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OBSAH / INDEX

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Ondřej Procházka

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The next editorial deadlines are on April 8 and June 28, 2018.

Ondřej Procházka

Pro autory

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The deadline of the next issue is on April 8, 2018, more on June 28, 2018.

Process grouping of transport systems within LCA system boundary

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Abstract

Environmental impacts of transport and transport systems are currently important. With the global development of transport, the importance of monitoring and assessing the concrete environmental impacts of transport is growing. Overall environmental impacts of transport systems using Life Cycle Assessment method are frequently evaluated in last years. One of principal steps of life cycle assessment is selection of system boundaries. Selection of system boundaries substantially influence obtained results. In this article, we have designed a way to determine boundaries for the LCA study of transport and transport-related processes such as fuel life cycles, biofuels, hydrogen transport systems, roads and related linear structures.

Keywords: *Life Cycle Assessment, LCA, transport systems, transportation construction, grouping*

Introduction

Transport systems are one of the biggest polluters of the environment. With the global development of transport, the importance of monitoring and assessment of the environmental impacts of transport is growing[1]. Adverse environmental impacts of transport generate not only direct emissions from vehicles, but also the processes involved in the operation of transport means (eg fuel production and distribution, road construction) and emissions of subsequent processes (eg road repairs, vehicle repairs and removals)[2]. As an example of the transport system, where the pre-processes are of great importance, let us introduce cars for hydrogen or electric drive. The very operation of these cars produces relatively low emissions, but production of the drive medium cannot be stated as emission free, although some producers of electric cars tend to promote their products as emission free. Liquidizing and maintaining hydrogen in the liquid state is relatively energy-intensive. The operation of an electric car is also just as "non-emission", such as "non-emission" the electric power generation needed for car operation is. Similarly, the CO_2 savings achieved through the use of biofuels are only as significant as significant are savings of CO_2 equivalents within all life cycle of biofuels, that means including for biomass needed fertilisers and herbicides production, processing of biomass, biofuels production and other[3].

Methodical and experimental part

As mentioned in the introduction, there is a need to assess the environmental impacts of transport systems in a comprehensive way and not to focus only on certain phases of the transport sector. Whole life cycle of the transport systems should be assessed together including all relevant related processes and operations. A comprehensive tool for assessing the environmental impacts of technologies, services, products or technical systems within whole-life perspective is the life cycle assessment method. Life Cycle Assessment (LCA) is an analytical method of assessing potential environmental impacts associated with the life cycle of a particular product, service, technology, and/or product in general. The LCA study consists of four basic phases: definition of objectives and scope, inventory, impact assessment and interpretation. Compilation of LCA studies is in accordance with ISO 14040 (2006) and ISO 14044 (2006) standards[4,5].

Individual phases of the life cycle are created by operations transforming the materials and energy inputs into outputs. These processes are interconnected by their material and energy flows. The entire system of processes taking a part in a product's life cycle is called the product system. LCA is an interactive methodology (see Figure 1), which means that if it is not possible to ensure a consistency of the processed phase with some of the previous phases, the previous phase and all the following phases have to be reprocessed. In order to fulfil the original goal of the study, some aspects regarding its scope may require modification[5].

The first step of LCA is to determine the goals of the study, who are the recipients, and what are the contributions. The key question is what product will be assessed and what its function is. The subject of the analysis is thus described from a functional point of view, which is quantified by the functional unit and reference flow, which is defined by the amount of product necessary to fulfil the functional unit. On this basis, the whole operational plan is further developed. The scope of the study includes requirements of input data quality, accepted preconditions and simplifications, as well as temporal and regional limitations. Further, also to be identified will be the confines of the system with respect to the complexity of the study, defining of the allocation procedures, and the choice of one characterization model which will enable the assessment of the environmental impacts[6,7].

Life Cycle Inventory (LCI) collects environmentally-significant information regarding those processes which fulfil the functional unit in the product system whose confines were specified in the phase of defining the goals and scope. The inventory phase contains these steps:

- Categorization of the product system
- Inventory data collection
- Calculation of the product system ecovector.

Ecovector describes both the amounts of resources consumed and the matter emitted in relationship to the reference flow of the product being assessed. The ecovector is a mathematical operator. Its size matches the emission of the elemental flows into the environment or the consumption of certain raw materials. The product system ecovector amounts to the sum of all the ecovectors of the partial processes[6,7].

The sequence of partial processes which are caused by the elemental flows overcoming the system boundary is called the impact chain. The impact chain leads to the final environmental impacts, i.e. calculation of impact category results[6,7]. Life Cycle Impact Assessment consist at least of classification and characterization of elementary flows and sometimes also consists of normalization and weighting.

The last phase of LCA is the life cycle interpretation, which is used for assessment and checking of the study results. For the large amounts of data in the previous phases of the life cycle assessment, it was necessary to sort them out and interpret them in an appropriate manner. Within the framework of inventory analysis, certain preconditions and simplifications can be accepted, or eventually accepted if they involve unclear data. Within the framework of the complexity of this study, these facts have to be placed besides the presented results, and their impacts needing to be assessed. The interpretation mostly consists of the following steps:

- Structuring of the data with respect to the most significant groups of processes.
- Discussion the meaning of data above, in relationship to the quality of the input data.
- A final summary and proposal of recommendations.

In the method of LCA for construction products and services[8] individual phases of the life cycle of individual products (buildings and works) are divided into modules A1 - A5, B1 - B7, C1 - C4 and D, where individual process groups are detail described in following table.

Table 1: General description of the system boundary of construction products and services systems [8]

A1 - A3 Product stage	Raw material supply	A1
	Transport	A2
	Manufacturing	A3
A4 - A5 Construction process	Transport from the gate to the site	A4
	Assembly	A5
B1 - B7 Use stage	Use	B1
	Maintenance	B2
	Repair	B3
	Replacement	B4
	Refurbishment	B5
	Operational water use	B6
	Operational energy use	B7
C1 - C4 End of life stage	De-construction	C1
	Transport	C2
	Waste processing	C3
	Disposal	C4
D Benefits and loads beyond the system boundaries	Reuse- Recycling - Recovery Potential	D

This arrangement and breakdown of individual stages of the life cycle of buildings is logical and builds on a practice that is already steady. Another situation is related to transport systems. Te life cycle of transport systems consists of a larger number of independent industries and industrial activities. While building manufacturers, energy and fuel distributors, transport and waste management are involved in the building industry, broad spectrum of stakeholders is involved in the life cycle of transport systems: fuel and energy producers, vehicle manufacturers, transport infrastructure manufacturers and, of course, number of related services providers. Consequently, transport systems are more complex than the construction industry, and it will be appropriate for LCA studies to open a discussion on how the system boundaries will be defined. ISO standards do not address the issue of transport systems more closely and the use of already established life cycle structure of construction products is not possible without larger adjustments.

In the preparation of LCA studies of products and projects related to transport systems, it has been shown that most of these projects involve some stages, and in some other cases some stages are not necessarily included. We have identified the following groups of processes that make up the overall framework of the lifecycle of transport systems.

In the stage of life cycle of fuel production, there are mainly processes involved in the extraction of resources needed for the production of fuels (Resources extraction). These processes are directly linked to the production of fuels (Fuel production). In some cases fuel distribution needs to be modelled in more details, such as hydrogen cells systems (Fuel storage and distribution). The distribution and use of fuels is linked to accidents and unwanted releases of harmful substances into the environment. At the moment when the operations repairing these damages are not negligible, they need to be added to the system under review (Recovery after potential accidents dealing with fuels). Some fuel raw materials can generate various environmental side effects, such as biofuels production and related impacts on landscape, biodiversity or environmental impact of pesticide (Potential consequences of fuel production).

An important place in transport systems carries a vehicles. In modelling the lifecycle of transport systems, it is logical to model resource extraction and vehicle material production. The use of means of transport leads to emmisions of harmful compounds into environments resulting in their direct environmental impacts (Vehicle use phase). Maintaining vehicles in a workable condition carries the need to run certain processes that also have the potential to damage the environment (Maintanance of vehicle). At the end of the vehicle's lifecycle, its eventual material use or final disposal (Vehicle End of Life) should be considered.

Traffic infrastructure entails requirements for material and energy inputs at the stage of obtaining raw materials and materials necessary for infrastructure development (Resources extraction and infrastructure material production; Infrastructure production). Some types of infrastructure, such as tunnels, need some inputs to be used for their operations, which should also be included in the studies (Infrastructure use phase). As infrastructure operation leads to more frequent damage, it needs to be continually repaired and renewed (Infrastructure maintenance). The end of the life cycle of the infrastructure entails a potential environmental burden, both at the stage of the eventual reworking of raw materials and in the case of end-of-life (Infrastructure End of Life).

Similarly, in the field of life cycle assessment of construction products and services, we propose the grouping of above mentioned processes involved in the lifecycle of transport systems into the above groups of modules, designated F1 – F5, V1 – V5 and I1 – I5.

Table 2: Process grouping of the transport system

F1 – F5 Fuel stage of life cycle of transport system	Resources extraction	F1
	Fuel production	F2
	Fuel storage and distribution	F3
	Recovery after potential accidents dealing with fuels	F4
	Potential consequences of fuel production	F5
V1 – V5 Vehicle stage of life cycle of transport system	Resources Extraction and vehicle material production	V1
	Vehicle production	V2
	Vehicle use phase	V3
	Maintanance of vehicle	V4
	Vehicle End of Life	V5
I1 – I5 Infrastructure stage of life cycle of transport system	Resources extraction and infrastructure material production	I1
	Infrastructure production	I2
	Infrastructure use phase	I3
	Infrastructure maintenance	I4
	Infrastructure End of Life	I5

Such a system of process grouping designed in each stage of transport system would appropriately classify the processes involved, and at the same time allow individual processes to be identified in order to be able to distinguish which environmental impacts arise from which sequence of transport system operations. In addition, it would be possible to distinguish emissions released from individual processes in such a way as to make it clear where they occur. For the evaluation of environmental impacts of transport systems it is important to know where emissions are released, if in cities with high density of human population or in isolated industrial plants. In the following paragraphs, we want to show the possibilities of segmentation of transport systems using our proposed grouping system.

Results and discussion

System boundary of any product system is defined by unit processes and the elemental flows which will be included into the product system. In accordance with ISO 14040[5], specification of the unit process is defined as the smallest part of the product system for which the inventory data are collected. The product system usually creates flows which come out of this, and exceed system confines in the form of emissions discharged into the environment. Such flows are called elemental flows. They include inputs and outputs exceeding the confines of the product system, and thus providing exchanges of materials and energy with the environment[7]. Process selection in the model product system depends upon the definitions of goals and the scope of the study, as well as its intended utilization(s), costs, limiting criteria, and on the accessibility of the necessary data. System boundary further defines the geographic and temporal scope of the validity of the study. The principle of "from cradle to grave" includes those processes which take some part from the acquisition of the raw materials all the way to the waste management processes.

Different system or system boundary choices affect the results obtained from the LCA study, although in all cases it is the entire life cycle. Lifecycle is, in the LCA, the assessment of the so-called cradle to the grave, but always for the group of processes included in the boundaries of the system. Interpretation of the LCA study may also differ in cases of different requirements for the assessment of the environmental and health aspects at the site, in the region or globally. For certain applications, the placement of environmental and health aspects can be important. Thus, the boundary of the system influences the technological scope of the study and the location of the environmental and health aspects makes it possible to determine where the particular environmental impacts may occur. Especially, but not exclusively the LCA studies focused on transport systems are to selection of system boundary very sensitive.

The following diagrams illustrate how the function and hence the boundaries of the system under consideration in the field of personal land transport can be chosen. The first diagram shows the basic groups of operations / processes involved in the complete life cycle of transport.

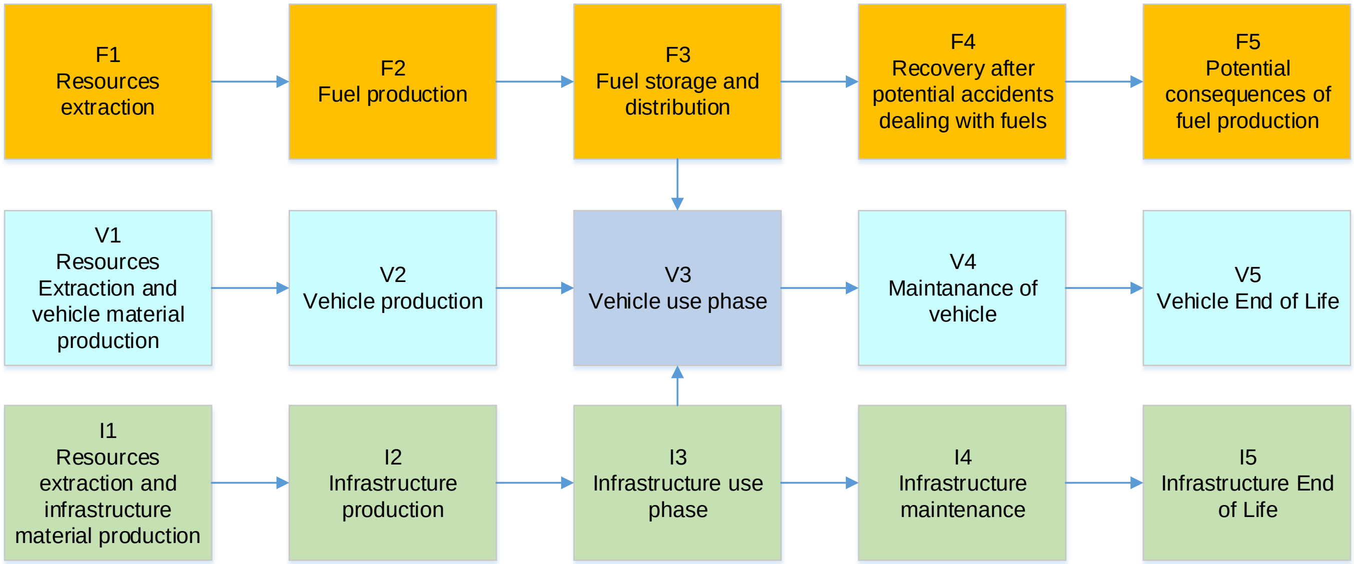

Figure 1: Scheme of system boundaries of the transport products and/or services in general. F indicates processes dealing with fuel life cycle; V with vehicle life cycle and I with infrastructure life cycle

This scheme expresses how the boundaries of the LCA system would be chosen to assess the environmental impacts of transport in a particular region from long time perspecive and also taking into account the global scale of environmental impacts. For example, a function of the system could be expressed as follows: providing land transport for the population of the very country for 20 years. It can be expected that some environmental aspects would be implemented directly in the area (eg exhaust gas), some environmental aspects would be implemented in another region (eg emissions from foreign cars production) and some environmental aspects would have a global scope (eg greenhouse gases or ozone depleting substances). However, some environmental aspects with a global scope may also be significant from a local point of view. Particularly greenhouse gases, which are related to the global category of impacts, are relevant also locally in terms of legislative requirements prescribing the reduction of greenhouse gas production. A narrower system boundary would be appropriate for the LCA for. This would include, for example, assessing the environmental impacts of biofuels, electric vehicles and the like. The system boundaries could then be selected as shown in the following figure.

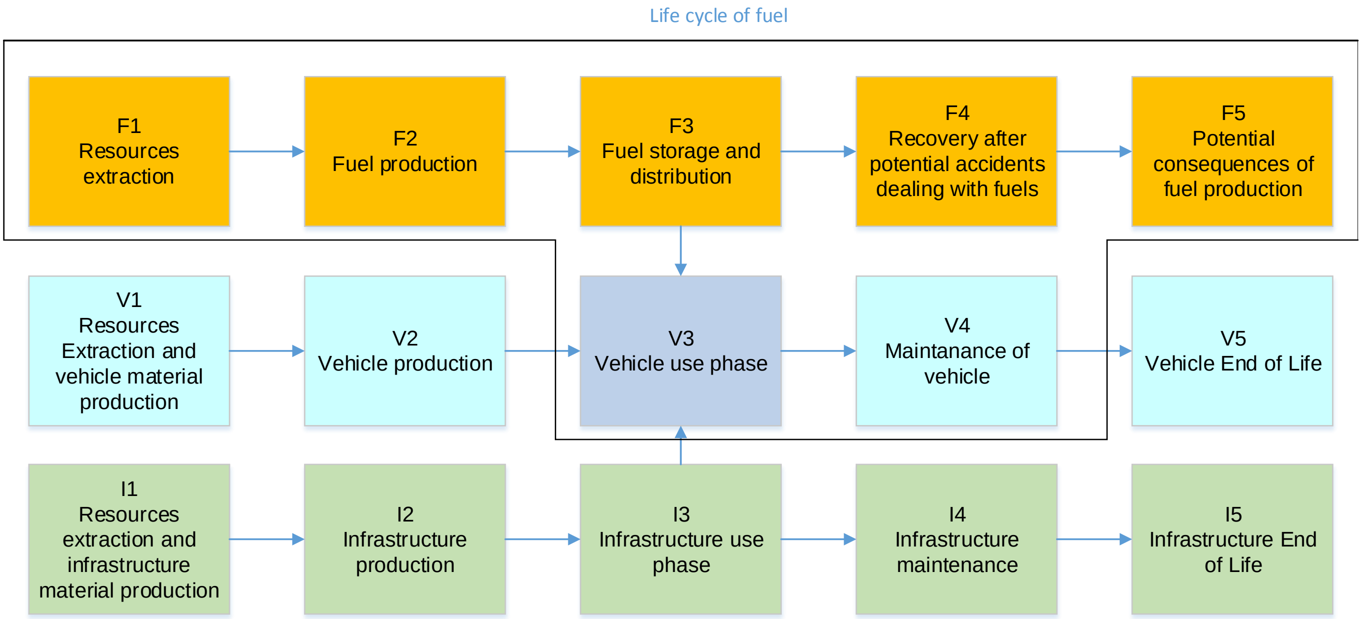

Figure 2: Scheme of system boundaries of fuels

The figure shows the difference in the range of system boundaries compared to what is normally considered when assessing the environmental aspects of the use of biofuels. While the use of biofuels can lead to a reduction in CO_2 emissions in the biofuel use phase, it does not have to apply if the environmental aspects of the production of biofuels and all the necessary materials (fertilizers, herbicides) are included in the system boundaries. At the same time, it is also necessary to include the possible higher environmental aspects of the transport equipment service that may be higher due to the use of biofuels. The boundaries of the transport system as such could be chosen as shown (Figure 4). This is how often the boundaries of the electro-mobiles system are chosen. This is misleading, however, because the production of electricity also has its specific quantifiable environmental aspects.

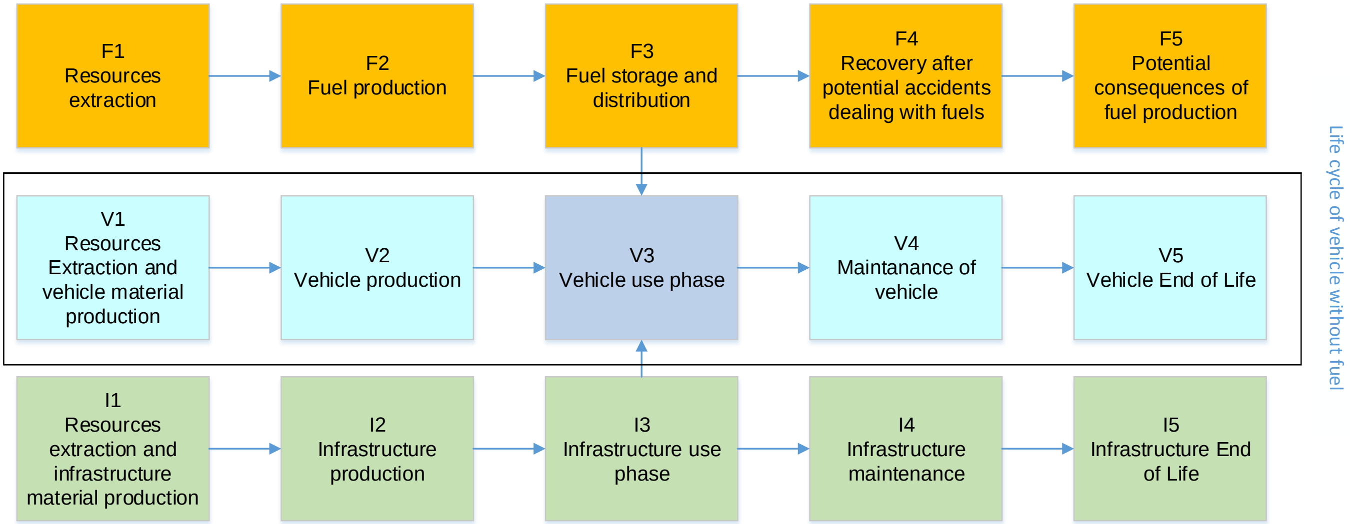

Figure 3: Insufficient system boundaries of the vehicle excluding fuel production

Since production and distribution of fuels cause particular environmental aspects, only the processes involved in the production and distribution of fuels are included in the system boundaries.

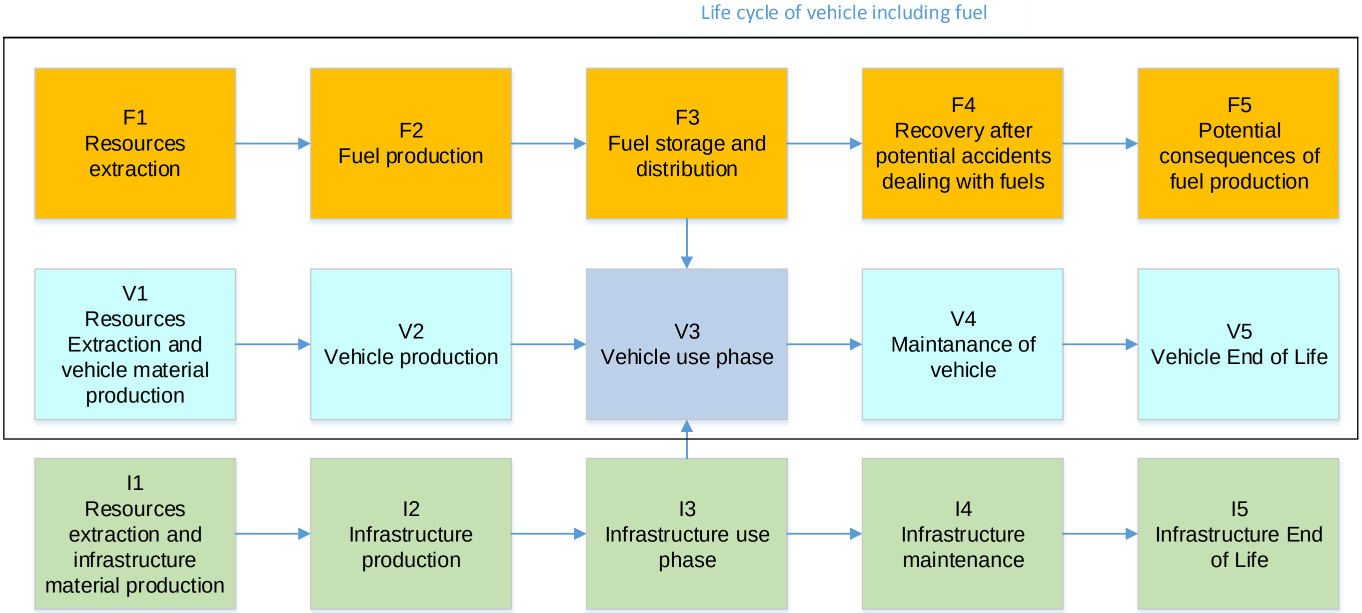

Figure 4: System boundaries of the vehicle including the production and distribution of fuels

While the study becomes more demanding on data, the information is growing. For the purpose of choosing building materials or technologies used to build the road itself, the boundaries of the system can be chosen in close connection with the road life cycle. If the roadway is not designed for a very specific traffic load, traffic from the proposed system boundaries can be excluded. The boundaries of the system are illustrated by the following diagram.

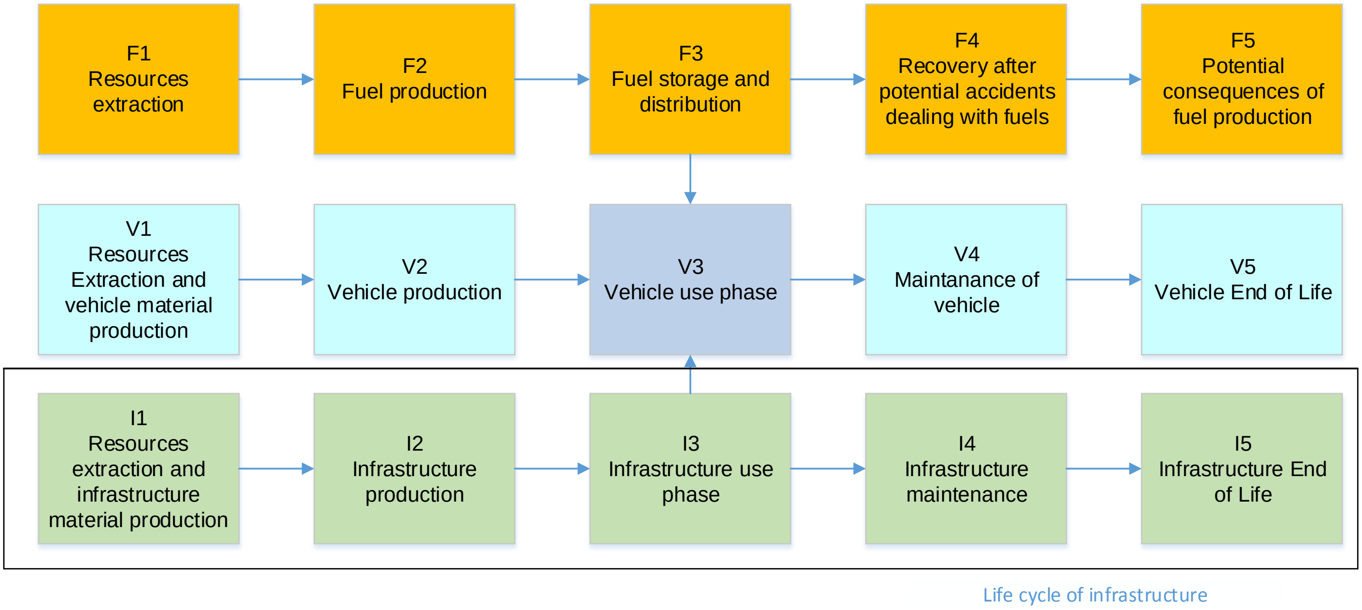

Figure 5: System boundaries of infrastructure

When designing transport systems, it is necessary to include in the assessment of environmental impacts to the boundaries of the system, in particular, the operation of transport means, its preliminary processes of obtaining and distributing fuels, as well as the processes of production, maintenance and, if necessary, the termination of the operation of the road itself. Such system boundaries are appropriate for assessing environmental impacts from a global perspective.

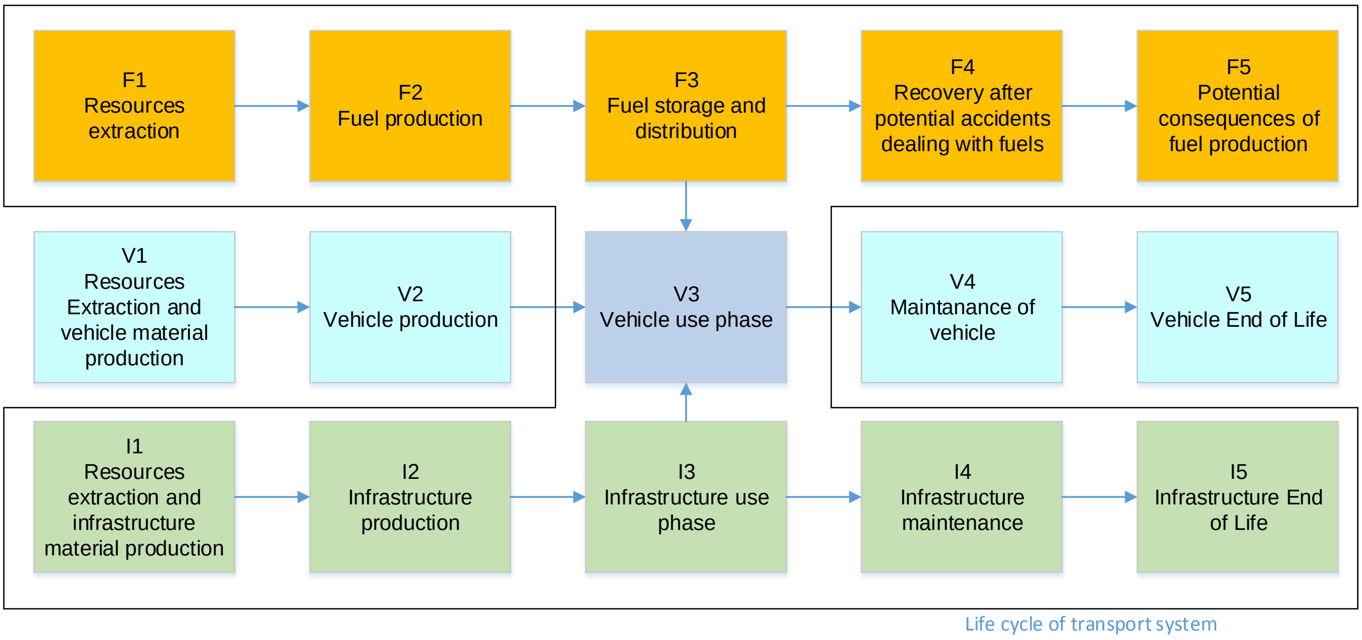

Figure 6: System boundaries of life cycle, excluding vehicles, ie included are only processes involved in local environmental aspects

In the case of assessing the potential impacts of traffic system, it may be important to organize the identified data so that it is possible to capture which potential environmental impacts directly or indirectly affect the territory in which the transport system is operated. For that purpose, it may be meaningful to exclude road construction from the boundaries of the system. This, of course, depends on the overall assignment. If we consider the construction of the road to be strategic and necessary, its construction can be considered inevitable and therefore its potential environmental aspects are acceptable. However, this does not always have to be the case. In certain situations, road construction may be very significant. Various variants of the construction or entire lifecycle of the pavements should then be assessed within the system boundaries proposed earlier in the Figure 6. Inclusion of road construction into the system boundaries then leads to a requirement to allocate environmental impacts emerged due the construction, what may introduce wider variability into the system. The local impacts of transport system are caused by those emissions that have been released from the processes included in the system boundaries shown in the following figure. These are emissions from local processes of the transport system.

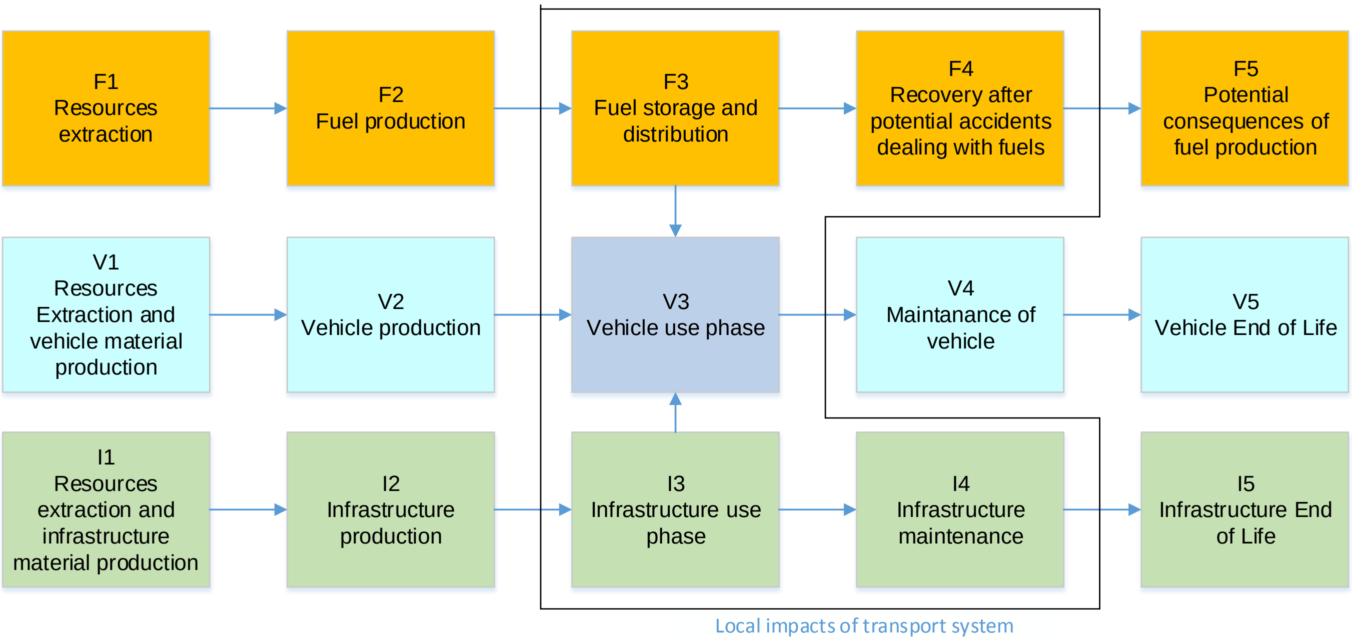

Figure 7: Local environmental impacts of the transport system

In the case of a more comprehensive study, it is also appropriate to include fuel production and distribution processes within the system boundaries. It is, however, appropriate to structure the inventory table in an appropriate manner.

It follows from the above that the choice of the boundaries of the system influences fundamentally the overall concept of the study, its interpretation and the results obtained. For the purpose of assessing the environmental impacts of transport systems, it seems expedient to choose the system boundary shown in the following figure 9 with the characterization of emissions (elementary flows) to localised and dislocated.

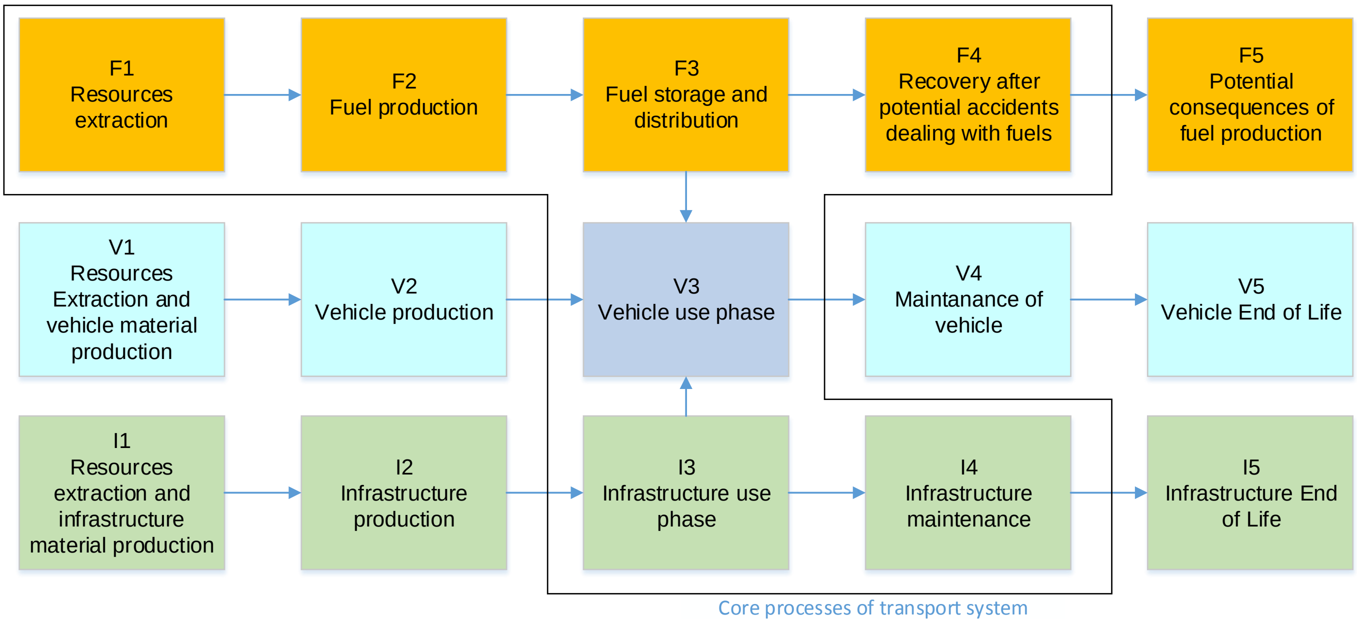

Figure 8: Core processes of the transport system

As localized we consider the environmental and health aspects (emission of matter, elementary flows), the release of which into the environment occurred directly due to the operation of the transport system and in its location. Dislocated are the environmental and health aspects that are triggered by elementary flows from pre-process or subsequent processes to the processes of the actual operation of the means of transport. Similarly, for processes that are dislocated, we consider those processes whose operation and environmental aspects are implemented outside of the transport system location. Localized are those processes that are directly related to the transport system operated in its place - on the transport route.

