journal of Environmental Management 102 (2012), 96 – 107.
11. Eze C. P. at all., Chemical, mineralogical and morphological changes in weathered coal fly ash: A case study of a brine impacted wet ash dump, Journal of Environmental Management 129 (2013), 479 – 492.
12. Carroll R. A., Coal Combustion Products in the United Kingdom and the Potential of Stockpile Ash, 6th World of Coal Ash Conference, Nasvhille, United States, 2015, 15 pp.
13. Mejeoumov G. G. at all., Beneficiation of stockpiled fluidized bed coal ash in road base course construction, Construction and Building Materials 24 (2010) 2072 – 2078.
14. Shon C-S. at all., Potential use of stockpiled circulating fluidized bed combustion ashes in controlled low strength material (CLSM) mixture, Construction and Building Materials 24 (2010) 839 – 847.
15. Jones M. R. at all., Experiences of Processing Fly Ashes Recovered from United Kingdom Stockpiles and Lagoons, their Characteristics and Potential End Uses, 3th World of Coal Ash Conference, Lexington, United States, 2009, 24 pp.
16. Shon C-S., Saylak D., Zollinger D. G., Potential use of stockpiled circulating fluidized bed combustion ashes in manufacturing compressed earth bricks, Construction and Building Materials 23 (2009) 2062 – 2071.
17. in PROJEKT LOUNY ENGINEERING s.r.o., Studie – Rekultivace odkaliště Panský les, 15-2112-01, 2015.
18. CEM I 42,5 R, Portlandský cement. Technický list, březen 2019. <https://www.heidelbergcement.cz/cs/cement/volne-lozeny-cement/cemi425r> [accessed 17/06/19]
19. ČSN 72 0103 Basic analysis of silicates - Determination of loss on ignition, Czech office for standards, metrology and testing, Prague (2009), 4 pp.
20. ČSN EN 196-3 Methods of testing cement - Part 3: Determination of setting times and soundness, Czech office for standards, metrology and testing, Prague (2017), 16 pp.
21. ČSN EN 196-1 Methods of testing cement – Part 1: Determination of strength, Czech office for standards, metrology and testing, Prague (2016), 32 pp.
22. Vassilev S. V., Vassileva C. G., Mineralogy of combustion wastes from coal-fired power stations, Fuel Processing Technology 47 (1996) 261 – 280.
23. Cheerarot R., Jaturapitakkul C., A study of disposed fly ash from landfill to replace Portland cement, Waste Management 24 (2004) 701 – 709.

# Vlastnosti českých deponovaných vysokoteplotních popílků

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## *Souhrn*

*Popílky, vedlejší produkty získávání energie ze spalování uhlí, jsou cennou surovinou používanou ve stavebnictví. V současné době dochází k postupnému ústupu technologie spalování a vzniká otázka, zda bude možné v budoucnosti využít dříve uložené vysokoteplotní popílky z elektrárenských deponií. Cílem práce bylo porovnat vlastnosti uložených vysokoteplotních popílků (aglomerátů) s čerstvým vysokoteplotním popílkem z elektrárny Mělník (CZ). Laboratorní testy byly provedeny za účelem stanovení chemického a mineralogického složení, ztráty žíháním, změn v morfologii, hustot (měrné, volně sypané a setřesné), jemnosti, přirozeného obsahu vlhkosti, standardní konzistence, doby tuhnutí a indexu účinnosti.*

*Zjistili jsme, že aglomeráty z povrchové vrstvy složiště Panský les (CZ) mladší než 4 měsíce měly podobné chemické složení jako čerstvý vysokoteplotní popílek. Chování aglomerátů v cementových kaších a maltách splňuje standardní požadavky na popílek pro betony. Proto by bylo možné uložené popílky z tohoto složiště používat ke stejným účelům jako čerstvé popílky.*

***Klíčová slova:*** *vysokoteplotní popílek, složiště, uložený vysokoteplotní popílek, aglomerát*

# Characterization of Czech coal combustion ashes and their hydrated products

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## Abstract

*Czech coal ashes and their hydrated products were characterized primary by X-ray diffraction analysis (XRD), followed by X-ray fluorescence analysis (XRF) and scanning electron microscopy (SEM). The aim of this paper was to determine the phase composition including an amorphous content in the selected pulverized coal combustion ashes (PCC FA), sulfocalcic ashes (SC ash, CFBC ash) and in hardened SC ash slurries. Amorphous phase was determined by the internal standard method using XRD. The phase composition of the slurries and its changes occurring during the time-dependent hydration were studied within 90 days. The results showed different phase composition of both types of ashes. It was found that the selected PCC ashes had about 55% of amorphous content and the SC ashes from 47 to 65%. The phase changes could be observed during the first 7 days of hydration by XRD analysis, then the phase composition remained practically constant until the observed 90 days. For the hydrated slurries, the amorphous content was time independent and ranged from 57 – 64%. Furthermore, it was found that the amount of ettringite and the amount of amorphous phase is affected by the amount of water; the higher the water to binder ration, the higher amount of the ettringite and the lower amount of the amorphous phase, respectively.*

***Keywords:*** *Coal combustion products, FBC ash, PCC fly ash, amorphous phase, XRD analysis, internal standard.*

## Introduction

Complete recycling of waste and its reuse is a big goal of the European Union nowadays. Great attention is paid to high-volume waste, including coal combustion products (CCPs) from coal power plants. The amount of the fly ash, bottom ash and slag represents a major environmental issue. It was estimated that the amount of produced CCPs was more than 105 million tons in Europe in the year 2012 (28 EU Member States)[1]. This large amount of CCPs is mostly deposited in the landfills, which results in considerable land occupation and other problems. PCC FA from high-temperature combustion can be used as a secondary raw material in cement pastes, mortars or concrete, which reduces the emission of $CO_2$. The use of SC ash from fluidized bed combustion is still questionable because of the high lime and calcium sulphate content[2,3]. SC ash has not been used yet in a wider range and mostly it is being deposited in the landfills. The phase composition of ashes firstly depends on the mineral matter in coal and on the type of coal combustion. The mineralogical composition of ashes is very diverse; the most important minerals are listed in Table 1. Czech brown coal contains mainly clay minerals followed by carbonate minerals and sulfide minerals[4].

Two types of the combustion process are the most widespread in the Czech power plants. The first type is pulverized-coal combustion (PCC) usually ranging between 1100 - 1700°C. The second, newer type of coal combustion is fluidized bed combustion (FBC) using much lower temperatures around

850°C. Due to the EU's requirements for reducing $SO_x$ and $NO_x$, desulphurization and denitrification processes play an important role in the ash phase composition. Desulfurization of coal flue gases in FBC boilers may take place directly in boilers in contrast to PCC process. An additive - the most commonly finely ground limestone, reacts with $SO_x$ to form anhydride AII in FBC boilers. The composition of PCC ash and SC ash is given in Table 1[5-8].

***Table 1. Main components of mineral matter from Czech coal mines (left); phase composition of fly ashes (right).***

| Group | Mineral | Formula |
|---|---|---|
| Clay minerals | kaolinite | $Al_2O_3.2SiO_2.2H_2O$ |
| | illite | $K_2O.2Al_2O_3.6SiO_2.2H_2O$ |
| | halloysite | $Al_2O_3.2SiO_2.4H_2O$ |
| | montmorilonite | $(Na,Ca)(Mg,Al)[(OH)_2Si_4O_{10}], 11H_2O$ |
| Carbonate minerals | calcite | $CaCO_3$ |
| | dolomite | $(Ca, Mg)(CO_3)_2$ |
| | siderite | $FeCO_3$ |
| | ankerite | $Ca, Mg, Fe, Mn (CO_3)$ |
| Sulfide minerals | pyrite, marcasite | $FeS_2$ |
| | pyrrhotine | $Fe_5S_6$-$Fe_{16}S_{17}$ |
| Sulfate minerals | gypsum | $CaSO_4.2H_2O$ |
| | | $MgSO_4$ |
| | | $Na_2SO_4$ |
| | | $FeSO_4.7H_2O$ |
| Oxide minerals | quartz | $SiO_2$ |
| | hematite | $Fe_2O_3$ |
| | magnetite | $Fe_3O_4$ |
| | rutile, anatase | $TiO_2$ |
| Others | chloride | NaCl, KCl |
| | orthoclase | $K, Al, Si_3O_8$ |

| SC (FBC) ash | PCC ash |
|---|---|
| Amorphous silicate and alumosilicate | Amorphous vitrious Si-Al phase |
| Anhydrite AII – $CaSO_4$ | mullite |
| Crystalline silicates and alumosilicates | Crystalline silicates and alumosilicates |
| Quartz | Quartz, cristobalite |
| Iron minerals (magnetite, hematite) | Iron minerals (magnetite, hematite) |
| Titanium minerals ($TiO_2$ - rutile, anatas) | Titanium minerals ($TiO_2$ - rutile, anatas) |
| Calcium compounds: CaO<br>Carbonates ($CaCO_3$ - calcite, vaterite)<br>$Ca(OH)_2$ - portlandite | Calcium compounds: Carbonates ($CaCO_3$ - calcite, vaterite)<br>CaO, $Ca (OH)_2$<br>$CaSO_4$ - anhydrite, basanite, gypsum |
| Accessory minerals:<br>Pericles – MgO, ettringite, hanebacit, thaumazite, etc. | Accessory minerals:<br>pyrit, ettringit, etc. |

The composition of an amorphous phase is different for both types of coal combustion ashes. Heating kaolinite clay minerals ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), dehydroxylation occurs above a temperature of 500 °C to produce metakaolinite ($Al_2O_3 \cdot 2SiO_2$), which is the major part of the amorphous content in SC ashes. Additional heating of metakaolinite above 1000 °C leads to the formation of mullite. This crystalline phase occurs in PCC ash. The main part of the amorphous content in PCC ash is a vitreous Si-Al phase[9].

Several authors deal with the hydration of SC ashes containing free lime and anhydrite AII[10,11,12]. These ashes have self-cementitious properties that means they harden with the water addition. Sheng et al.[13] showed, the cementing SC process was based on three main reactions: (1) generation of $Ca(OH)_2$ from lime, (2) generation of AFt phase - ettringite and (3) generation of amorphous CSH phase. The hydration process was studied for 7 days and a gypsum was found as a crystallization product obviously after 24 h along with ettringite. Ettringite appears after 12 h of hydration and gradually increases due to the reaction of $Ca(OH)_2$, anhydrite and active alumina. In addition Škvára et al.[9] showed, the presence of modified ettringite as well as an amorphouse CASH phase in which Al is incorporated in to the structure in comparison to CSH phase. Chen et al.[12] studied the development of hydration products of the mixtures consisted of OPC and SC ash within 180 days and they found ettringite and gypsum as the main crystalline hydration products.

In terms of qualitative and quantitative analysis of coal ashes, there are many methods for their characterization. The most important methods are X-ray fluorescence analysis (XRF) and X-ray diffraction analysis (XRD). Quantitative XRD analysis along with amorphous phase determination is usually performed by the internal standard method. This method has been used by many authors for the quantitative determination of PCC ashes[14-16]. Rutile ($TiO_2$), ZnO, $Al_2O_3$ and $CaF_2$ are the most commonly used standards. Homogenizing medium is ethanol or isopropanol.

The aim of this paper was to select a suitable standard for XRD analysis of the Czech brown coal ashes and their hardened slurries and to determine an amorphous and crystalline content in PCC and SC ashes. In addition, the crystalline and amorphous phases occurring during the hydration process were studied and quantified.

## Experimental part

Czech coal ashes from pulverized coal combustion (PCC ash) and fluidized bed coal combustion (SC ash) were studied in this work. Ashes were characterized primarily by XRD, followed by XRF and SEM.

### *SC and PCC ashes*

Elemental composition of PCC ashes from a locality 1 and 2 and SC ashes from a locality 3, 4, 5 and 6 calculated as oxides were determined by XRF analysis. Table 2 shows the composition of ashes from these six locations in the Czech Republic. The ashes were always taken as fresh samples from the coal power plant except the ash PCC ash 1S. This ash was taken from the ash landfill from a depth of 3 – 5 m from the locality 1. In addition, there is an elemental composition of the SC ash 3 for 4 different sampling times; year 2017 (3A), 2018 (3B, 3C) and 2019 (3D).

***Table 2: Composition of ashes by XRF analysis.***

| | $SiO_2$ | $Al_2O_3$ | CaO | $SO_3$ | $Fe_2O_3$ | $TiO_2$ | $Na_2O+K_2O$ | Others | LOI* |
|---|---|---|---|---|---|---|---|---|---|
| **PCC ash 1** | 47.5 | 34.5 | 1.9 | 0.5 | 7.6 | 3.1 | 1.7 | 1.7 | 1.5 |
| **PCC ash 2** | 43.1 | 34.9 | 1.8 | 0.0 | 5.1 | 9.2 | 1.1 | 2.4 | 2.6 |
| **PCC ash 1S** | 49.6 | 33.8 | 1.8 | 0.0 | 7.2 | 2.2 | 1.7 | 1.9 | 1.8 |

| | $SiO_2$ | $Al_2O_3$ | CaO | $SO_3$ | $Fe_2O_3$ | $TiO_2$ | $Na_2O+K_2O$ | Others | LOI* |
|---|---|---|---|---|---|---|---|---|---|
| **SC ash 3** | 35.4 | 27.2 | 17.2 | 6.3 | 4.5 | 2.3 | 1.3 | 0.2 | 5.6 |
| **SC ash 4** | 28.2 | 22.9 | 20.0 | 8.5 | 6.7 | 4.2 | 1.2 | 1.2 | 7.3 |
| **SC ash 5** | 38.9 | 27.3 | 10.3 | 6.2 | 3.4 | 1.7 | 1.1 | 1.1 | 10 |
| **SC ash 6** | 38.0 | 19.7 | 15.7 | 8.3 | 4.5 | 0.8 | 3.8 | 1.3 | 8 |

| | $SiO_2$ | $Al_2O_3$ | CaO | $SO_3$ | $Fe_2O_3$ | $TiO_2$ | $Na_2O+K_2O$ | Others | LOI* |
|---|---|---|---|---|---|---|---|---|---|
| **SC ash 3A** | 35.4 | 27.2 | 17.2 | 6.3 | 4.5 | 2.3 | 1.3 | 0.2 | 5.6 |
| **SC ash 3B** | 32.9 | 25.9 | 18.8 | 8.3 | 4.4 | 2.4 | 0.7 | 1.1 | 5.5 |
| **SC ash 3C** | 33.7 | 25.0 | 18.8 | 7.6 | 5.7 | 2.0 | 0.8 | 1.2 | 5.2 |
| **SC ash 3D** | 32.6 | 24.8 | 20.4 | 8.0 | 4.8 | 2.3 | 0.7 | 1.1 | 5.3 |

**LOI according to ČSN 72 0103*

All ashes were mechanically treated to obtain the similar granulometry curves, d50 for the ashes was in the interval d50 = 11 – 21 µm.

The ashes for XRD phase analysis were weighted and mixed with standard (ZnO, 7.5 mass %). The mixture was homogenized using isopropanol in an agate mortar for 10 min. Three diffractograms were evaluated for each sample and the average phase values for a given location and time are presented below.

The diffraction patterns were collected at room temperature with an X'Pert$^3$ Powder θ-θ powder diffractometer with parafocusing Bragg-Brentano geometry using Cu Kα radiation (λ = 1.5418 Å, Ni filter, generator setting: 40 kV, 30 mA). An ultrafast PIXCEL detector was employed to collect XRD data over the angular range from 5 to 90° (2θ) with a step size of 0.013° 2θ and a counting time of 180 s/step. The fixed divergence slit was used for the measurement. The back loading technique was used to eliminate preferred orientation.

The data were evaluated with software package HighScore Plus V4.6 (PANalytical, Almelo, Netherlands) and search-match performed in PDF4+ database containing 365.877 experimental and calculated cards. The qualitative and quantitative phase analyses were done. The Rietveld method was used to calculate mass content for present crystalline phases and amorphous phase.

ARL 9400 XP sequential WD-XRF spectrometer was used to perform XRF analysis. All peak intensity data were collected by software WinXRF in vacuum. The generator settings-collimator-crystal-detector combinations were optimized for all 82 measured elements with analysis time of 6s per element. The obtained data were evaluated by standardless software Uniquant 4. The analysed powders were pressed into pellets about 5mm thick and diameter of 40 mm and covered with 4 µm supporting polypropylene (PP) film. The time of measurement was about 15 min.

The morphology of powdered ashes and hydrated products (fracture surface) were studied using the SEM analysis with the aid of the scanning electron microscope Hitachi S 4700.

## *Hydrated slurries from SC ash*

Four ash slurries were prepared from the SC ash 3A, Table 3. The slurry I contained only SC ash and water with water to binder ratio 0.4. The slurry II, III and IV contained, in addition, a superplasticizer (SP) based on polycarboxylates, with the water to binder ratio 0.4, 0.3 and 0.36 respectively. The slurries were prepared in a standard mixer. After mixing, the slurries were immediately filled into 2 x 2 cm metal molds. Subsequently, these molds were placed into the BS VLH-203 Concrete System humidity chamber at the relative air humidity (RH) of 95% and 20 ± 2 °C. The slurries were unmolded after 24 hours, the samples were then placed back into the humidity chamber.

***Table 3: Composition of slurries I, II, III and IV, SP - superplasticizer.***

| | **w** | **SC ash 3A** | **SP** |
|---|---|---|---|
| **Slurry I** | 0.40 | x | |
| **Slurry II** | 0.40 | x | x |
| **Slurry III** | 0.30 | x | x |
| **Slurry IV** | 0.36 | x | x |

At precisely given intervals (1, 2, 3, 7, 14, 28, 56 and 90 days), XRD measurements were performed. The preparation and measurement of the slurries using XRD was similar to that of ash analysis. However, the slurries had to be crushed first, and then hydration was stopped with acetone. After the evaporation of acetone, the specimens were air dried at a temperature of 40 °C.

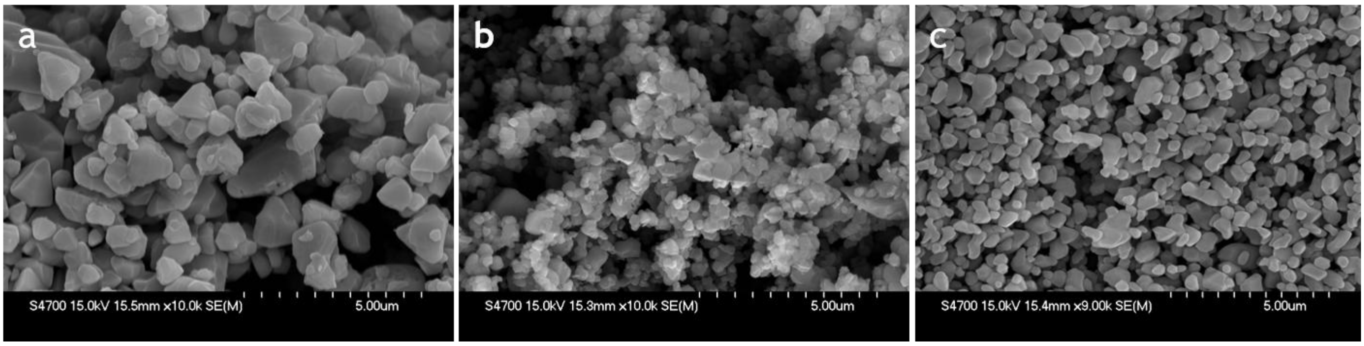
## Results and discussion

### *Standard for XRD analysis*

Zinc oxide (ZnO), rutile ($TiO_2$) and $CaF_2$ were considered as possible standards for XRD analysis. The most important criteria for the suitability of a standard are as follows:

- The standard must be fully crystalline or the amount of amorphous phase must be specified.
- The standard must not be present in the sample.
- The size and shape of the standard particles must be well defined, ideally spherical particles having the size comparable to the particles of the measured sample.
- The diffraction peaks of the standard must not overlap with those of phases present in the sample.

Figure 1 shows SEM images of the considered standards. The particles morphology of the individual standards does not differ significantly. Standards do not have a strictly spherical shape, but neither of them has a tabular or rod-like character of the particles. Concerning particle size, the smallest are $TiO_2$ particles, the largest are ZnO particles. In terms of the morphology, ZnO standard was chosen as the most suitable as the size of its particles is comparable to the particles of the analyzed ashes.