Table 3: Dislocated and localized environmental impacts in relation to processes coveren into systém boundaries of transport systems

	Dislocated	**Localized**
Processes	Processes related to the operation of transport systems but operated outside its locality	Processes operated at the site of the transport system
Elementary flows	Emissions and raw material inputs from processes outside the transport system	Emissions released at the area of the transport system
Environmental and health aspects	All environmental and health aspects of the dislocated processes - outside of the transport system	Environmental and health aspects at the area of the transport system
Environmental impacts	All relevant impact categories: acidification, eutrophication, global warming, photooxidants, stratospheric ozone depletion, human toxicity, ecotoxicity and others. Impact categories indicator results are determined for elementary flows of dislocated processes.	All relevant impact categories: acidification, eutrophication, global warming, photooxidants, stratospheric ozone depletion, human toxicity, ecotoxicity and others. The results of the impact categories indicators are determined for the elementary flows of the localized processes.

Conclusions

At this paper we propose to divide life cycle diagrams of transport systems into structured modules, similarly as in the field of life cycle assessment of construction products and construction services. We propose the breakdown of individual processes involved in the lifecycle of transport systems into the groups designated F1 - F5, V1 - V5 and I1 - I5, where modules *F* cover life cycle of fuel, *V* life cycle of vehicle and *I* life cycle of infrastructure.

Localized we consider the environmental and health aspects (emissions of matter, elementary flows), the release of which into the environment occurred directly due to the operation of the transport system and in its place. As dislocated we consider the environmental and health aspects that are triggered by elementary flows from pre-process or subsequent processes to the processes of the actual operation of the means of transport. Similarly, for processes that are deployed, we consider those processes whose operation and environmental aspects are implemented outside the transport system location. Localized are those processes that are directly related to the transport system operated in its place - on the transport route.

In LCA studies, processes are usually divided into groups for upstream processes, core processes, and downstream processes. This classification is particularly suitable for modeling the production of specific products. For the purpose of transport systems, it is also possible to use this classification, but for the assessment of possible environmental impacts at the traffic site, it is preferable to structure the processes on localized and dislocated. In current LCA studies, the production of energy or fuel is included in the central processes. This is not appropriate for transport systems, as the design of new transport systems is usually an effort to reduce emissions and environmental and health impacts at the point where the planned transport system will operate.

In this article, the proposed system boundaries the grouping of involved in these processes would certainly deserve demonstration on specific case studies. However, given the scope of this text, we have decided to exemplify this article no longer. We will prepare examples of these schemes for publication in a separate article.

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Návrh seskupování procesů při posuzování životního cyklu dopravních systémů

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Souhrn

Doprava je jedním z největších znečišťovatelů životního prostředí. S celosvětovým rozvojem dopravy vzrůstá význam sledování a hodnocení konkrétních environmentálních dopadů dopravy. Nepříznivé environmentální dopady dopravy způsobují vedle samotných výfukových plynů i emise látek z procesů předřazených samotnému provozu dopravních prostředků (např. výroba a distribuce paliv, stavba vozovek) i emise látek z procesů následných (např. opravy vozovek, opravy a odstraňování vozidel). V tomto článku jsme navrhli způsob určování hranic systému pro studie LCA dopravních procesů a procesů souvisejících s dopravou, například životní cykly paliv, biopaliv, vodíkových systémů pro dopravu, vozovek a souvisejících lineárních staveb. V článku navrhujeme seskupovat procesy při modelování LCA dopravních systémů do skupin F, V a I, které odrážení jednotlivé skupiny procesů zaměřené okruhy činností týkající se životního cyklu paliv, dopravních prostředků a infrastruktury.

Klíčová slova: *odpad, sanace ekologických zátěží, průmyslová a komunální ekologie*

Intermunicipal Cooperation in Municipal Waste Management and Its Effects on Cost-Effectiveness

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Abstract

This paper focuses on intermunicipal cooperation and provides a new and innovative approach to evaluating the cost effectiveness and cost efficiency of municipal waste management. We examine a sample of 710 municipalities in two regions in the Czech Republic between 2014 and 2016. We investigated two forms of intermunicipal cooperation: joint public procurements and intermunicipal waste collection companies. The results, based on an ordinary least squares regression, show that cost reduction is significantly influenced by both forms of intermunicipal cooperation. The impact is stronger for small municipalities of fewer than 1,000 inhabitants.

Keywords: *waste management; intermunicipal cooperation; public procurement; cost effectiveness.*

Introduction

Municipalities in the Czech Republic are obliged to provide a large number of public utilities; this obligation is delegated to them as part of their independent and devolved powers. These services include waste management. For the past fifty years, the academic world has been discussing the factors influencing the cost efficiency and cost effectiveness of providing these public utility services[1-4, 6-15]. Most papers have focused particularly on the form of production (public or private) and the form of provision (contracting out and in-house)[1-2, 8-10, 16-18]. Solid new evidence indicates that intermunicipal cooperation is among the most significant factors influencing the efficiency of waste management services[9, 13, 17, 21]. In the area of waste management, intermunicipal cooperation can take the form of intermunicipal contracting out (joined public procurement) or of an intermunicipal waste collection company.

Municipal waste management costs were more than 60% of the total current municipal costs for environmental protection and they accounted on average for 4% to 5% of the total current costs for municipalities in the Czech Republic in the 2012-2016 period. It is thus obvious that waste management is an integral and indispensable part of municipal budgets. Waste management is therefore a suitable target for measures aimed at saving public resources. Within this context, this paper is focused on waste management at the local level in the Czech Republic in general.

The increasing importance of municipal waste management and its efficiency and effectiveness is a broadly discussed topic, both in terms of theory and practical experience[1-21]. Our main intention with our research is to contribute to the ongoing academic debate and to go a bit beyond conventional approaches. Defining and measuring the efficiency, or, in other words, the process of using resources and their transformation into outputs and outcomes, seems to be one of the biggest issues of contemporary research. Over the course of several decades, evaluating efficiency and even evaluation methods have been greatly improved and advanced. However, an accurate evaluation still remains a conceptual challenge in relation to municipal costs. This issue is also complicated by the fact that public sector outcomes used to be off-market, lacking relevant data and thus making it impossible to quantify.

Many relevant factors influence the efficiency of public services. These factors have been widely analysed in the scientific literature worldwide. Although most international studies are strictly focused on the importance of the form of production (i.e. public, private, or mixed – PPPs), statistically more significant and clearer results are provided by the studies that are focused on the forms of provision (i.e. outsourcing or in-house provision), including contracting out and public procurement issues. In addition, different forms of production and provision lead to different results. Obviously, these issues are closely connected to the problem of suboptimal local government size as well as to the phenomena of economies or diseconomies of scale. More intensive research has recently been focused on intermunicipal cooperation. The authors who study these issues usually point out that intermunicipal cooperation enables the decrease of expenses and the saving of costs for municipalities and the improvement of the quality and accessibility of local services[22-25]. Bel and Costas[18] found intermunicipal cooperation to be an efficient tool for reducing costs, but the cost savings can disappear over time if contracting-out was chosen by the municipality. According to Bel and Mur[26], municipal cooperation can help especially the smallest municipalities to provide higher quality services at stable costs. This result corresponds with that of Steiner[27], who stated that municipal mergers resulted in a higher quality and increased quantity of services. According to Bel et al.[11], the decision of municipalities to cooperate is pragmatic, especially for municipalities of suboptimal size. Some authors[25, 28-29] have pointed out that although most research results show that intermunicipal cooperation has a significant impact on cost savings in waste management, it is important to examine the internal aspects of intermunicipal cooperation (such as management, institutionalization, and share of municipalities in cooperation). However, this research is still in the early stages.

Intermunicipal cooperation and its influence on increasing the efficiency of municipal expenses are also currently significant research issues in the Czech Republic. Because the expenses expended by municipalities on waste management have grown exponentially in the Czech Republic[30-34], the demand of municipalities for efficient and effective solutions has been increasing. The increasing municipal costs for waste collection and waste disposal, as well as increased wages, require measures that will enable the decrease of total expenses. Thus a space is created for making use of intermunicipal cooperation that will enable the decrease of expenses, for example by utilizing the positive effects of the economies of scale or the economies of density. In addition, municipalities themselves can influence this if they collaborate in the given area. The Czech Republic serves as an excellent data source on this point, contributing to the relevant academic debate with experiences from highly fragmented local government structures.

This paper studies the relation between municipal waste management costs and selected factors affecting cost efficiency. We pay special attention to (1) the form of production (public/private/PPPs), intermunicipal cooperation and its different forms (intermunicipal waste collection company, intermunicipal/joint public procurements), and economies of scale, and (2) the size structure of local governments. The following research questions were set:

RQ1: How is the cost efficiency of local waste collection services affected by selected factors?

RQ2: Is the cost efficiency of local waste collection services affected by intermunicipal cooperation? If so, how?

RQ3: How do the results differ between different population sizes?

The paper is structured to present answers to these three research questions, as follows: the first sub-chapter provides a concise description of the material and the scientific methods used, focusing on data and sources, and the empirical model. The second part of the paper contains the evaluation and exact description of the achieved results and their statistical significance and provides a discussion and comparison of the achieved results and previously published papers, our own opinion of the established differences, and our view of the results. We outline the need for further solutions and the importance of developing the research field, society, and practice. The paper concludes by providing a concise summary of the most important findings in relation to the paper focus.

Materials and Methods

Data and Sources

The research was carried out on data collected from 2014 to 2016. The sample consists of 710 municipalities located in two regions in the Czech Republic: Olomouc Region and Zlín Region. The analysis utilized linked open data on municipal areas and populations from the Czech Statistical Office (CZSO) and linked open data on the costs of the waste collection service for the Czech municipalities from MONITOR, the specialized information portal of the Ministry of Finance of the Czech Republic. The data relating to the forms of intermunicipal cooperation, forms of production, forms of provision, PPPs, and economies of scale were obtained via a questionnaire-based survey. The survey was carried out from September 2016 to the end of December 2017.

For processing the OLS regression, it was necessary to clean the data to achieve a standard data distribution. This was obtained after the data had been cleaned by 5% due to extreme values (18 lowest values and 18 largest values). The data set contained 674 municipalities after the sample was cleaned. In order to perform a statistical data analysis, the municipalities were divided into two population size categories: fewer than 1000 inhabitants and more than 1,000 inhabitants.

The Czech Republic has one of the highest territorial fragmentations of municipalities in Europe. There are many small municipalities with fewer than 1000 inhabitants (more than 82 % of all municipalities) in the Czech Republic. Municipalities with more than 1,000 inhabitants form only 17.3 % of all municipalities (see Table 1). The structure of the research sample corresponds relatively well to the structure of municipalities in the Czech Republic, even though it contains a smaller proportion of municipalities with fewer than 1000 inhabitants (see Table 1).

Table 1: Structure of the research sample

Population	*Number of municipalities in the Czech Republic*	*Percentage of all the municipalities in the Czech Republic*	*Number of municipalities in the research sample*	*Percentage of the sample*
fewer than 1000	5618	82.69 %	482	67.88 %
more than 1000	1176	17.31 %	228	32.12 %
total	6794	100.00 %	710	100.00 %

Source: The authors, according to CZSO

The Empirical Model

In order to enable the comparison of the results of the research with international parametric (econometric) studies[8, 16, 18-19, 26], an OLS regression model was used, as in those studies. The basic function for total municipal waste management costs per capita (*TMWCpc*) in relation to intermunicipal cooperation, as well as other factors, can be represented as:

$$TMWCpc = f(IWCC, IPP,\ Prod,\ Prov, PPP, Scale) \quad (1)$$

The dependent variable *TMWCpc* represents the total municipal waste costs per capita. It includes collection, transportation, disposal or treatment, and other waste collection services. The total costs incurred by each municipality are determined by the population of the municipality; therefore, we study the costs per capita.

They are mainly determined by the following factors, which were determined as explanatory variables:

- *Intermunicipal waste collection company (IWCC)*: This is a dummy variable expressing *intermunicipal cooperation* and *common municipal waste collection company*. The variable acquires a value of 1 when a municipality is one of the owners of waste collection company; otherwise it acquires a value of 0. The hypothesis for this variable is a negative correlation, which was confirmed by a number of studies [13, 18, 21, 26, 38].

- *Intermunicipal/joint public procurement (IPP)*: This is a dummy variable expressing *intermunicipal cooperation in public procurement* for municipal waste management. This variable acquires a value of 1 when a municipality submits a joint public procurement contract for waste management and a value of 0 otherwise.
- *Form of production (Prod):* This variable captures the influence of either *public or private delivery* of waste collection and services on costs. It is constructed as a dummy variable and takes a value of 1 if the service is produced by a public company and a value of 0 for cases of private delivery. A public company is defined as a company which is more than 50% under public ownership. The expected effect is ambiguous. According to Ohlsson[7], public delivery is more cost efficient than private delivery. In contrast, other authors[6, 9,13, 18,20-21, 26, 38-40] have concluded that there are no significant differences between public and private delivery.
- *Form of provision (Prov)*: This is a dummy variable for the *form of delivery* of waste collection services. It acquires a value of 1 for cases of contracting out and a value of 0 for cases of internal delivery. The results of empirical studies conducted in various European countries and in the US are ambiguous as regards this variable. According to Bel and Costas (2006) and Bel and Mur (2009), the form of delivery (internal/contracting out) does not have a significant impact on municipal waste collection costs. Dijkgraaf and Gradus (2013) and Gradus, et al. (2016) indicate that contracting out reduces municipal costs. For this reason, the hypothesis for this variable is ambiguous.
- *Public-private partnership (PPP)*: The impact of *the mixed (PPP) form* of waste collection companies is examined in a number of empirical studies[13, 15, 39]. In order to assess the influence of the PPP form of enterprise on waste collection costs, we use the PPP variable as a dummy variable that takes a value of 1 if waste collection services are provided by a mixed form of enterprise (PPP), and a value of 0 otherwise. The hypothesis for this variable is a positive correlation. In mixed ownership, the co-owner is a private company, which is expected to exert pressure on the waste collection company to achieve a higher profit.
- *Multinational waste collection corporation* (*MNC*): This is a dummy variable that acquires a value of 1 in cases in which a municipality is served by a waste *multinational corporation* (MNC) and a value of 0 if it is not. The hypothesis for this variable is a positive correlation. The globalization of the world economy has resulted in the rapid growth of MNCs; regions forge increasing numbers of links with other locations within and across national boundaries through the local technological development efforts of MNCs. This kind of ownership leads the owner or/and co-owner of the MNC to exert pressure on the waste collection company to achieve an increasingly higher profit. Subsequently, the MNCs are allowed to return the achieved profit to the municipality only in a minor degree; hence, the costs are increasing.
- *Economies of scale (Scale)*: This dummy variable acquires a value of 1 where economies of scale have been achieved in a waste collection area with more than 30,000 inhabitants and a value of 0 in the opposite situation. The hypothesis for this variable is a negative correlation, as was proved in a number of studies[1, 40].

The analysis, consisting of both exploratory data analysis and multiple OLS regression analysis, was conducted at the municipality level; the data used stemmed from 2016. We used the software packages Microsoft Excel 2011 and STATISTICA. Tables 2 – 5 shows descriptive statistics for the individual variables.

Table 2: Descriptive statistics for variables used in the OLS model (whole sample; N=710; 2016)

Variable	***Mean***	***Min***	***Max***	***St. dev.***
MWMCpc [CZK/capita]	533.53	283.79	1,406.30	152.46
IWCC	0.29	0.00	1.00	0.45
IPP	0.17	0.00	1.00	0.37
Prod	0.58	0.00	1.00	0.49
Prov	0.61	0.00	1.00	0.49
PPP	0.13	0.00	1.00	0.33
MNC	0.49	0.00	1.00	0.50
Scale	0.72	0.00	1.00	0.45

Table 3: Descriptive statistics of variables used in the OLS model (sample of Municipalities with fewer than 1000 inhabitants; N = 482; 2016)

Variable	***Mean***	***Min***	***Max***	***St. dev.***
MWMCpc	556.69	283.79	1,477.86	188.37
IWCC	0.35	0.00	1.00	0.48
IPP	0.17	0.00	1.00	0.38
Prod	0.68	0.00	1.00	0.47
Prov	0.57	0.00	1.00	0.50
PPP	0.07	0.00	1.00	0.25
MNC	0.57	0.00	1.00	0.50
Scale	0.69	0.00	1.00	0.46

Source: The authors

Table 4: Descriptive statistics of variables used in the OLS model (sample of Municipalities with more than 1000 inhabitants; N = 228; 2016)

Variable	*Mean*	*Min*	*Max*	*St. dev.*
MWMCpc	615.31	290.259	1,465.868	197.23
IWCC	0.15	0.00	1.00	0.36
IPP	0.15	0.00	1.00	0.36
Prod	0.38	0.00	1.00	0.48
Prov	0.71	0.00	1.00	0.46
PPP	0.25	0.00	1.00	0.43
MNC	0.33	0.00	1.00	0.47
Scale	0.78	0.00	1.00	0.41

Source: The authors

Results and discussion

Table 5 shows the results obtained for the whole sample and for two different population size subgroups. The results for all samples indicate that the explanatory power of the model is not very high, but in relation to the sample size the results are significant.

The results for the whole sample show that PPPs increase total municipal waste management costs per capita and show a significant relation to costs per capita (above 99 % of the confidence level). MNCs have a significant and positive relation to costs (above 95 % of the confidence level). In contrast, intermunicipal cooperation in both forms has a **cost-reducing effect**: for the *intermunicipal waste* *collection company* variable, the significance reaches above 95 % of the confidence level; for the *intermunicipal public procurements* variable, the significance reaches above 99 % confidence level. Finally, form of provision and economies of scale achieved from waste collection areas larger than 1000 inhabitants did not show a significant relation to costs; however, the result is not significant, and international studies indicate that, economies of scale have a positive relation with costs for municipalities with over 10,000 inhabitants.

Table 5: Empirical results of the regression analysis (OLS model) for the dependent variable of total costs of waste collection service per capita

Variable	***Whole sample***	***Municipalities with fewer than 1000 inhabitants***	***Municipalities with over 1000 inhabitants***
Const	874.378*** (25.643)	846.588*** (42.658).	920.881*** (45.251)
IWCC	**-31.704**** **(8.865)**	**-34.453***** **(4.111)**	**-20.516**** **(5.339**)
IPP	**-53,381***** **(12.146)**	**-64.907***** **(17.492)**	**-34.453***** **(20.811)**
Prod	-35.808* (1.999)	21.370 (20.617)	-38,298 (34.509)
Prov	-89,381 (59.146)	-112.471 (78.220)	-112.579 (50.576)
PPP	**49.404***** **(14.039)**	**65.703***** **(4.516)**	10.748 (29.833)
MNC	**30.691**** (15.467)	31.367 (33.939)	36.149 (23.845)
Scale	-13.366 (14.246)	-4.648 (25.023)	8.008 (44.849)
N	710	482	228
R^2	0.3419	0.3467	0.3432
adj. R^2	0.3001	0.2517	0.2472

Note : The values in brackets are the standard errors for individual variables. The results of the variables with a significance level higher than 95 % are marked in bold.
The numbers stand for the p-value of the significance of a variable: *** the significance level of 99 %, ** the significance level of 95 %, * the significance level of 90 %.*

Source: The authors

Table 5 also shows different results for different population size subgroups: municipalities with fewer than 1000 inhabitants and municipalities with over 1000 inhabitants. In the municipalities with fewer than 1000 inhabitants, the results for the variables *IPP* and *PPP* are quite similar to the total sample estimation. In both cases, **intermunicipal cooperation reduces waste collection costs** and is significant, but the confidence level differs. In the municipalities with fewer than 1000 inhabitants **intermunicipal public procurement** has a stronger effect; it is above 99 %. **Intermunicipal waste collection companies** have a significant effect in municipalities with over 1000 inhabitants.

The results indicate that intermunicipal cooperation shows a significant cost-reducing effect; however, this effect is relatively small when compared to the opposite effects of PPPs and MNC. Concerning the importance of intermunicipal cooperation and our RQ2, as shown by other studies focused on highly fragmented countries[19], it can produce positive effects especially for local governments with insufficient capacities, i.e. for small local governments, as is shown by our results for the intermunicipal public procurements variable. According to Bel and Warner[25], economies of scale exist especially for small local governments. Small local governments could benefit more from cooperation than larger ones, as the smaller ones are more likely to achieve a reduced average cost of service delivery[25]. The same point was made by Koprić[5], who stresses that intermunicipal cooperation can serve as a surrogate or functional substitute for territorial consolidation under the conditions of small units and fragmented local structure in particular. Larger local governments do not need intermunicipal cooperation in order to properly perform their own tasks. Our results correlate with these findings[5, 9-11, 25, 31-34].

On the other hand, the PPPs have a significant positive relation to the costs in both cases in relation to increasing costs, but in the smallest municipalities with fewer than 1000 inhabitants, the effect is stronger. The results of the OLS model show a significant positive relation between the PPPs and cost increase in the total sample and for municipalities with population sizes of fewer than 1000 inhabitants. Chong, et al. [20] obtained similar results based on the data from 5000 local French authorities. The choice made by local authorities to engage in a PPP is not random; further, conditional on the choice of the PPP, consumer prices are significantly higher on average. Considering these results, it is possible to ask: *Do the PPPs lead to failure in terms of efficiency?* The results obtained in the estimation indicate that the form of provision (especially contracting out) has no significant effects on municipal waste collection costs for either sample. It seems surprising in contrast that the results for intermunicipal public procurement (contracting out in the form of intermunicipal cooperation) have a significant cost-reducing effect. The result for the form of production variable shows a small cost-reducing effect for the service produced by a public waste collection company. This effect is not so strong; the significance level is above 90 % and cost reduction is only 35.8 CZK for the whole sample. In the economies of scale achieved from a waste collection area larger than 30,000 inhabitants, the results for municipalities with fewer than 1000 inhabitants have a positive effect and for municipalities with over 1000 inhabitants a negative effect (increasing costs). These results were not significant. The achieved results enable us to provide a contrast with previously published papers, to present an opinion of established differences, and to express a view of the results with a relevant explanation. This enables us to open a space in which to outline the need for further possible solutions and for the development of science, society, and practices in the area of local waste management, even beyond the borders of conventional ways of thinking in regards to different factors and variables.

Conclusions

The paper is focused on the relation between local waste collection costs and selected factors affecting cost efficiency. We paid special attention to the forms of production and provision, to intermunicipal cooperation in two forms (intermunicipal waste collection company and intermunicipal public procurements), to economies of scale, and to PPPs. Based on the data set, the paper provides clear answers to the established research questions and contributes to ongoing academic debates while going beyond conventional approaches.

The empirical analysis of factors influencing waste collection costs returned interesting findings. In addressing RQ1, the obtained results show a significant positive relation between intermunicipal cooperation and cost savings in the total sample and for all population size subgroups. Concurrently we found that the cost efficiency of local waste collection services is negatively affected by PPPs but only for smaller municipalities with populations of fewer than 1000 inhabitants.

RQ2 and RQ3 help us to understand this issue in a deeper way. In addressing RQ2, we found that the cost efficiency of local waste collection services is more strongly affected by intermunicipal waste collection companies, but the significance is higher for intermunicipal public procurements. In addressing RQ3, we found that intermunicipal cooperation more reduces waste collection costs in the smaller municipalities with fewer than 1000 inhabitants.

The paper provides clear answers to the research questions and contributes broadly to the field of cost effectiveness in waste management studies. The policy implications could involve pointing out the importance of intermunicipal cooperation in cost savings and offering a new and innovative solution to the decision-making processes of municipal representatives. It is clear from numerous studies that local governments prefer to collaborate with other local governments. From this perspective, it is no surprise that intermunicipal cooperation is considered a sufficient measure of cost reduction for the municipality. In addition, our results allow us to support the assertion that intermunicipal cooperation is often accompanied with decreases in costs per capita. However, as was stressed by Lackowska[42], intermunicipal cooperation is not a panacea. When policy makers seek to identify an “optimal” population size for delivering services, even the high diversity of local services can lead to different recommendations. Taking this fact into account, it is impossible to state the sizes and the number of local governments that must cooperate in order to achieve cost efficiency and cost effectiveness in all cases of delivering the local services for which they are responsible. More precisely, while collaborating local governments can be very efficient in delivering one service, at the same time they may fail to achieve efficiency in the delivery of another service.

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Meziobecní spolupráce obcí v odpadovém hospodářství a její efekty na nákladovou efektivnost

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Souhrn

Článek se zaměřuje na meziobecní spolupráci a její efekty v oblasti nákladové efektivnosti odpadového hospodářství obcí ČR a poskytuje nový a inovativní přístup k nákladové efektivnosti služeb nakládání s komunálním odpadem. Byl zkoumán vzorek 710 obcí ze dvou regionů v České republice (Olomoucký a Zlínský kraj) pro data výdajů na odpadové hospodářství za období 2014 až 2016. Byly zkoumány dvě formy meziobecní spolupráce: svozové společnosti ve společném vlastnictví obcí a veřejné zakázky zadáváné společně obcemi. Výsledky analýzy zpracované pomocí obecné lineární regrese metodou nejmenších čtverců ukazují, že meziobecní spolupráce má výrazný vliv na snižování výdajů na odpadové hospodářství obcí, a to zvláště u malých obcí do 1 000 obyvatel.

Klíčová slova: *odpadové hospodářství, meziobecní spolupráce, veřejné zakázky a nákladová efektivnost*

Co-firing of coal with a solid recovered fuel as a route for reduction of sulphur dioxide emissions

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Abstract

This work focuses on co-firing of coal with specially separated waste marked as a solid recovered fuel (SRF) for the purpose of decreasing sulphur dioxide emissions. Nowadays, it starts to be very challenging for coal fired boilers to reach tightened emission limits for SO_2 which are currently set at 1 500 mg/m^3 for solid fuel and power inputs from 5 to 50 MW. The main contribution of this work is that there were done long term experiments with co-firing at the real industrial boiler with real operating parameters.

Three mixtures with increasing amount of SRF were proven at the grate type of boiler having power output 5.14 MW. Used mixtures obtained 10, 25 and 40% of SRF in heat input. Experimental results show that only the mixture with the highest amount of SRF decreases SO_2 concentration under the current SO_2 emission limits. However, this percentage of SRF in the mixture created several problems which should be sorted out. The biggest problems with this co-firing were increased concentrations of particular matter, increased concentration of NO_x and higher emissions of HCl. Due to the different specific volume and mechanical properties of used fuels some potential problems with fuel preparation and fuel feeding should be taken into consideration.

Keywords: *co-firing of waste, solid recovered fuel, sulphur dioxide*

Introduction

In the Czech Republic energy industry has a strong position. There are more than 38.1 % of households heated from the central heating systems where one half of the delivered heat comes from coal fired sources [1]. Nowadays, coal fired heating plants faces new challenges in terms of fulfilling new emission limits. For the stationary power systems those are stated in the Air Protection Act 201/2012 Coll. [2] and the directive 415/2012 [3] and divide the sources to the categories according to the power input and type of the fuel. Current emission limits are being tightened by legislation of European Union. In the Czech legislation there are emission limits stated up to year 2025 and further as can be seen in Table 1. This work mainly focuses on sulphur emission targeting sources with power thermal input in the range from 5 to 50 MW.

For coal fired boilers meeting the newly stated emission limits starts to be very challenging. This article focuses on fulfilling emission limits of SO_2 in the grate type of boiler.

Sulphur dioxide emissions

Sulphur is contained in each type of solid fuels and its content in the Czech coals varies most commonly in the range from around 0.5 wt% up to 3 wt% related to the combustible matter. Sulphur in coal has only negative impacts on the fuel quality. The main problem is the production of harmful sulphur oxides, but it also decreases the calorific value and it contributes to the easier self-ignition on the fuel storage. Sulphur in coal is found in several forms and the problematic of sulphur type determination is very wide. The major forms are pyritic, organic, sulphates and traces of elemental sulphur [4].

Table 1: Specific emission limits for combustion in stationary sources with thermal input 5 – 50 MW [mg/m^3] [2]

Validation		***Fuel***	***SO_2***	***NO_x***	***PM***	***CO***
Before 31. 12. 2017		Solid fuel	2500 1500 1)	650 500 1)	150 100 1) 250 2)	400 300 1) 650 2)
1. 1. 2018 – 19. 12. 2018	Sources in operation before 1. 9. 2014	Solid fuel	2500 1500 1)	650 500 1)	150 100 1)	400 300 1)
	Sources in operation after 1. 9. 2014	Solid fuel	1500 3)	500	30	300 500 4)
20. 12. 2018 – 31. 12. 2024	Sources in operation before 21. 12. 2018	Solid fuel	1500 3)	500	30	300 500 4)
	Sources in operation after 20. 12. 2018	Solid fuel except biomass	400	300	20 5)	300
From 1. 1. 2025	Sources in operation before 21. 12. 2018	Solid fuel except biomass	400 6)	500	30	300
	Sources in operation after 20. 12. 2018	Solid fuel except biomass	400	300	20 5)	300

1) Applies for stationary sources with fluidized bed.
2) Applies for biomass combustion in stationary sources.
3) For brown coal combustion in stationary sources which are operating maximally 3200 hours per year applies specific emission limit of 2000 mg/m^3.
4) Valid for biomass combustion in stationary sources except for seed cakes.
5) For stationary sources having thermal input lower or equal 20 MW applies emission limit of 30 mg/m^3.
6) For stationary sources having thermal input lower or equal 20 MW applies emission limit of 1100 mg/m^3.

The product of sulphur oxidation - sulphur dioxide (SO_2) is non-explosive, non-flammable, colourless toxic gas [5]. SO_2 is also dangerous for whole combustion system, because it is causing both high-temperature and low-temperature corrosion. When released to the atmosphere, the sulphur dioxide can be converted to sulphur trioxide, which later by reactions with water vapour creates sulphuric acid H_2SO_4. Sulphuric acid has a damaging effect in atmosphere, it is usually marked as acid rain. Acid rains damage vegetation, due to their acidification they are dangerous for water sources and have devastating effect on water organisms. Acid rains are also damaging a wide variety of building materials – mortar, marble and roofing slate. There are several possibilities of SO_2 reduction. Generally we consider:

- desulphurization of fuel
- flue gas desulphurization
- in-situ desulphurization during combustion
- changing of high sulphuric fuels for low sulphuric fuels.

Desulphurization of coal covers methods removing sulphur directly from coal just before its combustion. These methods were under the main scope of research in 1970s and 1980s. With increasing requirements on SO_2 emissions and usually very high energy demands and complicated processes, these methods are neither competitive with desulphurization of flue gas nor with other methods.

Flue gas desulphurization are methods removing SO_2 after the combustion processes. FGD is a relatively complicated process where it is necessary to remove relatively small concentrations of SO_2 from a large volume of flue gas. Generally it can be divided into wet, dry or semi-dry methods. These methods covers proven technologies with known operation but they are usually more suitable for larger scale heating or power plants, due to their relatively expensive operation and high investment costs. Using these technologies always means growth of the final heat price.

Desulphurization during combustion is based on the reaction between gaseous SO_2 and solid sorbent, which is added directly to the combustion process. The most commonly used additives are limestone ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). The summarized reaction of SO_2 retention can be stated as [6]:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$$

The product of desulphurization is stable calcium sulphate which is removed from the combustion process commonly with ash. The process of in-situ desulphurization is suitable mainly for fluidized bed combustion due to the optimal combustion temperatures and improved mass and heat transfer which are typical for fluidized beds. [6]

The last mentioned possibility of decreasing the SO_2 emissions with relatively low investment cost is substitution of the fuel. Changes between the coals in terms of the Czech Republic does not bring any important benefits, because even the usage of coal with the lowest available sulfur content does not meet the emission limit of 1500 mg/m^3. The only possibility is co-firing with other types of low sulphur fuels, usually with biomass, although usage of other fuels is also possible.

This work focuses on co-firing of coal with certificated solid recovered fuel coming from sorted waste on a grate fired type of boiler for the purpose of decreasing the sulphur dioxide emissions.

Experimental part

Used fuels

The original fuel used for the experiments is Czech brown coal. It should be mentioned that the quality of used coal was slightly improved in comparison with catalogue values due to the fact that it was stored in dry storage, protected against rain and its particular water draining. The fuel which is co-fired is marked as Solid Recovered Fuel (SRF) and is made of non-dangerous waste. It is produced from scrapped products that have already ended their lifetime and became waste – such as textile, plastic, rubber etc. The original items were put on market therefore they cannot have dangerous properties. The proximate and ultimate analyses of both fuels is stated in Table 2. The composition of SRF is shown in Table 3. It can be seen that majority of the fuel comes from automotive industry, mainly from automotive textile.

Table 2: Proximate and ultimate analyses of the brown coal

Fuel	C^r	O^r	H^r	S^r	N^r	A^r	W^r	Q_i^r	Cl^d
Coal	50.1	15.4	3.9	0.8	0.6	10.7	18.5	20.1	< 0,01
SRF	54.9	26.5	7.4	0.07	1.1	9.3	0.79	25.6	0.07

Table 3: Composition of the SRF

Component	***Average amount (wt. %)***
Automotive textile	60 – 80 %
Fiberglass with carton filling	Up to 20 %
Rubber hose and rubber granulate	Up to 10 %
Document shredding	Up to 10 %
Plastic covers from food industry	Up to 10 %
Plastic parts from automotive, plastic films	Up to 10 %
Other	Up to 10 %

Description of the boiler

Experiments were done on steam boiler with moving grate of a belt type running in opposite direction than fuel addition. It is supplied via pneumatic fuel spreader. Combustion air is preheated. The boiler has a drum and is equipped with membrane walls where water circulation is natural. The nominal parameters of the boiler are shown in Table 4.

Table 4: Parameters of the boiler

Parameter	***Value***
Steam output [t/h]	6.3
Heat output [kW]	4,266
Heat input [kW]	5,140
Steam pressure [bar]	1.2
Steam temperature [°C]	220

The boiler is newly equipped with secondary air distribution in order to decrease emissions of CO. Secondary air is supplied by 13 nozzles at the front and side walls above the grate. Flue gases are dusted off in dry vortex and secondly in electrostatic precipitator.

Experimental set-up

Performed experiments with co-firing of above mentioned fuels have taken place within 20 days on the described boiler. The boilers power output was set between 65 to 95% of nominal parameters. The experiments were started with combustion of 100% coal to set the common state. Later on, three different fuel compositions were tested. SRF was stored in outdoor storage with protection against rain and blowing off the fine particles. Tested combination of co-combusted fuels was premixed in required ratio outside and put inside the hopper from which it was transported via the conveyor belt to the combustion chamber. The tested mixtures are stated in Table 5.

Table 5: Tested mixtures

	Energy ratio Coal / SRF		***Mass ratio Coal / SRF***		***LHV [MJ/kg]***	***Sulphur content [wt.%]***	***Theoretical SO_2 concentration [mg/m^3]***
Coal	100	0	100	0	20.1	0.8	2 273
Mixture I	90	10	92	8	20.6	0.75	2 081
Mixture II	75	25	79	21	21.2	0.66	1 787
Mixture III	60	40	66	34	22.3	0.57	1 484

Table 5 shows that increasing amount of SRF in the mixture increases the low heating value and oppositely decreases SO_2 theoretical concentration. In case of the mixture III we can see that the theoretical SO_2 concentration is below the emission limit of 1500 mg/m^3 and it should be possible to use this mixture as the fuel for further operation of the boiler.

Measuring consists of continual analysis of SO_2, CO and NO_x using IR analyser Ultramat 23 equipped with electrochemical module for O_2 analyses. Particulate matter was measured continually using optical in situ analyser Dusthunter SP100 and HCl was measured using IR analyser EcoChem MC3. All the analysers were calibrated by certified laboratory.

Results and discussion

The results of SO_2 decrease from above mentioned measurements are stated in Table 6. It can be clearly seen that the theoretical calculation of SO_2 concentration have relatively good accordance with the measurements, having the highest deviation under 10%. The calculation of the theoretical SO_2 concentration takes into consideration 100% conversion of sulphur to sulphur dioxide SO_2. However it is known that some part of the sulphur contained in the fuel is in a non-combustible form - e.g. sulphates. The second reason explaining the difference between the measurement and theoretical concentration is that the sulphur from the fuel can create also sulphur trioxide at lower temperatures, which is not under emission measurement and is not standardly watched. Another explanation of the lower measured concentrations is the presence of calcium carbonate in the coal ash and consequent particular SO_2 self - retention in the ash. However, the difference can be also caused by fluctuating amount of sulphur in both fuels.