(a) (b) (c)

***Figure 1: SEM images of standards for XRD analysis: ZnO (a), $TiO_2$ (b), $CaF_2$ (c).***

The XRF analysis showed that some of the ashes contain $TiO_2$. The XRD analysis showed the possibility of $TiO_2$ presence in rutile modification. Therefore, rutile is not a suitable standard for XRD analysis for the Czech ashes.

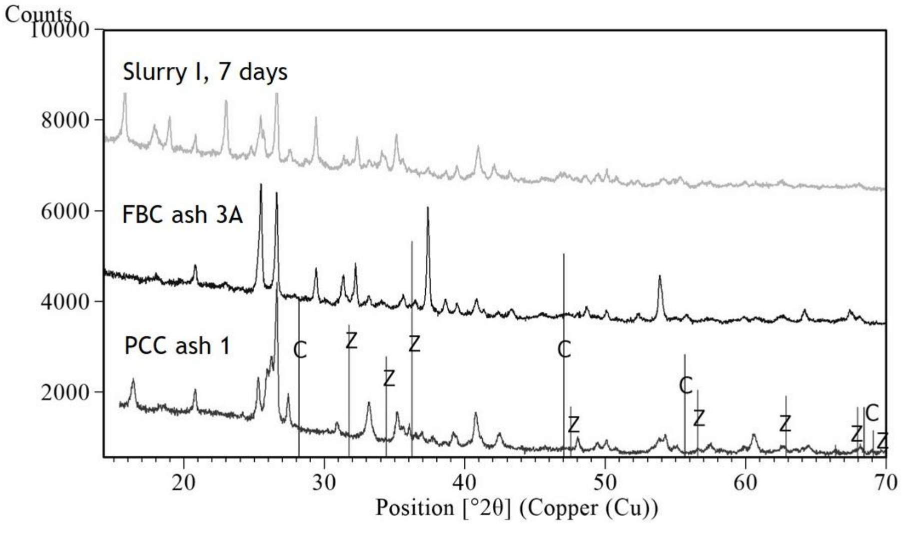


***Figure 2: Comparison of diffraction lines for standards ZnO (Z) and $CaF_2$ (C) with powder patterns for the PCC fly ash, SC ash and the hardened slurry.***

Figure 2 shows diffraction lines for ZnO and $CaF_2$ standards and powder patterns for PCC fly ash 1, SC ash 3A and the hardened slurry prepared from SC ash 3A (the slurry I, 7 days hydration). It is clearly seen that the diffraction lines for both standards have got negligible overlaps with ash lines and therefore ZnO and $CaF_2$ are suitable as internal standards. This conclusion is in a good agreement with the literature data. The powder patterns of hardened slurries have more diffraction lines (contain more crystalline phases) compared to ashes and the overlaps among the slurry and standard lines become more serious. ZnO as a standard seems to be more suitable than $CaF_2$ because of a higher number of non-overlaped diffraction lines.

## SC and PCC ashes

Phase composition of ashes was determined by XRD including three measurements for each sample at a given location at the same time. The phase composition of ashes for each location did not change significantly. In addition, for the SC ash 3, the composition was also monitored within the time of 2 years (SC ash 3A, 3B, 3C, 3D). The Rietveld method was used to quantify crystalline phases and an amorphous content. The results are presented in Table 4.

***Table 4. Composition of ashes by XRD quantitative phase analysis (wt. %) of selected PCC and SC ashes, * the phase is below 1%.***

| | Amorph. | mullit | $SiO_2$ | $Fe_2O_3$ | $Fe_3O_4$ | anatas | rutil | Rw |
|---|---|---|---|---|---|---|---|---|
| PCC ash 1 | 55 | 33 | 7 | 2 | 2 | * | * | 2.1 |
| PCC ash 2 | 56 | 26 | 12 | * | 2 | 2 | * | 4.0 |
| PCC ash 1S | 56 | 34 | 8 | * | 2 | * | * | 2.6 |

| | Amorph. | $SiO_2$ | Anhydrite | CaO | $Ca(OH)_2$ | $CaCO_3$ | $Fe_2O_3$ | $Fe_3O_4$ | anatas | Rw |
|---|---|---|---|---|---|---|---|---|---|---|
| SC ash 3 | 57 | 8 | 11 | 7 | * | 4 | * | * | * | 3.4 |
| SC ash 4 | 48 | 8 | 17 | 6 | 9 | * | 2 | 3 | 3 | 3.1 |
| SC ash 5 | 65 | 11 | 13 | 3 | 2 | * | * | * | * | 3.6 |
| SC ash 6 | 47 | 22 | 12 | 3 | * | 0 | * | * | 0 | 5.0 |

| | Amorph. | SiO2 | Anhydrite | CaO | $Ca(OH)_2$ | $CaCO_3$ | $Fe_2O_3$ | $Fe_3O_4$ | anatas | Rw |
|---|---|---|---|---|---|---|---|---|---|---|
| SC ash 3A | 57 | 8 | 11 | 7 | * | 4 | * | * | * | 3.4 |
| SC ash 3B | 53 | 8 | 15 | 5 | 6 | * | * | * | * | 3.3 |
| SC ash 3C | 54 | 8 | 14 | 6 | 5 | * | * | * | * | 3.6 |
| SC ash 3D | 53 | 8 | 14 | 6 | 6 | * | * | * | * | 3.5 |

Mullite and quartz are the main crystalline phases, while hematite, magnetite, anatas and rutile are the minor phases in PCC fly ashes. Anhydrite, quartz and lime are the main crystalline phases, while portlandite, calcite, hematite, magnetite and anatase are the minor phases in SC ashes. Phases such as muscovite, gehlenite, illite or anortite were also presented in some ash samples. Amorphous content calculated by Rietveld method was about 55% for the PCC fly ashes and in the range of 47 – 65% for the selected SC ashes. The SC ash 3A shows a higher content of calcite, which was likely caused by the reaction of portlandite with air $CO_2$. This was probably caused by poor sealing of the container during the sample collection. The weighted agreement indice-$R_{wp}$, was used to judge the quality of a Rietveld refinement and its value was lower than 4% for all evaluated samples.

Figure 3 shows SEM images of PCC and SC ashes. The morphology of both ashes is very different. PCC ash contains mostly spherical glassy particles whereas SC ash has the original coal morphology.

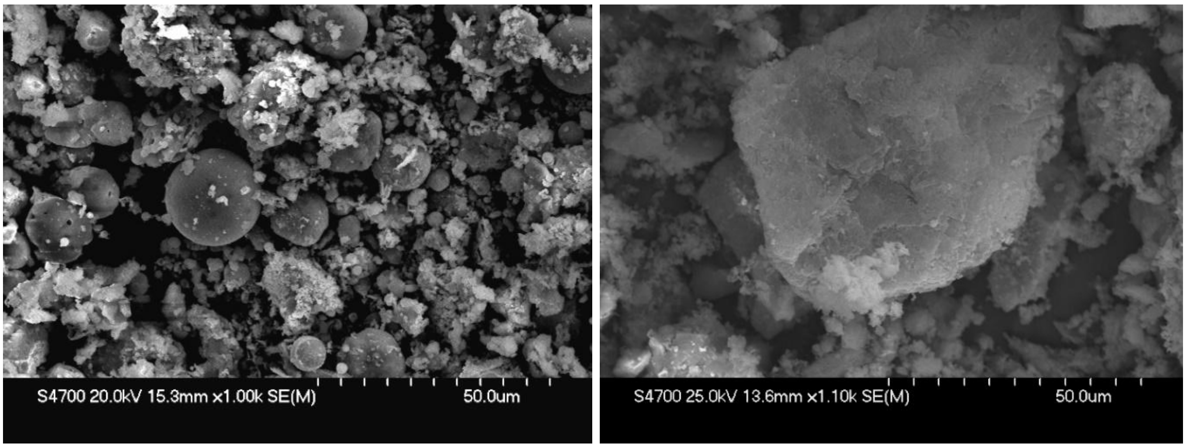


***Figure 3: SEM images of PCC fly ash 1 (left) and SC ash 3A (right).***

## *Hydrated slurries from SC ash*

SC ash 3A was used to prepare hardened slurries. Four slurries I, II, III and IV were prepared and crystallization kinetics of individual phases during hydration process was studied. Graphs on Figure 4 show changes of selected phases of the hardened slurries I, II, and III in time determined by the XRD analysis. The quantitative analysis was performed by the Rietveld method.

The content of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) increases with hydration time and between 3rd and 7th day stops at a constant value of 29(1)% in the slurry I, of 28(1)% in the slurry II, resp. 23(1)% in the slurry III. Simultaneously, the content of anhydrite decreases between 3rd and 7th day of hydration and finally anhydrite completely disappears in the sample I, resp. stops at a constant value of 1(0.5)% in the sample II and III. The content of portlandite decreases with time and after 14 days portlandite was not identified in the hardened slurry I and II and stops below 1% in the hardened slurry III. Quartz, hematite, magnetite and anatase do not participate in the hydration process. The content of the last three phases in hardened slurries is about 1%. The amount of quartz is about 6(1)% for all slurries and reminds practically unchanged. The content of $CaCO_3$ keeps unchanged in the range 4 – 5%. The amorphous content does not show changes at the time interval of 1 - 90 days and is about 57 – 60% for the slurries I and II, and 61 – 64% for the slurry III. There is no evident time dependence of an amorphous content on time. The hydration proceeds slower in the slurry III compared to the slurries I and II. The amount of ettringite is lower and the amount of anhydride is higher in the slurry III during the entire hydration period compared to the slurries I and II. The residua of anhydrite in the slurry III can cause volume instability of the mixtures as the residual anhydrite can react with the environmental moisture to the ettringite, which is accompanied by volume expansion. It could be concluded, the phase changes could be observed during the first 7 days of hydration by XRD analysis, then the phase composition remained practically constant until the observed 90 days.