Table 6: Comparison of average values of SO_2 with theoretical calculation

	Measured SO_2 concentration [mg/m^3]	***Theoretical SO_2 concentration [mg/m^3]***	***Difference [mg/m^3]***	***Difference [%]***
Coal	2 225 ± 134	2 273	48	2.1
Mixture I	1 877 ± 173	2 081	204	9.8
Mixture II	1 660 ± 206	1 787	127	7.1
Mixture III	1 369 ± 171	1 484	115	7.7

There has to be mentioned that the values of measured SO_2 concentration are the averages from several day lasting measurements. The time runs of the measurements with the given fuel mixtures are stated in diagrams in Figure 1. Those diagrams are created from the points representing the average values of the given emission from 30 minutes periods. It can be seen that addition of other type of fuel have significant effect on SO_2 emission without any negative effect on combustion stability and some dramatic increase of other gaseous emissions. The effect on other emissions is stated in Table 7.

Table 7: Average values of other measured emissions and their standard deviations during co-firing experiments

	PM [mg/m^3]	***CO [mg/m^3]***	***NO_x [mg/m^3]***	***SO_2 [mg/m^3]***	***O_2 [%]***	***HCl [mg/m^3]***
Coal	6.2 ± 5.9	388 ± 76	458 ± 94	2 225 ± 134	14.7 ± 0.8	6.4 ± 3.4
Mixture I	40.2 ± 47	407 ± 64	463 ± 66	1 877 ± 173	13.9 ± 1.7	18.2 ± 10.5
Mixture II	118 ± 54	402 ± 64	527 ± 82	1 660 ± 206	15.1 ± 1.7	17.6 ±17.7
Mixture III	154 ± 23	359 ± 71	499 ± 54	1 369 ± 171	14.8 ± 1.2	30.8 ± 23.1

It can be seen that increasing amount of SRF in the fuel mixture have significantly negative impact on particulate matter emissions which increases from 6.2 mg/m^3 up to 154 mg/m^3 in case of using Mixture III. This effect is probably caused by the high amount of light and fine particles which are entrained with combustion gases from combustion chamber and their different characterization. The emission limit of 30 mg/m^3 is exceeded more than five times therefore further operation optimization or extension of PM removing should be done. In order to learn more about the problem of higher PM emissions there should be done more comprehensive analyses of particle size distribution of PM or e.g. elemental composition of fly ash. However, this was not the main focus of presented work and thus these analyses are missing.

In case of CO emissions there is not seen any definite dependence with increasing amount of SRF in the fuel. The emission limit of 300 mg/m^3 for CO was exceeded also for reference measurement with coal. Although the CO concentrations are higher for Mixture I and Mixture II in comparison with reference state, this increase cannot be dedicated to the SRF addition, as Mixture III having the highest amount of SRF shows oppositely the lowest emissions of CO. Emissions of CO could be decreased by improvement of combustion process by optimization of air supply.

In case of NO_x the limit 500 mg/m^3 was exceeded only in case of measurement with Mixture II. The increased NO_x emissions in comparison with reference case are caused because of two reasons. The first reason is higher amount of nitrogen presented in SRF, which is nearly two times higher in comparison with coal and could increase production of so called fuel nitrogen oxides. The second reason of higher production of NO_x are increased local combustion temperatures caused by the higher low heating value of the mixed fuel and thus increased production of thermal nitrogen oxides. Also the process of combustion was not directly optimized for NO_x reduction, due to the low experience of the operators with the new mixtures of fuel and their different behaviour. Although there are several reasons for increase nitrogen oxides concentrations, the final NO_x emissions ranges around the emission limit and they can be reduced by optimization of combustion process, such as optimization of secondary air supply.

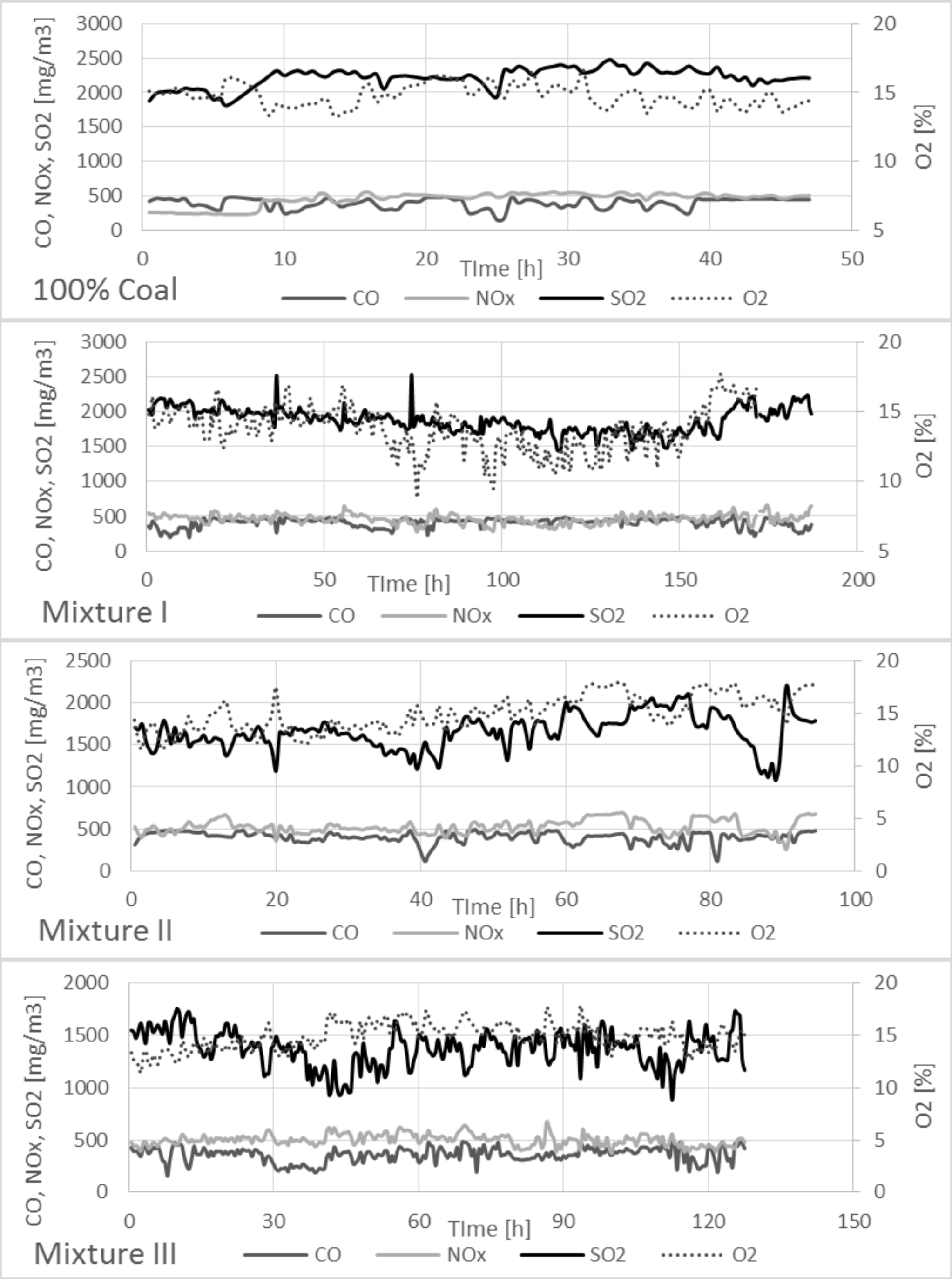

Figure 1: Emission behaviour during combustion of different fuel mixtures

It should be mentioned that the boiler was operated with high excess of air, having O_2 concentration in flue gas around 15%. This measure has several combined effects on emission production. The main reason for such a high excess of air was to decrease the combustion temperature and thus decrease the production of thermal NO_x. Among negative effect of this measure belongs increased production of CO, which is given by incomplete oxidation to CO_2 under lower temperatures and by shorter residence time in the zone of combustion. On the other side, higher CO emissions participate on reduction of NO_x back to N_2. Therefore, it is important to find some optimal settings of the boiler in order to meet these emission limits. However, the construction of the boiler (with belt grate and pneumatic throwing of fuel) do not enable further significant decrease of these emissions and it will be quite challenging to find an optimal setting.

The last monitored pollutant was hydrogen chloride HCl. Chlorine which is released during combustion is very dangerous for the construction of the boiler due to the fact that it causes corrosion. It can be seen that with increasing amount of SRF in the mixture increases also the concentration of HCl. This fact is connected with the higher amount of chloride obtained in the SRF. However, the process of chlorine corrosion is relatively complicated and does not dependent only on the concentration of released chloride but depends also on the local operational parameters. The real effect of chloride corrosion was not studied during the experiments in detail.

Potential risks of using co-firing

According to the experiments that were done in the real industrial boiler it is possible to reduce the concentration of SO_2 by co-firing of waste (SRF) with coal. Using this method brings some potential risks that should be taken into consideration. These risks could be summarized as:

- ensuring the sufficient mixing of the fuel
- potential problems with fuel feeding
- decreased capacity of the fuel hoppers
- problems with meeting the emission limits of CO
- problems with increased PM emissions due to the different characteristic of ash particles
- ensuring the properties of used co-combusted fuel.

It is very important to ensure sufficient mixing of the used fuels. Insufficient mixing could cause instable combustion with potential exceed of emission limits and instable power output of the boiler.

Different physical characteristic of the co-combusted fuel could cause problems with fuel feeding. The most problematic feature is probably the different bulk density of the co-combusted fuels. Table 8 shows increase of the volume of used mixtures of the fuel. The bulk density of used coal is 720 kg/m^3 which is more than 3,5 higher than the bulk density of SRF which is around 200 kg/m^3. Values of the specific volume in table 8 shows that for mixture III we get nearly two times higher volume of the fuel in comparison with coal. This fact can affect the volume capacity of the fuel conveyors and also decreases the capacity of the fuel hoppers. Another problem could be the fact, that the fuel contains high amount of the fine and light particles that can be entrained by wind from the fuel storage, which increases the requirements for its storage.

Table 8: Specific volume of the fuel mixtures

	Energy ratio Coal / SRF		*Mass ratio Coal / SRF*		*Specific volume of the fuel [m^3/kg]*
Coal	100	0	100	0	1.39
Mixture I	90	10	92	8	1.68
Mixture II	75	25	79	21	2.14
Mixture III	60	40	66	34	2.63

Potential exceed of CO concentration can be caused by the fact than the operators of the boiler do not have enough experiences with operation of such boilers with this type of fuel.

Emissions of the particulate matter seem to be also problematic. The reason is probably different characteristic of the entrained particles and insufficient efficiency of the electrostatic precipitators. The additional improvement of the particles removing is expected. Possible solution could be further adjustment of SRF in order to increase its density using e.g. extrusion or pelletization. However, such a type of certificated SRF or processing method is currently missing on the Czech market.

Potential risk comes also from the characteristic of the additional fuel. According to the analyses from the last 5 years the amount of sulphur varied from 0.05 wt.% up to 0.25 wt %, with the average amount around 0.11 wt %. Increase in sulphur content for given mass ratio of the fuels could cause growth in SO_2 production. The effect of different heat ratios of the fuel with different sulphur content in SRF is shown in Figure 2. The lower curve at the diagram shows expected SO_2 concentrations while co-firing the fuel with lower amount of S (0.05 wt %). Oppositely the upper curve shows presumable SO_2 emissions while co-firing the fuel with the higher amount of S (0.25 wt %). The diagram supposes constant sulphur content in the coal, although this can also varies and assumes 100% conversion of the sulphur on SO_2.

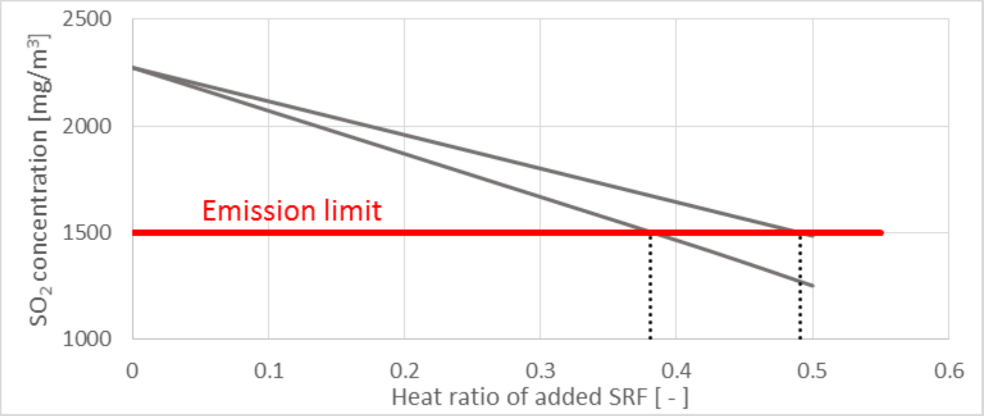

Figure 2: Effect of different amounts of SRF addition on SO_2 concentration for two different amounts of S in SRF

Conclusions

Above mentioned experiments that were done in the real scale industrial boiler successfully proved that co-firing of this exact low sulphuric solid recovered fuel can be used as a tool for decreasing of the SO_2 concentrations and reaching the legislative emission limit of SO_2. In this exact case it was necessary to use about 40% of SRF (heat ratio) in order to reach the emission limits of 1 500 mg/m^3 SO_2. However, the experiments uncovered several problems with using this co-combusted fuel.

It is always necessary to individually consider the construction of the fuel feeding system and its suitability for transporting SRF to the combustion chamber. The reason is the different characteristic of the SRF and its higher specific volume. It is also necessary to ensure the stored SRF against the inconvenient atmospheric conditions.

Meeting the emission limits for particular matter seems to be problematic. The measurements showed increase of PM concentration from 6.2 mg/m^3 to 154 mg/m^3 in case of using Mixture III. The material which is entrained from the boiler during co–combusting have different physical characteristic than the ash entrained from the original fuel. This leads to insufficient efficiency of electrostatic precipitators. Necessity of additional investment costs on improving this technology are expected.

During co-combustion there were recognized almost five times higher concentration of HCl which could cause problems with corrosion of the boiler. The expected emission limit of HCl in future will be probably set at about 10 mg/m^3, which could cause another problem with co-firing of this fuel.

Without solving above mentioned problems that were recognized during the experiments, mainly the problems with meeting the emission limits of PM, the co-firing of SRF cannot be currently used in practice.

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Spoluspalování uhlí s tuhým alternativním palivem jako způsob snižování emisí oxidu siřičitého

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Souhrn

Tato práce se zabývá problematikou spoluspalování uhlí s tuhým alternativním palivem pocházejícím z odpadu za účelem snížení emisí oxidu siřičitého. Pro kotle o tepelném příkonu 5 až 50 MW spalující uhlí dochází od 1. 1. 2018 ke značnému snížení emisního limitu SO_2 na 1 500 mg/m^3. Hlavním přínosem této práce je prezentace výsledků z dlouhodobých experimentů spoluspalování provedených na skutečném průmyslovém kotli při reálných provozních podmínkách.

Celkově byly spalovány tři směsi paliv obsahující vzrůstající obsah TAP (10, 25 a 40 % tepelného příkonu). Spalování probíhalo na roštovém kotli o celkovém tepelném příkonu 5,14 MW. Výsledky měření ukázaly, že pouze v případě využití směsi s největším obsahem TAP je možné plnit požadované emisní limity SO_2. Použití takto bohaté směsi paliva ovšem způsobuje i řadu negativních dopadů, které je třeba dále řešit. Mezi nejzávažnější problémy patří výrazné zvýšení emisí tuhých částic, zvýšená koncentrace NO_x a rovněž vyšší emise HCl. Díky rozdílnému měrnému objemu a mechanickým vlastnostem paliva mohou nastat problémy s přípravou směsi paliva a její následnou dopravou do kotle.

Klíčová slova: *spoluspalování odpadu, tuhé alternativní palivo, oxid siřičitý*

Effective ventilation strategy for indoor air polluted by gas appliances operation

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Abstract

Indoor environmental quality of average family house in the Czech Republic is the most problematic in the kitchen equipped with combined gas and electrical appliances. Especially gas continuous flow water heaters can be source of significant pollution in the buildings which were recently refurbished and their façade changed into air – tight building envelope. Kitchen hood (exhaust air ventilation equipment located above stove) was found completely insufficient in keeping adequate indoor air quality. This study shows set of requirements on kitchen hood operation (exhaust of polluted air to outdoor environment) and states the necessity of multiple ventilation strategies cooperation (natural ventilation – window opening and kitchen hood operation) based on a few day measurement of typical kitchen operation and appliances use. These stated requirements were necessary to reach standard indoor environmental parameters values together with minimum heat losses.

Keywords: *indoor environmental quality, indoor air quality, ventilation rate, gas appliances, air change.*

Introduction

According to the recent trends of energy savings in building services operation and building envelope insulation, the minimum air change rate is calculated considering heat retention. Ventilation system control is usually based on the CO_2 measured concentration. The air change rate is dependent on the occupant behavior. This paper is focused on experimental description of the investigated pollutants in a naturally ventilated room during both occupied and unoccupied hours.

In this kitchen operation typically many pollutants are produced during cooking – combustion of gas. The real question is which pollutant is the most important and decides the exact ventilation need rate. The ventilation need is highly dependent on the real use of the room. These are two main challenges for this sort of operation.

Gas Appliances in the Investigated Room

In the investigated kitchen the following appliances are used: a gas cooker and a gas continuous flow water heater. The cooker top has four burners. These burners have three essential considerations: 1 kW; 1. 75 kW and 2 times 2.0 kW. The gas continuous flow water heater has following characteristics: stand-by flame 0. 2 kW and output during hot water generation: 8 kW.

Ventilation Strategies

Possible ventilation strategies are natural ventilation and forced ventilation (Table 1). Natural ways of used ventilation strategies are apart from infiltration partially open window and open door to the corridor. This corridor is connected to another three rooms with operable windows. It interconnects spaces with different temperatures. The forced ventilation possibility is a kitchen hood located above the kitchen cooker. The kitchen hood output characteristics are 3 levels. The highest level enables the ventilation rate of 205 m^3/h. The output of kitchen hood fan engine is 120 W. The outlet duct diameter is Ø 120 mm. The kitchen hood is used only during times of cooking. The occupants use mostly only 1st level. The estimation of this ventilation rate was determined as 130 m^3/h.

Table 1: Ventilation strategies used during measurement

	YES	**NO**
partially open window	x	
open window		x
closed window	x	
door to corridor open	x	
door to corridor closed	x	
kitchen hood on	x	
kitchen hood off	x	
infiltration	x	

Methods

Following methods were used to investigate indoor environment in the kitchen. Measurements were taken of carbon dioxide, carbon monoxide, TVOC and formaldehyde. There were Innova air quality sensors used to measure their concentrations. The measurement was carried out by Innova 1412 device. This device is photoacoustic multi gas monitor which works on the photoacoustic spectroscopy (PAS) principle.

This device works as a system which consists of centrally located datalogger with multi gas monitor and a multiple point sampler. The monitoring works as continuous – flow – PAS detector. The samples can be taken from up to 5 different locations. This system is connected to PC (laptop) for activation of process controllers[1]. All these pollutants were measured in three selected standpoints. The standpoints were chosen to determine air flows in a room.

A tracer gas was used to calculate air exchange in time when every window and door is closed and when there is some sort of ventilation schedule. The occupants registered their schedule of a kitchen use and ventilation behavior – the schedule of their ventilation habits, their presence in the room, their activity – for better comprehension of room operation.

The tracer gas sulfur hexafluoride (SF_6) was dosed into the investigated kitchen in the beginning of the measurement. The concentration uniformity was provided by the use of mixing fan. The tracer gas concentrations were also measured by the Innova air quality sensors.

Measurements and experimental part

For indoor air quality measurements three standpoints (Figure 1) were chosen closed to freezer I1, sink I2 and door to pantry I3. Indoor air quality parameters were measured to examine the environment under the combustion of natural gas conditions. Especially CO concentrations are expected to be interesting because this gas is a main product of dangerous imperfect combustion of natural gas. Other notable sources of the natural gas are tobacco products and exhaust gasses.

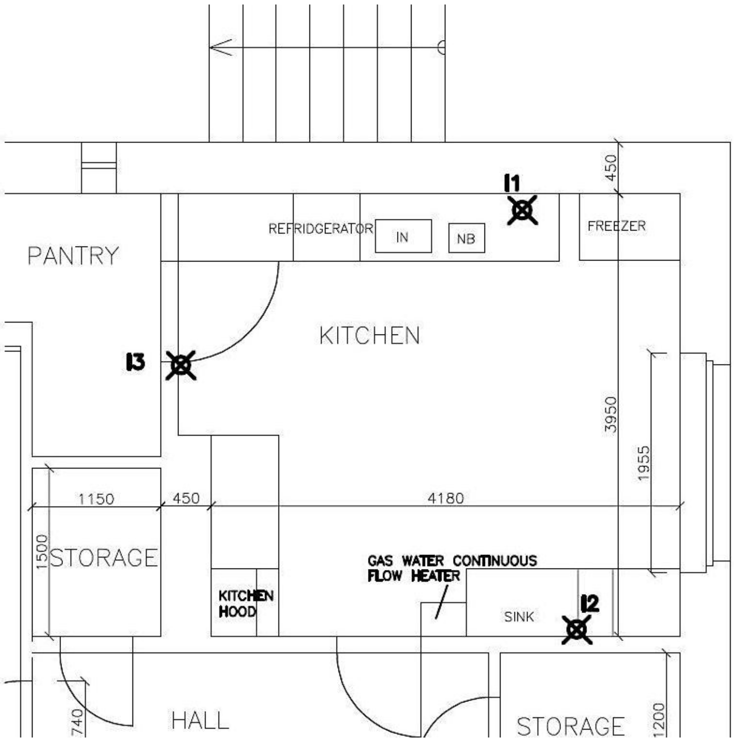

Figure 1: Scheme of IAQ measurement standpoints (I1; I2; I3) in the investigated kitchen

IAQ measurements and gas appliances

CO, CO_2, formaldehyde and TVOC concentrations were measured (Figure 3, 4, 5, 6). For better understanding the cooker schedules are included. Combustion of gas influences the measured concentrations. CO_2 concentration is often used as indicator of occupant's presence in the investigated area. This CO_2 value is an average value of these 3 standpoints. (Figure 6) According to the directive[3] the acceptable CO_2 concentration is in the value of 1500 ppm. According to the opening schedule the open door can better the situation only a little. The partially open window helps much more.

Occupational Behaviour

Occupants were present during the test time for a couple of times. Their presence is shown in the Fig. 4. Mostly just one occupant is present. For only one time two occupants were present. During those times occupants produce pollutant CO_2 and they also use gas appliances. Occupant presence influences the air quality and its requirements on ventilation rate. On the following graph Fig. 4 there is an occupancy profile. This profile is represented together with openings schedule and CO_2 concentration.

Mostly one occupant was present in the kitchen; exceptionally two of them were present. Occupant usually cooked or washed the dishes. Cooking produces pollutants and water vapour. Washing dishes also produces water vapour.

There is this relation between occupancy presence and the requirements on ventilation. Also the occupant behavior can very much influence the indoor air and indoor environmental quality as whole. According to their behavior in terms of using different ventilation strategies the indoor environment can very much be changed into more satisfactory state.

Schedules of Gas Appliances Use and Kitchen Use

The investigated kitchen is used every day through the whole day because of occupants. Occupants are elderly retired persons who stay at home usually for most of the time of a day. They work partly during the day at home. During cooking time kitchen hood is turned on. Most of the day a window is partially open. The upper part of the window is folded inward. The water heater operates in two positions on-position and off position. Gas appliances are in operation for a few times a day. For the following calculations all the values were chosen properly on the safe side of values for the biggest burners.

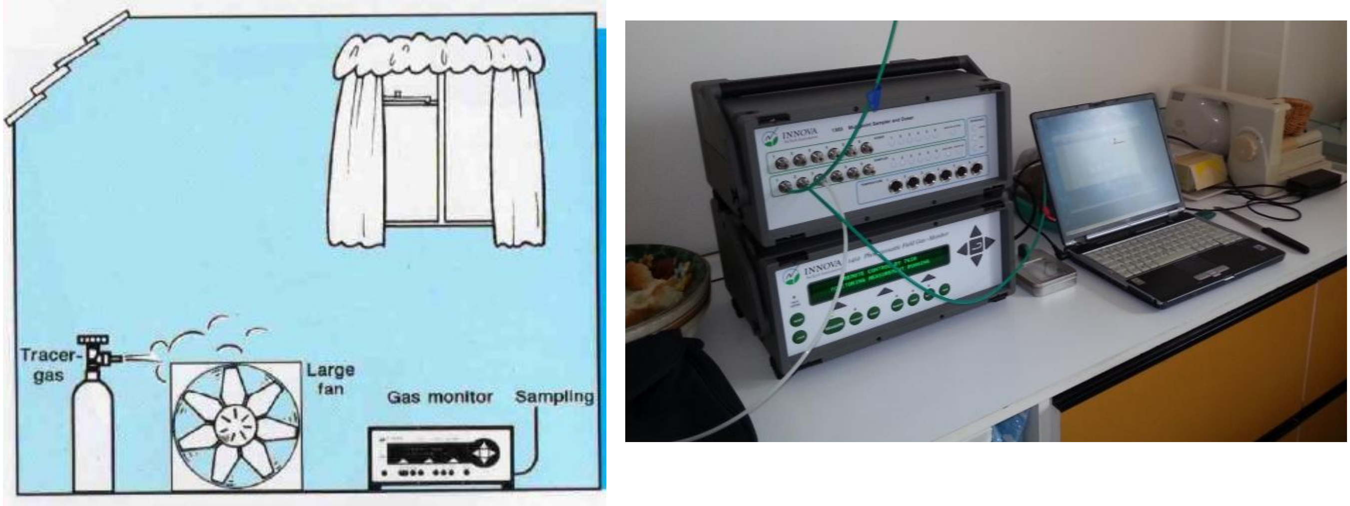

Figure 2: The Concentration-decay method measurement scheme[2]; Picture taken by the papers author of Innova PAS detector and multi point sampler connected to laptop during the measurement in the investigated kitchen

Calculations

Air change calculation

Recently the plastic windows were installed to this family house. This family house façade has also a thermal insulation of 100 mm thickness. These factors give the assumption that the building envelope was changed to the tighter one. The question was how effective can this kitchen ventilate through building envelope? This assumption also brings out the hypothesis that the indoor air quality would have changed for the worse.

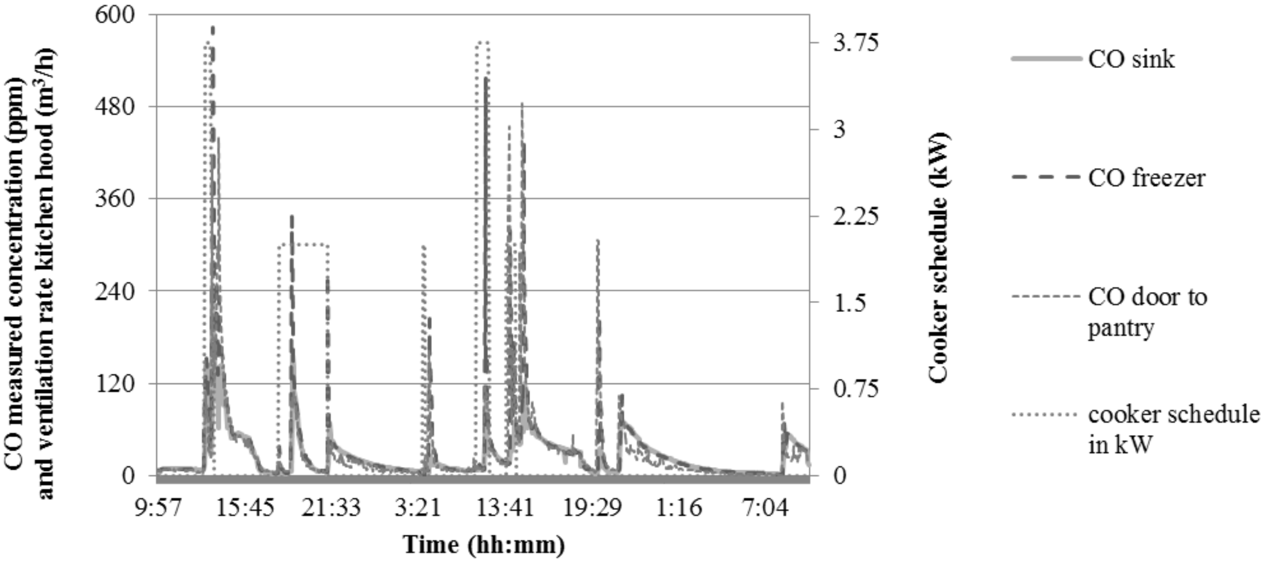

Figure 4: CO – measured standpoint concentrations and cooker schedule

The idea was to investigate this issue with the use of a tracer gas SF_6. Tracer gas concentrations were measured (Fig. 7) on the three standpoints during the whole day. That means during the period of closed openings and during the period of open window and door. The rate was calculated from the measured concentrations of SF_6. The air change was calculated according to the following equation.[4]

$$AC = \frac{\int_0^\infty C(\tau)d\tau}{C(0)}\left[\frac{1}{h}\right] \tag{1}$$

AC air change rate [1/h]
C (τ) measured concentration at τ = ∞ [ppm]
C (0) measured concentration at τ = 0 [ppm]
τ time of measurement [h]

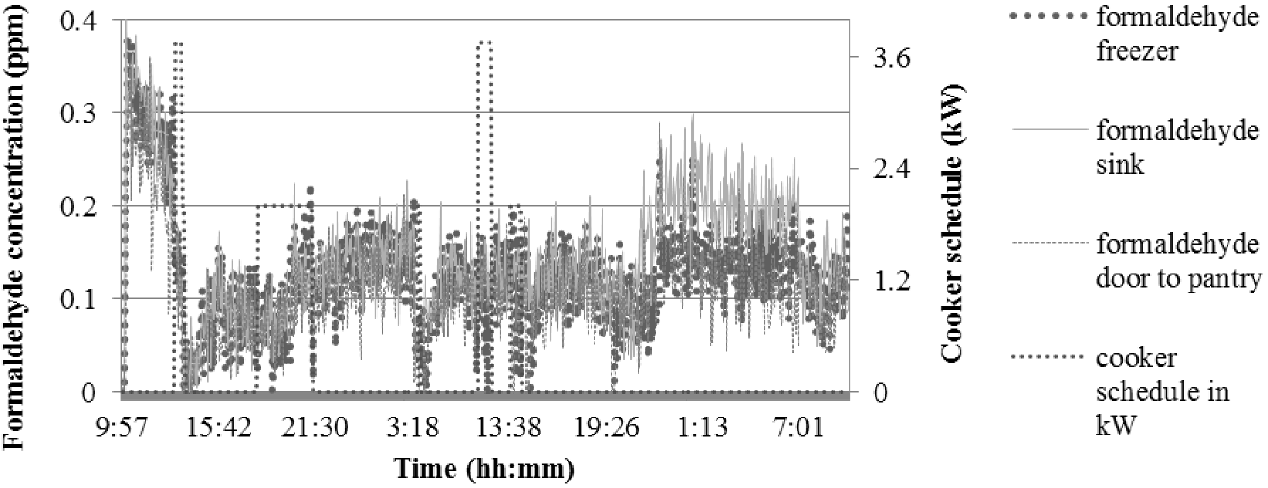

Figure 5: HCHO – 3 measured standpoint concentrations and cooker schedule

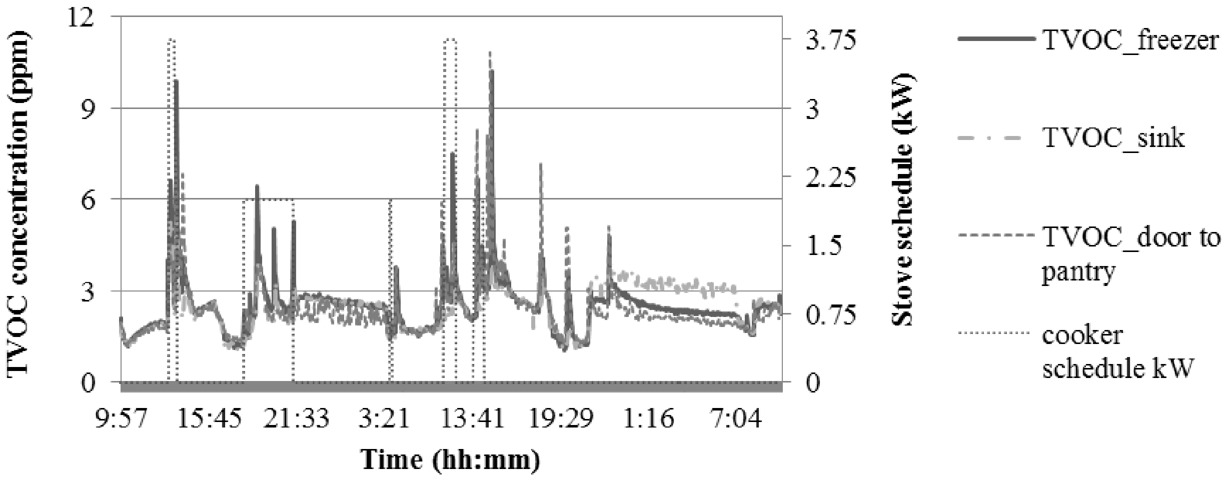

Figure 6: TVOC – 3 measured standpoint concentrations and cooker schedule

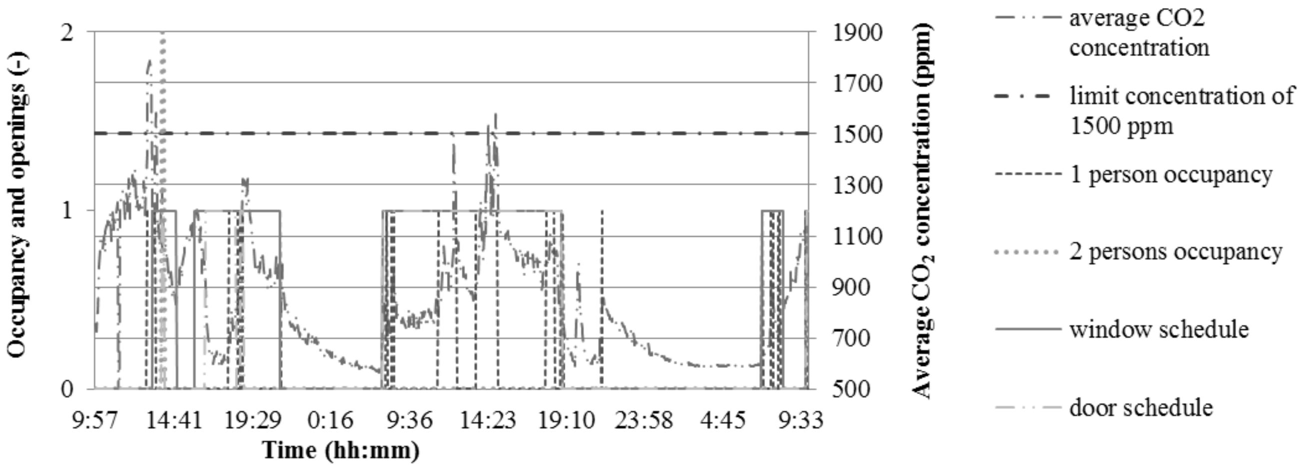

Figure 6: Occupancy, openings schedule and CO_2 concentration

Natural ventilation rate

A temperature difference between an outdoor temperature and an average indoor temperature was calculated. In order to find out a natural ventilation efficiency of a partially opened window the temperature difference was calculated. This difference shows that the natural ventilation is possible and efficient during these times of the measurement. That means that the ventilation through the partially open window is not negligible. Thus the strategy of the ventilation with partially open window was effective and should be taken into the consideration.

Formulation of required ventilation rate according to occupant´s presence

Calculations of required ventilation rates were done. According to the standard[5] the required ventilation rate per person is 25 m^3/h. Analogically the rate for two present occupants is then supposed to be 50 m^3/h. Also during unoccupied hours there is this required value according to standard[5] of a multiple air change n = 0.1 1 / h. Then the required rate is calculated as:

$$V_{unocc} = n * V_m \ (m^3/h) \qquad (2)$$

V_{unocc} – ventilation rate for occupied hours (m^3/h)
n – multiple air change dependent on room purpose and operation (1/h)
V_m – volume of investigated room (m^3)

Calculation of required ventilation rate according to gas appliances

Every used gas appliance has its own known installed wattage. The ventilation rate needed to get rid of these pollutants emitted by gas appliances was calculated. Every watt of this wattage is known and the use was written down during the measured time. The relation between wattage used and ventilation input required was estimated[6] as following:

$$1\ kW \approx 0.2\ m^3/s \quad \text{i.e. } 1\ kW \approx 720\ m^3/h \qquad (3)$$

Into the calculations following appliances and their schedule were taken: a cooker and gas continuous flow water heater. Operation of the kitchen hood was also considered. The kitchen hood was used just once. Its ventilation rate was estimated as 130 m^3/h. Balance calculations were taken in order to find out the real ventilation rate needed during the occupied hours and occupants activities in the kitchen. The balance was calculated from a gas appliance output and its conversion to carbon dioxide and to ventilation rate of fresh air.

Situation in the world

According to the available sources[7] the gas appliances and their influence on indoor air quality was examined since the 1970´s. There were experiments held in the laboratories, (see Fig. 8 - there are the following AC values shown: A) 0. 24; B) 1; C) 2. 5 and D) 7 (1 / h), as well as in summary field measurements (in the kitchens of apartments and residential houses). Traditionally CO and CO_2 concentrations were measured [8, 10, 11, 12]. For some cases NO, NO_2 and NO_x concentrations were also measured [8, 10, 12, 13]. In the Californian (USA) study formaldehyde and acetaldehyde concentrations were also measured. The goal was to find out if the examined gas appliances operation could have had an impact on these concentrations. It was not prooved[10]. Ultrafine particles (particles with diameters of 6 nm or larger (PN)) and fine particulate matter (PM2.5) were measured[13].

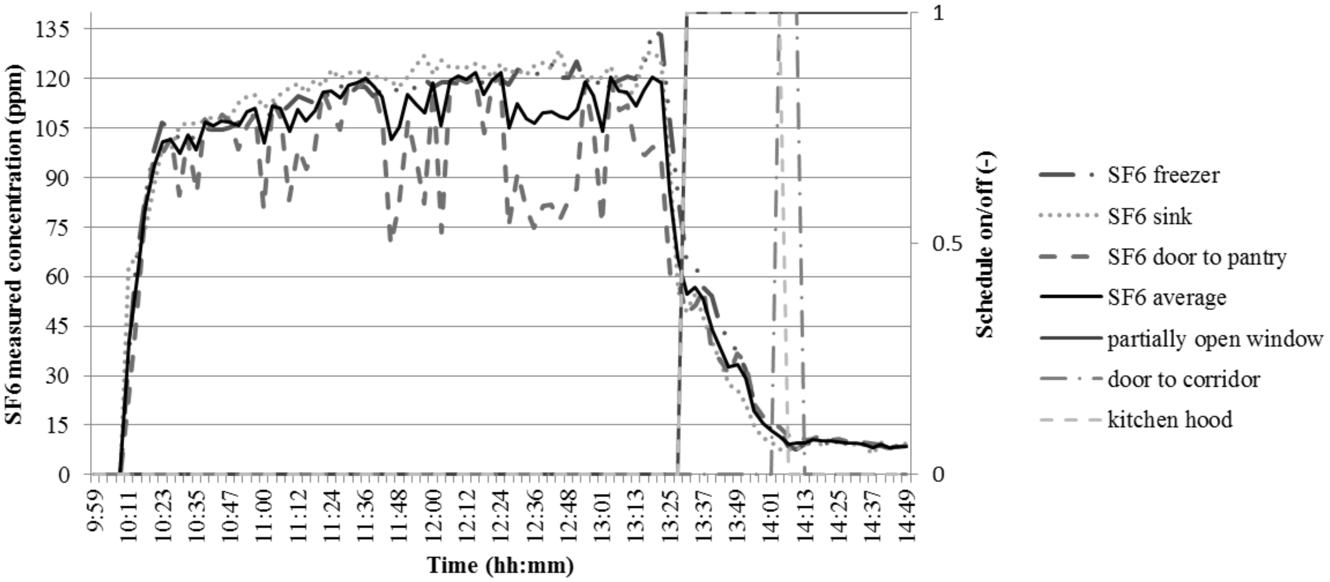

Figure 7: SF_6 - 3 measured standpoint concentrations, average concentration and ventilation schedule – Morning of Day 1

A study conducted in Utah (USA) was focused on CO emission and decay time periods observed in homes during every day activities[14]. Measurements were carried out for gas oven operation[7,13], gas-fired space heaters [8,14] and residential gas cooking systems [10,11,12,13,14]. In Europe in the Netherlands a study was conducted which was focused on pollutants stratification. The study introduces the new concept of CACP. CACP expresses the Chance of Accumulation of Combustion Products[11].

Use of kitchen hoods and increased awareness of the need to ventilate when cooking, along with building standards for minimum range hood flow rates and volume, could substantially reduce exposures to the pollutants[9, 10, 11]. Topic becomes more important with the tight building envelopes and lower air changes. Concentrations of pollutants can affect health. Simulation results suggest that regular use of even moderately effective venting range hoods would dramatically reduce the percentage of homes in which concentrations exceed health-based standards[12].

Results

Air change results

The calculated value was taken from the concentration measured during the period of closed window and door. In the Tab. 3 initial values can be seen and also calculated results. These concentration values are taken from the period of time with no occupancy and all openings closed. These values were measured during the day 1 of the measurement. The outdoor conditions were summer extreme conditions with no rain. Outdoor temperatures were the interval of 17.1° C – 26.6 °C through day and night.

Table 2: Air change calculated results from values obtained by measurement

standpoint	**freezer**	**sink**	**door to pantry**
day	10. 7.	10. 7.	10. 7.
T1 (hh:mm)	13:19	13:19	13:19
T2 (hh:mm)	13:22	13:22	13:22
C1 (ppm)	134.38	127.17	99.12
C2 (ppm)	133.11	125.88	96.33
AC (1/h)	0.063	0.097	0.190

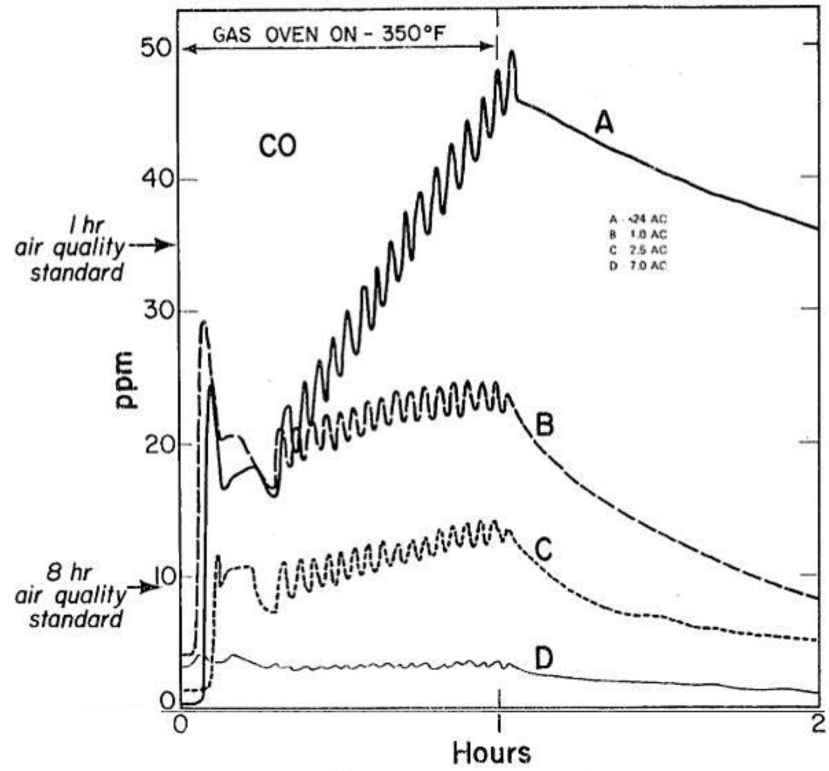

Figure 8: CO concentrations in a 27 m^3 experimental room at various air change rates AC (1/h). Gas oven operated for 1 hour at 180 ^{0}C (approximately 350 ^{0}F).[7]

According to the measured values the measured concentrations of pollutants are higher than it is required. There was no ventilation strategy applied during this time. The calculated air change through the building envelope with closed window and door from SF_6 concentrations in three standpoints was calculated as 0.063; 0.097 and 0.190 (1/h).

Required ventilation rate results according to occupancy

The required ventilation rates for times during occupancy are 25 and 50 m^3/h (one occupant and two occupants present). The calculated result with no occupancy is 5.41 m^3/h according to the standard multiple air change. This value was calculated according to standard requirements. These requirements were added into the Figure 11. The calculated rates changes over a 50 %. The rate is very variable.

Required ventilation rate results according to occupancy and gas appliances operation

In the following Figures (Figure 11, 12, 13) operation of gas appliances was documented. Firstly Figure 10 represents quantification of kilowatts for each gas appliance separately. Secondly Figure 11 represents their summed operation in kilowatts. The sole values were under the value of 12 kW, the summed values were up to 11. 75 kW. A total of appliances produce about 30 m^3/h diluted flue gases to be fed through a fan.

In the following Figure 12 all ventilation requirements can be seen through time. The required ventilation input was calculated according to the appliances operation and the above mentioned equation (3) and is in line with the previous estimate for kitchen. After the time 13:05 there were openings (partially opened window, open door) open in a various arts. The openings schedule was graphically illustrated but due to a lack of space it was not published. The ventilation rates are time dependent and occupancy dependent. The highest requirements are during time of 2 occupant´s presence and cooking. The required ventilation rate changes according to the occupant´s activity in the kitchen and appliances operation schedule.

Discussion

Air change through the building envelope is not sufficient when the door and window are closed. The calculated values of air change based on measurement are really small which means that the building envelope is tight, air is mixed inside the room and doesn´t move outside much despite of the fact that outdoor temperature is lower than indoor temperature. The highest air change is close to the door to pantry which is understandable because the air can move slowly through the door. There is a solution needed to find an effective way to cope with this issue. The ventilation rate is negatively influenced by the summer conditions so it is an extreme state.

Four pollutants were measured. It is interesting to observe pollutants movement inside room volume and its meaning to the occupant. Different measured values for three different places make a good question of how one correct point should be chosen and how the exact concentration measurement should be done.

The following questions are if there is a way how the occupants can change the environment for themselves? Is there a way how to ventilate the volume efficiently and with the favorable operation costs?

Conclusions

The ventilation rate is not sufficient after the refurbishment of building envelope. The pollutants weren’t able to be ventilated away sufficiently. This room with tight windows and gas appliances is high-risky. The carried out measurements show that use of gas appliances increases dangerous pollutants concentrations and worsen environmental quality. This room with episodic operation is a complicated case of indoor environment. The air change solution based on the episodic appliances schedule and assumed behavior of pollutants is neither sufficient nor safe. A sophisticated smart solution should be designed which shouldn´t be dependent on human factor. In the future there should be a change in standards which should take into account special solutions of ventilation of recently refurbished rooms equipped with air-tight windows and with gas appliances operation with possible polluted indoor air exhaust.

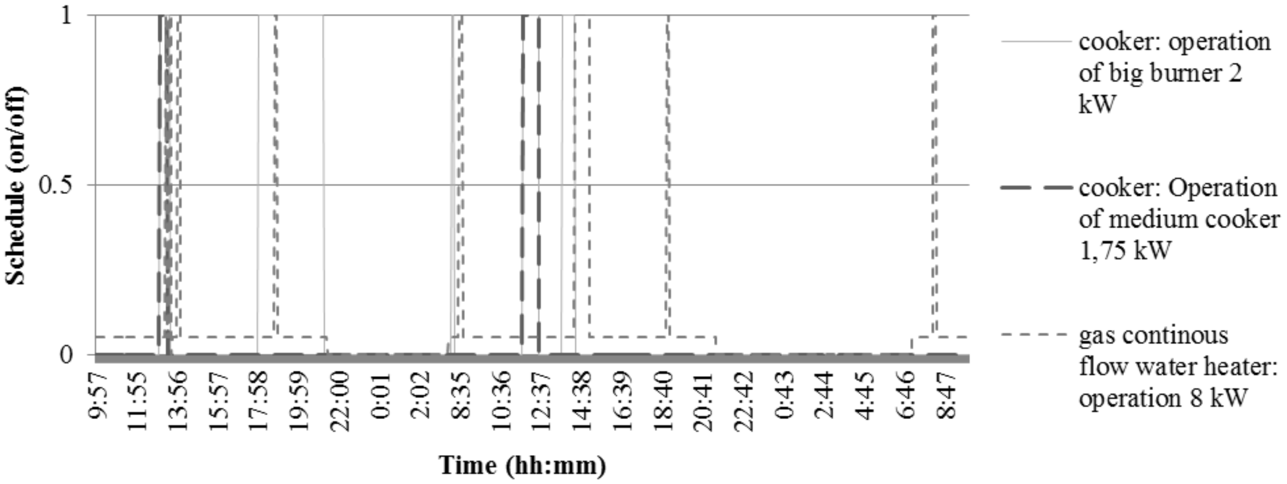

Figure 9: Operation of gas appliances during measurement: on/off

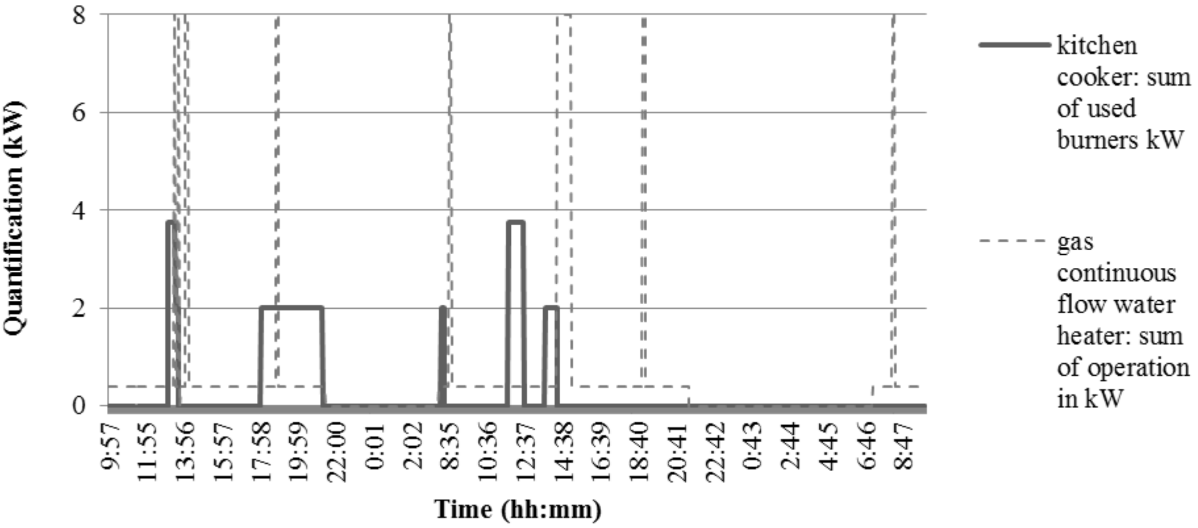

Figure 10: Operation of gas appliances during measurement: quantification in kW

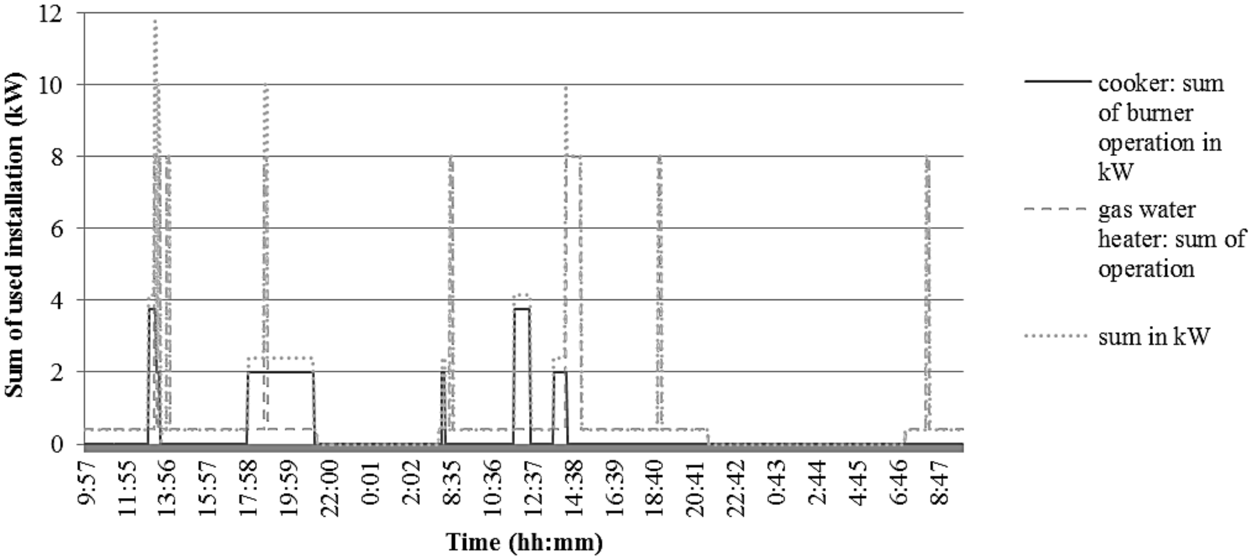

Figure 11: Operation of gas appliances: quantification in kW – sum

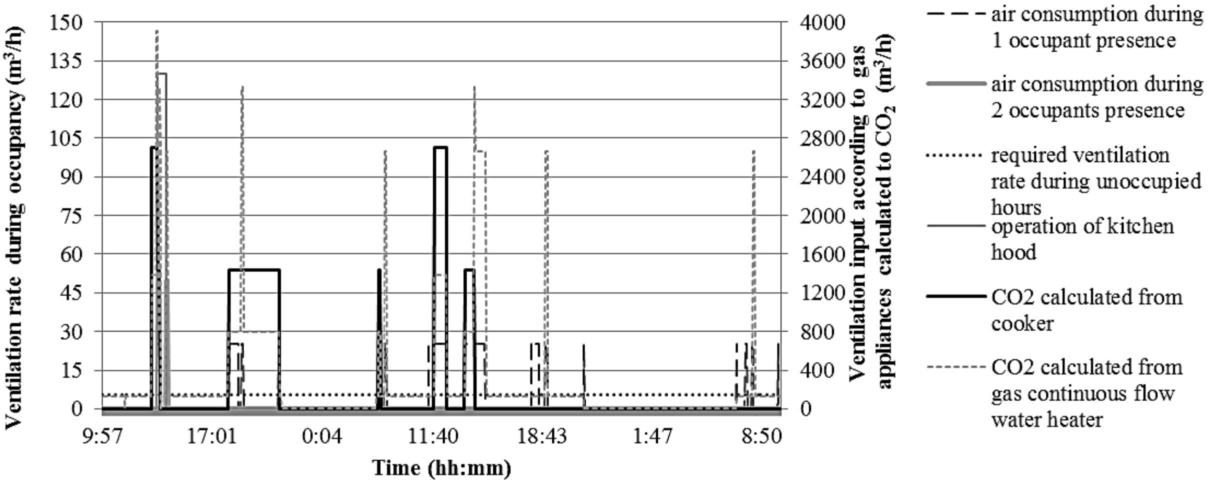

Figure 12: Overview of required ventilation rate and ventilation input and CO_2 production calculated to m^3/h

List of symbols

PC – personal computer
PAS – photoacoustic spectroscopy
CO_2 – carbon dioxide
CO – carbon monoxide
HCHO - formaldehyde
kW – kilowatts
Ø – diameter
ppm – parts per million
TVOC – total volatile organic compounds
SF_6 – sulfur hexafluoride, tracer gas
AC – air change
CACP – Chance of Accumulation of Combustion Products

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Efektivní větrací strategie pro vnitřní ovzduší znečištěné provozem plynových spotřebičů

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Souhrn

Kvalita vnitřního prostředí běžného rodinného domu v České republice je nejproblematičtější v kuchyni s kombinovanými spotřebiči (elektřina, plyn). Zejména otevřené plynové spotřebiče mohou být zdrojem významného znečištění, a to zejména u objektů po zateplovacích opatřeních s těsnými okny a těsnou obálkou budovy. Digestoř (odsávací zařízení pro přímotopný spotřebič) se ukázala jako zcela nedostatečná pro udržení přiměřené kvality vnitřního ovzduší.

Studie na základě výsledků průběžného měření typického průběhu několikadenních činností v kuchyni a používání spotřebičů přináší soubor požadavků na provoz digestoře (odsávání do vnějšího prostředí) s nezbytnou kombinací přirozeného větrání okny pro dosažení normativních hodnot vnitřního prostředí s minimalizací tepelných ztrát.

Klíčová slova: *kvalita vnitřního prostředí, kvalita vnitřního ovzduší, průtok větracího vzduchu, plynové spotřebiče, výměna vzduchu*

Landfill leachate treatment using membrane separation: summary of laboratory testing experiences

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Abstract

This study deals with the problem of landfill leachate treatment using membrane separation processes Large experience was performed in this field using samples of various landfill leachates from landfills for municipal and hazardous waste disposal. Screening of the samples composition in the Czech Republic showed their large variability. Large spectrum of inorganic components was analysed and the following maximal concentrations were measured: Na 2124 mg.L^{-1}*, K 1912 mg.L*$^{-1}$*, ammonia nitrogen 3178 mg.L*$^{-1}$*, chlorides 3108 mg.L*$^{-1}$*, nitrates 491 mg.L*$^{-1}$*, sulphates 1300 mg.L*$^{-1}$*, carbonates 9870 mg.L*$^{-1}$ *and TOC 1554 mg.L*$^{-1}$*. The conductivity values of leachates were between 6.1 – 22 mS.cm*$^{-1}$ *and pH values between 7.5 – 8.7. A set of membrane separation experiments using different operating conditions was performed on every landfill leachate with complete analyses of all streams. The combination of reverse osmosis and pretreatment reduced the volume of landfill leachate by approximately 80 % using one separation stage; the next stage improves the composition of permeate. The number of treatment stages may be ruled by local legislation. Reverse osmosis showed high separation efficiency (over 95 % in most cases) regardless of the feed quality for all pollutants and the decrease in conductivity was also considerable. The designed and verified treatment schema allows optimization of the treatment process with regard to the output streams disposal.*

Keywords: *Landfill leachate, pollutant, ammonia nitrogen, membrane separation, reverse osmosis.*

Introduction

Landfilling belongs in the Czech Republic still to the most used techniques for waste removal and this situation does not seem to change in the near future. Nowadays around 70 % of municipal waste generated in the Czech Republic is still landfilled[1]. Even if we stopped landfilling right now, the technical maintenance of landfills would take decades. Incineration of waste as an alternative to landfilling produces ash, which will be probably landfilled again[2]. The landfill body as an uncontrolled chemical reactor produces solid, liquid and gaseous emissions[3]. Landfill leachate is formed when rainwater and groundwater infiltrate the body of the landfill. The volume of the leachate depends to a large degree on the climate. Its composition is very variable and depends on the total rainfall, the kind of deposited waste, the chemical reactions taking place in the landfill and the age of the landfill. Landfill leachate usually contains large quantities of dissolved solids and organic pollutants4, usually determined in total as the TDS (Total Dissolved Solids) and COD/TOC (Chemical Oxygen Demand/Total Organic Carbon), respectively. Some of them represent a potential risk for local fauna, flora and potable water sources in case of uncontrolled release into the environment[5]. These are mainly ammonia nitrogen[6], heavy metals[7,8] and drugs[9]. Over-balanced volume of landfill leachate must be treated or removed. A conventional wastewater treatment plant is designed to remove only substances of organic character, heavy metals and various forms of nitrogen. It cannot handle dissolved inorganic salts; in certain cases it even increases their concentrations[10]. The biodegradability of organic matter is limited, because most organic compounds presented in leachates are persistent[11].

Pressure-driven membrane separation processes have found firm place in many industrial branches as an alternative to conventional processes; landfill leachate treatment is one of them[12]. Reverse osmosis is used for the purification of landfill leachate usually as the main step because the treated is usually pure water[13]. It is included in the BAT (Best Available Techniques) for landfill leachate treatment[14]. The principle of nanofiltration and reverse osmosis is the same. But the separation ability of nanofiltration is usually considerably lower. This separation technology can separate especially monovalent ions with lower efficiency than reverse osmosis; the separation level of polyvalent ions is comparable. The mechanism is based on the diffusion. Microfiltration and ultrafiltration are most similar to the classical filtration. They are suitable for the removal of suspended particles, colloids, bacteria and viruses, high-molecular substances etc. The separation is based on the sieve-effect. These processes are commonly used as pretreatment to extend the cleaning interval of membrane modules and to increase permeate flux and total efficiency of membrane separation[15,16]. Pretreatment combining various steps (filtration[17], pH adjustment by acid[18], antiscalant dosing[19] etc.) is necessary for the proper running of separation device and for ensuring the long life of membrane modules[20]. Scaling, fouling and bio-fouling have to be eliminated for these reasons.

Landfill leachate is probably the most complicated wastewater a membrane can encounter. Reverse osmosis operates at high pressure gradients at a range of 10 – 100 bar (1 – 10 MPa). In this process the feed is divided with the help of a semipermeable membrane into two streams - the permeate and the concentrate. The permeate is formed by the solvent and particles which passed through the membrane, while the concentrate contains all the chemicals that were held by the membrane. The operating pressure of this separation process grows with increasing concentration of dissolved particles in the feed.

The permeate can be released into the environment if it fulfils limit concentrations, finds use in the landfill area for restoration purposes (e.g. ammonia nitrogen is a nutrient) or can be used as technological water without limitation. But general limits for release in the Czech Republic do not exist and have to be defined individually. The concentrate disposal has to be more sophisticated. Compared to the input landfill leachate, the concentrations of pollutants are significantly higher and the biodegradability is worse[21]. Simple return to the landfill body makes the composition of landfill leachate worse as practical samples showed[22]. Evaporation or stabilization/solidification[23] technology can solve this stream disposal.

Based on the information survey during sampling, disposal of over-balance landfill leachate in landfills is limited by the wastewater treatment plant capacity or with the sewerage system, if there is any available at closer range. In some cases, wastewater treatment plants accept landfill leachate only for limited time periods and in limited volumes. Different role play the costs for the treatment and transport by tank. These costs could be comparable. For these reasons landfill managers are looking for a complex technology with a simple arrangement which operates in the landfill area and saves costs with regard to the Czech law. Currently some landfills dispose of a stabilisation/solidification technology.

The focus of this work is a study, which describes the composition of landfill leachates and the application of reverse osmosis for landfill leachate treatment in laboratory scale using single stage and multi stage separation experiments with simple pretreatment focused on ammonia nitrogen removal and elimination of precipitation. The experience abroad showed various treatment strategies and therefore we selected and adjusted some steps for local conditions with regard to the costs. Despite the variability of landfill leachates we wanted to design a treating process and optimization of the operating conditions to achieve good quality permeate and to minimize the volume of concentrate with discussion of its further disposal.

Materials and Methods

Materials

During three years, a total of 12 different samples of landfill leachate were collected in 10 Czech landfills for disposal of municipal and hazardous waste and subjected to separation experiments. The landfills were located in various areas across the Czech Republic. The volumes of the leachate samples ranged from 50 to 200 L. Concurrently we prepared particular samples for analytical determination of ammonia nitrogen (sample without the headspace) and of metals (sample with addition of high-purity nitric acid). Samples are marked only with numbers 1 – 10 (condition of anonymity).

Analytical Methods

The landfill leachates and all streams were analysed using the following methods. Metal concentrations were measured by an AAS SensAA (GBC Scientific Equipment, Australia) according to following standards: Ca, Mg – ČSN ISO 7980; Fe, Mn - ČSN 75 7385; Na, K – ČSN ISO 9964-3.

Anion concentrations were measured by a capillary electrophoresis Capel 105M (Lumex, Russia), total inorganic carbon (TIC) and total organic carbon (TOC) by a Liqui TOCII analyser (Elementar Analysensysteme GmbH, Germany). Both methods worked according to standard operational procedure with following conditions. Capillary electrophoresis based on electromigrating principle of charged particles in a electric field: original patented Lumex buffer for anions analysis, injection time 10 s under pressure 30 mbar, standard bare fused – silica capillary length 60 cm, capillary diameter 75 µm, voltage -17 kV, temperature 20°C, detection – absorption in UV (254 nm). Carbon analysis based on two-step procedure with acidification and thermal decomposition method: decomposition of substances containing inorganic carbon by addition of hydrochloric acid (automatic dosage of HCl solution for carbonates and hydrogencarbonates decomposition) with stripping of rising CO_2, then heating to the temperature of 850 °C and decomposition of organic substances with rising of CO_2. Formed CO_2 is purified through a halogen trap with a subsequent intensive gas drying system for interfering substances capture. CO_2 is detected by a non-dispersive infrared photometer.

The ammonia nitrogen was determined by an indophenol method using a UV-VIS spectrophotometer Cintra 101 (GBC Scientific Equipment, Australia) according to standard ČSN ISO 7150-1, the conductivity by a conductivity-meter GMH3430 according to standard ČSN ISO 27888 and the pH values on a pH-meter GMH3530 (Greisinger Electronic GmbH, Germany) according to standard ČSN ISO 10523. Detail pictures of harmed membrane were taken using a microscope Evo MA15 (Carl Zeiss, Germany).

Membrane Separation Unit

The separation experiments were performed on a membrane separation unit LAB-M20 (Alfa Laval, Sweden). This device allows the membrane separation in laboratory scale. The device was customized for batch processing. The volume of the feed tank was ca. 12 L. The actual separation took place on a plate-and-frame module DSS equipped with membranes for reverse osmosis RO98pHt (Alfa Laval, Sweden). In all experiments, also in the second stage of separation the same type of membrane was used. The flow rate of treated feed was 8,9 – 9,1 l/min. Permeability was determined experimentally to value of 3 $L.m^{-2}.h^{-1}.bar^{-1}$ for used RO98pHt membrane. The rejection of NaCl solution of this composite membrane is higher than 97 % (NaCl 2 $g.L^{-1}$, 1.6 MPa, 25°C). The following operation conditions could be applied: pH range 2 – 11, typical operating pressure range: 1.5 – 4.2 MPa, maximum operating pressure: 5.5 MPa, temperature 5 – 60°C[24]. Maximal number of membranes was 36 with a total membrane area of 0.63 m^2. A Rannie piston pump with a maximum operating pressure of 6 MPa was used. A separate water supply was used to maintain the pistons of the pump moist. The membrane module was cooled by a flow liquid-liquid heat exchanger. Water from the faucet served as the cooling medium.

The device was cleaned after every experiment using an alkali and acid to allow the comparison of experiments. Permeate flux at 2 MPa and 20°C using potable water as feed determines the purity level of membranes. For bio-fouling prevention, membrane module was kept in a biocide solution.

Separation Process

The separation experiments were focused on the minimization of the feed volume to gain good quality permeate. The operating conditions were set up to achieve the stability of the separation process and to minimize the negative influences (membrane fouling, precipitation of salts, damage of membranes, etc.) while maintaining high separation level. For these purposes, a pretreatment step was included using a two-stage separation process to achieve sufficient treatment level evaluation. Special attention was paid to the removal of ammonia nitrogen, which will always represent one of the limits evaluated when released into the environment. In principle our effort was pointed to design the treating process as simple as possible.

All experiment were carried up at an operating temperature of 20 °C because the permeate flux grows with increasing temperature and invariable value of temperature allows the results comparison. Among other factors that affect reverse osmosis belong rejection R, volume reduction factor and permeate flux. Rejection indicates the separation efficiency of a component or in total. For the calculation of rejection serve concentration values in the feed and in permeate (c_F and c_P, respectively), or conductivity values κ can be used.

$$\mathrm{R} = \frac{c_F - c_P}{c_F} \cong \frac{\kappa_F - \kappa_P}{\kappa_F} \qquad (1)$$

The volume reduction factor (VRF) is defined like the ratio between the feed and concentrate volumes, respectively. The permeate flux is an hourly flux of permeate through the membrane with an area of 1 m^2. Its values are different for setting up the operating conditions of the separation process and its decrease can indicate membrane fouling.

Results and Discussion

Composition of Landfill Leachates

Sampled landfill leachates were characterized by brownish to brown-black colour and by mild smell. The colour was caused by humic acids as demonstrated by their precipitation in acid conditions. Mildly alkaline pH values (~8) were measured in all samples. The range of conductivities was wider (6.1 – 22 mS.cm^{-1}). Based on analytical determinations we characterized the main compounds/pollutants in samples - ammonia nitrogen, inorganic salts and organic matter. The concentrations of said compounds differed largely across the leachate samples. Large variability of leachates was found. But we can find similarity across parameters. Ammonia nitrogen, carbonates (determined as TIC) and organic matter (as TOC) occur everywhere in considerable concentrations. Table 1 and Figure 1 give a comprehensive overview of the leachates composition.