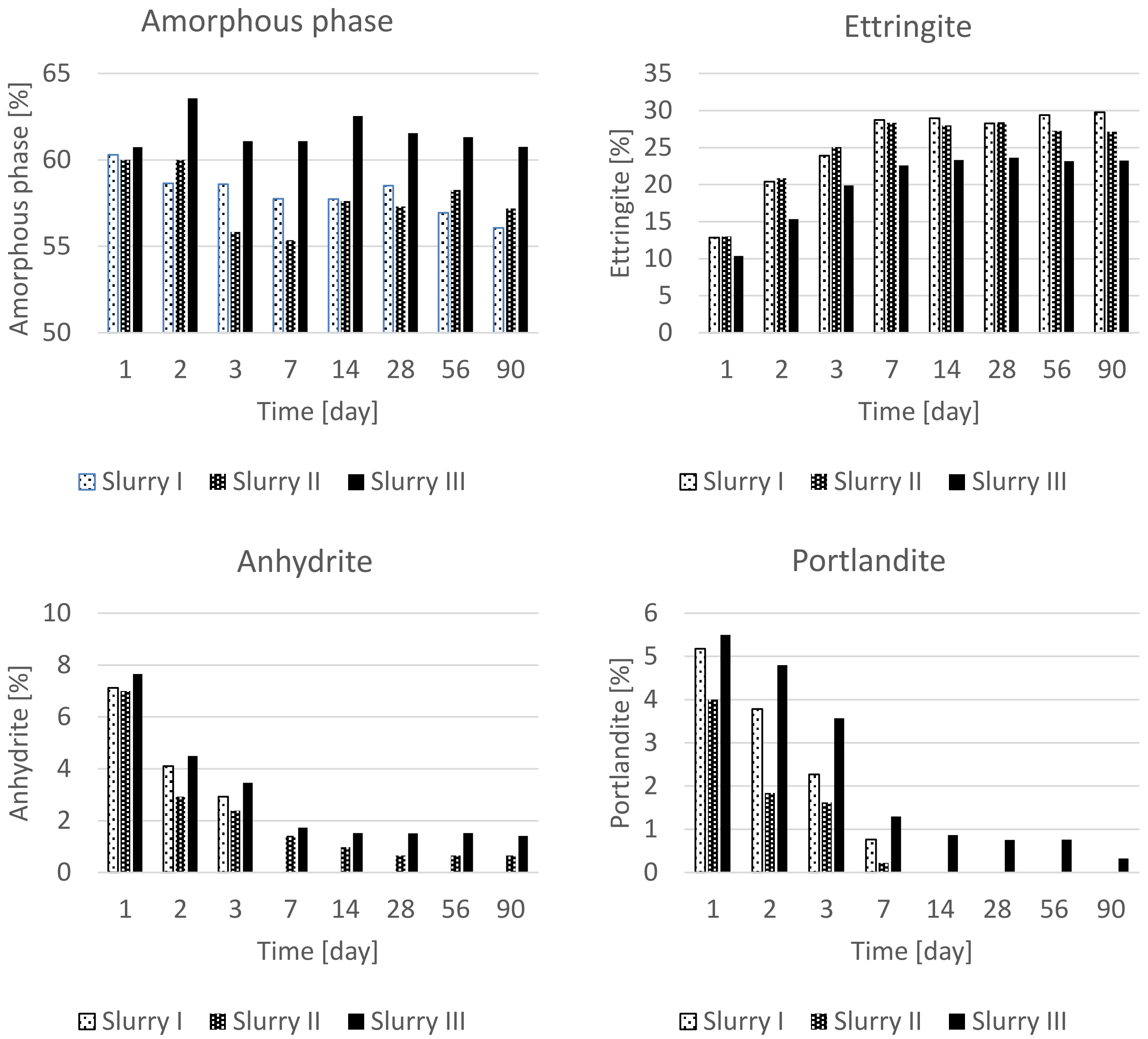


***Figure 4: Quantitative changes (wt. %) of selected phases of hardened slurries I, II and III by Rietveld method.***

Furthermore, it was found that the amount of ettringite and the amount of amorphous phase is affected by the amount of water, Figure 5. It can be clearly seen that the higher water to binder ration leads to the higher amount of ettringite and to lower amount of the amorphous phase, respectively. Comparing the amount of ettringite in the slurries I and II, which have the same water to binder ratio and the different amount of the superplasticizer, it can be assumed that the superplasticizer may affect the amount of the ettringite during hydration. Further experiments are needed to confirm the effect of the superplasticizer on the amount of ettringite by XRD.

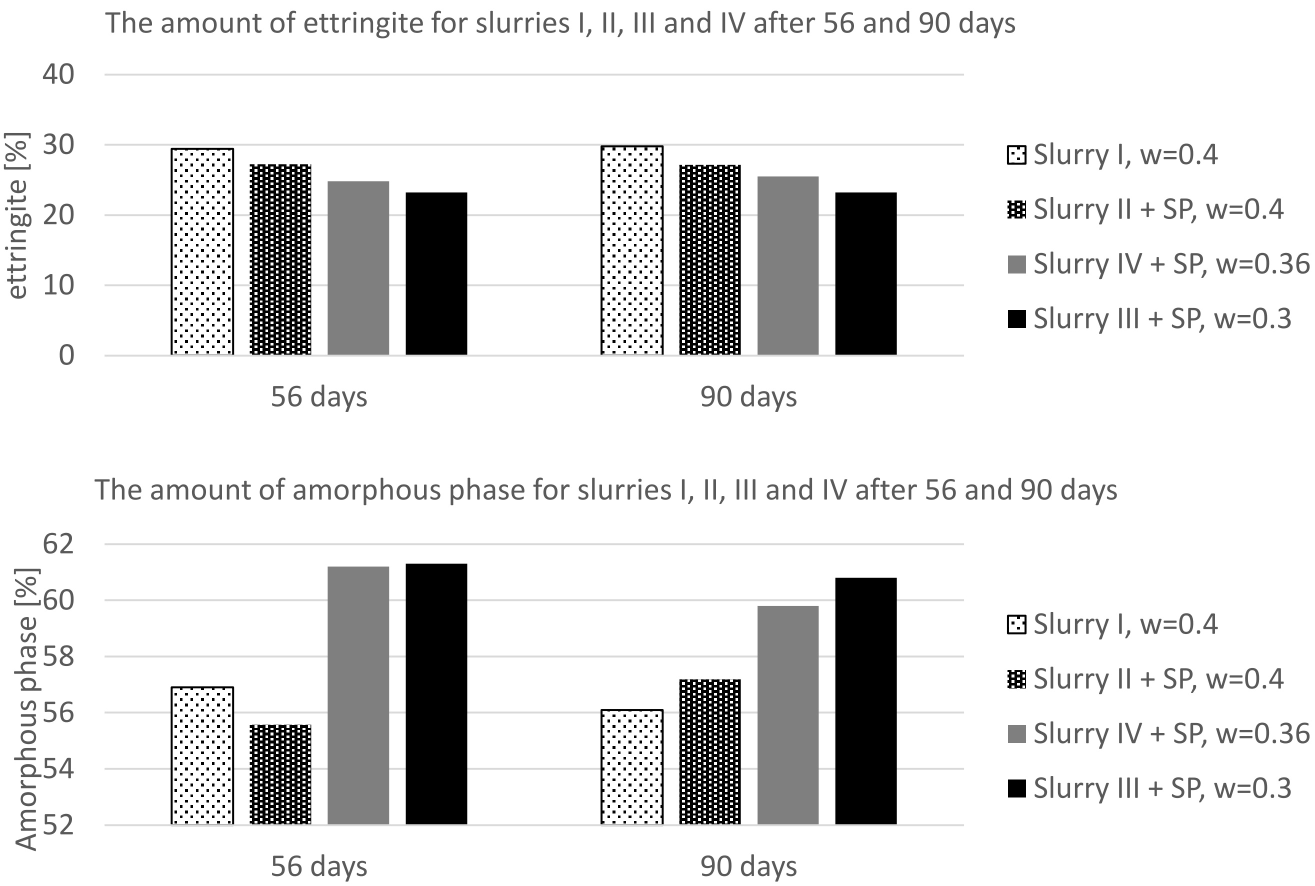


***Figure 5. The amount of ettringite and the amorphous phase for hardened slurries I, II, III and IV after 56 and 90 days of hydration by XRD analyses.***

Figure 6 shows SEM images of the fractured surface of hardened slurries I and III after 14 days. The ettringite particles are visible on both images. It was found that ettringite particles were presented in cracks (more evident in the slurry I) and in pores (more evident in the slurry III) where the ettringite particles had enough space to grow. It is a question if cracks occur due to volume expansion accompanying ettringite formation (for the slurry I), or whether ettringite grows predominantly at cracks. Homogeneous dispersion of ettringite needles in the hardened slurries was not observed.

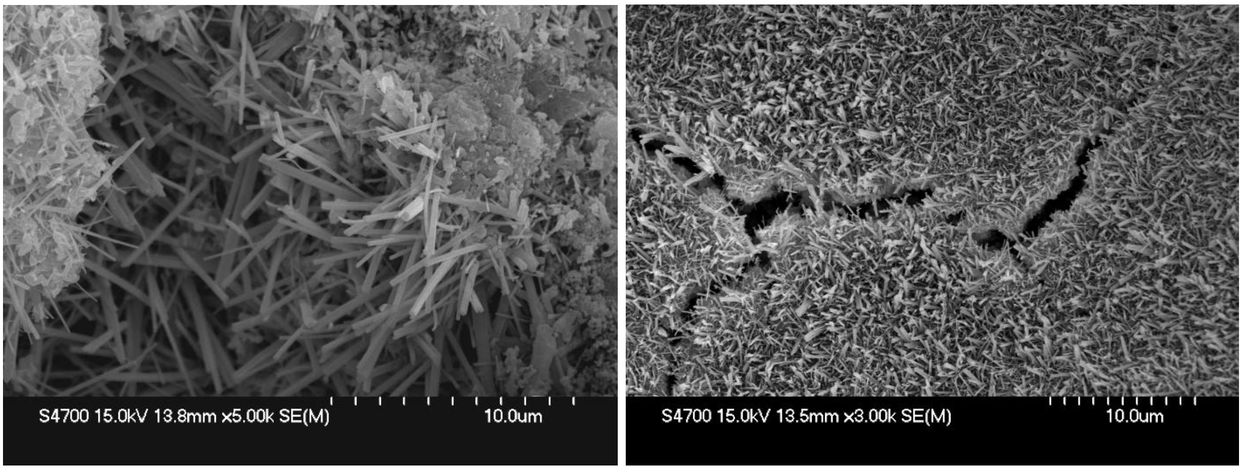


***Figure 6: SEM images of the fractured surface of the slurry I (left) and the slurry III (right) after 14 days of hydration.***

Previously, Škvára et al.[9] showed that binders with Czech SC ashes could be used in the building industry with respect to flexural strength and long-term volume stability (linear length change measurements). The present paper showed the phase changes during the hydration process of the SC ashes and confirmed the phase stability of the hardened slurries within 90 days; further, long-term monitoring of the phase composition stability will follow.