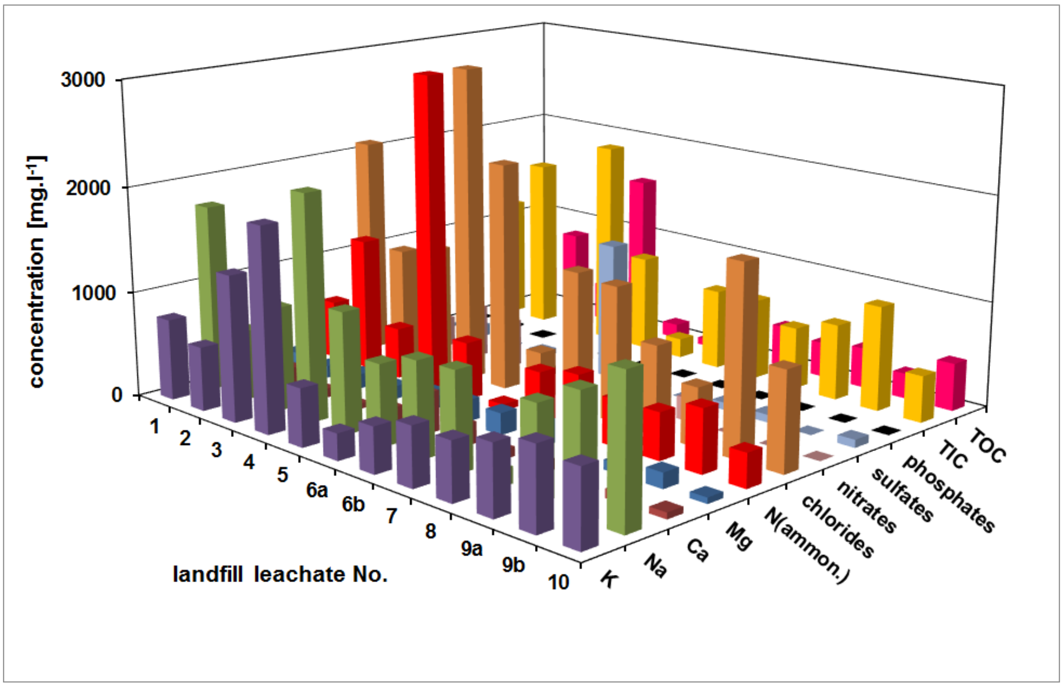
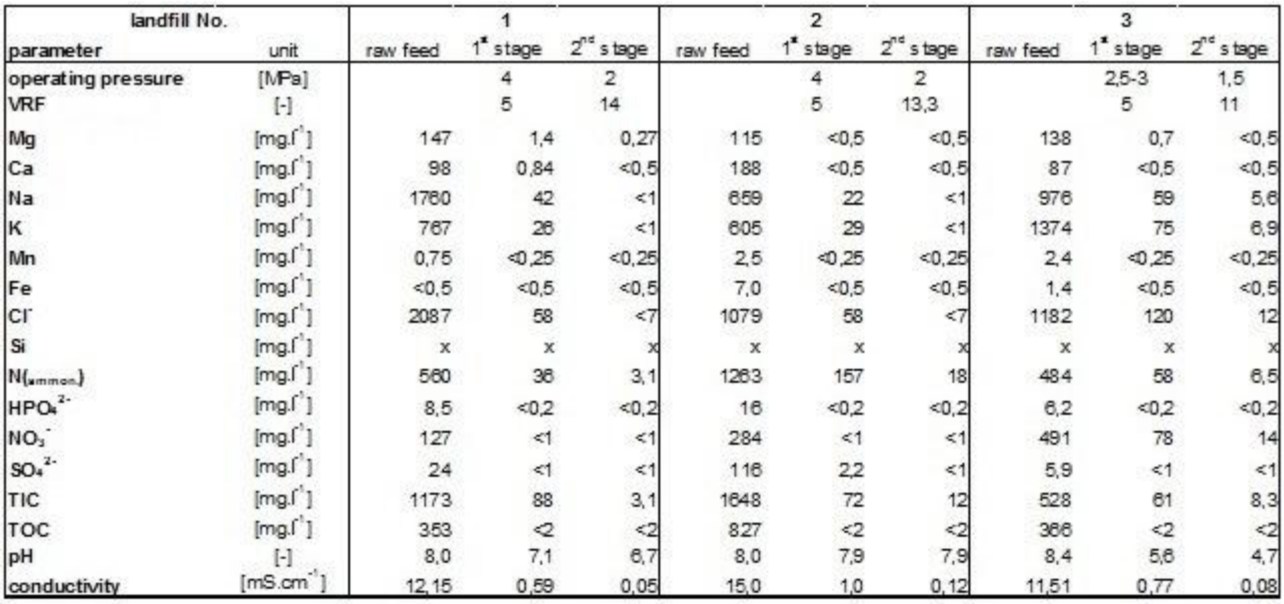
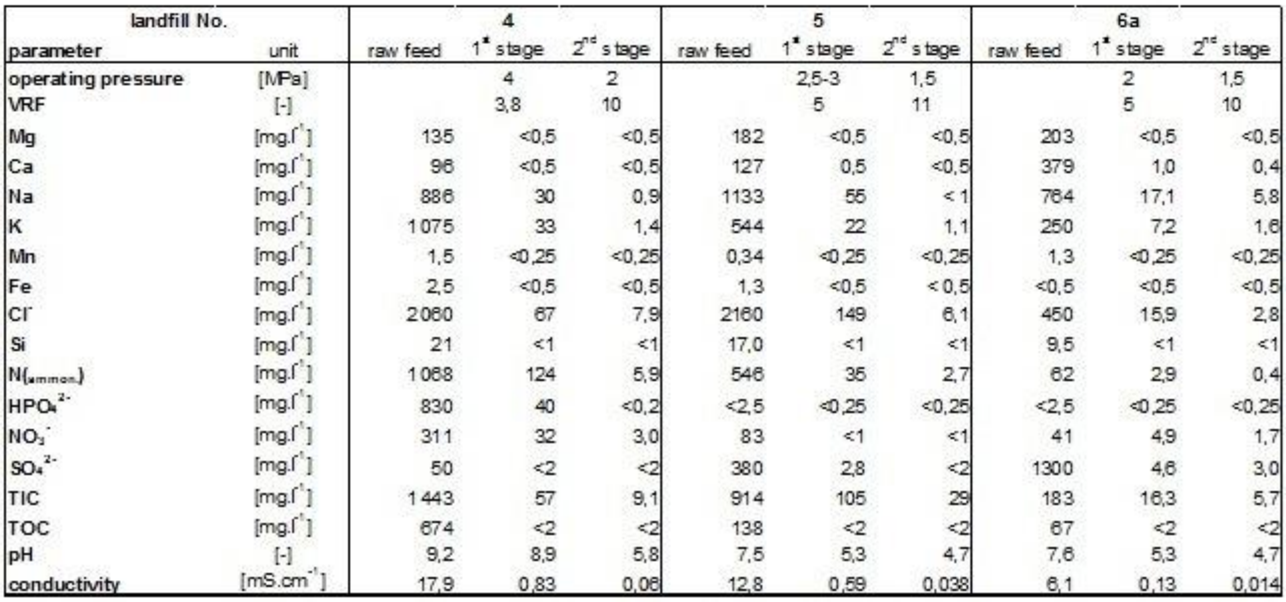


Figure 1: Landfill leachates composition: visualization of variability

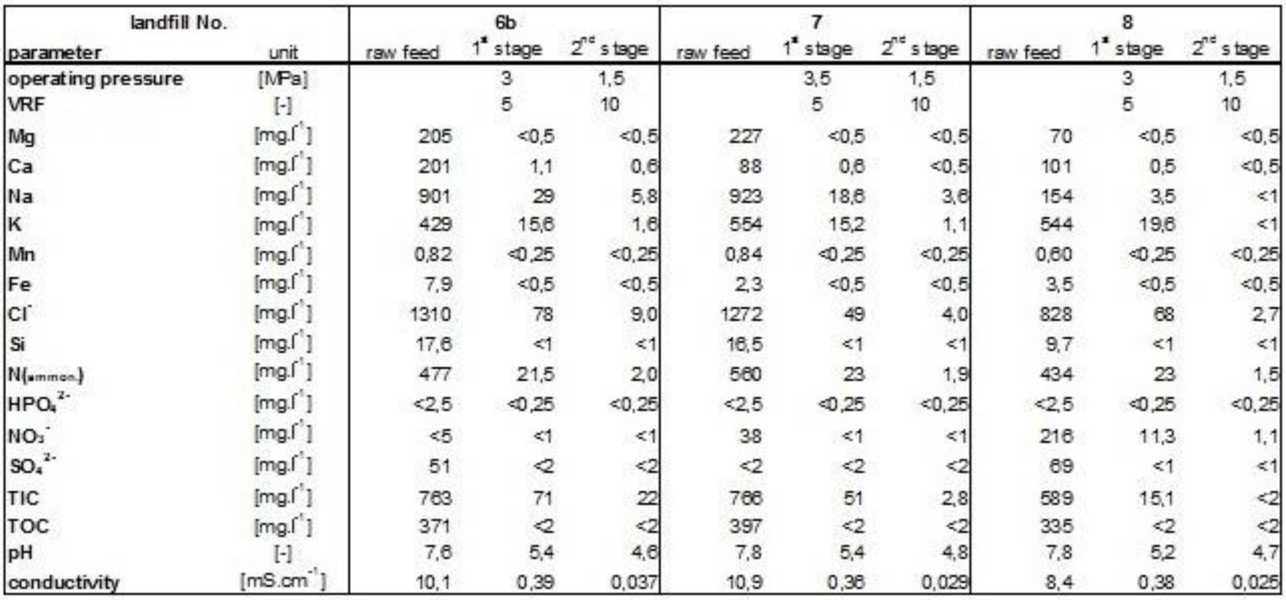
Table 1: Composition of raw feed and permeates from two-stage separation experiments



landfill No.		1			2			3		
parameter	unit	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage
operating pressure	[MPa]		4	2		4	2		2,5-3	1,5
VRF	[-]		5	14		5	13,3		5	11
Mg	[mg.l^{-1}]	147	1,4	0,27	115	<0,5	<0,5	138	0,7	<0,5
Ca	[mg.l^{-1}]	98	0,84	<0,5	188	<0,5	<0,5	87	<0,5	<0,5
Na	[mg.l^{-1}]	1760	42	<1	659	22	<1	976	59	5,6
K	[mg.l^{-1}]	767	26	<1	605	29	<1	1374	75	6,9
Mn	[mg.l^{-1}]	0,75	<0,25	<0,25	2,5	<0,25	<0,25	2,4	<0,25	<0,25
Fe	[mg.l^{-1}]	<0,5	<0,5	<0,5	7,0	<0,5	<0,5	1,4	<0,5	<0,5
Cl^{-}	[mg.l^{-1}]	2087	58	<7	1079	58	<7	1182	120	12
Si	[mg.l^{-1}]	x	x	x	x	x	x	x	x	x
$N_{(ammon.)}$	[mg.l^{-1}]	560	36	3,1	1263	157	18	484	58	6,5
HPO_4^{2-}	[mg.l^{-1}]	8,5	<0,2	<0,2	16	<0,2	<0,2	6,2	<0,2	<0,2
NO_3^-	[mg.l^{-1}]	127	<1	<1	284	<1	<1	491	78	14
SO_4^{2-}	[mg.l^{-1}]	24	<1	<1	116	2,2	<1	5,9	<1	<1
TIC	[mg.l^{-1}]	1173	88	3,1	1648	72	12	528	61	8,3
TOC	[mg.l^{-1}]	353	<2	<2	827	<2	<2	366	<2	<2
pH	[-]	8,0	7,1	6,7	8,0	7,9	7,9	8,4	5,6	4,7
conductivity	[mS.cm^{-1}]	12,15	0,59	0,05	15,0	1,0	0,12	11,51	0,77	0,08

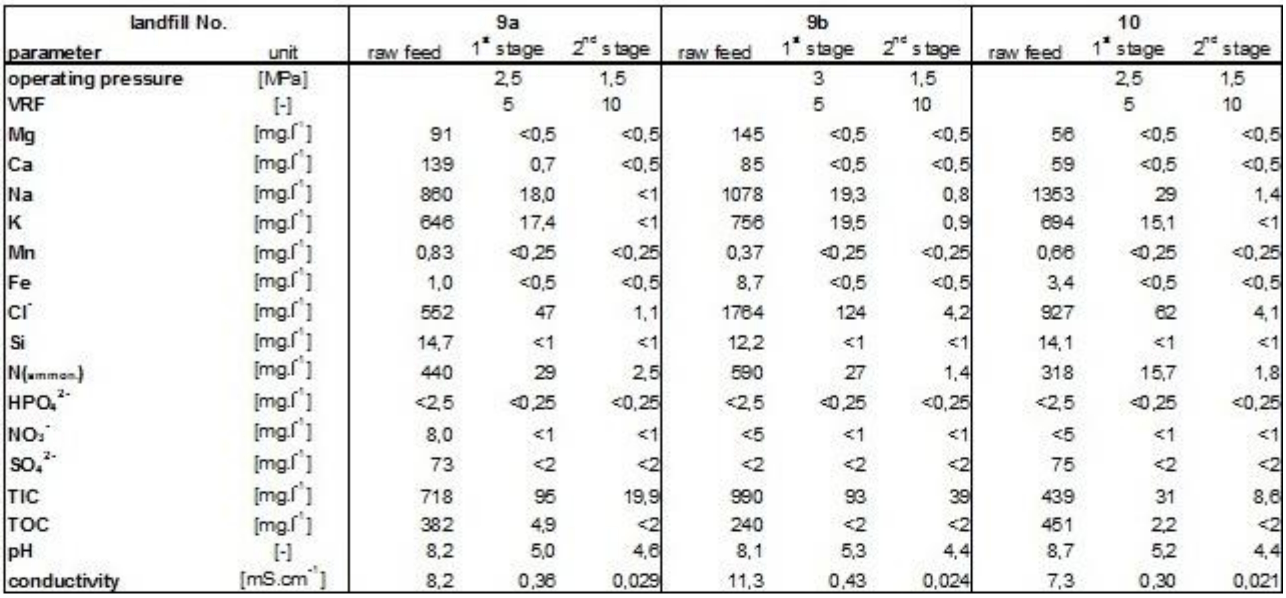


landfill No.		4			5			6a		
parameter	unit	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage
operating pressure	[MPa]		4	2		2,5-3	1,5		2	1,5
VRF	[-]		3,8	10		5	11		5	10
Mg	[mg.l^{-1}]	135	<0,5	<0,5	182	<0,5	<0,5	203	<0,5	<0,5
Ca	[mg.l^{-1}]	96	<0,5	<0,5	127	0,5	<0,5	379	1,0	0,4
Na	[mg.l^{-1}]	886	30	0,9	1133	55	< 1	764	17,1	5,8
K	[mg.l^{-1}]	1075	33	1,4	544	22	1,1	250	7,2	1,6
Mn	[mg.l^{-1}]	1,5	<0,25	<0,25	0,34	<0,25	<0,25	1,3	<0,25	<0,25
Fe	[mg.l^{-1}]	2,5	<0,5	<0,5	1,3	<0,5	< 0,5	<0,5	<0,5	<0,5
Cl^{-}	[mg.l^{-1}]	2060	67	7,9	2160	149	6,1	450	15,9	2,8
Si	[mg.l^{-1}]	21	<1	<1	17,0	<1	<1	9,5	<1	<1
$N_{(ammon.)}$	[mg.l^{-1}]	1068	124	5,9	546	35	2,7	62	2,9	0,4
HPO_4^{2-}	[mg.l^{-1}]	830	40	<0,2	<2,5	<0,25	<0,25	<2,5	<0,25	<0,25
NO_3^-	[mg.l^{-1}]	311	32	3,0	83	<1	<1	41	4,9	1,7
SO_4^{2-}	[mg.l^{-1}]	50	<2	<2	380	2,8	<2	1300	4,6	3,0
TIC	[mg.l^{-1}]	1443	57	9,1	914	105	29	183	16,3	5,7
TOC	[mg.l^{-1}]	674	<2	<2	138	<2	<2	67	<2	<2
pH	[-]	9,2	8,9	5,8	7,5	5,3	4,7	7,6	5,3	4,7
conductivity	[mS.cm^{-1}]	17,9	0,83	0,06	12,8	0,59	0,038	6,1	0,13	0,014



landfill No.		6b			7			8		
parameter	unit	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage	raw feed	1st stage	2nd stage
operating pressure	[MPa]		3	1,5		3,5	1,5		3	1,5
VRF	[-]		5	10		5	10		5	10
Mg	[mg.l^{-1}]	205	<0,5	<0,5	227	<0,5	<0,5	70	<0,5	<0,5
Ca	[mg.l^{-1}]	201	1,1	0,6	88	0,6	<0,5	101	0,5	<0,5
Na	[mg.l^{-1}]	901	29	5,8	923	18,6	3,6	154	3,5	<1
K	[mg.l^{-1}]	429	15,6	1,6	554	15,2	1,1	544	19,6	<1
Mn	[mg.l^{-1}]	0,82	<0,25	<0,25	0,84	<0,25	<0,25	0,60	<0,25	<0,25
Fe	[mg.l^{-1}]	7,9	<0,5	<0,5	2,3	<0,5	<0,5	3,5	<0,5	<0,5
Cl^{-}	[mg.l^{-1}]	1310	78	9,0	1272	49	4,0	828	68	2,7
Si	[mg.l^{-1}]	17,6	<1	<1	16,5	<1	<1	9,7	<1	<1
$N_{(ammon.)}$	[mg.l^{-1}]	477	21,5	2,0	560	23	1,9	434	23	1,5
HPO_4^{2-}	[mg.l^{-1}]	<2,5	<0,25	<0,25	<2,5	<0,25	<0,25	<2,5	<0,25	<0,25
NO_3^-	[mg.l^{-1}]	<5	<1	<1	38	<1	<1	216	11,3	1,1
SO_4^{2-}	[mg.l^{-1}]	51	<2	<2	<2	<2	<2	69	<1	<1
TIC	[mg.l^{-1}]	763	71	22	766	51	2,8	589	15,1	<2
TOC	[mg.l^{-1}]	371	<2	<2	397	<2	<2	335	<2	<2
pH	[-]	7,6	5,4	4,6	7,8	5,4	4,8	7,8	5,2	4,7
conductivity	[mS.cm^{-1}]	10,1	0,39	0,037	10,9	0,36	0,029	8,4	0,38	0,025

Table 1: Composition of raw feed and permeates from two-stage separation experiments – continuation



landfill No.		9a			9b			10		
parameter	unit	raw feed	1^{st} stage	2^{nd} stage	raw feed	1^{st} stage	2^{nd} stage	raw feed	1^{st} stage	2^{nd} stage
operating pressure	[MPa]		2,5	1,5		3	1,5		2,5	1,5
VRF	[-]		5	10		5	10		5	10
Mg	[mg.l^{-1}]	91	<0,5	<0,5	145	<0,5	<0,5	56	<0,5	<0,5
Ca	[mg.l^{-1}]	139	0,7	<0,5	85	<0,5	<0,5	59	<0,5	<0,5
Na	[mg.l^{-1}]	860	18,0	<1	1078	19,3	0,8	1353	29	1,4
K	[mg.l^{-1}]	646	17,4	<1	756	19,5	0,9	694	15,1	<1
Mn	[mg.l^{-1}]	0,83	<0,25	<0,25	0,37	<0,25	<0,25	0,66	<0,25	<0,25
Fe	[mg.l^{-1}]	1,0	<0,5	<0,5	8,7	<0,5	<0,5	3,4	<0,5	<0,5
Cl^{-}	[mg.l^{-1}]	552	47	1,1	1764	124	4,2	927	62	4,1
Si	[mg.l^{-1}]	14,7	<1	<1	12,2	<1	<1	14,1	<1	<1
$N_{(ammon.)}$	[mg.l^{-1}]	440	29	2,5	590	27	1,4	318	15,7	1,8
HPO_4^{2-}	[mg.l^{-1}]	<2,5	<0,25	<0,25	<2,5	<0,25	<0,25	<2,5	<0,25	<0,25
NO_3^{-}	[mg.l^{-1}]	8,0	<1	<1	<5	<1	<1	<5	<1	<1
SO_4^{2-}	[mg.l^{-1}]	73	<2	<2	<2	<2	<2	75	<2	<2
TIC	[mg.l^{-1}]	718	95	19,9	990	93	39	439	31	8,6
TOC	[mg.l^{-1}]	382	4,9	<2	240	<2	<2	451	2,2	<2
pH	[-]	8,2	5,0	4,6	8,1	5,3	4,4	8,7	5,2	4,4
conductivity	[mS.cm^{-1}]	8,2	0,36	0,029	11,3	0,43	0,024	7,3	0,30	0,021

Single Stage Separation Experiments

Every landfill leachate sample was filtered through a fabric filter to remove suspended solids. In the first experiment, an operating pressure in the range 2.5 – 4.0 MPa was applied on untreated landfill leachates depending on the values of conductivity and permeate flux. We usually in most experiments used 30 L of feed in single stage separation experiments. The first experiments were carried out in order to determine whether the maximum recovery rate of the feed could be achieved at the given operating conditions. The experiments were stopped at achieved volume reduction factor equals 5 because precipitation of some salts occurred in many cases and the separation of ammonia nitrogen was unsatisfactory. From these purposes we adjusted the pH of filtered landfill leachates using hydrochloric acid to a value near pH ~5.5. In this area ammonia nitrogen is mostly in ion form NH_4^+ and the separation efficiency increases. The positive effect of this pretreatment is particular decomposition of carbonates and delay of precipitation. On the other hand, addition of hydrochloric acid increases the concentrations of chlorides in permeates; sulfuric acid could solve this problem because separation level of divalent sulphates is higher than separation of monovalent chlorides using reverse osmosis.

The concentration of the soluble substances with the charge has a direct effect on the conductivity value. Substitution of the concentration of the individual components is technologically acceptable and corresponds to the subject of the research where the purpose of the experiments was not to evaluate the rejection of the individual components of the landfill leachate. The quality of the resulting mixed permeate in terms of concentration of the individual components is mediated in the Table 1. Reported rejection is only indicative of the progress of the experiment and the gradual concentration of the inlet solution, and thus the higher penetration of the substances into the permeate.

Rejection of all pollutants (replaced with conductivity) stays on high levels (>95%) through the entire separation experiment despite the worsening of composition of circulating feed with every next litre of permeate as shown in Figure 2. The conductivities of permeates are comparable to the values in potable water. Nevertheless it is visible the effect of the gradual concentration of the batch on the worsening permeate quality due to substances penetration. However, ammonia nitrogen is in most cases the key parameter and it could happen that a single stage treatment with pH adjustment will not be sufficient or the requirements on the permeate composition for further disposal will be stricter for various reasons. Table 1 contains the analyses of permeates from first separation stage. Permeate flux values for single stage separation experiments with pH adjustment are shown in Figure 3.

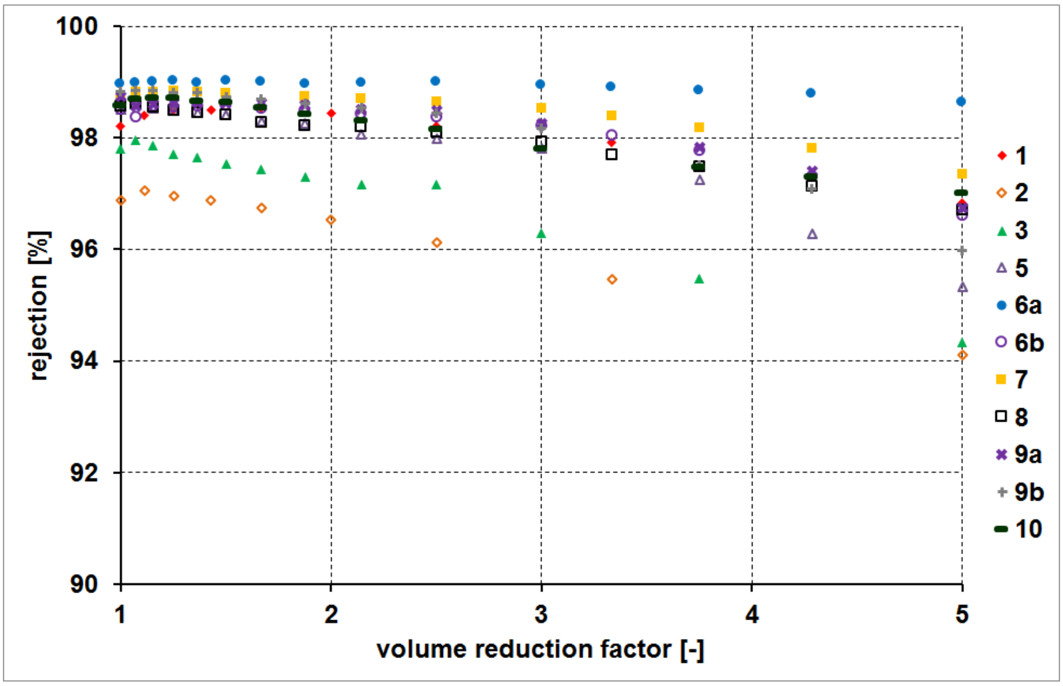


Figure 2: Rejection values obtained during single stage separation experiments with pH adjustment

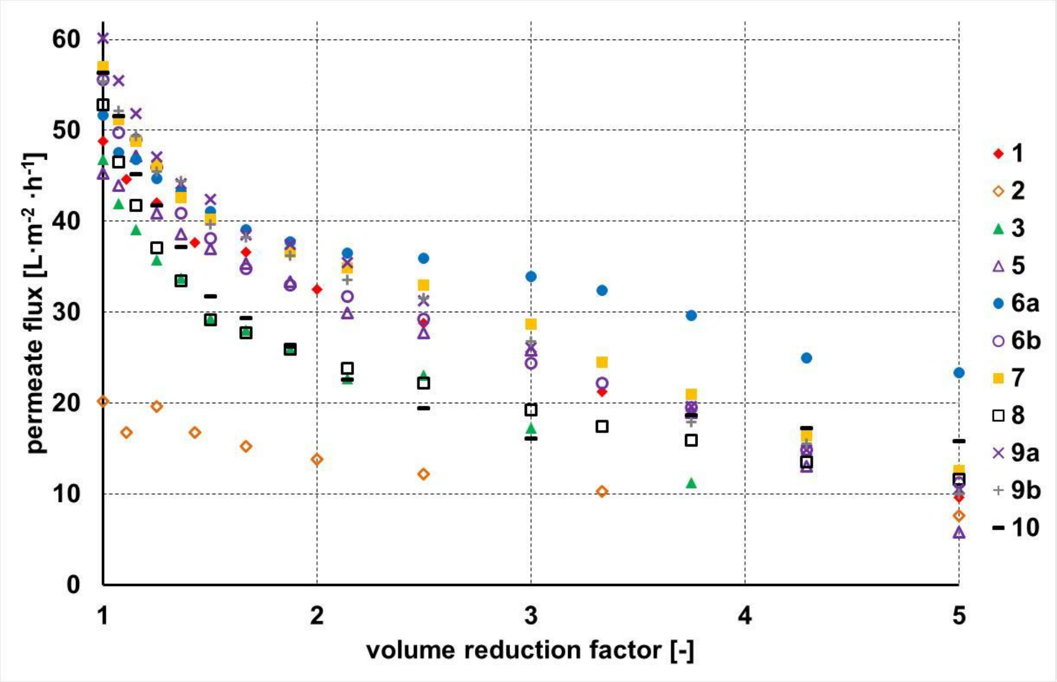


Figure 3: Permeate flux values obtained during single stage separation experiments with pH adjustment

The impact of insufficient pretreatment on the membrane used for the reverse osmosis combined with the effort to achieve maximal reduction of concentrate volume (VRF = 20) is shown in Figure 4a and Figure 4b. Total blockage of surface caused by organic compounds occurred and finally the rupture of membrane followed.

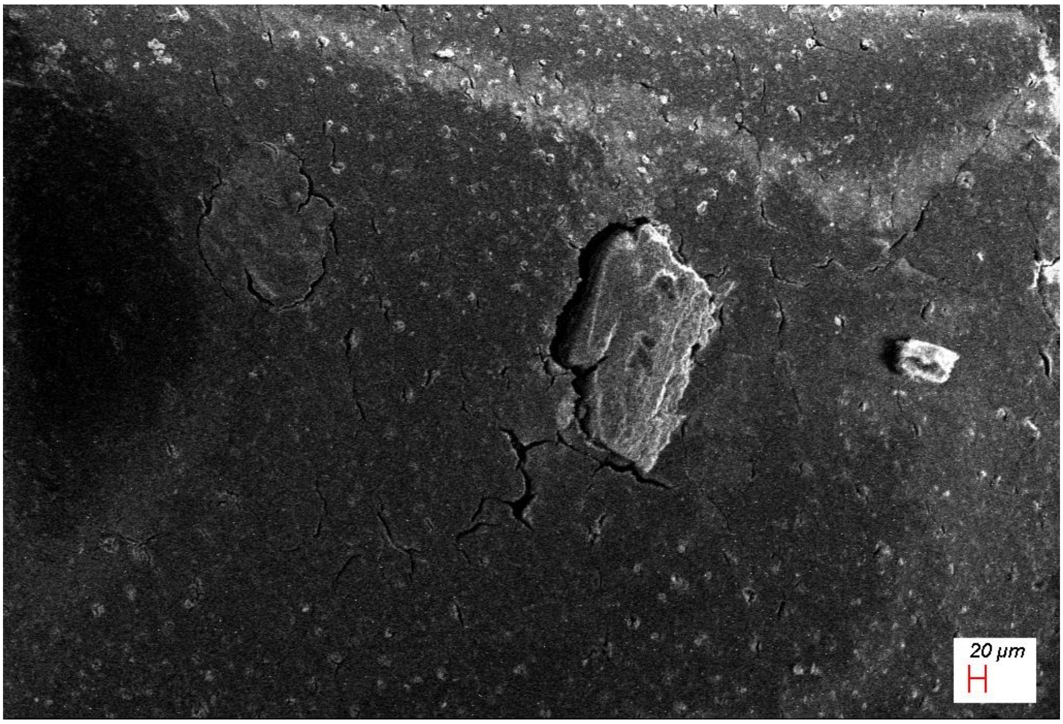


Figure 4a: Membrane surface with cracks

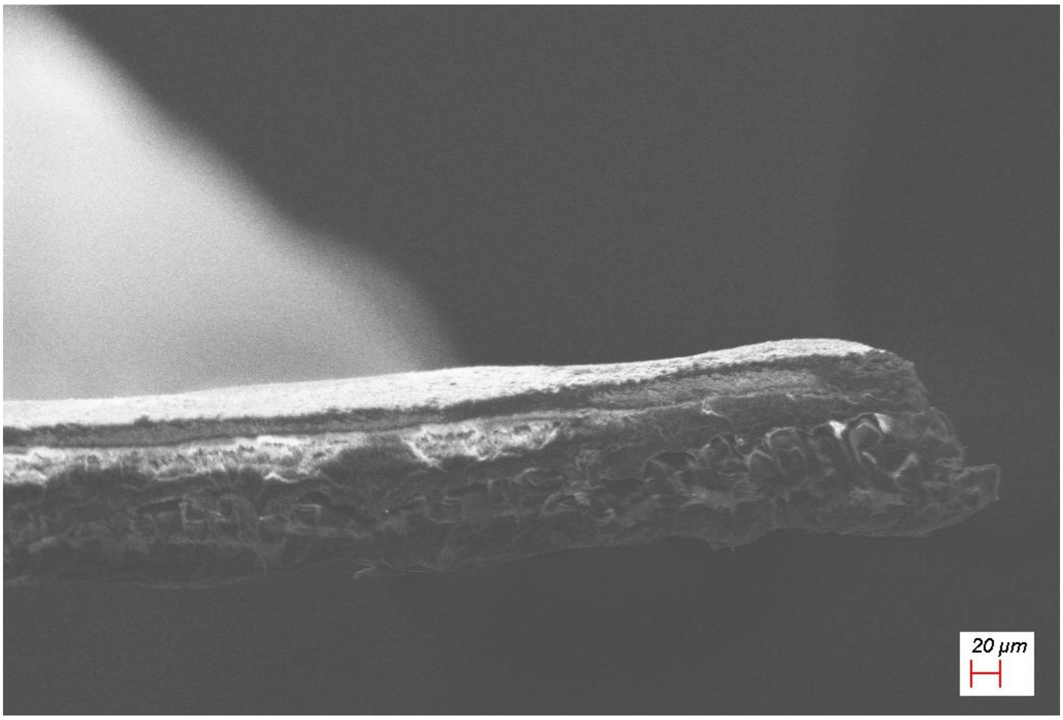


Figure 4b: Membrane cross-section

Two-stage Separation Experiments

Last experiments were employed as the second reverse osmosis stage, which were used to further purify the permeates that were produced in the single stage experiments with pH adjustment. No pretreatment was applied to the samples (with one exception) and the operating pressure was decreased to 1.5 MPa. The aim was to achieve the highest recovery rate possible in regard to the minimal needed liquid volume in device. Due to the small volume of circulating liquid in the device, the experiment was stopped at a volume reduction factor of 10 which means a 90% yield of the permeate. We used 20 L of permeate obtained from the single stage separation experiments as feed in this step. Permeate flux values for two-stage separation experiments are shown in Figure 5.

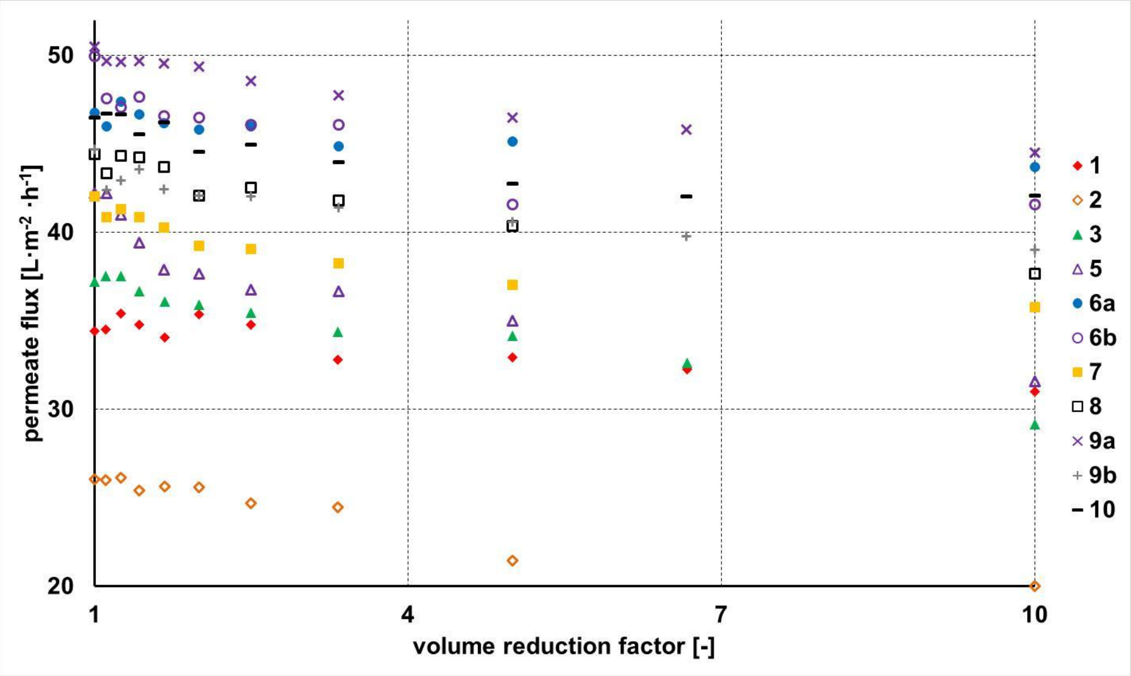


Figure 5: Permeate flux values obtained during two-stage separation experiments

The conductivities of permeates were under conductivity level of potable water and the composition is very close to distilled water. In regard to the low pH of permeate, the TIC concentration is formed by CO_2xH_2O according to carbonaceous equilibrium; this form was separated by the membrane with worse efficiency. Table 1 contains the analyses of permeates from second separation stage.

Experience

The decisive criterion for the number of treatment stages is the quality of permeate, which depends on its final purpose (use as technological water in landfill areas, release into the environment, etc.). This way we can formulate general requirements on permeate quality. As these requirements are not known, we designed two treatment possibilities. Irrespective of the landfill leachate composition, the following steps will be included: pretreatment, pH adjustment and one or two reverse osmosis stages. Commercial antiscalant may additionally be dosed in the first stage. This arrangement represents a very simple treatment scheme.

In many examples the product from the first stage is so clean that there is a high probability of approval from the state administration. But we cannot confirm this information. For this purpose, the second treating stage was added. Figure 6 describes the designed treatment process for landfill leachate which was used by experiments in laboratory scale (without antiscalant). This schema is based on the schema published by Linde et all[25]. based on real landfill leachate treating plants in Wijster (Netherlands) and Rastorf in Plön (Germany). Although landfill leachates differ in their composition, treating schema could be similar in some range of operating conditions.

From the perspective of streams balance it is possible to decrease the feed volume in the first stage by up to 80 % (based on our results); using even higher pressure. The remaining volume of concentrate must be removed. The second stage treats the permeate from further stage and concentrate from this stage can be returned into reservoir where based on its composition enhances the composition of feed.

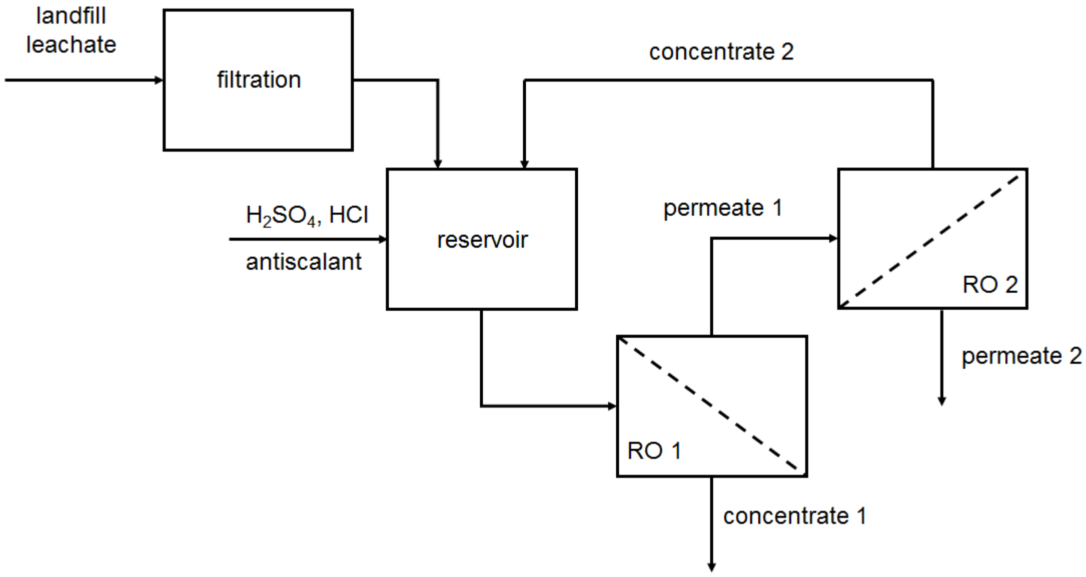


Figure 6: Two-stage schema for landfill leachate treatment

The concentrate from membrane separation processes contains 5 – 10times higher amounts of pollutants compared to the feed. Back flush of the concentrate into the landfill body is not a solution of this problem and can cause increase in pollutant concentrations in the landfill leachate[22]. According to the composition of this stream, the following technologies come into consideration: stabilization/solidification[23], evaporation, precipitation and advanced oxidation processes[26]. The choice of the technology depends on the concentrate composition and on the requirements on final product (for example leaching tests for solidification blocks disposal). We can also use a combination of more technologies – for example the evaporation and solidification.

Conclusions

Our work generalised the experience with landfill leachate treatment using reverse osmosis in laboratory scale. We sampled 12 landfill leachates in 10 landfills in the Czech Republic which represented relatively wide spectrum of physico-chemical parameters. Based on a large set of separation experiments we formulated the following conclusions.

- Individual approach to every landfill leachate is necessary. Landfill leachates with similar composition could separate distinctly differently using the same operating conditions. The reason of this phenomenon is probably the influence of organic compounds in the leachate. For this reason laboratory and pilot plant experiments have to be performed before full-scale technology installation.
- Single stage reverse osmosis is capable to decrease the amount of most pollutants with high efficiency. Depending on required limits and technology performance, a single stage treating process could be sufficient for desired quality of permeate also in the case of ammonia nitrogen. In the first step we applied the operating pressure up to 4 MPa, not high-pressure reverse osmosis. The volume of leachate was reduced usually by 80 %. A two-stage separation process will always meet the requirements on permeate quality.

- Pretreatment of landfill leachate is needed for the following reasons: removal of solid particles by coarse filtration to protect the membranes and to reduce fouling of the membranes, increasing of the efficiency for ammonia nitrogen separation by pH adjustment, elimination of precipitation by preventive dosing of antiscalant.

The investment and operating costs for the technology are not low. However, the current state of insufficient capacity of wastewater treating facilities and their costs make reverse osmosis technology as one of possible and effective solutions.

Acknowledgements

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Čištění skládkových výluhů pomocí reverzní osmózy: souhrn laboratorních zkušeností

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Souhrn

Tato studie se zabývá problematikou čištění skládkových výluhů pomocí membránových separačních procesů. Na základě rozsáhlých zkušeností v této oblasti byly vyvozeny závěry vyplývající ze zpracování vzorků skládkového výluhu ze skládek komunálního a nebezpečného odpadu. Byla provedena detailní analýza vzorků výluhů z České Republiky, které ve svém složení vykázaly značnou variabilitu. Bylo analyzováno velké spektrum anorganických látek, přičemž jejich maximální koncentrace byly následující: Na 2124 mg.l^{-1}*, K 1912 mg.l*$^{-1}$*, amoniakální dusík 3178 mg.l*$^{-1}$*, chloridy 3108 mg.l*$^{-1}$*, dusičnany 491 mg.l*$^{-1}$*, sírany 1300 mg.l*$^{-1}$*, uhličitany 9870 mg.l*$^{-1}$ *a TOC 1554 mg.l*$^{-1}$*. Hodnoty měrné vodivosti výluhů byly mezi 6,1 – 22 mS.cm*$^{-1}$ *a hodnoty pH mezi 7,5 – 8,7. S každým skládkovým výluhem byla provedena série membránových separačních experimentů za různých provozních podmínek a byla provedena analýza technologických proudů. Kombinace reverzní osmózy a předúpravy snížila objem skládkového výluhu zhruba o 80 % při použití jednoho stupně separace; další stupeň zlepšuje složení permeátu. Počet separačních stupňů může být určen místní legislativou. Reverzní osmóza vykázala vysokou účinnost separace (ve většině případů více než 95 %) pro všechny znečišťující látky bez ohledu na kvalitu vstupu a pokles měrné vodivosti byl také značný. Navržený a ověřený postup zpracování výluhu umožňuje optimalizaci procesu čištění s ohledem na další nakládání s výstupními proudy.*

Klíčová slova: *skládkový výluh, polutant, amoniakální dusík, membránová separace, reverzní osmóza*

Use of recycled aggregate from blast furnace slag in the design of asphalt mixtures

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Summary

Within a research study, blast furnace slag was used as an alternative substitute of natural crushed aggregate. Slag is in general a by-product mainly of iron and steel production and it has been used in transport engineering for many years, but only as aggregate for unbound layers or as an additive for hydraulically bound layers. Applications of steel slags in asphalt mixtures are known form several regions in the world. Any other application is currently not used. This can be also due to some problems of large road constructions (swelling) or insufficient knowledge of characteristics, source and origin of specific types of slags. This material is often being deposited in landfills, although it could be an aggregate with high quality, improved strength and anti-skid properties. In this paper there are presented data of the ongoing research, where crushed and sorted slag aggregates were used in asphalt mixtures. In the asphalt mixtures, one aggregate fraction was always fully replaced by the blast furnace slag aggregate. A number of tests was performed on the control and alternative asphalt mixtures to verify the effect of this alternative aggregate on the asphalt mixture properties. Performed tests included the determination of stiffness, determination of resistance to permanent deformation, the indirect tensile strength test, the determination of moisture susceptibility, and others.

Keywords: *Furnace blast slag, asphalt mixture, asphalt mixture testing, recycling*

Introduction

Blast furnace slag is produced by melting iron ores in blast furnaces during production of iron and steel. Metallurgical industry is worldwide industry with one of the largest interests of the world economy. Therefore, the slag as the waste product of this industrial production is one of the most voluminous waste from the entire manufacturing industry.

Metallurgical slag is divided into two basic groups – blast furnace slag and steel slag. Blast furnace slag (BFS) is produced by melting iron ores in blast furnaces. Steel slag is a by-product from the production of steel from iron in converters or from melting scrap in the production of steel in electric arc furnaces. The primarily function of steel slag is to protect the liquid metal from oxidation.

The chemical composition of the slag depends primarily on the properties of the input ores. For blast furnace slags, it depends on the type of produced iron and the amount of coke used during the production. The basic component are CaO, MgO, Al_2O_3, SiO_2, which comprise about 80 – 90 % of slag weight. Blast furnace slag is often added to cement due to hydraulic properties. For steel slags, the composition is significantly more diverse then for previous kind. The composition might even vary within individual batches of production.

In the Czech Republic and generally in Europe slag has been used in transport engineering for several decades. A number of harmonized European standards permits the use of blast furnace slag as an alternative filler or binder (in fine grain form) in hydraulically bound mixtures.

Nowadays, in many places in the Czech Republic or wherever else around the world there are large amounts of slag, which was developed in the past decades and can be considered fully stable at present. These materials have a certain heterogeneity, however by suitable crushing and sorting it is possible to obtain sufficiently homogeneous materials usable (depending on the properties of the aggregate) for various applications in road construction as well as for asphalt mixtures.

There are many research studies focusing on the use of slag aggregate in asphalt mixtures. The problem of generalization of the result is the input material. The properties of slag aggregate is very depending on the input material (steel ore source, quality of steel ore etc.) and used manufacture procedure. Slag aggregate produced from the same steel ore source can very differ only due to the used manufacturing procedure.

Based on these reasons it is impossible to generalize the research data. It is always important to apply the testing on direct slag source. It might be possible to generalize the workability of the mixtures. The study[4] emphasises the angular and rough textured surface of the slag particles that increases the interlocking mechanism and therefore increases the strength performance of the asphalt mixtures. On the other hand the studies[6,7] investigated that with increasing content of slag in the asphalt mixture it is necessary to sufficiently increase the amount of bituminous binder (in 100 % slag asphalt mixture by at least 0,5%). The aggregate has porous surface, which can partially absorb part of the binder. The study[8] also mentioned worsened workability because of the high angularity and texture of the particles.

Problem observed in some research projects (e.g.[9, 10, 11]) was bulking/swelling. Not fully chemically stable slags are highly susceptible to bulking, which can cause problem specially, when it is used in unbound layers of road construction or hydraulic bound layers. When the slag is covered by bituminous binder film, the potential expansion should be eliminated. This problem relates specially to steel slags. The steel slag contains high percentages of free lime and magnesium oxides, which have not reacted with the silicate structures. When it hydrates, there is expansion reaction.

Most of the studies result in recommendations to use only stable blast furnace slag, and are more concerned about use of steel slag.

The intention of this study was to prove the suitability of the use of one certain type of stabilized blast furnace slag (BFS) as a partial replacement of natural crushed aggregate. In the first phase of the presented study, one fraction of crushed stone was replaced by slag aggregate. The intention of the study was not to improve the properties of bituminous mixtures, but to prove that it is possible to produce asphalt mixtures, which comply with the standard requirements with recycled aggregate, excluding any potential risks, which might occur based on previous practical international experience.

The use of slag aggregate can also have significant economic benefits for the asphalt plant. The price of slag aggregate is lower than the price of natural crushed aggregate. Another aspect that should not be avoided is the possible environmental benefit. The metallurgical industry has a long history in many countries as the Czech Republic, so there are hundreds and thousands tonnes of material stored in the waste disposals. Being exposed for years to the climate, humidity, precipitations and changing temperatures, we can assume they are stabilized.

Asphalt mixtures

In the presented research study three types of asphalt concrete were selected – AC_{surf}11, AC_{bin}16 and AC_{base}22. AC_{surf} is asphalt concrete used traditionally in the wearing courses of pavement structures, AC_{bin} is used in binder courses (middle layer) and the AC_{base} is used in the base layer (the lowest asphalt layer). Later stone mastic asphalt for low noise (acoustic) wearing courses SMA 8 NH was added. The number following the asphalt mix acronym stays for maximum used aggregate size - the maximum size of aggregate in AC_{bin} 16 is according to that 16 mm.

Input materials

Aggregate

For asphalt mixtures production three types of aggregates were used. Aggregates from the Zbraslav quarry (spilit), from Lašovice quarry (hornstone, gneiss) and crushed and screened blast furnace slag from industrial area Kladno, which origin is from the high quality iron production of Poldi Kladno performed in the 20th century. The aggregates from the Zbraslav quarry were used as a solid skeleton of all the mixtures. The aggregate from Lašovice quarry was used only in fraction 0/4 mm to increase the bulk density of mixtures and reduce the air voids content. The slag was used in mono-fraction 4/8 mm and later in 0/4 mm.

All types and fractions of the aggregates have been subjected to fundamental tests, such as density, shape index, water absorption, granularity, resistance to abrasion etc. All the aggregates met the parameters of asphalt concrete product standard EN 13108-1 and the Czech technical specifications for low noise wearing courses, TP 259. The granularity of all used aggregates is shown in Figure 1.

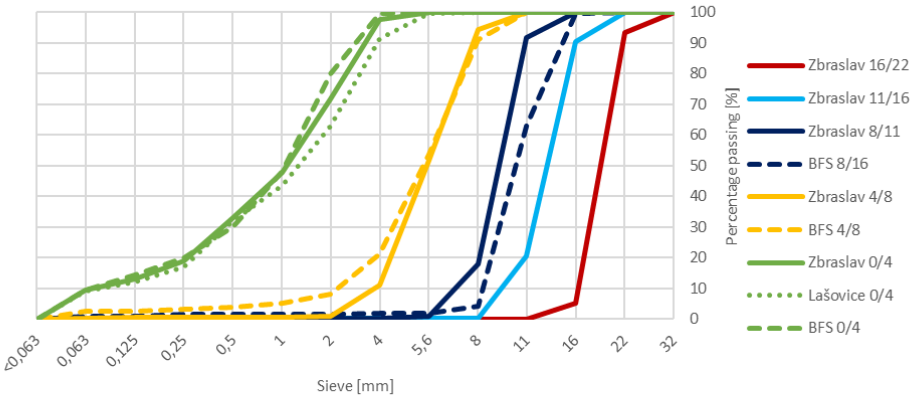

Figure 1: The granularity of all used aggregates

For asphalt concrete mixtures, the fraction Zbraslav 4/8 mm was fully replaced by blast furnace slag (BFS) of the same particle size. The mix design and content of particular components of the mixture was slightly modified so the resulting granularity of the reference asphalt mixture and asphalt mixture containing BFS were as close as possible. In case of stone mastic asphalt for low noise wearing course (SMA NH) the aggregate fraction 0/4 mm was replaced by the BSF of the same gradation. The SMA NH consisted of approx. 80 % of fraction 4/8 mm and 20 % of fraction 0/4 mm, so the substitution of 0/4 mm seemed to be more consistent causing less changes in determined characteristics if reference and BSF containing mixtures have been compared.

Blast furnace slag

The blast furnace slag was obtain from industrial area Kladno, where were historically grand metallurgical furnaces. The metallurgic industry is currently reduced, but the area contains enormous amount of blast furnace and steel slags. Some of the slag were deposited separately and structural companies are slowly extracting, crushing, sorting and selling the stabilized material – e.g. the material used in this project from “Halda Kladno”. Some of the slags were disposed with all the kinds of materials, including furnace muds, fly ash, cinders and other undefined material – e.g. “Buštěhradská halda”. These disposals contain heterogeneous material, which has only very narrow possible use, if any.

The BFS used in the presented experimental study can be classified as artificial aggregates regularly sold for unbound base layers or hydraulically bound mixtures for base layers. The material is periodically controlled. The results of last laboratory control testing are summarized in Table 1. The BFS used in this study was screened to different fraction, because of intended usage. This is the reason why the fractions of control testing vary from aggregate fractions used in the experimental study. The sorting to narrower fraction would not have any significant influence on the tested aggregate properties. All controlled properties met the standard requirements for the asphalt mixtures.

Table 1: Properties of BFS [22 23 24]

Test method	Standard	BFS 0/4	BFS 2/8	BFS 8/22	Limits according to national annex of ČSN EN 13108-1
particle size distribution - fine particle volume (%)	EN 933-1	5.7	0.7	0.2	f_{10}
particle density (Mg/m^3)	EN 1097-6	2.414	2.394	2.381	-
water absorption (%)	EN 1097-6	7.6	6.8	5.7	WA_{24}
shape index (%)	EN 933-4	NRQ	15.3	8.3	SI_{30}
resistance to fragmentation (LA method) (-)	EN 1097-2	NRQ	23.4	23.4	LA_{25}
resistance to freezing and thawing (%)	EN 1367-1	NRQ	1.8	1.8	F_2

NOTE: NRQ = not required

The BFS was during the project testing subjected to XRD analyses (X-ray diffraction crystallography analysis). The XRD analysis helps to determine the material composition. This method uses a monochromatic beam of X-rays which passes through the test sample. During the passing through the sample X-ray beams are flexibly bent (so called diffraction). The direction and intensity of the flexible beam bending depends on the internal structure of the sample. The results of this test method are only semi-quantitative and it is not possible to exactly determine the ratio of individual components. It is only possible to estimate which components are dominant in the sample according to the intensity of the peaks.

The result of XRD analysis of used BFS is refractive curve and summary of established minerals. For shortage of the article, only the summary of minerals is published. The results show that the main identified minerals are gehlenite ($Ca_2Al(AlSi)O_7$) and grossular ferrian ($Ca_3AlFe(SiO_4)_3$). Less dominant are quartz, gypsum and thaumasite.

Table 2: Mineral composition of the BFS sample[1]

Compound name	Score	Total lines	Scale Factor	Semi-Quant [%]
Gehlenite, syn	57	23	1.000	64 %
Grossular ferrian	27	18	0.137	29 %
Quartz	20	7	0.041	2 %
Gypsum	8	16	0.024	2 %
Thaumasite	12	51	0.034	3 %

The actual chemical composition of the slag sample can be determined from the composition of minerals determined by XRD analysis. The result of this analysis is only indicative as it is based on semi-quantitative values, which do not consider the glass phase of the slag. Nevertheless the glass phase should not differ dramatically from the crystalline phase. It is possible to obtain the approximate information about the main component in the sample, but it is not possible to define the trace components.

Using the table from [21] (the chemical composition of mineral) the percentage chemical composition of the crystalline phase of the BFS was determined. The results are summarized in Table 3.

Table 3: Chemical composition of the used BFS sample[1]

Sample	Chemical composition [%]										M_Z
	CaO	SiO_2	FeO	Fe_2O_3	Al_2O_3	MgO	Na_2O	CO_2	H_2O	SO_3	
K 1	38.3	27.9	0	0	30.4	0	0	0.2	1.5	1.3	0.66

The content of CaO and SiO_2 is typical for this type of stabilized blast furnace slag. Slightly atypical is the higher content of Al_2O_3. Such a high content of Al_2O_3 is typical only for cast irons. this detection indicates the possible origin of the slag. It is important to emphasize. that the values are indicative and based on one sample. For more exact determination of chemical composition it would be necessary to use additional test methods. such as spectral analysis or others. Since slag aggregates used in an asphalt mixture is in a regular contact with water and at the same time is affected by climatic effect – mainly thaw-freezing cycles – additional tests like ferrous. silicate or manganesian decay are important. At the same time it is always important to determine alkalinity modulus which is given by following equation[14]:

$$M_Z = \frac{CaO + MgO}{SiO_2 + Al_2O_3}$$

The alkalinity modulus of used BFS is 0.66. If M_z is < 1. the slag aggregate is specified as acid and if Mz ≥ 1 the slag is defined as alkalaine. The alkalinity modulus is performed on fraction 0/4 mm. because the fine fraction is most susceptible to volume changes. The results only indicates in case of asphalt mixtures. that the slag aggregate might be more hydrophilic. which can influence the water susceptibility of the asphalt mixture. Following result shown later in Fig. 4 this was seen as an impact only in case of the SMA 8 NH mixture.

The ferrous decay was determined according to EN 1744-1. the result of which should indicate number of particles which show indication of such decay. From the results done repeatedly in 2015 and 2016 there were no such particles. The silicate decay was determined following the same European standard. Also in this case the result was negative, e.g. no particles indicating the potential of such type of chemical disintegration have been found [22.23.24].

Bitumen

For asphalt concrete design and laboratory production a paving grade 50/70 according to CSN EN 12591:2009 was used. Additionally for the second variant of $AC_{bin}16$ mixture. PMB 25/55-60 was used (labelled as PMB in the experimental results). A modified bituminous binder with a higher polymer content PMB 40/100-65 was used for stone mastic asphalt for low noise wearing courses.

Results and discussion

Volumetric characteristics

The volumetric characteristics were compared with the standard EN 13108-1 and TP 259 in case of SMA 8 NH. The standard limit and threshold values for the initial type tests are highlighted for each mixture in the Figure 2. For each test. data are presented for the control mixture (labelled as “ref.”) and the mixture with the replacement of one fraction by slag aggregate (labelled as "BSF").

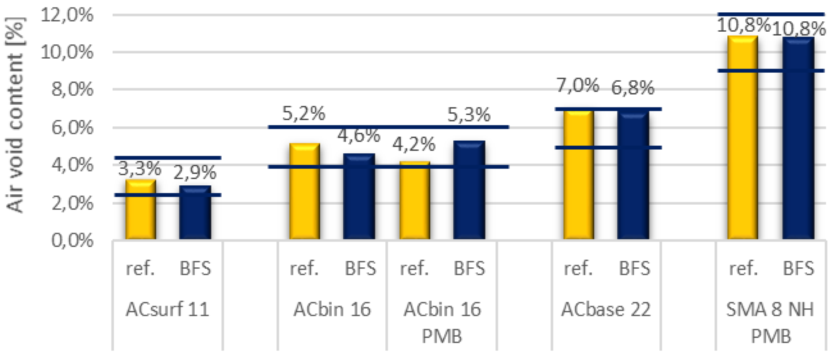

Figure 2: Volumetric characteristics

In the case of volumetric characteristics. there are not visible any significant changes due to BSF usage. For most of the mixtures. the air voids content was slightly reduced. Slag aggregates 4/8 mm have a finer grading curve then the crushed aggregate. so it was a predictable trend. In the case of the AC_{bin}16 PMB. substitution by BSF led to an increase in air voids content by about 1 %. This trend was unexpected and it is unexplainable.

Resistance to water damage and frost immersion

The determination of water and frost resistance was performed in accordance with EN 12697-12 and AASHTO T283-3 (own modified procedure). The U.S. testing method was included to extend the procedure by a freezing cycle. The freeze cycles is not standardly required neither in the Czech Republic nor in Europe.

For each mixture a set of 9 Marshall specimens was compacted by 2x25 blows by Marshall hammer (EN 12697-33). These specimens were divided into three groups where each group was subjected to another conditioning process. The dry specimens ("ref.") were stored dry at room temperature and at normal relative humidity. The specimens ("EN") were subjected to a saturation procedure according to EN 12697-12. when the specimens were saturated and stored in a water bath at 40 °C for 72 hours. The last set of test specimens ("AASHTO") was saturated and stored in a plastic bag for 18 hours in a freezer at -18 °C and then stored in a water bath at 60 °C for 24 hours. The indirect tensile strength testing temperature for all of the specimens was 15 °C with conditioning of at least 4 hours.

As can be seen from the Figure 3. the indirect tensile strength values in some types of mixtures has increased if aggregates were partly replaced by BSF and on the contrary. This disparateness is the reason why different mixtures with different maximum grain sizes were included in the study to verify the impact of BSF aggregates. The verification was performed on a wider range of asphalt mixtures and not just on one type.

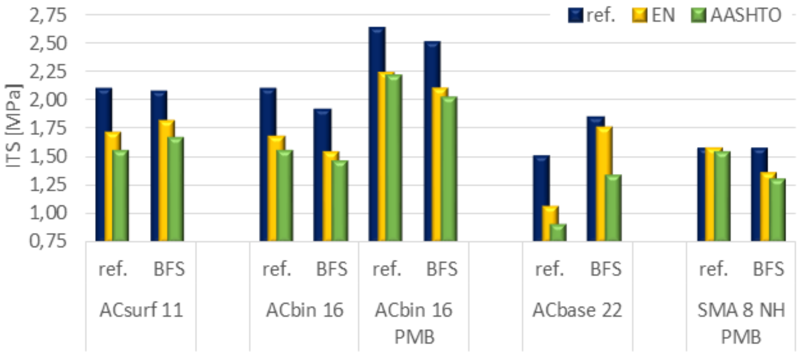

Figure 3: Indirect tensile strength (ITS) results

As it was stated above. the intention of this study is not to improve the properties of asphalt mixtures. but to prove the suitability of the slag usage in selected asphalt mixtures. The standard requirement of this test is specified by a minimum value of ITSR ("indirect tensile strength ratio"). ITSR is the ratio of strength of unconditioned ("dry") and conditioned ("EN") specimen. All tested mixtures comply with the standard parameter of indirect tensile strength ratio for EN test method. $ITSR_{min}$= 80 %. or 70 %. For AC_{base} mixtures. the $ITSR_{min}$ is not determined. because this test is not required for initial type test. Nevertheless test was performed for further comparison.

The ITSR of tested asphalt mixtures varies similarly as the strength results. The AC_{surf} and AC_{base} mixtures with BSF reached higher parameters. In case of AC_{base} the difference is almost 25 % in EN method and 12 % in AAHSTO method. The AC_{bin} mixtures reached very similar ratios for both bituminous binders. The SMA NH evince the last case. where the presence of blast furnace slag decreases the strength ratio.

There is no possible way to generalize the behaviour of BSF in asphalt mixtures.

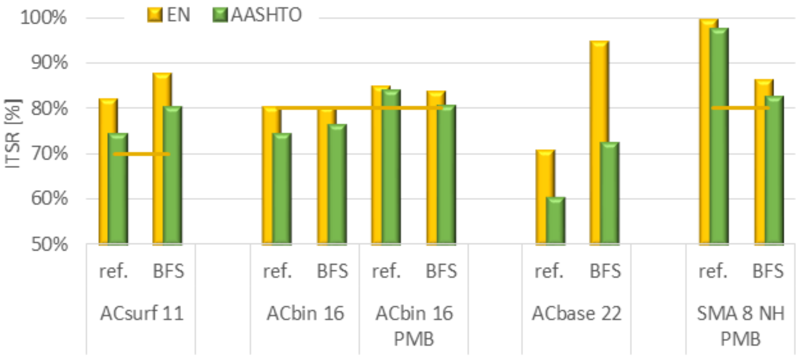

Figure 4: Indirect tensile strength ratio - ITSR

Resistance to permanent deformation

The resistance to permanent deformation was determined in accordance with EN 12697-22 in a small test device using air bath at a test temperature of 50 °C. The product standard ČSN EN 13108-1 and for low noise wearing course asphalt mixture national technical specifications TP 259 set maximum values for the two test parameters – PRD_{AIR} and WTS_{AIR}. PRD_{AIR} is the average rut depth and WTS_{AIR} is the increment of rut depth. calculated as an average value of rut depth increase determined during the application of repeated test wheel load cycles.

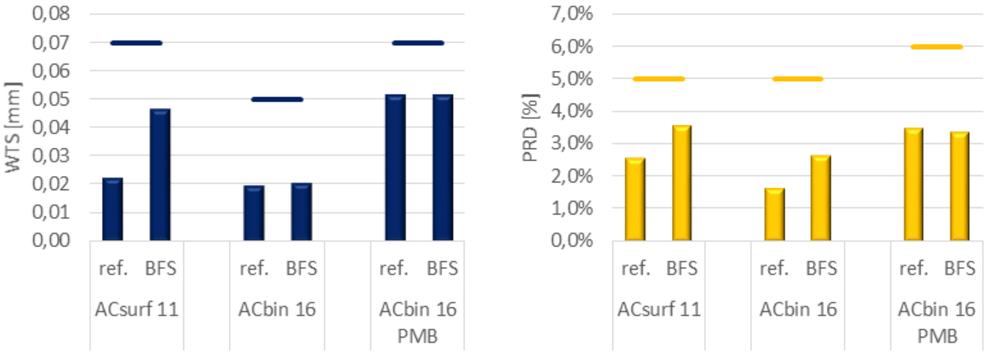

Figure 5: Results of resistance to permanent deformation

The results are summarized in Figure 5. which highlights the limits according to EN 13108-1 or TP 259 depending on assessed mix type. For AC_{base} mixture this test was not performed because this parameter is not required for the initial type test.

AC_{surf} and AC_{bin} mixtures with BFS aggregates show slightly higher values in the permanent deformation test than the control mixtures. but these values are still deeply below the required standard limits. The SMA NH mixtures evince the same parameters.

The standard EN 13108-1. or TP 259 requires for initial type testing only bituminous binder content. grading curve. air voids content. ITSR and resistance to permanent deformation parameters. No further characteristics are demanded. By evaluating only these parameters. BSF aggregates improves to some extent water and frost resistance (ITSR) but. on the other hand slightly reduces resistance to permanent deformation.

Since the results of only three material characteristics do not seem to be relevant for performance prediction and do not evaluate asphalt mixtures for example in the low temperature range. additional tests have been added. The further tests do not have any limiting values required in the Czech Republic for tested types of asphalt mixtures but they give an appropriate perspective how the mixture can perform. To evaluate the effect of aging. some tests were performed even on laboratory aged specimens.

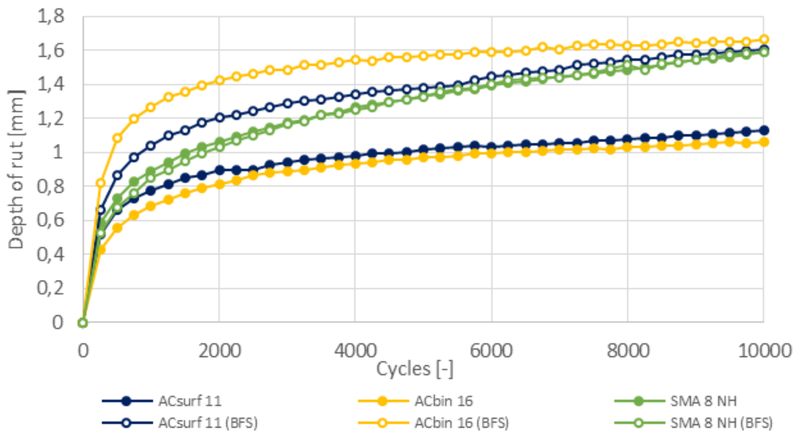

***Figure 6:* Development of the wheel tracking test for 10 000 cycles**

Stiffness

The first test performed beyond the initial type testing was the stiffness modulus determination. The stiffness was determined on Marshall specimens by IT-CY method according to EN 12697-26 (non-destructive repeated indirect tensile stress test) at three selected test temperatures: 0 °C. 15 °C and 27 °C.

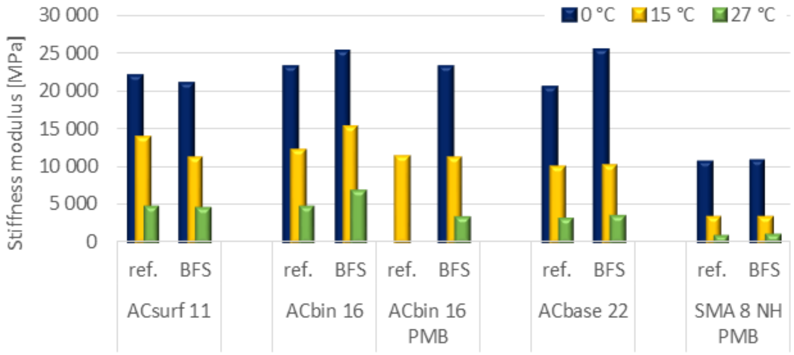

***Figure 7:* Stiffness results for three selected test temperatures**

Figure 7 shows that BSF aggregates have a different effect on the stiffness modulus in different types of asphalt mixtures. These results fairly support the indirect tensile strength results. For AC_{surf}. the stiffness modulus at 15 °C decreased by 20 % due to BSF use. but on the contrary the AC_{bin} with a paving grade bitumen increased the stiffness modulus by 25 %.

The test specimens were further extended by a group of specimens exposed to laboratory aging. Aging was performed according to one of the procedures described in prEN 12697-52. The specimens were stored in heating oven under a constant air supply (ventilation) at 85 °C for 5 days. Due to the oxidation of bituminous binder in the mixture. the strength characteristics increased to some extent. The oxidized bitumen becomes harder (its penetration decreases and the softening point increases) and thus the strength characteristics of the mixture are affected. as is generally known and expected.

The graph in Figure 8 shows stiffness values at 15 °C of virgin and aged test specimens. The increases of stiffness modules due to laboratory aging (ageing index) are calculated. The higher the ageing index is, the more the mixture is influenced by the ageing; is more ageing susceptible.

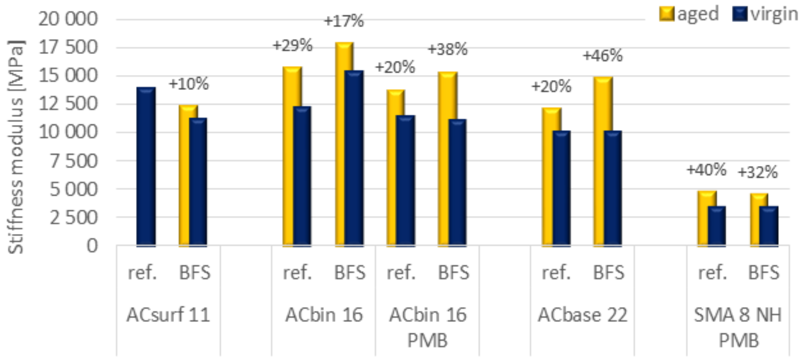

Figure 8: Comparison of stiffness modules of virgin and aged specimens

Resistance to crack propagation

The resistance to crack propagation test was performed in accordance with EN 12697-44. Contrary to the standard procedure Marshall specimens with diameter of 100 mm were use dividing them in two semi-circular test specimens. The required width of 50 mm was achieved by cutting of specimens on laboratory saw.

The essence of the test is a three-point bending of semi-circular specimens with a defined notch of 10 mm depth in the middle of bottom specimen face. The test procedure was performed on at least 6 test specimens at a temperature of 0 °C applying a standardized loading rate of 5 mm/min.

The set of specimens was again extended to the specimens exposed to laboratory aging. In this test it cannot be generally said that the oxidized bitumen would result in a higher fracture toughness. The ageing index depends on number of factors - type of used bituminous binder. type of asphalt mixture. presence/amount of reclaimed asphalt. amount of additives. etc.

The higher the value of fracture toughness is. the better resistance to thermal cracking of the mixture should be. It is apparent from Figure 9 that mixtures with only crushed aggregate reached higher fracture toughness than mixtures with BSF. The decrease is apparent for all types of tested asphalt mixtures.

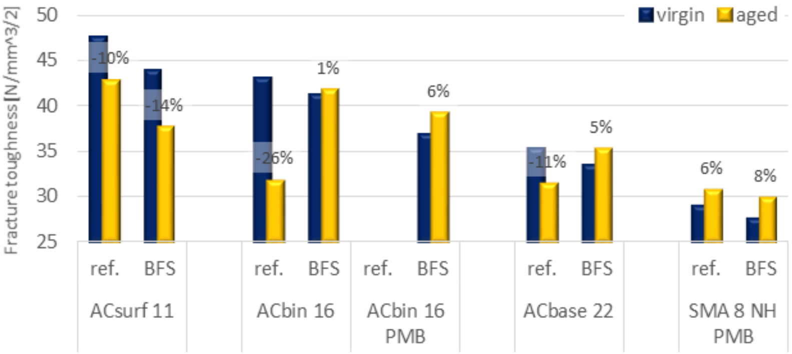

Figure 10: Fracture toughness of virgin and aged specimens

The fracture toughness of almost all mixtures with only crushed aggregates decreased due to the aging. but for the mixtures with BFS the trend is inverse. Most of the mixtures responded with increase of the parameter due to the aging. With adequate circumspection it can be summarized that asphalt mixture with BSF being exposed to climatic conditions (aging) shall have better characteristics at low temperatures than asphalt mixture using only traditional crushed aggregates. Nevertheless from other studies done at the Czech Technical University in Prague it is evident that fracture toughness is only in limited extent suitable for describing the thermal cracking behaviour and these characteristics should always be compared with fracture energy calculated from the load-displacement diagram.

Flexural strength (3-point bending test)

Flexural tensile strength is another simple destructive non-LVE test performed in the range of low temperatures. Flexural strength was tested according to Czech technical specifications TP 151. This test is in the Czech Republic required only for HMAC mixtures. The test was included for its representative results with all types of mixtures and a simple reproducibility.

The test is performed by a three-point bending of unnotched beam test specimens. The test temperature was 0 °C applying a loading rate of 1.25 mm/min. In total eight beam test specimens were divided into two groups. where one group was exposed to laboratory aging according to prEN 12697-52 (5 days at 85 °C), the second group was tested in virgin state.

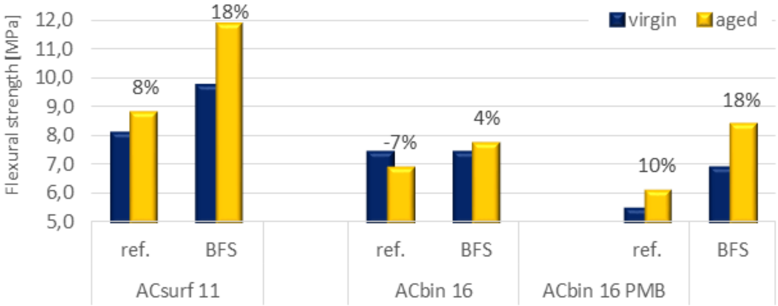

Figure 11: Flexural strength of virgin and aged specimens

The tensile bending strength of asphalt mixtures containing BSF is in all cases higher than the value for control test specimens with only crushed aggregates. These results show that BSF containing asphalt mixtures might better withstand low temperature stresses (thermal cracking). However. this conclusion must be taken with circumspection. The crack propagation test results on semi-circular test specimens show the exact opposite. In that test. mixtures with BSF obtained lower fracture toughness. That implies that it is always necessary to evaluate the mixtures at a complex range - to evaluate independently as many tests as possible. Additionally a more suitable test. which would be run in linear viscoelastic range might be more suitable to explain the cracking behaviour of the asphalt mixture.

The flexural tensile strength test defines only the maximum force and the displacement at the moment of failure. For the purpose of the research study. these parameters were additionally expanded by the fracture energy. The fracture energy is the energy necessary for getting the test specimen fully collapsed. The fracture energy was calculated as the area under the load-displacement diagram to the point of failure.

It can be demonstrated on the example of AC_{bin} mixture. why the addition of this parameter is so important. Both AC_{bin} mixtures achieved almost the same flexural strength. It can be therefore said that both mixtures will behave in terms of thermal cracking similarly. However, in the case of fracture energy. it is clear that the mixture with crushed aggregate needs significantly higher amount of energy to fully collapse the specimen than the mixture with BSF aggregates. The asphalt mixture with crushed aggregate will take much longer to break (terminally crack). even though the maximum force is the same.

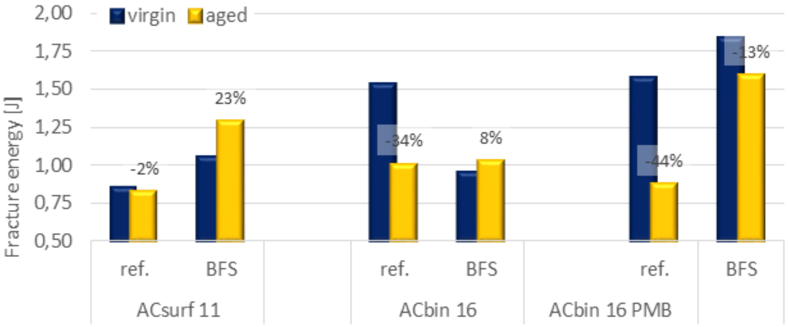

Figure 12:* *Fracture energy of virgin and aged specimens

Conclusion

As it was emphasized in the introduction. the aim of the presented ongoing research study was to prove the suitability of the use of BSF aggregates as a substitute for natural crushed aggregate. For the study three asphalt concrete types with different maximum aggregate particle size and one stone mastic asphalt mixture for low noise surface layers were selected. Several tests have been performed to demonstrate the suitability of this artificially born material.