## Conclusions

The phase composition and the amorphous content of selected Czech brown coal ashes and their hydrated products was determined primary by the XRD quantitative analysis using the internal standard method. ZnO was chosen as the most suitable standard for the analyses. The Rietveld method was used for the data evaluation.

The results showed that the phase composition of ashes depends on the type of coal combustion process. The main crystalline phases were mullite and quartz in the PCC fly ashes and the anhydrite, lime, quartz, portlandite and calcite in the SC ashes. Iron and titanium-rich phases were also presented in both ashes followed by muscovite, gehlenite, illite or anortite in some ash samples. Amorphous content was about 55% for the PCC fly ashes and in the range of 47 – 65% for the selected SC ashes. Study of the hydration process of SC ashes by XRD showed that the phase changes could be observed during the first 7 days, then the phase composition remained practically constant until the observed 90 days. The amount of amorphous phase in hydrated slurries was time-independent. Furthermore, it was found that the amount of ettringite and the amount of amorphous phase is affected by the amount of water; the higher the water to binder ration, the higher amount of the ettringite and the lower amount of the amorphous phase, respectively.

This work is a part of a wider effort to find out possible utilization of SC ashes from the fluidized bed combustion process with limestone addition and reutilization of the PCC fly ashes from ash landfills.

## *Acknowledgment*

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## References

1. Robl T.; Oberlink A., Jones R., Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation, 1st ed., Woodhead Publishing, 2017.
2. Anthony E. J., Jia L., Burwell S. M., Najman J., Bulewicz E. M.: Understanding the behavior of calcium compounds in petroleum coke fluidized bed combustion (FBC) ash, J. Energy Resour. Technol. *128 (4),* 290 (2006).
3. Brandstetr J., Havlica J., Odler I., Properties and use of solid residue from fluidized bed coal combustion, Waste Materials Used in Concrete Manufacturing, William Andrew Publishing, Westwood, 1996, pp. 1 – 52.
4. Teyssler J.: Spalování popelnatých hnědých uhlí, Nakladatelství technické literatury, Prague, 1998, „in Czech“.
5. Fečko P.: Popílky, Vysoká škola báňská - Technická univerzita, Ostrava, 2003, „in Czech“.
6. Vávra V.: Kvantitativní fázová analýza ve směsích s obsahem elektrárenských popílků, Geologické výzkumy na Moravě a ve Slezsku, *5,* 115 (1998), „in Czech“.
7. Sulovský P., Vávra V.: Fázové složení popílků ze spalování ve fluidním loži, Geologické výzkumy na Moravě a ve Slezsku *4,* 123 (1997), „in Czech“.
8. Škvára F., Šulc R., Snop R., Zlámalová-Cílová Z., Peterová A., Kopecký L., Formáček P.: Czech fluid sulfocalcic fly ash, Ceram.-Silik. *60(4),* 344 (2016).

9. Škvára F., Šulc R., Snop R., Peterová A., Šídlová M.: Hydraulic clinkerless binder on the fluid sulfocalcic fly ash basis, Cement Concr. Compos. *93,* 118 (2018).
10. Li Xg., Chen Qb., Huang Kz., Ma Bg., Wu B.: Cementitious properties and hydration mechanism of circulating fluidized bed combustion (CFBC) desulfurization ashes, Construct. Build. Mater. *36* 182 (2012).
11. Hlaváček P., Šulc R., Šmilauer V., Roßler C., Snop R.: Ternary binder made of CFBC fly ash, conventional fly ash, and calcium hydroxide: Phase and strength evolution, Cement Concr. Compos. *90,* 100 (2018).
12. Chen X., Gao J., Yan Y., Liu Y.: Investigation of expansion properties of cement paste with circulating fluidized bed fly ash, Construct. Build. Mater. *157* 1154 (2017).
13. Sheng G, Li Q., Zhai J.: Investigation on the hydration of CFBC fly ash, Fuel *98* 61 (2012).
14. Chancey R. T., Stutzman P., Juenger M. C., Fowler D. W.: Comprehensive phase characterization of crystalline and amorphous phases of a Class F fly ash, Cem. Concr. Res. *40,* 146 (2010).
15. Winburn R. S., Lerach S. L., Jarabek B. R., Wisdom M. A., Grier D. G., McCarthy G. J.: International Centre for Diffraction Data *42,* 387 (2000).
16. Scrivener K., Snellings R., Lothenbach B.: A practical guide to microstructural analysis of cementitious materials, CRC Press, 2016.

# Charakterizace českých hnědouhelných popílků a jejich hydratačních produktů

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## *Souhrn*

*České popílky a jejich hydratované produkty byly charakterizovány primárně rentgenovou difrakční analýzou (XRD), dále pak rentgenovou fluorescenční analýzou (XRF) a skenovací elektronovou mikroskopií (SEM). Cílem práce bylo stanovit fázové složení, včetně amorfního podílu, u vybraných vysokoteplotních popílků (PCC FA), fluidních, resp. sulfáto-vápenatých popílků (SC) a zatvrdlých kaší připravených z SC popílku. Množství amorfní fáze bylo stanoveno metodou vnitřního standardu za použití XRD analýzy. Bylo studováno fázové složení zatvrdlých kaší v závislosti na době hydratace v horizontu 90 dní.*

*Výsledky ukázaly rozdílné fázové složení obou typů popílků. Amorfní podíl pro vysokoteplotní popílky byl kolem 55 %, pro fluidní popílky se pohyboval v rozmezí 47 – 65 %. Změny fázového složení během hydratace pomocí XRD analýzy bylo možno sledovat během prvních 7 dnů, pak zůstalo fázové složení prakticky konstantní až do sledovaných 90 dnů. Nebyla prokázána časová závislost množství amorfní fáze na čase. Dále bylo zjištěno, že množství ettringitu, resp. množství amorfní fáze je ovlivněno množstvím záměsové vody. S rostoucím vodním součinitelem kaší roste množství ettringitu, resp. klesá množství amorfní fáze.*

***Klíčová slova:*** *vedlejší energetické produkty, fluidní popílky, vysokoteplotní popílky, amorfní fáze, XRD analýza, vnitřní standard.*

# Prieskum a riešenie brownfields veľkého priemyselného areálu v Žiari nad Hronom

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## *Souhrn*

*Brownfields vznikajú ako vedľajší dôsledok priemyslovej alebo inej reštrukturalizácie využívaných území v ktorejkoľvek krajine a v ktoromkoľvek čase. Napriek tomu, že je táto téma z hľadiska existencie legislatívy na Slovensku relatívne nová, v priemyselnom areáli v Žiari nad Hronom a predovšetkým v samotnej spoločnosti ZSNP, a.s. bolo a je vysporadúvanie sa so starými environmentálnymi záťažami bežnou súčasťou fungovania podniku. Vďaka aktívnemu prístupu spoločnosti ZSNP, a.s., a dobrej spolupráci s orgánmi štátnej správy a samosprávy na úseku ochrany životného prostredia zaraďujeme dnes Žiarsku kotlinu medzi územia so slabým znečistením a nie medzi zaťažené územia, ako tomu bolo donedávna. Príspevok sa venuje komplexnému prieskumu a riešeniu brownfields veľkého priemyselného areálu v Žiari nad Hronom vrátane sanačných prác realizovaných v dotknutom priemyselnom areáli..*

***Klíčová slova:** brownfields, sanácie, priemyselné podniky.*

## Úvod

V súčasnosti sa do popredia čoraz viac dostáva problematika riešenia brownfields ako starých environmentálnych záťaží. Je to dané stavom životného prostredia a neustálou snahou o jeho zlepšenie. Nové využívanie brownfields vyžaduje významné finančné zdroje aj zo strany verejného sektora a doba nápravy môže trvať desaťročia[1].

Na Slovensku ale i vo svete existuje celý rad veľkých priemyselných areálov. Z pohľadu využívania ich môžeme rozdeliť nasledovne [1,2]:

- staré veľké nevyužívané a opustené priemyselné areály,
- staré veľké priemyselné areály, ktoré prechádzajú postupnou rekonštrukciou,
- nové veľké priemyselné areály.

Z pohľadu vzťahu k životnému prostrediu sú najproblematickejšími staré priemyselné areály. Väčšina z nich vznikala a bola prevádzkovaná v období, keď ešte nejestvoval potrebný legislatívny rámec zabezpečujúci ochranu životného prostredia, resp. len čerstvo vznikal. V súčasnosti je však nevyhnutné takéto areály prispôsobiť požiadavkám platnej legislatívy v oblasti ochrany životného prostredia, čo si vyžaduje nemalé finančné náklady. Mnohí investori preto radšej uprednostňujú investovanie na zelenej lúke, tzv. greenfields[3]. Toto je na úkor záberu kvalitnej poľnohospodárskej pôdy, pričom pôvodné priemyselné areály ostávajú opustené a bez náležitej starostlivosti.

Priemyselný areál v Žiari nad Hronom vznikal postupne od roku 1951. Vtedy boli vybudované prvé prevádzky, ktoré sa postupne rozrastali a zároveň pribúdali ďalšie, ktoré priamo alebo nepriamo súviseli s výrobou a spracovaním hliníka. Celý areál bol známy ako Závod slovenského národného povstania Žiar nad Hronom. Postupom rokov, predovšetkým v posledných 25 rokoch prešiel areál rozsiahlymi zmenami. V prvom rade to boli zmeny vlastníckych vzťahov a obchodných foriem až po konečné rozdelenie jedného veľkého podniku na niekoľko menších so strategickými investormi. Tak sa postupne z národného podniku Závod slovenského národného povstania stal ZSNP, a.s. s rozlohou 1 673 612 m$^2$. A pokiaľ v minulosti areál tvoril jeden podnik s jedným vedením a teda aj strategickými rozhodnutiami, v súčasnosti v areáli podniká takmer 50 spoločností. V rámci toho je nesmierne obťažne robiť akékoľvek spoločné rozhodnutia. Avšak riešenie environmentálnych problémov sa týkalo celého areálu a začalo sa s ním dávno pred rozdelením podniku.