The results of the present research show that the use of BSF aggregates in asphalt mixtures does not influence the quality or durability of the mixture. on the contrary in some cases the BFS can even improve the properties.

The use of slag in asphalt mixes could have a significant positive impact on the environment. The extraction of natural crushed aggregate is an environmental burden and the appropriate aggregate resources are getting smaller. It is necessary to search for new suitable quarry sites. The expansion of the current quarries is not possible infinitely. At the same time by using suitable alternative materials which are defined as waste materials or by-products the principles of circular economy and sustainable construction is supported.

There are enormous amounts of different slags stored in waste disposals in current or old (brownfield) industrial metallurgical areas. These waste materials are deposited there without any appropriate usage having less or better potential to be applied in different areas of construction industry. Another advantage of such material might be its economic aspect. Slag or any other recycled aggregate is usually cheaper than natural aggregates being a waste material or industrial by-product. The cost of crushed. screened and sorted slag aggregates is about half of the costs of natural aggregates.

In the next stages of the presented research study, a coarser fraction of BSF aggregate will be used in asphalt mixtures to verify its effect on strength characteristics. After confirming the assumed properties with a coarse fraction. mixtures with 100 % slag aggregate will be produced.

Acknowledgement

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Využití umělého kameniva z vysokopecní strusky při výrobě asfaltových směsí

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Souhrn

V rámci výzkumného projektu byla použita stabilní kladenská vysokopecní struska jako alternativní náhrada k běžnému drcenému kamenivu. Struska je vedlejším produktem především výroby železa a oceli. V dopravním stavitelství je používaná již řadu let, ale pouze jako kamenivo do nestmelených vrstev, případně jako příměs pro výrobu hydraulicky stmelených vrstev. Jakákoliv jiná aplikace není v současné době používána, a to i díky některým problémům některých velkých silničních staveb nebo z nedostatečné znalosti charakteristik a historie vzniku a původu konkrétních strusek. Tento materiál je proto mnohdy spíše ukládán na skládky, ačkoli by se mohlo jednat o kvalitní kamenivo se zlepšenými pevnostními a protismykovými charakteristikami.

V tomto příspěvku jsou prezentována data probíhajícího výzkumu, kdy bylo předrcené a přetříděné struskové kamenivo aplikováno do asfaltových směsí typu AC. Ve směsích byla jedna frakce kameniva kompletně vyměněna kamenivem struskovým. Na referenčních a alternativních asfaltových směsích byla provedena celá řada zkoušek pro ověření vlivu tohoto alternativního kameniva na výsledné vlastnosti asfaltové směsi. Příkladem provedených zkoušek je stanovení modulu tuhosti, stanovení odolnosti vůči trvalým deformacím, provedení zkoušky pevnosti v tahu za ohybu, stanovení odolnosti vůči účinkům vody a mrazu a další.

Klíčová slova: *Vysokopecní struska, asfaltové směsi, zkoušení asfaltových směsí, recyklace*

Hodnocení energetické efektivity tepelné izolace z celulózových vláken ve dvouplášťových střechách

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Souhrn

Článek se zabývá energetickým hodnocením doplňkové tepelné izolace z celulózových vláken ve skladbách plochých dvouplášťových střech. Pro výpočtové vyhodnocení je zvolena modelová konstrukce dvouplášťové ploché střechy, která nesplňuje normové tepelně technické požadavky. Splnění těchto požadavků je řešeno doplněním tepelně izolační vrstvy o tepelnou izolaci z foukaných celulózových vláken. Jedná se o materiál, který je vyroben z více než 75 % recyklovaného papíru.

Energetická náročnost tohoto recyklovaného materiálu je na ploše 1m^2 modelové konstrukce porovnána s jinými druhy tepelných izolací. Hodnocena je spotřeba svázané energie doplňkového tepelně izolačního materiálu, spojené s jeho životním cyklem. Dalším hodnoceným parametrem je energetická návratnost svázaných energií, která je porovnána s úsporou potřeby tepla na vytápění.

Klíčová slova: *celulózová vlákna, tepelná izolace, svázané energie, energetická náročnost.*

Úvod

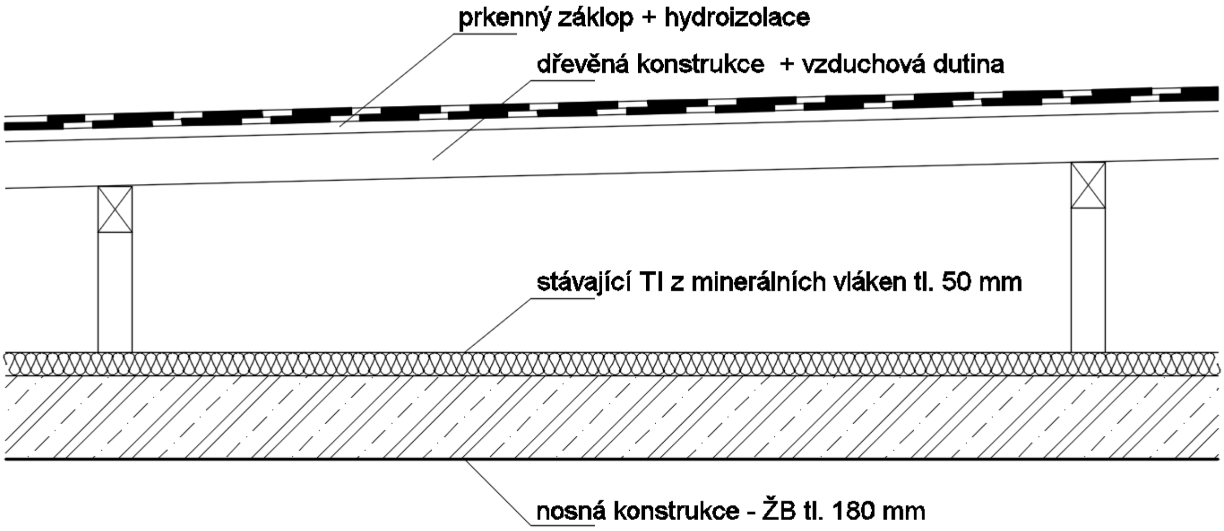
Cílem příspěvku je výpočtově prokázat efektivnost návrhu dodatečného zateplení celulózovými vlákny z hlediska celkové energetické náročnosti v porovnání s ostatními materiály tepelných izolací.

Tepelné izolace z celulózových vláken reprezentují recyklované materiály, které přispívají ke globálnímu snižování produkovaných odpadů a spotřeby nových surovin. Svou funkcí významně pomáhají snižovat spotřebu provozních energií budovy. Energetická náročnost celulózových vláken v průběhu definovaného životního cyklu je významně nižší[1,2] než energetická náročnost standardních tepelných izolací z minerální vlny nebo expandovaného polystyrenu[3]. Hodnocení životního cyklu (LCA) materiálů a stanovení jejich energetické náročnosti je popisováno v souboru mezinárodních norem ČSN ISO 14040-49[4].

Princip výpočtu pro porovnání svázaných energií tepelně izolačních vrstev je proveden a hodnocen dle vzoru metodiky SBToolCZ[5] s využitím databází environmentálních charakteristik materiálů[1,2,3]. Pro relevantní výsledky a možnost vyhodnocení energetické efektivnosti je zvolena funkční jednotka 1 m^2 plochy střechy, která svou skladbou splňuje doporučený normový požadavek[6] součinitele prostupu tepla konstrukcí U = 0,16 W/m^{2}K. Pro vyhodnocení celkové energetické návratnosti je bilance svázané energie doplněné tepelně izolační vrstvy porovnávána s vypočtenou úsporou provozní energie, stanovené dle výpočtového postupu ČSN EN 12831[7].

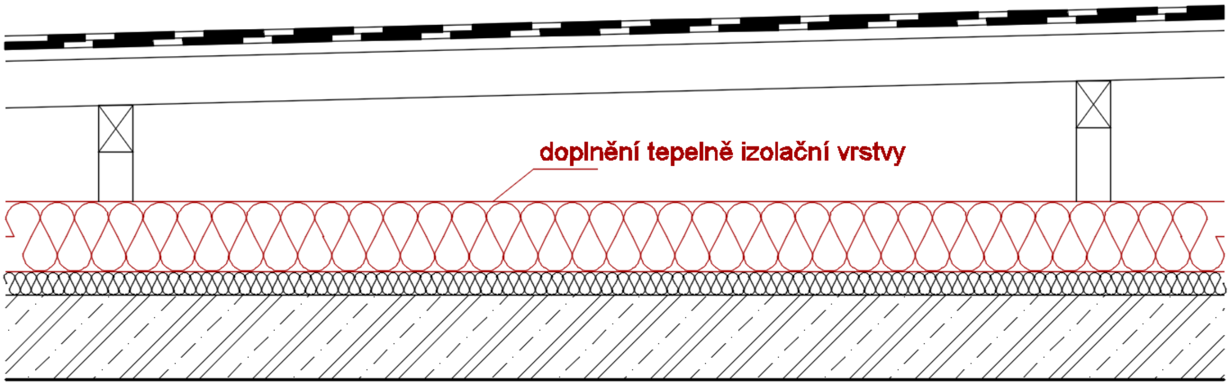
Experimentální část

Základní modelovou konstrukcí pro výpočet je dvouplášťová plochá střešní skladba (obrázek 1) s větranou vzduchovou vrstvou. Hlavní nosná konstrukce střechy je z železobetonové monolitické desky tl. 180 mm s hodnotou λ = 1,74 W/m.K, na které je aplikována tepelná izolace z minerální vlny tl. 50 mm s hodnotou λ = 0,06 W/mK. Větranou vzduchovou vrstvu vymezuje dřevěná konstrukce, na jejíž horní pásnici je zhotoven dřevěný záklop a krytina z asfaltového souvrství. Při tepelně technickém zhodnocení základní modelové konstrukce, bez vlivu tepelných mostů, je vypočten součinitel prostupu tepla U = 0,93 W/m^{2}K a nesplňuje normové požadavky dle ČSN 73 0540-2[6].



Obrázek 1: Základní modelová konstrukce střechy

Pro splnění normových tepelně technických požadavků konstrukce je navrženo doplnění tepelně izolační vrstvy (obrázek 2).



Obrázek 2: Doplnění tepelně izolační vrstvy do základní modelové konstrukce střechy

Pro modelové porovnání energetické efektivnosti tepelných izolací jsou zvoleny materiály z databáze Ecoinvent[2] včetně uvedených vlastností objemové hmotnosti, součinitele tepelné vodivosti a hodnoty svázaných energií PEI, (viz tabulka 1). Z uvedených vlastností je následně vypočtena minimální tloušťka tepelné izolace pro splnění normového požadavku[6] součinitele prostupu tepla U = 0,16 W/m^{2}K na definovanou funkční jednotku 1m^2. Výpočet je proveden bez uvažování vlivu tepelných mostů. Při reálném hodnocení konstrukce je vždy nutné zohlednit skutečné vlastnosti zvolených materiálů.

Tabulka 1: Vlastnosti hodnocených tepelně izolačních vrstev dle databáze Ecoinvent [2] a výpočet minimální tloušťky

Materiál tepelně izolační vrstvy	PEI [MJ/kg]	kg/m^3	λ [W/mK]	minimální tl. tepelné izolace pro splnění U = 0,16 W/m^{2}K
celulózová vlákna	7,2	50	0,040	200 mm
minerální vlna kamenná	20,2	32	0,036	180 mm
minerální vlna skelná	45,6	40	0,040	200 mm
EPS expandovaný polystyren	105,1	30	0,035	180 mm

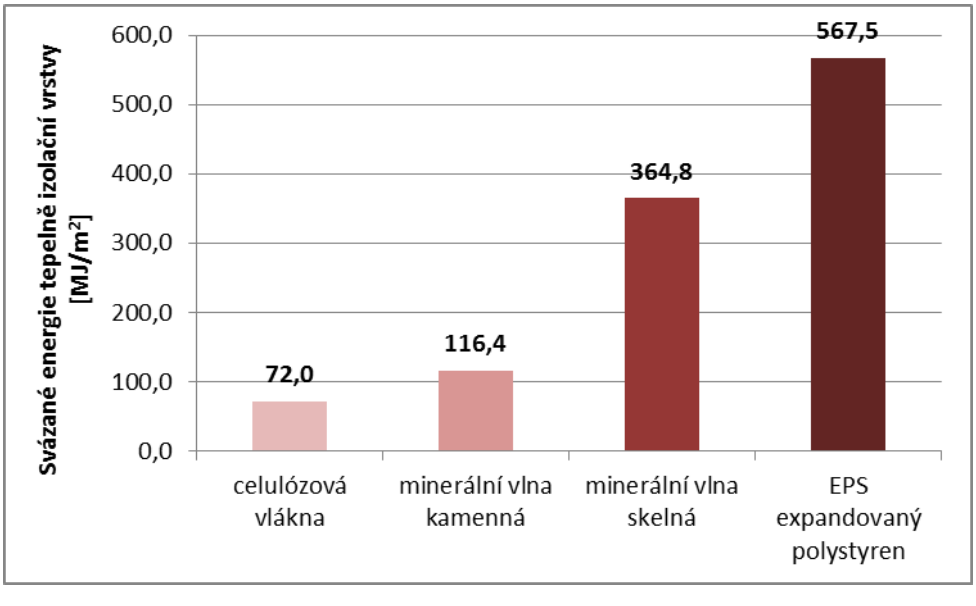
Dle výpočtu normové doporučené minimální tloušťky tepelné izolace v tabulce 1 jsou vzájemně porovnány svázané energie jednotlivých materiálů pro zvolenou funkční jednotku 1 m^2. Vzájemné porovnání energetické efektivnosti dodatečně vložených tepelných izolací je uvedeno na obrázku 3.

Dalším hodnoceným kritériem je efektivní materiálová volba tepelně izolační vrstvy vzhledem k návrhové tloušťce materiálu a celkové energetické návratnosti. Hodnocení je provedeno s okrajovými podmínkami teploty interiéru +20°C, teploty exteriéru -13°C, průměrná roční exteriérová teplota +4°C a počet ročních dní na vytápění 216. V první výpočetní fázi je stanovena potřeba tepla na vytápění základní modelové konstrukce a poté konstrukce s nově aplikovanou tepelně izolační vrstvou v rozmezí tlouštěk 40 - 400 mm. Výpočet potřeby tepla na vytápění je proveden dle výpočtového postupu uvedeného v ČSN EN 12831[7]. V druhé výpočetní fázi jsou porovnány bilance svázaných energií aplikované tepelně izolační vrstvy s vypočtenou úsporou potřeby tepla na vytápění. Vliv tloušťky doplňkové tepelně izolační vrstvy na nárůst energetické návratnosti a vzájemné porovnání je uveden na obrázku 4.

Výsledky a diskuse

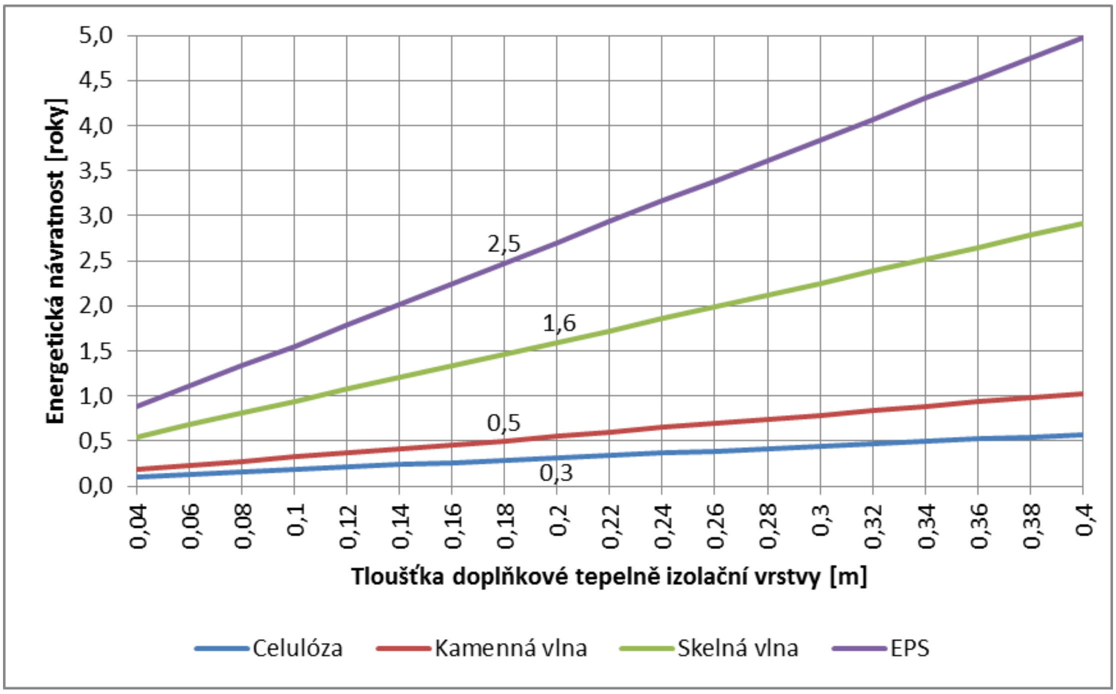
Výsledky vypočtených svázaných energií tepelně izolační vrstvy jsou shrnuty do obrázku 3. Z porovnání uvedených hodnot vyplývá, že nejnižší hodnota svázané energie a energeticky efektivní volbou je využití tepelné izolace z celulózových vláken. Nízká energetická náročnost tohoto materiálu je dána především svou hlavní výrobní surovinou, kterou je tříděný recyklovaný novinový papír s objemem více jak 75 % finálního produktu. Energeticky hospodárná je také samotná výroba celulózových vláken, která je realizována rozdrcením a následným rozmělněním papíru s impregnací z přírodních produktů proti škůdcům.

Dle výsledků uvedených v grafu na obrázku 3 je nejvyšší hodnota svázaných energií uvedena u expandovaného polystyren. Důvodem je především základní surovina zpěňovaného polystyrenu ve formě perlí, vyrobené suspenzí polymerací monomeru, s obsahem 4 – 7 % pentanu - nadouvadel[3]. Expandovaný polystyren je tedy energeticky náročný nejen svou základní surovinou, ale i samotnou výrobou finálního produktu a likvidací po konci své životnosti. Z konstrukčního hlediska je tento materiál pro zvolenou modelovou konstrukci nevhodný, do hodnocení je zařazen pro komplexnost porovnání standartních tepelně izolačních materiálů.



Obrázek 3: Porovnání energetické efektivnosti tepelně izolační vrstvy

Obrázek 4 je graf, z něhož je patrná vypočtená doba energetické návratnosti doplňkové tepelně izolační vrstvy dle návrhové tloušťky tepelné izolace. U jednotlivých tepelných izolací je vyznačena doba návratnosti při minimálních tloušťkách tepelné izolace, stanovené dle tabulky 1. Nejkratší doba návratnosti 0,3 roku a nejnižší lineární nárůst je uveden u celulózových vláken. Z hlediska doby návratnosti jsou celulózová vlákna nejefektivnější volbou. Nejdelší dobu návratnosti 2,5 roku a nejvyšší lineární nárůst je uveden u tepelné izolace z expandovaného polystyrenu.



Obrázek 4: Celková energetická návratnost

Závěry

Na modelové konstrukci dvouplášťové ploché střešní skladby s výpočetním výsekem plochy 1m^2 bylo prokázáno, že aplikace tepelné izolace z celulózových vláken je v porovnání s ostatními hodnocenými izolanty energeticky efektivní. Efektivnost je prokázána výpočtem svázaných energií tepelně izolačních vrstev a výpočtovou bilancí energetické návratnosti. Efektivita tohoto materiálu je vztažena především k základní výrobní surovině recyklovaného novinového papíru.

Podobných parametrů jako celulózová vlákna dosahuje i tepelná izolace z minerální vlny kamenné. Důvodem nízké energetické náročnosti je základní vstupní surovina (čedič, diabas a struska).

Využití novinového papíru ve formě celulózových vláken je uplatnitelné ve stavebnictví nejen ve formě foukaných tepelných izolací, ale i jako surovina kompozitních materiálů, která zlepšuje pevnost a tepelně izolační vlastnosti základního materiálu[8].

Pro minimalizaci energetické náročnosti staveb a zlepšování životního prostředí by mělo být upřednostňováno využívání produktů obsahující druhotné a přírodní surovinové zdroje.

Seznam symbolů

U	Součinitel prostupu tepla [W/m^{2}K]
λ	Součinitel tepelné vodivosti [W/mK]
PEI	Primary Energy Input – Spotřeba primární energie [MJ]
EPS	Expandovaný polystyren

Poděkování

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Energy efficiency evaluation of cellulose fibers thermal insulation in double-skinned roofs

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Summary

This extract discusses energy evaluation of additional thermal insulation from cellulose fibres in the composition of flat double skin roofs. The model construction of double skin roof which doesn´t meet thermal-technical requirements of standards was chosen for computational evaluation. The fulfillment of these requirements is solved by addition of thermal insulation from blown cellulose fibres into thermal insulation layer. It is a material which is made from more than 75 % recycled paper.

Energy demand of this recycled material is compared to other types of thermal insulations on area of 1 m^2 *of model construction. The evaluated parameter is the associated energy consumption of additional thermal insulation material connected with its life cycle. Other evaluated parameter is energy return of connected energies which is compared with the heat saving for heating.*

***Keywords**: cellulose fibres, thermal insulation, primary energy, energy demand.*

Hodnocení obsahů minerálních živin a rizikových prvků v anaerobně stabilizovaných kalech z ČOV

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Souhrn

Kaly z čistíren odpadních vod (ČOV) jsou významným zdrojem minerálních živin a organické hmoty, ale zároveň jejich aplikace na zemědělskou půdu představuje možné riziko vnosu rizikových prvků do půdy. V roce 2017 bylo odebráno celkem 20 vzorků anaerobně stabilizovaných kalů ze 17 provozů ČOV napříč Českou republikou. Kaly byly analyzovány z hlediska obsahu sušiny, hodnoty pH a obsahů minerálních živin a rizikových prvků dle platných norem daných aktuální legislativou. Sušina kalů se nejčastěji pohybovala okolo 25 hm. %, pH pak v naprosté většině případů okolo 7,1. Obsahy živin ve vzorcích kalů byly mezi jednotlivými provozy mnohem méně variabilní, než obsahy rizikových prvků. V žádném vzorku nebyl překročen limitní obsah olova, které navíc vykazovalo velmi nízkou variabilitu mezi vzorky. Limity pro aplikaci na zemědělskou půdu byly nejčastěji překračovány pouze v jednom ze sledovaných rizikových prvků, kdy největší četnost překročení tohoto limitu byla v případě arsenu. Celkově nesplnilo limity obsahů rizikových prvků přibližně 35 % sledovaných provozů.

Klíčová slova: *čistírenský kal, monitoring, rizikové prvky, živiny, sušina,*

Úvod

Přísun kvalitní organické hmoty do zemědělských půd dlouhodobě klesá v důsledku poklesu produkce statkových hnojiv. Z tohoto důvodu je ohrožena půdní úrodnost, půdy degradují a narůstá riziko půdní eroze. Tyto skutečnosti jsou dále umocněny klimatickou změnou, která mimo jiné přináší odlišné rozložení srážek v průběhu vegetačního období a zvyšuje tak nároky na retenci vody v půdě a krajině. Vedle toho je zde významná produkce čistírenských kalů, které obsahují jak velké množství organické hmoty, tak i cenné množství živin, především fosforu a dusíku. Z tohoto důvodu je žádoucí čistírenské kaly aplikovat na zemědělskou půdu, zvýšit tak obsah půdní organické hmoty a uzavřít koloběh některých minerálních živin.

Čistírenský kal je jedním z konečných produktů procesu čištění odpadních vod a jeho produkce je nedílnou součástí těchto procesů. V EU se v roce 2013 dle dostupných informací vyprodukovalo nejméně 6 470 000 tun sušiny kalu[1]. Produkce kalu v České republice v roce 2016 činila přibližně 174 000 tun sušiny kalu. To při průměrné sušině 25 % představuje přibližně 700 000 t čerstvého kalu. Z tohoto množství bylo přibližně 36 % přímo aplikováno na půdu, 37 % kompostováno, 24 % uloženo na skládky (6 % jako odpad, 18 % jako technická vrstva skládky) a 3 % byly spáleny[2].

Suchý čistírenský kal obsahuje v průměru 50 – 70 % organické hmoty a 30 – 50 % minerální složky. Obsah dusíku se v sušině kalu pohybuje v rozmezí 1,6 – 6 % a obsah fosforu v rozmezí 1 – 4 %[3,4]. Z pohledu výživy rostlin je obsah draslíku v kalech většinou nízký a ve srovnání s obsahem dusíku a fosforu lze obsah draslíku považovat za nedostatečný[5]. Obsah dalších makro- a mikroživin, stejně jako rizikových prvků, se významně liší dle jednotlivých čistíren odpadních vod[3].

Kaly však dále mohou obsahovat značná množství rizikových a často velmi perzistentních látek, jako jsou např. polycyklické aromatické uhlovodíky[6], polychlorované bifenyly, halogenované uhlovodíky[7], polychlorované dibenzo-p-dioxiny a dibenzofurany[8], pesticidy, přípravky osobní potřeby[9,10], látky hormonální povahy, léčiva a jejich metabolity[11,12], mikroplasty[13] nebo nanočástice[14]. Dále se v kalu mohou vyskytovat různé druhy patogenních organismů, jako jsou bakterie[15], viry nebo prvoci[3].

Cílem této práce je zhodnotit aktuální stav obsahu rizikových prvků a základních minerálních živin v anaerobně stabilizovaných kalech z čistíren odpadních vod v rámci České republiky.

Experimentální část

Během roku 2017 bylo odebráno celkem 20 vzorků anaerobně stabilizovaných kalů, celkově ze 17 provozů čistíren odpadních vod. Jednotlivé provozy byly vybírány především na základě velikostní diverzifikace testovaného souboru. Pokud bylo součástí kalového hospodářství ČOV i sušení či hygienizace kalů, byly odebrány vzorky před a po této úpravě. Rozložení vzorkovaných ČOV dle jejich velikosti je uvedeno v tabulce 1.

Tabulka 1: Rozdělení souboru vzorkovaných ČOV dle konstrukční kapacity vyjádřené počtem ekvivalentních obyvatel (EO)

Konstrukční kapacita (EO)	**< 50 000**	**50 000 – 100 000**	**> 100 000**
Počet ČOV	5	7	5

Při každém vzorkování bylo odebráno minimálně 15 kg odvodněného kalu. Každý vzorek se skládal z alespoň 30-ti dílčích vzorků (ČSN EN ISO 5667-13). Jako vzorkovnice byly použity uzavíratelné neprůhledné nádoby z polypropylenu, v kterých byl vzorek následně transportován do laboratoře při teplotě 4 °C. Z těchto byl vytvořen vždy jeden směsný vzorek, který byl důkladně homogenizován, a následně byla pomocí kvartace odebrána reprezentativní část vzorku. Tato část byla dále manipulována a analyzována ve třech nezávislých analytických opakováních.

Kaly byly následně zmraženy (-40 °C) a lyofilizovány. Sušina vzorků byla stanovena gravimetricky po vysušení (105 °C) do konstantní hmotnosti. pH kalů bylo stanoveno v suspenzi kalu a roztoku 0,01 M $CaCl_2$ (1:5; v/v) (ČSN EN 15933) po vytřepání (1 h; 150 ot. /min) pomocí pH metru s ISFET elektrodou (SI400, Sentron Europe BV, Leek, Nizozemsko). Celkové obsahy živin a rizikových prvků byly ve vzorcích stanoveny pomocí optické emisní spektrometrie s indukčně vázaným plazmatem (ICP-OES) po mikrovlnné digesci lučavkou královskou (ČSN EN 13657, ČSN CEN/TS 16171).

Výsledky a diskuse

Základní statistické údaje sledovaných parametrů testovaného souboru vzorků (n = 20) anaerobně stabilizovaných čistírenských kalů jsou uvedeny v tabulce 2. Ústřední kontrolní a zkušební ústav zemědělský v Brně v roce 2016 analyzoval 82 vzorků kalů napříč celou Českou republikou a pro obsahy rizikových prvků uvádí následující hodnoty mediánu (mg/kg): As (6,49); Cd (1,26); Cr (41,7); Cu (204); Ni (31,1); Pb (31,6); Zn (841)[16]. Srovnáním těchto hodnot lze tedy konstatovat, že námi vzorkovaný soubor představuje reprezentativní vzorek produkovaných kalů v ČR.

V testovaném souboru vykazovaly obsahy rizikových prvků obecně mnohem vyšší variabilitu než obsahy sledovaných živin. Hodnoty variačního koeficientu (KV) byly pro jednotlivé rizikové prvky v pořadí: Ni >> Cr > Cd > Cu > As > Zn > Pb. Z toho obsahy Ni, Cr, Cd a Cu vykázaly hodnoty KV vyšší než 100 %. To poukazuje na silnou variabilitu těchto prvků v souboru a lze to přisuzovat možné silné kontaminaci některých kalů těmito prvky pravděpodobně průmyslovou činností v dané oblasti.

Obsahy sledovaných živin (Ca, Fe, K, Mg, P a S) vykázaly relativně konstantní rozložení mezi jednotlivými vzorky, jelikož ani u jedné živiny KV nepřesáhl 100 %. Nejvyšší variabilita ze sledovaných živin byla nalezena pro Ca (KV = 72 %). To lze přisuzovat skutečnosti, že některé z analyzovaných kalů byly po odvodnění vápněny. Tyto kaly následně vykazovaly silně zásadité hodnoty pH s maximální naměřenou hodnotou 12,7. Obecně obsahy živin ve sledovaných kalech byly nalézány v pořadí: Ca ~ Fe > P > S >> Mg ~K.

Sušina vzorkovaných odvodněných, anaerobně stabilizovaných kalů se pohybovala okolo 25 %. Maximální hodnoty (nad 90 % sušiny) byly nalezeny u kalů, které byly průmyslově sušeny. Hodnoty pH se mezi jednotlivými kaly lišily jen minimálně a většina kalů vykazovala pH okolo hodnoty 7,1 (vyjma kalů vápněných).

Tabulka 2: Deskriptivní statistika obsahů živin a rizikových prvků ve vzorcích kalů z ČOV (n = 20)

Rizikové prvky (mg/kg)	**Průměr**	**Medián**	**Min.**	**Max.**	**KV^a (%)**
As	14,2	8,65	3,05	51,6	99
Cd	2,31	1,34	0,27	16,3	148
Cr	111	49,6	24,9	1 219	229
Cu	412	201	72,2	2 021	125
Ni	49,4	37,6	17,6	208	856
Pb	40,0	36,7	8,87	114	48
Zn	1017	841	346	4318	78
Živiny (g/kg)					
Ca	39,0	32,2	15,2	157	72
Fe	35,5	32,7	14,8	64,6	35
K	3,98	3,71	2,73	8,30	29
Mg	5,84	4,98	3,38	9,90	33
P	25,9	26,6	19,2	33,4	14
S	13,3	13,5	7,62	19,3	21
Ostatní parametry					
Sušina (hm. %)	28,2	26,6	16,0	96,2	57
pH	7,37	7,13	6,47	12,7	17
Cd/P^b	87,1	53,7	9,80	583	142
Ni/P^c	1 888	1 400	664	7 520	80
Pb/P^d	1 550	1 386	342	4 056	46

*^{a} Variační koeficient (směrodatná odchylka / aritmetický průměr * 100); ^{b} mg Cd/kg P; ^{c} mg Ni/kg P; ^{d} mg Pb/kg P*

Získané výsledky byly dále srovnány s mezními hodnotami koncentrací RP v kalech daných aktuální legislativou. Tyto výsledky jsou uvedeny v tabulce 3. Z ní je patrné, že limitní obsahy RP v kalech použitelných na zemědělskou půdu v ČR dané Vyhláškou č. 437/2016 Sb. jsou pro všechny RP přísnější, než požaduje Směrnice Rady 86/278/EHS.

Dle tabulky 3 je patrné, že ze sledovaného souboru ČOV byla nejčastěji překročena limitní hodnota pro As (3krát), následně pak Cd společně s Cu (2krát) a limit pro Cr, Ni, a Zn byl překročen vždy v jednom případě. Žádný vzorek pak nepřekročil limitní hodnotu obsahu Pb. Vzhledem k nízkému KV pro tento prvek lze říci, že kontaminace anaerobně stabilizovaných kalů z ČOV olovem aktuálně nepředstavuje významné riziko pro životní prostředí.

Rozdělení sledovaných ČOV dle jejich konstrukční kapacity neprokázalo významný vliv velikosti ČOV na obsah rizikových prvků v kalu. Pro tento účel by zřejmě bylo třeba sledovat větší množství provozů. Srovnání bylo dále provedeno dle hmotnostních poměrů obsahu rizikových prvků na kg fosforu, resp. Cd/P, Ni/P a Pb/P daných aktuální dánskou legislativou[17], která umožňuje producentům odpadů si zvolit kritérium hodnocení buď dle celkového množství RP na kg odpadu anebo právě dle přepočtu na kg fosforu. V rámci těchto kritérií byl hlavní rozdíl oproti České legislativě nalezen u ČOV střední velikosti (50-100 tis. EO), kdy všechny vzorkované provozy splňovaly sledovaná dánská kritéria pro aplikaci kalů na zemědělskou půdu. Výsledky Ni/P mohou naznačovat, že tento poměr je spíše negativně ovlivněn v kalech pocházejících z větších aglomerací, jelikož kritická hodnota byla ve sledovaném souboru překročena pouze u ČOV s kapacitou vyšší než 100 000 EO.

Celkově byly limitní koncentrace alespoň jednoho ze sledovaných RP překročeny v 6-ti provozech z celkových 17-ti sledovaných. To představuje přibližně 35 % z testovaného souboru. Z pohledu RP lze tedy říci, že 65 % sledovaných kalů lze aplikovat na zemědělskou půdu. Průměrný obsah P dosahoval ve sledovaných kalech přibližně 26 g/kg suš. Při srovnání tohoto obsahu např. s obsahem P v hnoji skotu (6,1 g/kg suš.[17]), hnoji prasat (10,9 g/kg suš.[17]) nebo koňském hnoji (4,8 g/kg suš.[17]) je patrné, že kaly obsahují 2-5 krát více fosforu než hospodářský hnůj. Při jejich aplikaci na zemědělskou půdu pak tedy dochází nejen k vnosu cenné organické hmoty do půdy, ale také ke zlepšení celkové bilance fosforu na národní úrovni.