Veľký priemyselný areál v Žiari nad Hronom patrí medzi staré priemyselné areály, ktoré prechádzajú postupnou rekonštrukciou, čím vznikajú priestory pre nové investičné akcie. V celom areáli prebehli rozsiahle prieskumy zamerané na kvalitu zložiek životného prostredia. Predovšetkým sa jednalo o prieskumy horninového prostredia a prieskumy a následné monitorovacie práce v oblasti kvality podzemných vôd. Na základe uvedených prieskumov boli identifikované kritické miesta areálu, ktoré bolo potrebné riešiť úpravami, revitalizáciou, prípadne sanáciou. Po realizácii takýchto zásahov bolo možné pokračovať vo výrobe produktov modernejším spôsobom, resp. tak vznikli priestory pre rozširovanie pôvodných prevádzok alebo priestory pre nových investorov, ktorí mohli začať podnikať v dotknutej priemyselnej zóne. Príspevok sa venuje komplexnému prieskumu a priebehu riešenia brownfields veľkého priemyselného areálu v Žiari nad Hronom vrátane sanačných prác realizovaných v dotknutom priemyselnom areáli počas 25 rokov.

## Materiál a metodika

Metodika výskumu vyplýva predovšetkým z platnej legislatívy upravujúcej problematiku sanácie environmentálnych záťaží.

Samotnou záujmovou lokalitou je priemyselný areál Žiar nad Hronom, ktorý bol v minulosti tvorený spoločnosťou ZSNP, a.s., prípadne jej dcérskymi spoločnosťami. Dnes v tejto priemyselnej zóne podniká zhruba 50 väčších či menších právnických subjektov. Ich zameranie je predovšetkým na výrobu a spracovanie hliníka, ale aj na obslužné činnosti súvisiace s výrobou a spracovaním hliníka (výroba a distribúcia rôznych druhov energií, strojárska výroba, stavebné činnosti a pod.).

## Výsledky a diskusia

Prieskum stavu životného prostredia v roku 1994 vykonali na základe požiadavky EBRD holandské spoločnosti IWACO B.V., DHV Consultant B.V[4] a slovenská spoločnosť GEOS, a.s.[5] Audit jednotlivých prevádzok vykonala rovnako holandská spoločnosť HASKONING. Celkovo bolo zo záujmového územia odobratých 70 vzoriek podzemných vôd a 60 vzoriek zemín. Kvalita vzoriek bola vyhodnocovaná na základe odporúčania bývalej Komisie pre životné prostredie, dnes Ministerstvo životného prostredia, ktoré stanovovalo parametre a normy pre sanáciu kontaminovaných pôd a podzemných vôd označené ako hodnoty A, B a C. V sledovaných vzorkách boli na rôznych lokalitách prekročené tieto ukazovatele: Cd, Mo, As, olej, F, PAU, VOX, BTX, benzo(a)pyrén, chryzén.

V rámci prieskumných prác bola celá záujmová lokalita rozdelená na nasledovné oblasti:

| | |
|---|---|
| A1 | Nová elektrolýza |
| A2 | Nová anodáreň |
| A3 | Nová odlievareň |
| B1 | Kysličnikáreň |
| B2 | Stará elektrolýza |
| B3 | Stará anodáreň |
| B4 | Stará odlievareň |
| B5 | Zlievarne |
| B6 | Povrchové úpravy |
| B7 | Tepláreň |

Prieskum firmy IWACO potvrdil, že na väčšine územia areálu je vrchná vrstva do hĺbky 0,5 až 1,0 m antropogénne porušená. Ďalej presne stanovil rozsah zisteného znečistenia. Rovnako bola za pomoci programu HESP určená aj miera zdravotných rizík z jednotlivých druhov znečistenia a dennej expozície pôsobeniu týchto faktorov.

Ďalší prieskum vykonávala firma Hydros[6], ktorá sledovala problematické vrty, ktoré v prvom cykle vzorkovania v roku 1994 určila firma IWACO ako problematické, to znamená, že niektorý zo sledovaných ukazovateľov dosahoval v rámci hodnotenia hodnotu B alebo vyššiu. Tieto ostali zaradené do ďalšieho monitoringu, ktorý bol realizovaný na vybraných pozorovacích objektoch jedenkrát za štvrťrok v období rokov 1995 až 1998.

V tomto období monitoringu sa preukázalo, že veľký rozsah a stupeň znečistenia podzemnej vody fluoridmi síce za štvorročné obdobie poklesol, ale i napriek tomu je zostatkové znečistenie presahujúce C limit značné. Taktiež sa preukázalo, že znečistenie podzemnej vody PAU pokleslo od roku 1994 natoľko, že v marci 1998 bolo možné podzemnú vodu považovať za nekontaminovanú týmto druhom znečistenia. Znečistenie podzemnej vody benzo(a)pyrénom sa znížilo účinkom likvidácie zdrojov znečistenia a autosanácie do takej úrovne, že v marci 1998 boli všetky hodnoty pod detekčným limitom použitého analytického laboratórneho prístroja.

Následne boli od roku 1999 do roku 2001 monitorovacie práce realizované na 12 vybraných monitorovacích objektoch. Vyhodnotenie analytických výsledkov uskutočnila v máji 2002 spoločnosť EnviGeo, s.r.o., Banská Bystrica[7]. Monitorovaním bolo zistené, že z monitorovacej siete sa môžu vylúčiť vrty, v ktorých koncentrácie fluoridov počas celého monitorovania v rokoch 1999 až 2001 dosahovali úroveň kategórie A. Bolo vypustené sledovanie POX, As, Mo a NEL v podzemnej vode. Ďalej sa sledovali iba koncentrácie fluoridov. Od roku 2002 sa teda pravidelne monitoruje lokalita na obsah fluoridov v podzemnej vode.

V roku 2003 realizovala spoločnosť GEOS, a.s., Bratislava geologický prieskum zameraný na znečistenie zemín v areáli spoločnosti SLOVALCO, a.s. a VUM. V rámci prieskumu odobrali a analyzovali 22 vzoriek. V ukazovateľoch As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sn, V, Zn, $CN^-$, EOX, PAU (BaP a chryzén) a NEL bolo celé územie v roku 2003 na hranici kategórie A, resp. B. a preto navrhli realizáciu sanácie kontaminovaných zemín a vypracovanie rizikovej analýzy.

Pri prevode niektorých častí výrobných oblastí si niektorí strategickí investori dali posúdiť stav kontaminácie podzemných vôd a horninového prostredia (environmentálny audit)[8]. Napríklad v júli 2001 vykonala spoločnosť HES-COMGEO, s.r.o., Banská Bystrica environmentálny audit[8] pre spoločnosť Rautenbach ZSNP, s.r.o. s cieľom zhodnotiť mieru znečistenia územia (pôda, podzemná voda) z hľadiska vplyvu na životné prostredie v širšom okolí a stanoviť primerané revitalizačné opatrenia. Prieskum bol realizovaný v oblasti B5 (na území zlievarní – dnešné územie spoločnosti NEMAK). V rámci prieskumu zhodnotili predchádzajúce výsledky prác a vybudovali 2 monitorovacie vrty do hĺbky 7,0 a 10,0 m a 10 vrtov na odber vzoriek zemín. Stanovili obsahy NEL, EOX, fenoly, As, Cd, Cr, Hg, Ni, Pb, F, Al v zeminách a NEL, EOX, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V, Zn, $NH_4$, B, F, CN a S v podzemnej vode. Kontaminácia podzemnej vody a zemín nebola zistená, sledované polutanty dosahovali koncentrácie, ktoré zodpovedajú fónovým obsahom.

V roku 2004 vykonala environmentálny audit v oblasti B6 (povrchové úpravy) – pri vstupe spoločnosti SAPA – spoločnosť Golder Associates, Turín, Taliansko[9]. Predmetom auditu bolo aj posúdenie stavu kontaminácie horninového prostredia a podzemnej vody. Spoločnosť zhodnotila stav daných zložiek životného prostredia (voda, pôda) ako uspokojivý a nepožadovala žiadne finančné prostriedky na sanáciu pôd, resp. podzemných vôd.

V roku 2008 bol areál skupiny spoločností ZSNP, a.s., Žiar nad Hronom zaradený do Registra environmentálnych záťaží SR s vysokou prioritou riešenia. Zaradenie bolo vykonané na základe prieskumu znečistenia realizovaného spoločnosťou IWACO B.V. z roku 1994 pre EBRD. Na základe uvedenej skutočnosti zadal ZSNP spoločnosti B & J ESO, s.r.o., Bratislava[10] geologickú úlohu „Prieskum znečistenia horninového prostredia a podzemnej vody v priestore areálu skupiny spoločností ZSNP, a.s., Žiar nad Hronom“ a spracovanie rizikovej analýzy.

Pre prehľadnejšiu interpretáciu rozsahu možnej kontaminácie (hlavne čo sa týka podzemnej vody) bola celá lokalita spojená do dvoch väčších skupín [11]:

- VÝCHODNEJ SKUPINY - oblasti B7, B1, B5 a B6
- ZÁPADNEJ SKUPINY - oblasti A1, A2, A3, B2, B3 a B4.

V jednotlivých oblastiach bola realizovaná inventarizácia jestvujúcich hydrogeologických objektov a na základe ich prehodnotenia boli vybraté jestvujúce vrty ako monitorovacie objekty pre podzemné vody a jednotlivé oblasti boli doplnené novými vrtmi.