Tabulka 3: Počet vzorků a ČOV nesplňujících kritéria pro aplikaci kalu na zemědělskou půdu v ČR

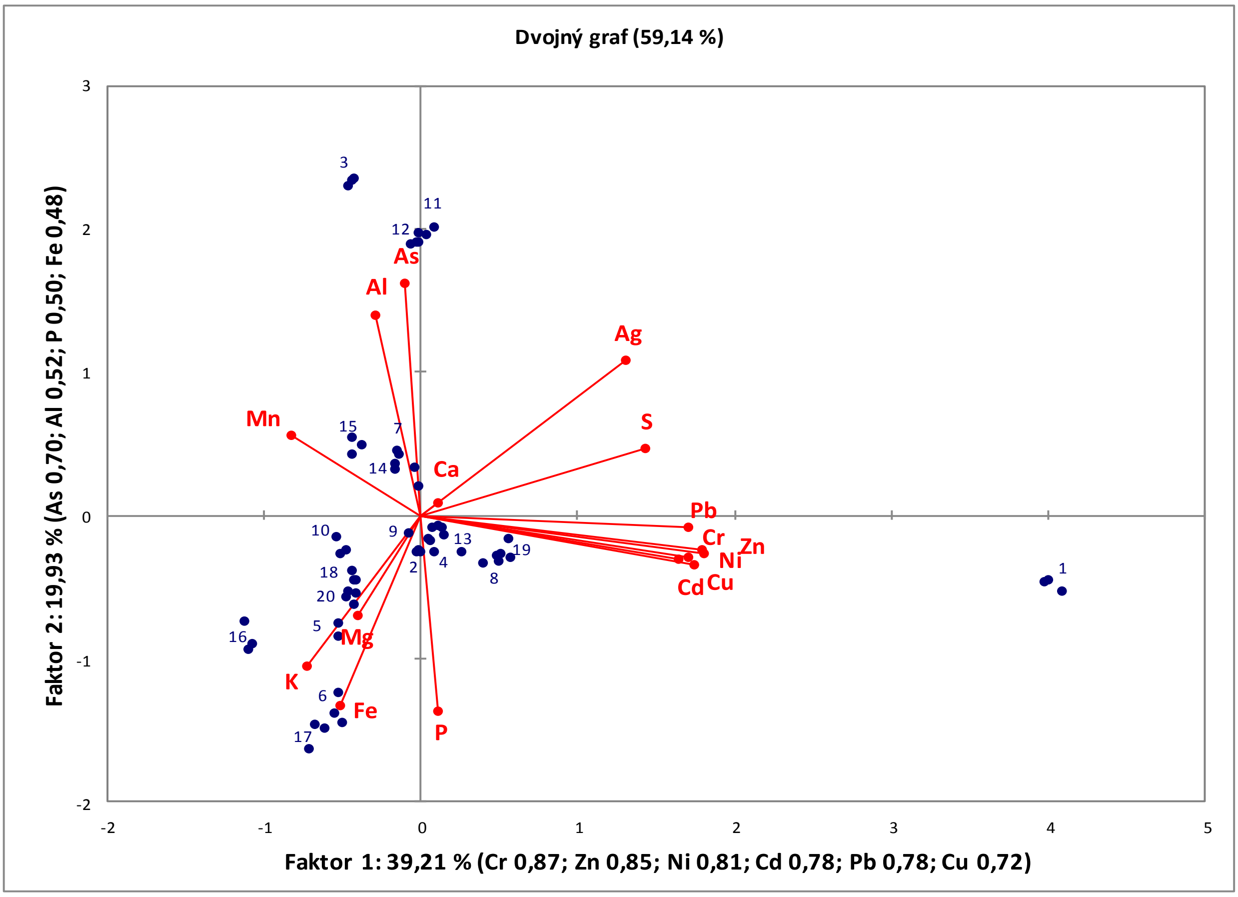
Rizikové prvky (mg/kg)	**Limit ČR[a]**	**Limit EU[b]**	**Konstrukční kapacita ČOV (EO)**		
			< 50 000	**50 000 – 100 000**	**> 100 000**
As	30	-	1	2	0
Cd	5	20-40	1	0	1
Cr	200	-	0	0	1
Cu	500	1 000-1 750	0	1	1
Ni	100	300-400	0	0	1
Pb	200	750-1 200	0	0	0
Zn	2 500	2500-4 000	0	0	1
Celkem ČOV			2	3	1
Cd/P	-	100[c]	1	0	2
Ni/P	-	2 500[c]	0	0	3
Pb/P	-	10 000[c]	0	0	0
Celkem ČOV			1	0	4

[a] *mezní koncentrace rizikových prvků v kalech dle Vyhlášky č. 437/2016 Sb.*

[b] *mezní hodnoty koncentrací rizikových prvků v kalech dle Směrnice 86/278/EHS*

[c] *mezní poměr (mg RP/kg P) pro kaly z ČOV dle Dánské legislativy*[18,19]

Analýza hlavních komponent obsahů živin a rizikových prvků ve sledovaných kalech je uvedena na obrázku 1. Z rozptylového diagramu komponentního skóre je patrná přítomnost přibližně deseti shluků objektů. To značí celkovou heterogenitu složení sledovaných kalů a poukazuje to na skutečnost silné proměnlivosti obsahů především rizikových prvků mezi jednotlivými provozy. Kaly označené čísly 1, 3, 11 a 12 jsou silně izolované od ostatních vzorků. Lze je tudíž považovat za extremy sledovaného souboru.



Obrázek 1: Analýza hlavních komponent obsahu živin a rizikových prvků v kalech z ČOV
(číselné hodnoty v grafu představují označení jednolivých vzorků)

Na grafu komponentních vah jsou pak patrné tři skupiny silně korelujících proměnných. Nejsilnější korelace lze pozorovat mezi Pb, Cr, Zn, Ni, Cu a Cd, tedy rizikovými prvky přítomnými v prostředí především v kationtové formě. Je třeba však poznamenat, že pozorovaná silná korelace může být silně ovlivněna přítomností extremního vzorku (č. 1) díky jeho vysokým obsahům těchto RP. Dále je patrná silná korelace mezi As a Al. To může být způsobeno silnou adsorpcí As k hydratovaným oxidům hliníku popř. srážením s hlinitými solemi. Obdobně pak koreluje P s Fe, jelikož většina P je během procesu čištění srážena právě železitými solemi.

Závěry

V rámci této práce bylo analyzováno celkem 20 vzorků anaerobně stabilizovaných kalů z ČOV ze 17-ti různých provozů. Pokud nebylo do provozu zařazeno průmyslové sušení, pohybovala se sušina kalů nejčastěji okolo 25 hm. %. S průmyslovým sušením pak byla sušina vyšší než 90 hm. %. Většina kalů vykázala hodnotu pH přibližně 7,1, avšak kaly, které byly po odvodnění ošetřeny vápnem, měly pH vyšší než 11. Obecně obsahy živin ve sledovaných kalech byly nalézány v pořadí: Ca ~ Fe > P > S >> Mg ~K.

Analýza hlavních komponent prokázala silnou variabilitu v prvkovém složení kalů mezi jednotlivými provozy. Rizikové prvky v testovaném souboru vykazovaly mnohem vyšší proměnlivost než sledované živiny. Nejvyšší variabilita mezi provozy pak byla nalezena pro Ni. Naproti tomu Pb dle výsledků nepředstavuje vážnější riziko kontaminace sledovaných kalů. Limitní hodnoty RP pro aplikaci kalů na zemědělskou půdu byly nejčastěji překročeny u As. Celkově nesplnilo limity obsahů RP přibližně 35 % sledovaných provozů, přičemž v naprosté většině případů provozy překračovaly limit pouze v jednom ze sledovaných RP.

Seznam symbolů

ČOV – čistírna odpadních vod; EO – ekvivalentní obyvatel; RP – rizikový prvek

Poděkování

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Evaluation of mineral nutrient and trace element concentrations in anaerobically stabilized sewage sludge

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Summary

Sewage sludge (SS), or biosolids, represent an important source of mineral nutrients and organic matter. However, SS application on agricultural soil is related with the risk of soil contamination by trace elements. Twenty sewage sludge samples from 17 different waste water treatment plants in the Czech Republic were collected in 2017. Subsequently, dry matter content, pH and concentrations (aqua regia digestion) of nutrients and trace elements were determined. Analysed samples showed dry matter content most often around 25 % and pH around 7.1. The variability of nutrients concentrations was significantly lower when compared to variability of trace elements. No sample exceeded the limit value of Pb (200 mg kg^{-1}) given by Czech legislation for sewage sludge application on agricultural soils. The concentrations of Pb also showed the least variability among trace elements studied. The limit values were usually exceeded only for one trace element and it was most frequently As (30 mg kg^{-1}). Generally, 35 % of studied samples did not meet law requirements for soil application.

***Keywords**: sewage sludge, biosolids, trace elements, nutrients, dry matter,*

Denitrifikace odpadních vod s vysokou koncentrací dusičnanů pomocí imobilizovaného kalu

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Souhrn

Směsná bakteriální kultura získaná aklimatizací aktivovaného kalu z ČOV byla imobilizována jednak na uměle vytvořeném materiálu – geopolymeru, jednak na přírodních materiálech – zeolitu a lignitu. V kontinuálních testech byla ověřována možnost využití imobilizovaných bakterií pro biologickou denitrifikaci vod s extrémní koncentrací dusičnanů a závislost průběhu a účinnosti denitrifikace na typu použitého nosiče, době zdržení a vstupní koncentraci dusičnanů. Nejvyšší účinnosti odstranění dusičnanů byly dosaženy s použitím lignitu jako nosiče mikroorganismů, nicméně vzhledem k velké rozpadavosti je pro tyto účely nevhodný. Jako nosič bakterií se z testovaných materiálů nejlépe osvědčil makroporézní geopolymer, jehož členitý povrch přispěl k zachycení denitrifikačních bakterií a alkalická povaha k omezení tvorby dusitanů.

Klíčová slova: *biologická denitrifikace, geopolymer, zeolit, lignit*

Úvod

Koncentrace dusičnanů v některých typech průmyslových odpadních vod výrazně přesahují hodnoty běžné pro komunální odpadní vody. Příkladem mohou být například odpadní vody z výroby výbušnin, hnojiv, nebo zpracování kovů, které často obsahují i více než 1000 $mg.l^{-1}$ $N\text{-}NO_3^-$.

Ekonomicky nejvýhodnější metodou odstranění dusičnanů z odpadních vod je v současné době biologická denitrifikace, která využívá schopnosti přirozeně se vyskytujících organismů používat dusičnan (případně dusitan) v anoxických podmínkách jako konečný akceptor elektronů místo molekulárního kyslíku. Dusík je z oxidačního stupně N^{V} nebo N^{III} redukován na plynný dusík [1]. Z biochemického hlediska se jedná o proces podobný respiraci s molekulárním kyslíkem, kterého je proto schopna většina (až 80 – 90 %) běžných organotrofních bakterií (např. rody *Pseudomonas*, *Micrococcus*, *Denitrobacillus*). Denitrifikační mikroorganismy mohou být v systému čištění odpadních vod přítomny ve formě aktivovaného kalu, nebo mohou být imobilizovány např. v biofilmu či enkapsulací ve vhodném materiálu.

Imobilizace mikroorganismů (biomasy) na vhodném nosiči umožňuje zvýšení jejich koncentrace v systému a ulehčuje separaci kapaliny a pevné látky. Mikroorganismy se v těchto systémech vyskytují zejména na nosiči, zpracovaná voda tedy obsahuje výrazně méně mikroorganismů než při použití aktivovaného kalu. Další výhodou imobilizace na nosiči je vyšší odolnost biomasy vůči nepříznivým podmínkám (přítomnost toxických sloučenin, nedostatek živin) [2]. Použití imobilizovaných mikroorganismů je tedy vhodné při biologickém zpracování vod s „nestandardním“ složením např. s častými výkyvy složení nebo extrémními koncentracemi některých složek.

Jako nosič mikroorganismů byla testována a dovedena do praxe celá řada materiálů, a to jak přírodních, tak uměle vytvořených – písek, čedič, aktivní uhlí, biologické materiály, jíl, plasty, PVC kroužky, keramické kroužky. Údaje o využití imobilizované biomasy pro zpracování průmyslových dusičnanových vod s koncentrací $N\text{-}NO_3^-$ větší než 120 $mg.l^{-1}$ jsou nicméně vzácné. Publikováno je využití imobilizace směsné bakteriální kultury např. na tkanině [3], nebo na přírodním zeolitu či písku [4]. Další možností je např. chemická imobilizace pomocí polymerů [5] nebo enkapsulace do polyvinylalkoholových čoček [6].

Nejjednodušší a cenově nejméně náročnou metodou imobilizace je spontánní adhese (adsorpce) biomasy na pevném nosiči, která má proto i nejširší využití v praxi biologického čištění odpadních vod [7] byla využita v níže popsaných testech. Jako možné nosiče bakterií byly pro účely testování vytipovány zeolit a lignit jako přírodní materiály a geopolymer jako materiál uměle připravený.

Geopolymery jsou anorganické polymerní materiály, které jsou připravovány z hlinitokřemičitanových materiálů jejich geopolymerací v zásaditém prostředí za normální teploty a tlaku. Při geopolymeraci vzniká trojrozměrná aluminosilikátová síť empirického vzorce $M_n[\text{-Si-O}_2)_z\text{-Al-O}]_n.wH_2O$, kde M je K, Na či Ca, n je stupeň polykondenzace, z je 1,2,3 nebo více než 3. Síťovité útvary jsou složeny z tetraedrů SiO_4 a AlO_4 a jsou spojené kyslíkovými můstky. Z chemického hlediska jsou geopolymery syntetickým ekvivalentem přírodních zeolitů, které mají podobné chemické složení (hydratovaný hlinitokřemičitan) a amorfní strukturu. Tato struktura se pro daný účel vyznačuje dobrými mechanickými vlastnostmi a trvanlivostí [8]. Výhodou geopolymerů je možnost ovlivňovat metodou přípravy jejich vlastnosti. V našem případě byla použita alternativa vedoucí k vytvoření převahy makropórů ve struktuře geopolymeru.

Experimentální část

Použitý zeolit, klinoptilolit, pocházel z lokality Nižný Hrabovec na Slovensku, lignit z lokality Mikulčice na Moravě. Makroporézní geopolymerní nosič byl připraven z draselného vodního skla se silikátovým modulem 1,7, suroviny obsahující metakaolinit (Mefisto K05 – České lupkové závody, a.s.), mleté vysokopecní strusky (Kotouč Štramberk, s.r.o.) a vápenného hydrátu (Čerťák – Vápenka Čertovy schody, a.s.). Tvorba makropórů v geopolymeru byla iniciována přidáním práškového hliníku do homogenní směsi složek. V důsledku reakce hliníku s alkalickými složkami došlo k vývoji vodíku a také intenzivnímu ohřevu materiálu, čímž se urychlila geopolymerní reakce a vodíkem napěněný materiál rychle ztuhnul.

Nejvyšším měrným povrchem z testovaných nosičů disponuje klinoptilolit (22,3 $m^2.g^{-1}$), jako jediný také obsahuje mikropóry, lignit je prakticky neporézní s měrným povrchem 2,5 $m^2.g^{-1}$. Makroporézní geopolymer se vyznačuje členitým vnějším povrchem, ale měrný povrch je pouze 4,6 $m^2.g^{-1}$.

Vlastností, která ovlivňuje adhezi mikroorganismů k nosiči, je jeho acidita. Zkouška acidity nosiče byla provedena podle [9]: 1 g nosiče byl suspendován v 20 ml destilované vody prosté CO_2 v plastové lahvi. Konečné pH suspenze (po ustálení pH po 48 hodinách) odpovídalo pH_{pzc} (pH of the point zero charge). Vzhledem k metodě přípravy je nejalkaličtějším nosičem geopolymer (tabulka 1), alkalita se z něj vymývá postupně; nelze ji odstranit jednorázovým promytím. Naproti tomu klinoptilolit reaguje v roztoku mírně kysele.

Tabulka 1: Vlastnosti nosičů (po promytí a vysušení při 105 °C)

	geopolymer	**klinoptilolit**	**lignit**
měrný povrch ($m^2.g^{-1}$)	4,6	22,3	2,5
sypná hmotnost ($g.cm^{-3}$)	0,446	0,902	0,582
acidita nosiče pH_{pzc}	10,73	5,49	7,48

Před zahájením vlastních denitrifikačních pokusů byly všechny nosiče rozdrceny a byla vysítována frakce 4 – 8 mm, následně byly promyty pitnou vodou pro odstranění prachového podílu a vysušeny při 105 °C.

Pro testy byla připravena modelová odpadní voda simulující složení neutralizované odpadní vody z moření nerezových ocelí s přídavkem biogenních prvků a zdroje uhlíku. Modelová voda byla připravena rozpuštěním 6,85 g $NaNO_3$, 2,0 g KH_2PO_4, 0,1 g $MgSO_4.7H_2O$ a 0,3 g NaCl v litru pitné vody. Stopové prvky byly zajištěny přidáním 1 ml zásobního roztoku stopových živin do 1 litru modelové vody. Zásobní roztok byl připraven rozpuštěním 5,54 g $CaCl_2$, 5,0 g $FeSO_4.7H_2O$, 5,06 g $MnCl_2 .H_2O$, 2,2 g $ZnSO_4.7H_2O$, 1,51 g $CuSO_4.5H_2O$, 1,61 g $CoCl_2.H_2O$, 1,1 g $(NH_4)_6Mo_7O_{24}.xH_2O$ a 50 g EDTA v 1 litru destilované vody [3]. Jako zdroj uhlíku sloužil ethanol dávkovaný v poměru CHSK:N 4:1 (v imobilizační fázi 8:1). Hodnota pH modelové vody byla v rozmezí 7 – 7 ,5, koncentrace rozpuštěného kyslíku se pohybovala mezi 7 až 9 $mg.l^{-1}$.

Zdrojem mikroorganismů byla směsná kultura aktivovaného kalu z regenerační nádrže ČOV Neštěmice. Směsná bakteriální kultura byla získána z aktivovaného kalu aklimatizací na koncentraci 1130 mg.l^{-1} N-NO_3^- po dobu 30 dní při teplotě 30 °C za anoxických podmínek.

Metodika

Testy byly prováděny za laboratorní teploty ve skleněné koloně o průměru 3,7 cm a vnitřním objemu 300 ml, objem nosiče byl 250 ml. Průtok v koloně v rozsahu 50 až 170 ml.h^{-1} byl zajištěn peristaltickým čerpadlem. Směr průtoku byl zdola nahoru, aby napomáhal uvolňování vznikajících plynů (N_2 a CO_2). Na dně kolony byla umístěna plastová síťka s velikostí ok 1 mm, sloužící jako dno a současně zajišťující distribuci přitékající vody na celý průřez kolony. Proces probíhal při teplotě 23 °C ± 2°C. Na vstupu a výstupu z kolony byly odebírány vzorky, ve kterých byla zjišťována koncentrace dusičnanů, dusitanů, dále pH, teplota, vodivost, zákal a koncentrace rozpuštěného kyslíku.

Koncentrace dusičnanů v odebraných vzorcích byla stanovována pomocí dusičnanové iontově selektivní elektrody. Koncentrace dusitanů byla určována spektrofotometrickou metodou při 540 nm po použití vybarvovacího činidla tvořeného amidem kyseliny sulfanylové a N-(1-naftyl)-1,2-ethylendiamin dihydrochloridem. Koncentrace rozpuštěného kyslíku byla stanovována přenosným přístrojem Hanna HI 9146. Hodnota zákalu vody na výstupu z denitrifikace byla určována měřením na turbidimetru Lovibond TB210 IR.

Výsledky a diskuse

Imobilizace – vsádkový režim

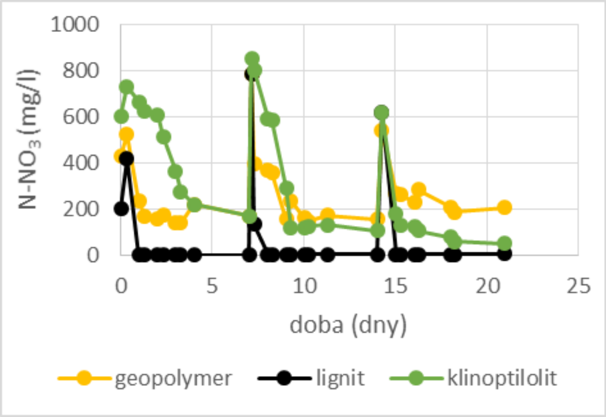
V první fázi testů, imobilizační, byl do kolony postupně načerpán roztok připravený smícháním modelové vody s koncentrací dusičnanového dusíku 1130 mg.l^{-1} N-NO_3^-, aklimatizované biomasy (0,1 g biomasy na 1 litr modelové vody) a ethanolu v množství odpovídajícím poměru CHSK:N 8:1. Roztok byl ponechán cirkulovat do poklesu koncentrace N-NO_3^- pod 10 mg.l^{-1}, poté byl nosič promyt 1000 ml pitné vody, čímž byly odstraněny volné baktérie, a do kolony byla načerpána čerstvá modelová voda s ethanolem v poměru CHSK:N 8:1. Při poklesu koncentrace N-NO_3^- pod 10 mg.l^{-1} byl roztok vždy vyměněn. Celý proces imobilizace byl prováděn 14 dní, což byla dostatečná doba k ustálení rychlosti denitrifikace.

K nejrychlejší denitrifikaci došlo v přítomnosti volné biomasy v koloně s geopolymerem (51 hodin), dále v koloně s lignitem (71 hodin), nejpomalejší byla denitrifikace v koloně se zeolitem - k poklesu koncentrace N-NO_3^- pod 10 mg.l^{-1} došlo až po 120 hodinách. Vyšší rychlost denitrifikace může být připsána vyššímu pH v koloně s geopolymerem. I přes intenzivní promývání stále docházelo k uvolňování alkality z nosiče a pH v koloně se pohybovalo okolo 9, oproti koloně se zeolitem a lignitem, kde bylo v rozmezí 7,5 až 8.

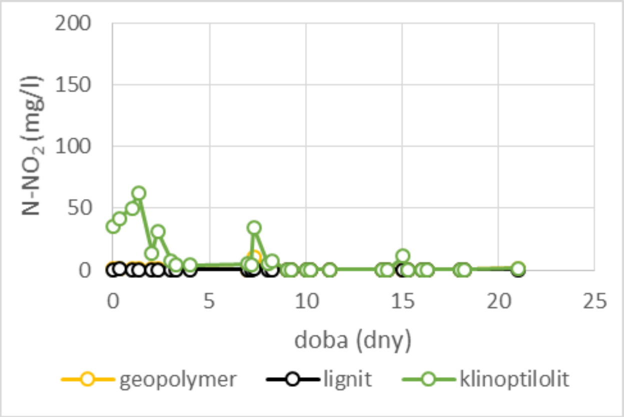
Kontinuální testy denitrifikace

Po imobilizační fázi byly kolony s biomasou imobilizovanou na nosičích promyty každá 1000 ml pitné vody a byly zahájeny kontinuální testy. Byl sledován vliv koncentrace dusičnanů a doby zdržení v náplni na rychlost a průběh denitrifikace. Testy za různých podmínek na sebe navazovaly v následujícím pořadí: 1) koncentrace 1130 mg.l^{-1} N-NO_3^-, doba zdržení 5 h, 2) koncentrace 1130 mg.l^{-1} N-NO_3^-, doba zdržení 2,5 h, 3) koncentrace 565 mg.l^{-1} N-NO_3^-, doba zdržení 2,5 h, 4) koncentrace 565 mg.l^{-1} N-NO_3^-, doba zdržení 1,5 h.

V první sérii testů se vstupní koncentrací N-NO_3^- 1130 mg.l^{-1} a dobou zdržení v koloně 5 hodin dosáhla výstupní koncentrace N-NO_3^- stabilní hodnoty u lignitu a geopolymeru za 2 dny, u klinoptilolitu za 4 dny. Podobná situace byla i u dusitanového dusíku, nejdéle přetrvával ve výstupu z kolony s klinoptilolitem, naopak u lignitu k jeho akumulaci prakticky nedocházelo. Průběh testů dokumentují obrázky 1 a 2. V této sérii testů docházelo na částicích nosiče i mezi nimi k tvorbě velkého množství biomasy, v důsledku toho se postupně zvyšoval hydraulický odpor a bylo nutno kolony po 7 dnech promýt, aby byly nánosy uvolněny. Nárazové propláchnutí kolon pitnou vodou nebylo dostatečné, proto bylo promytí v této sérii testů prováděno vyjmutím nosiče, a jeho propláchnutím pitnou vodu. Po promytí došlo k přechodnému zvýšení výstupní koncentrace dusičnanového dusíku., což naznačuje, že došlo k částečnému oddělení imobilizovaných baktérií. K obnovení původní aktivity biomasy došlo po prvním promytí u lignitu do 24 hodin, u geopolymeru a klinoptilolitu za 48 hodin, po druhém promytí již byl biofilm na všech nosičích stabilnější a aktivita se po přechodném zvýšení koncentrace dusičnanového dusíku na odtoku rychle obnovila.



Obrázek 1: Průběh výstupní koncentrace N-NO$_3^-$, vstup N-NO$_3^-$ 1130 mg.l^{-1}, doba zdržení 5 h



Obrázek 2: Průběh výstupní koncentrace N-NO$_2^-$, vstup N-NO$_3^-$ 1130 mg.l^{-1}, doba zdržení 5 h

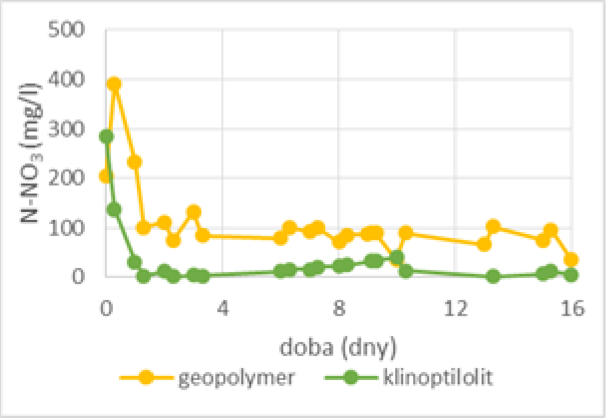
Průměrná výstupní koncentrace dusičnanového dusíku při vstupní koncentraci N-NO$_3^-$ 1130 mg.l^{-1} a době zdržení 5 hodin byla po ustálení stavu u lignitu 3 mg.l^{-1} N-NO$_3^-$, u geopolymeru 230 mg.l^{-1} a u klinoptilolitu 121 mg.l^{-1}. Koncentrace dusitanového dusíku byly po 5 dnech ve všech případech menší než 1 mg.l^{-1} N-NO$_2^-$, kromě přechodného zvýšení po promytí kolon (7. a 14. den), kdy jeho koncentrace u geopolymeru byla 10 mg.l^{-1} N-NO$_2^-$ a 2 mg.l^{-1}, u klinoptilolitu 35 mg.l^{-1} a 11 mg.l^{-1}.

Při době zdržení 5 hodin byly dosaženy vysoké účinnosti odstranění N-NO$_3^-$ (u lignitu 99,7 %, u geopolymeru 79,6 %, u zeolitu 89,3 %), ale průtok nebyl dostatečně velký, aby vymýval velké množství vznikající biomasy z nosiče a proto docházelo k rychlému ucpávání kolon a zvyšování hydraulického odporu. Promývání kolon bylo potom obtížnější.

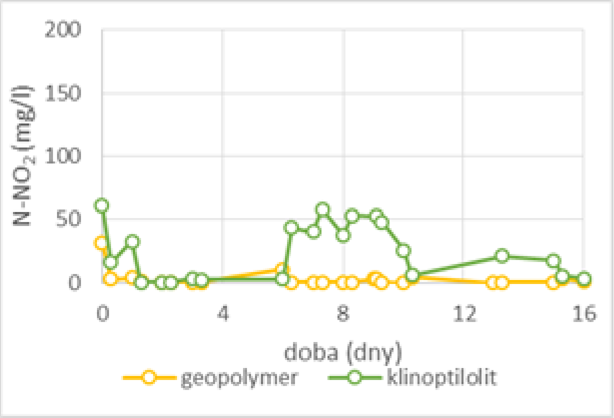
Při zvýšení průtoku v koloně a snížení doby zdržení v koloně na 2,5 hodiny se výstupní koncentrace dusičnanového dusíku ustálily na průměrných hodnotách 308 mg.l^{-1} N-NO$_3^-$ pro lignit, 403 mg.l^{-1} N-NO$_3$ pro geopolymer a cca 400 mg.l^{-1} N-NO$_3^-$ pro klinoptilolit. I v této sérii ale docházelo vlivem tvorby biomasy k ucpávání kolon a nosiče musely být pro promytí z kolony vyjmuty. U lignitu došlo postupně k masivnímu rozpadu částic a kolona se stala téměř neprůchodnou. Tvořily se velké agregáty částic spojených biomasou. Po vyjmutí lignitu z kolony, jeho promytí a vysušení, bylo zjištěno, že částic > 3 mm zbylo pouze 45 % z původního množství.

Další série testů byla provedena s modelovou vodou naředěnou na koncentraci dusičnanového dusíku 565 mg.l^{-1} N-NO$_3^-$ a s dobou zdržení 2,5 hodiny. Jako nosič byl použit geopolymer a klinoptilolit.

V této sérii testů již nebylo nutné nosiče pro promytí vyjímat z kolon, promývání bylo prováděno in situ pitnou vodou při zvýšeném průtoku. Promytím byly odstraněny vytvořené nánosy, ale nedocházelo k porušení vrstvy bakterií na nosičích, což se projevilo stabilními výstupními koncentracemi dusičnanového dusíku, obrázek 3. Koncentrace N-NO$_3^-$ na výstupu byla po ustálení (cca 48 h) u klinoptilolitu průměrně 16 mg.l^{-1} N-NO$_3^-$, u geopolymeru 84 mg.l^{-1} N-NO$_3^-$. Koncentrace dusitanového dusíku u geopolymeru byla průměrně 0,9 mg.l^{-1} N-NO$_2^-$, u klinoptilolitu kolísala (zejména po promytí) až k hodnotě 50 mg.l^{-1} N-NO$_2^-$, obrázek 4.

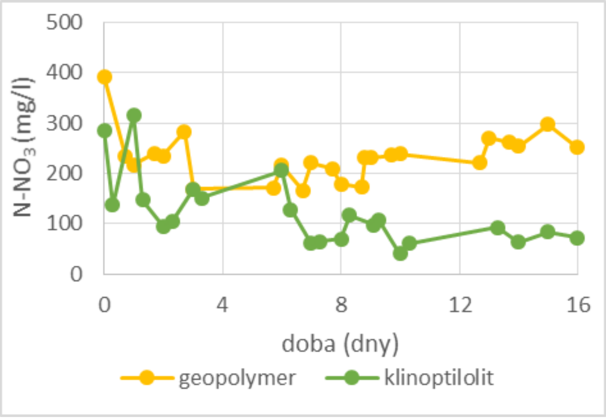


Obrázek 3: Průběh výstupní koncentrace $N\text{-}NO_3^-$, vstup $N\text{-}NO_3^-$ 565 mg.l^{-1}, doba zdržení 2,5 h

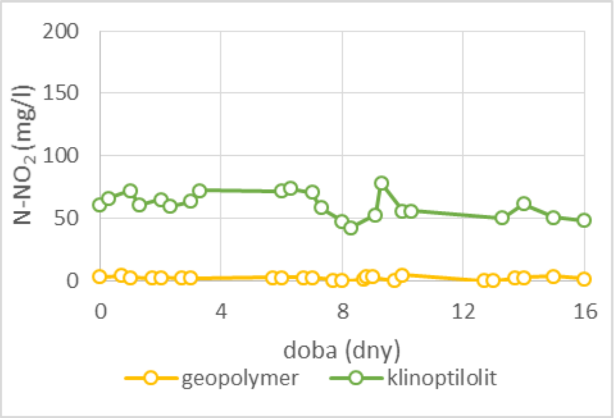


Obrázek 4: Průběh výstupní koncentrace $N\text{-}NO_2^-$, vstup $N\text{-}NO_3^-$ 565 mg.l^{-1}, doba zdržení 2,5 h

Po snížení doby zdržení na 1,5 hodiny se průměrná výstupní koncentrace dusičnanového dusíku zvýšila u geopolymeru na 226 mg.l^{-1} $N\text{-}NO_3^-$, u klinoptilolitu na 123 mg.l^{-1} $N\text{-}NO_3^-$, viz obrázek 5, což odpovídá účinnosti odstranění $N\text{-}NO_3^-$ 58,8 % a 78,2 %. Zatímco ale výstupní koncentrace dusitanového dusíku u geopolymeru byla průměrně 2 mg.l^{-1}, u klinoptilolitu se pohybovala mezi 50 až 60 mg.l^{-1} $N\text{-}NO_2^-$ – obrázek 6.



Obrázek 5: Průběh výstupní koncentrace $N\text{-}NO_3^-$, vstup $N\text{-}NO_3^-$ 565 mg.l^{-1}, doba zdržení 1,5 h



Obrázek 6: Průběh výstupní koncentrace $N\text{-}NO_2^-$, vstup $N\text{-}NO_3^-$ 565 mg.l^{-1}, doba zdržení 1,5 h

Průměrná hodnota pH vody na výstupu z kolon se příliš nelišila – u geopolymeru byla 8,2, u klinoptilolitu 7,8. Nicméně alkalická povaha povrchu geopolymeru se ukázala jako přínosná pro denitrifikaci. Pozitivně ovlivňovala adhezi mikroorganismů i rychlost odbourávání dusitanů.

Naopak kyselá povaha povrchu částic klinoptilolitu vedla k horší adhezi mikroorganismů a jejich slabé vazbě, která se snadno porušila promýváním. Největším problémem byla ale kumulace dusitanového dusíku, která dosahovala při použití klinoptilolitu až desítek mg.l^{-1} $N\text{-}NO_2^-$, což je z hlediska ekologických limitů nepřijatelné. Mikroporézní struktura klinoptilolitu je pro baktérie sice nevyužitelná, ale přispěla ke zvýšení kvality vody na odtoku – hodnota zákalu na výstupu z kolony dosahovala hodnot okolo 30 NTU, u geopolymeru cca 50 NTU, u lignitu byla nejvyšší – průměrně 158 NTU, což bylo dáno rozpadem jeho částic. Koncentrace rozpuštěného kyslíku na výstupu z kolon byla při všech měřeních menší než 0,7 mg.l^{-1}. Spotřeba organického substrátu se lišila podle použitého nosiče. U geopolymeru odpovídala poměru CHSK:N 3,5, u lignitu a klinoptilolitu méně než 3.

Obsah organických huminových látek v lignitu napomáhal adhezi mikroorganismů a podporoval jejich množení a tím i účinnost denitrifikace, vzhledem k rychlému rozpadu částic je ale lignit jako nosič mikroorganismů v tomto uspořádání nepoužitelný.

Průměrné hodnoty účinnosti odstranění dusičnanového dusíku pomocí imobilizace bakterií na jednotlivých nosičích uvádí tabulka 2.

Tabulka 2: Účinnost denitrifikace

vstup **mg.l^{-1} N-NO$_3^-$**	**doba** **h**	**účinnost odstranění N-NO$_3^-$ %**		
		geopolymer	**lignit**	**klinoptilolit**
1130	**5**	79 ± 8	99 ± 1	89 ± 4
1130	**2,5**	64 ± 9	73 ± 9	64 ± 8
565	**2,5**	83 ± 4	x	97 ± 2
565	**1,5**	59 ± 6	x	78 ± 12

Získané výsledky ukazují, že v použitém uspořádání je z hlediska zajištění stabilní koncentrace dusičnanového dusíku na odtoku a dlouhodobého provozu kolon, vzhledem k tvorbě nánosů v kolonách, vhodnější použití doby zdržení 2,5 h a nižší vstupní koncentrace dusičnanového dusíku – 565 mg.l^{-1} N-NO$_3^-$.

Závěr

Denitrifikace pomocí imobilizované směsné bakteriální kultury je účinnou metodou pro odstranění dusičnanů z průmyslových odpadních vod. Imobilizace proběhla úspěšně na geopolymeru, lignitu i klinoptilolitu. V kontinuálních testech byla nejvyšší účinnost denitrifikace pozorována při použití lignitu jako nosiče mikroorganismů (až 99 %). Jeho využití je ale limitováno velkou rozpadavostí. Využití klinoptilolitu je i přes dosaženou vysokou účinnost odstranění dusičnanů problematické kvůli přetrvávání dusitanů a jejich zvýšené koncentraci na odtoku z kolony. Připravený makroporézní geopolymer se jako nosič bakterií osvědčil. Jeho členitý povrch přispěl k zachycení denitrifikačních bakterií a alkalická povaha k omezení tvorby dusitanů. Získané výsledky budou, po optimalizaci druhu a množství organického substrátu, využity při návrhu procesu denitrifikace reálných odpadních vod z povrchové úpravy kovů.

Poděkování

Tato práce je výsledkem projektu řešeného s finanční podporou Ministerstva průmyslu a obchodu České republiky, které poskytlo prostředky v rámci institucionální podpory na dlouhodobý koncepční rozvoj výzkumné organizace. Projekt byl začleněn do Národního programu udržitelnosti I Ministerstva školství, mládeže a tělovýchovy České republiky prostřednictvím projektu Rozvoj centra UniCRE, identifikační kód LO1606.

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Denitrification of high nitrate waste water using immobilized sludge

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Summary

Mixed bacterial culture obtained by an acclimatization of activated sludge from the waste water treatment plant was immobilized both on artificially formed material - geopolymer and on natural materials - zeolite and lignite. In the continuous tests, the possibility of using immobilized bacteria for biological denitrification of water with extreme nitrate concentration and the dependence of the course and efficiency of denitrification on the type of carrier, the residence time and on the nitrate concentration were tested. The highest nitrate removal efficiency was achieved using lignite as a carrier of microorganisms, however, due to the high disintegration, lignite is inappropriate for these purposes. The macroporous geopolymer is a suitable denitrification bacteria carrier, the ragged surface of geopolymer contributes to the capture of bacteria and the alkaline nature of surface helps to limit the formation of nitrite.

***Keywords**: denitrification, geopolymer, zeolite, lignite*