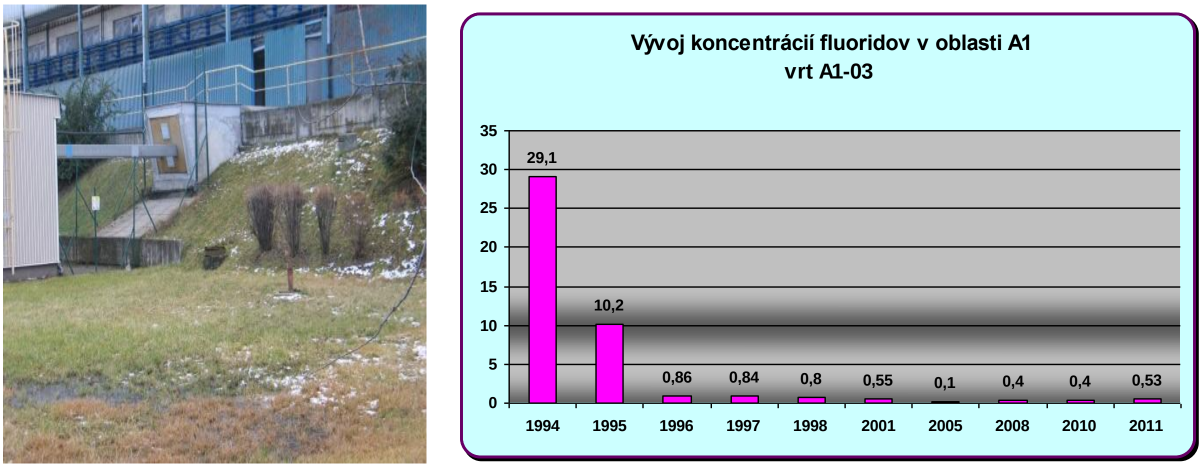
Na základe zhodnotenia skutkového stavu na lokalite sa realizátor geologickej úlohy rozhodol doplniť monitorovaciu sieť o nových tridsať hydrogeologických objektov (monitorovacích vrtov). Na základe rekognoskácie lokality a po zosumarizovaní výsledkov doterajších prieskumných prác boli určené miesta odberov vzoriek zemín a vytýčené miesta nových monitorovacích vrtov tak, aby bolo možné získať komplexný obraz o kvalite podzemnej vody (vstupujúcej aj odchádzajúcej).

Z existujúcich vrtov, po ich prečistení a začerpaní, bolo odobraných 29 vzoriek podzemnej vody a 30 vzoriek vody bolo odobraných z novovybudovaných monitorovacích vrtov. Na základe vyhodnotenia doterajších prác a zohľadniac nový skutkový stav jednotlivých oblastí bolo odobratých 58 vzoriek zemín na stanovenie vybraných ukazovateľov. Väčšina vzoriek bola odobraná z tzv. podstatnej kontaktnej zóny (hĺbka do 1,0 m) a realizátor sa snažil dodržať hĺbkové intervaly ako v roku 1994. Všetky odobrané vzorky (zemín a podzemnej vody) boli analyzované v akreditovanom laboratóriu INGEO-ENVILAB, s.r.o. v Žiline. V podzemnej vode boli stanovené obsahy As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V, Zn, F, PAU, NEL, BTX, VOX a EOX. V zeminách bol stanovený obsah ukazovateľov cielene, na základe vyhodnotenia doterajších skutočností. Stanovené ukazovatele boli fluoridy, As, PAU, NEL, Cd, Hg, Pb, Cu.

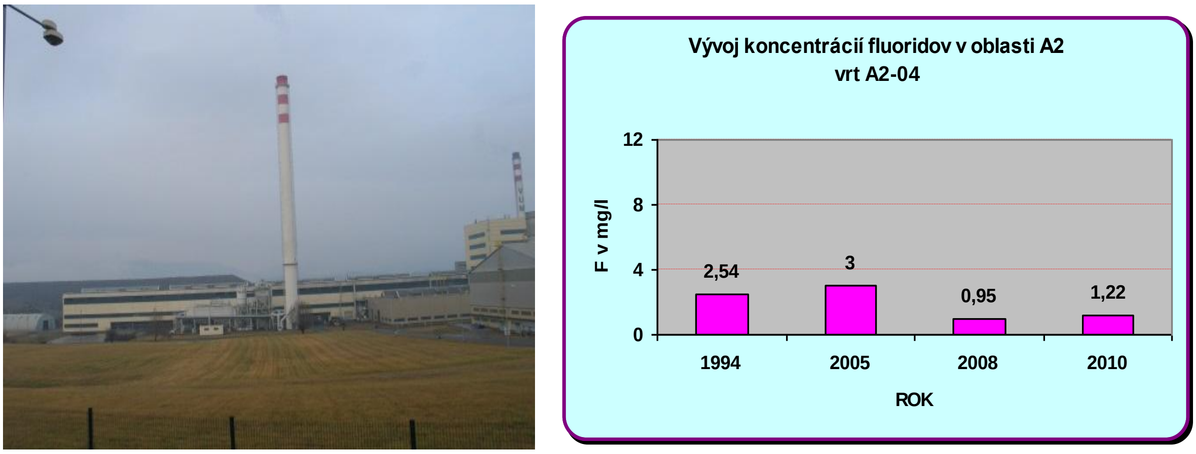
Všetky novovybudované vrty, ako aj existujúce staršie vrty, boli polohovo a výškovo zamerané firmou Geodetická spoločnosť, s.r.o., Žiar nad Hronom.

V závere hodnotiacej správy realizátor geologickej úlohy konštatuje, že pod vrstvou navážky sa nachádza tesniaca vrstva ílov a hlín, pod nimi je niekoľko metrová súvislá vodonosná vrstva štrkopieskov a pod nimi sa nachádza nepriepustné neogénne podložie. Prieniku kontaminácie z povrchu do podzemnej vody bráni niekoľko metrová tesniaca vrstva ílov vyvinutá skoro v celej sledovanej oblasti (chýba v severnej časti oblasti B5 a B6).

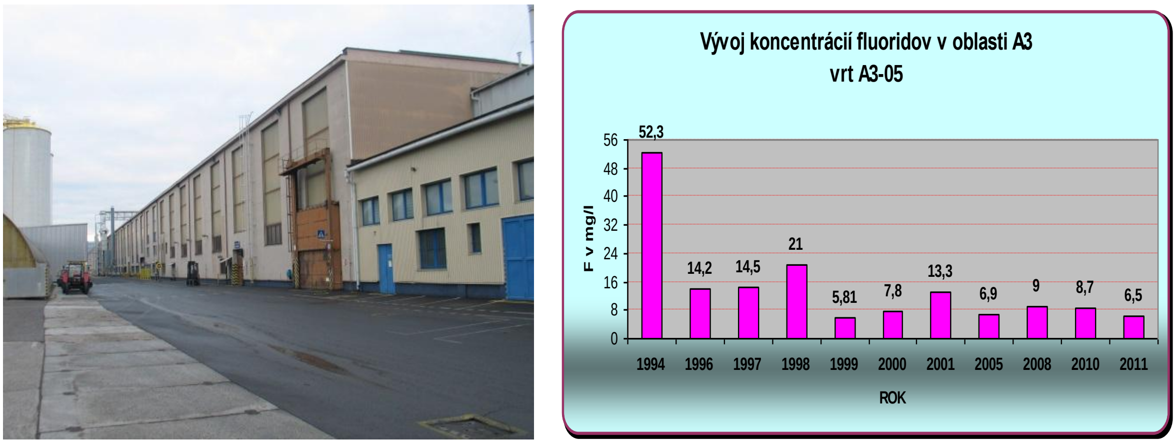
Na obrázku 1 až 4 je vizualizácia oblastí A1, A2, A3, B2 a grafy vývoja koncentrácii fluoridov v daných oblastiach.



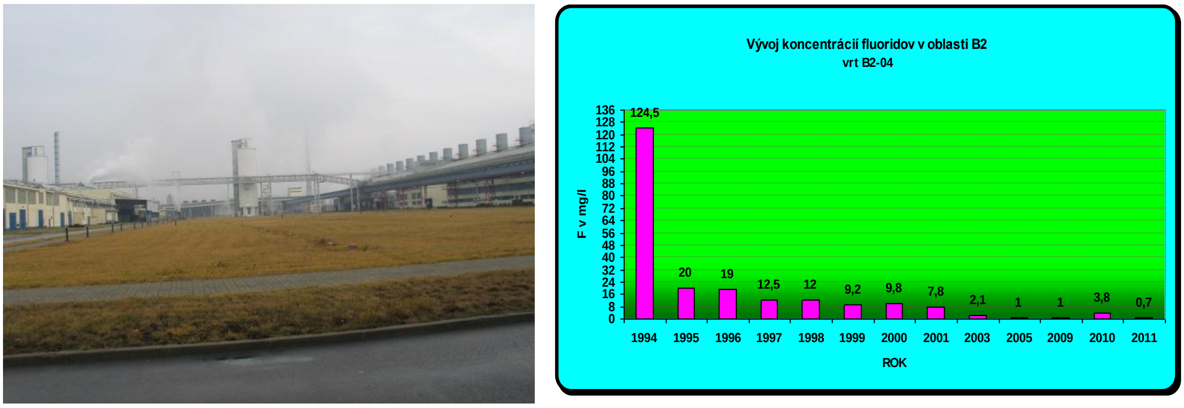
***Obrázok 1: Vizualizácia oblasti A1 – nová elektrolýza a graf vývoja koncentrácií fluoridov v oblasti A1***



***Obrázok 2: Vizualizácia oblasti A2 – nová anodáreň a graf vývoja koncentrácií fluoridov v oblasti A2***



***Obrázok 3: Vizualizácia oblasti A3 a B4 – nová a stará odlievareň a graf vývoja koncentrácií fluoridov v oblasti A3***



***Obrázok 4: Vizualizácia oblasti B2 – stará elektrolýza a graf vývoja koncentrácií fluoridov v oblasti B2***

Realizáciou významných ekologických opatrení došlo k výraznému zlepšeniu (netýka sa to oblasti B1-KYSLIČNIKÁREŇ) kvality podzemnej vody v danej oblasti. Z 58 vzoriek podzemnej vody bolo zistené prekročenie kategórie C metodického pokynu iba v 3 vzorkách. V západnej skupine (A1-nová elektrolýza, A2-nová anodáreň, A3-nová odlieváreň, B2-stará elektrolýza, B3-VUM a B4-stará odlieváreň) vo východnej oblasti síce doznieva ešte znečistenie fluoridmi (prekročenie kategórie C iba v okolí vrtu A3-05), ale vývoj znečistenia má výrazne klesajúcu tendenciu (porovnaním s rokom 1994) a podzemná voda v západnej skupine si nevyžaduje realizáciu sanačných opatrení. Vo východnej skupine (B5-zlievárne, B6-povrchové úpravy a B7-tepláreň) nebola zistená žiadna kontaminácia podzemnej vody, ktorá by si vyžadovala aplikáciu sanačných opatrení. V oblasti B1-kysličnikáreň sa od roku 1997 (odstavenie výroby) neudiali žiadne pozitívne zmeny týkajúce sa ekológie a daná oblasť bola vyhodnotená ako vysoko riziková. Ako v jedinej z oblastí skupiny spoločností ZSNP, a.s. tu dochádza k nárastu kontaminácie podzemnej vody (fluoridy, As, Mo). Preto bolo stanovené, že je potrebné realizovať komplexné opatrenia na zlepšenie jej kvality a zabrániť šíreniu kontaminácie do oblasti B6, prípadne B5. Oblasť B-1 predstavovala vysoké riziko pre životné prostredie.

V záujmovej lokalite bolo odobratých 58 vzoriek zemín a iba v 4 vzorkách bola prekročená kategória C metodického pokynu. V troch prípadoch sa jednalo o kontaminované miesta identifikované v roku 1994. Kontaminované miesta boli viazané na pochované polohy uhlíkatých materiálov. V západnej skupine sa prekročenie povolenej hodnoty pre sanáciu zistilo v oblasti A1 v hĺbke do 0,5 metra pod terénom (ukazovatele fluoridy a PAU benzo(a)pyrén) a v oblasti B3 v hĺbkovej úrovni do 0,4 metra pod terénom (ukazovateľ PAU). V oblasti A1 bola kontaminovaná zemina v okolí miesta vrtu A1-03. Oproti roku 1994 však bol pozorovaný výrazný pokles znečistenia (o cca 90 %). Znečistenie v oblasti B3 v okolí miesta vrtu B3X-16 bolo spôsobené nesprávnym uskladnením uhlíkatých zvyškov na skládke č.5. Vo východnej skupine sa kontaminácia zeminy nad povolené hodnoty preukázala v oblasti B7 a B1. V oblasti B7 bola kontaminácia zeminy zistená do hĺbky 0,7 m v okolí miesta odberu B7-05 (obsah As a fluoridy). Aj v tejto oblasti bol pozorovaný pokles znečistenia oproti roku 1994 (cca 50%-ný pokles v obsahu As a 60%-ný pokles v obsahu fluoridov). V oblasti B1 bola potvrdená kontaminácia v okolí vrtu B1-01 v ukazovateli PAU. Aj v tejto oblasti bol pozorovaný pokles znečistenia v obsahu PAU (zhruba o 25 % oproti roku 1994).

Rozsiahle prieskumné a monitorovacie práce zložiek životného prostredia prebiehali v areáli priemyselnej zóny v podstate od začiatku 90-tych rokov minulého storočia. Na základe výsledkov týchto prác bolo v areáli realizovaných niekoľko menej náročných, ale aj veľmi rozsiahlych projektov revitalizácie a sanácie. Bola to hlavne sanácia pôd v okolí prevádzky VUM, sanácia podzemných vôd znečistených fluórom v priestoroch bývalého závodu Kysličnikáreň a najrozsiahlejšou akciou bola sanácia odkaliska kalové pole.

Posledná menovaná sanácia pozostávala z troch samostatných úloh, a to konkrétne z vybudovania podzemnej tesniacej steny okolo odkaliska, vybudovania technológie na spracovanie alkalických vôd a z izolácie odkaliska proti priesakom zrážkových vôd do telesa odkaliska. Realizácia týchto, ale aj iných sanačných prác menšieho rozsahu, prispela k tomu, že momentálne sa v celej priemyselnej zóne nachádza iba jedna časť opustenej výrobnej prevádzky, ktorá nie je využívaná[11].

## Záver

Prehľad výsledkov preukazuje, že preskúmanosť územia veľkého priemyselného areálu Žiar nad Hronom je dostatočná na získanie relevantných výsledkov potrebných pre zhodnotenie kvality zložiek životného prostredia (predovšetkým sa jedná o pôdy a podzemné vody) a návrh prípadných ďalších revitalizačných či sanačných opatrení, ktoré by mohli prispieť k zvýšeniu využiteľnosti územia predmetného brownfield z pohľadu rozšírenia jestvujúcich priemyselných činností, resp. realizácie úplne nových výrobných a prevádzkových investičných zámerov.

## Poďakovanie

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## Literatúra

1. Ferber, U. et al. 2006. Brownfields příručka [online]. Praha: IURS – Institut pro udržitelný rozvoj sídel, 2006. 90 s. Dostupné na internete: http://fast10.vsb.cz/lepob/index2/handbook_cz_screen.pdf
2. Rusko, M. 2017. Environmentálne záťaže ako sprievodný jav hospodárskeho rozvoja územia. Zborník zo VII. medzinárodnej vedeckej konferencie, Bratislava, 24.11.2017, Žilina: Strix ex SSŽP, s. 62 – 75.
3. Petríková, D., Vojvodíková, B., Samson, N., Jackson, J.B., Finka, M., Toptchiyski, S., Rusu, O.C., Zubková, M., Grigorovschi, M., Ladzianska, Z., Toptchiyska, D., Pletnická, J., Jamečný, L., Ciolacu, D., Jaššo, M., Bláha, P., Maturová, M., Lukš, J., Kralchevska, A. Murínová, T., Bergatt, B. (2013). Príručka pre regeneráciu brownfieldov – BROWNTRANS. Editori: Dagmar Petríková, Barbara Vojvodíková. Vydavateľ: ROAD Bratislava, 2013, 265 s. Dostupné na: http://fast10.vsb.cz/browntrans/document/Brownfields_handbook_Slovak%20version.pdf
4. Správa z prieskumu firiem IWACO B.V., DHV Consultant B.V., GEOS, HASKONING, 1994.
5. Správa z geologického prieskumu firmy GEOS, a.s. Bratislava, 2003.
6. Správa z prieskumu firmy Hydros, 1995 až 1998.
7. Správa z prieskumu firmy EnviGeo, s.r.o. Banská Bystrica, 1999 až 2001.
8. Environmentálny audit pre spoločnosť Rautenbach ZSNP, s.r.o.; spracovateľ HES-COMGEO, s.r.o., Banská Bystrica, 2001.
9. Environmentálny audit v oblasti B6 (povrchové úpravy) pre spoločnosť SAPA, spracovateľ Golder Associates, Turín, Taliansko, 2004.
10. Geologická úloha a spracovanie rizikovej analýzy - Prieskum znečistenia horninového prostredia a podzemnej vody v priestore areálu skupiny spoločností ZSNP, a.s. Žiar nad Hronom, B & J ESO, s.r.o., Bratislava, 2008.
11. Ťahúňová, M. Komplexný prieskum a riešenie brownfields veľkého priemyselného areálu v Žiari nad Hronom. Projekt dizertačnej práce, jún 2018.

## Research and investigation of brownfields of a large industrial area in Žiar nad Hronom

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### *Summary*

*Brownfields are formed as a by-result of an industrial or other restructuring of the used territories in any country and at any time. Despite the fact that this topic is relatively new in terms of the existence of legislation in Slovakia, in the Žiar nad Hronom industrial site and especially in the company ZSNP itself, dealing with old environmental burdens has been and it is also now days considered as a normal part of the business. Thanks to the active approach of the company ZSNP and good cooperation with the state administration and self-government authorities in the field of environmental protection, today we rank Žiarska kotlina between the territories with weak pollution and not between the burdened areas as has been the case until recently. The paper focuses on the complex research and investigation of the brownfields of the large industrial complex in the locality of Žiar nad Hronom, including the remediation works carried out in the concerned industrial area.*

***Keywords**: brownfields, remediation, industrial enterprises.*

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- ☐ Bezpečnost a hygiena práce

## ODPADOVÉ FÓRUM 2020

15. ročník symposia, jehož plný název je „**Výsledky výzkumu a vývoje pro průmyslovou a komunální ekologii**", pokračuje ve svém rozšířeném záběru na celou oblast průmyslové a komunální ekologie:

### VODA

- ☐ Čištění průmyslových odpadních vod
- ☐ Získávání cenných látek z odpadních vod
- ☐ Recyklace vody
- ☐ Nakládání s kaly, kapalné odpady

### OVZDUŠÍ

- ☐ Čištění odpadních plynů a spalin
- ☐ Snižování a měření emisí
- ☐ Doprava a lokální zdroje
- ☐ Kvalita ovzduší a zdravotní dopady znečištění ovzduší

### ODPADY

- ☐ Systémové otázky odpadového hospodářství
- ☐ Materiálové, biologické a energetické využití
- ☐ Nebezpečné odpady, odstraňování odpadů
- ☐ Sanace ekologických zátěží a následků havárií
- ☐ Radioaktivní odpady a jejich ukládání

### VĚDA A VÝZKUM PRO OBĚHOVÉ HOSPODÁŘSTVÍ

- ☐ Šance a bariéry cirkulární ekonomiky
- ☐ Nové zdroje surovin a energie
- ☐ Inovativní technologické postupy a technologie
- ☐ Nové materiály a jejich aplikace (bio- a nanomateriály)

## KLÍČOVÉ TERMÍNY

| | | | |
|---|---|---|---|
| Přihlášky příspěvků | **15. 1. 2020** | Přihlášky účasti | **1. 3. 2020** |

## PŘIHLÁŠKY A PREZENTACE PŘÍSPĚVKŮ

Příspěvky na TVIP mohou mít povahu přednášky v odborné sekci (15 min. přednáška a 5 min. diskuse) nebo vývěsky. Termín přihlášek příspěvků, včetně jeho abstraktu, je **15. 1. 2020.** Přihlášky je možné zasílat výhradně prostřednictvím elektronického formuláře na **www.tvip.cz**.

Jednací jazyk je čeština a slovenština. Zahraniční přednášející (i posluchači) jsou vítáni, ale tlumočení nezajišťujeme. Komerční prezentace na konferenci je možná, více na **www.tvip.cz**.

## PŘIHLÁŠKY ÚČASTI

K účasti na TVIP se přihlašuje prostřednictvím formuláře na **www.tvip.cz**, **termín je 1. 3. 2020**. K účasti se přihlašují (a vložné platí) i autoři příspěvků, přednášky nejsou honorované.

## PUBLIKACE VE WASTE FORUM

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