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This results in greater workload in preparation of numbers. That's why the publisher decided to partially increase the publishing fee starting with 2019. The publication fee in this journal will be 500 CZK per page regardeless of the language in which the paper is.

The editorial closure of the nearest number is on October 8, 2018, the next one on January 8, 2019.

Ondřej Procházka

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The deadline of the next issue is on October 8, 2018, more on January 8, 2019.

The mechanism of separation of heavy metals from waters by means of cellulose carboxyl derivatives

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Summary

A mechanism of CS (Colloid – Sorption filtration) and CSF (Colloidal-Sorption – Filtration) separations are dynamic processes where, depending on intensity of media flowing in filter pores, also shear forces participate on trapping process of hydro-colloid particles. The adsorption capacity of cellulose carboxyl derivatives increases with increasing –COOH group content and is distinctly increased by the presence of other competitive ions in the aqueous solution.

***Keywords**: Colloid – Sorption filtration, Colloidal-Sorption – Filtration, oxycellulose, carboxymethyl cellulose*

Introduction

The treatments of heavy metals are of special concern due to their recalcitrance and persistence in the environment. Recently various methods for heavy metal removal from waste water have been extensively studied[1]. Adsorption characteristic of polysaccharides, cellulose and its derivates including oxycellulose in relation to cations, particularly[2] heavy metals, have drawn more attention. Their knowledge is important in the field of purification and treatment of water as well as from the medical point of view, because especially[3,4] metals plays an important role in metabolism of animals and humans. Heavy metal pollution has become one of the most serious environmental problems today.

Currently, there have been efforts to turn away from traditional sources of raw materials and to focus on their green alternatives (cellulose, starch, oils). Many research-production groups in the entire world have engaged to solve three tasks: bioenergy, biomaterials, biochemical utilization. Oxidized cellulose pertains to the group of biocompatible materials (biomaterials) used especially as healthcare products in medicine. Other opportunities include the use of oxycellulose in technical applications (absorbent, filtration materials, ion exchangers). As usually, products for technical applications are characterised by large volumes with requirements on the minimisation of product variable costs.

Oxidized cellulose is a product prepared by oxidation of cellulose to such an extent that almost all glucose units of cellulose are transferred to units of glucuronic acid, which is a biopolymer. It is a biopolymer characterised by various perspectives (complicated structure, polymerization degree, character of oxidation, character of fibres) and other factors affecting useful features of the product.

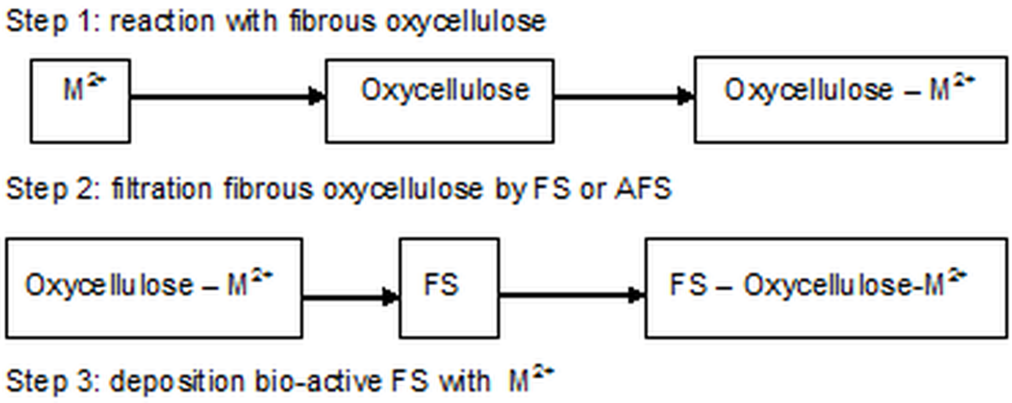
The most widely spread separation procedures include filtration working on various spatial levels (common filtration, micro filtration, ultrafiltration, nano filtration etc.)[5]. What is typical for these mechanical separation methods is a sharp decrease of the specific flow capacity of the filtered medium with a decrease in the size of particles contained in this medium. Moreover, there is another unpleasant effect which is polydispersity of the flow area pores of the filter[5].

Colloid – sorption filtration (CS separation)

This process is schematically illustrated on the Scheme 1. It is a separation process combining advantages of the reaction of colloid particles with a heavy metal, such as, M^{2+} and their following separation by use of filtration.

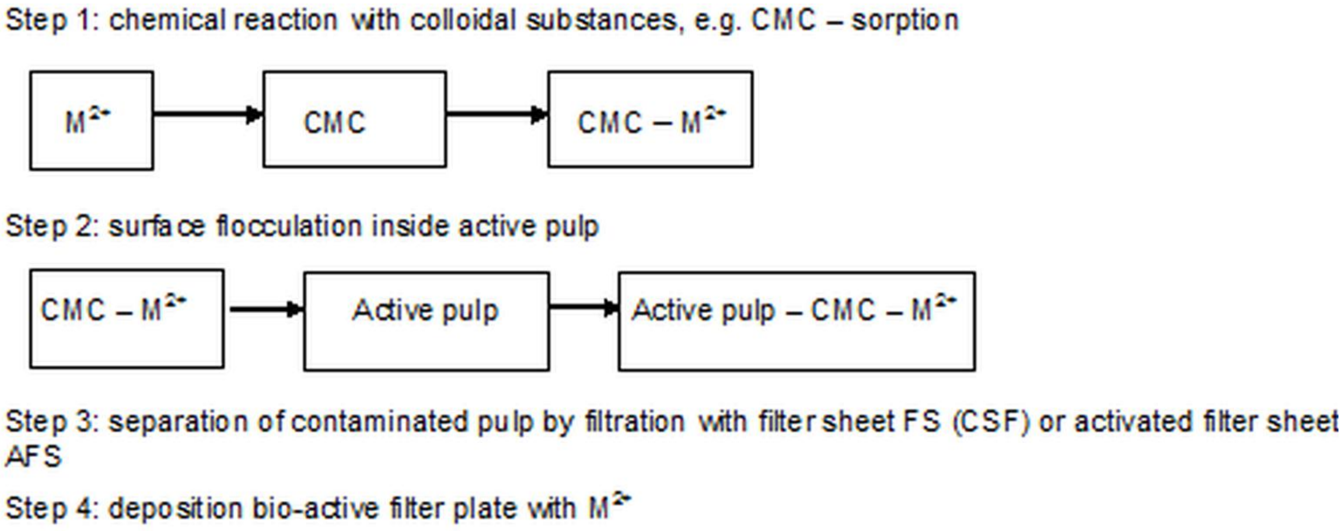
The process consists of two steps. The first step includes mixing polluted water with a suitable substance – carrier, preferably a fibrous, easily drain able substance such as fibrous oxycellulose in case of heavy metals. The dissolved impurities, e.g. heavy metals, adsorbed (chemisorption) to this carrier. The second step includes filtration through the common filter sheet (FS) or activated filter sheet (AFS) followed by deposition in the similar way as in the adsorption filtration (SF) process[6].

An advantage in comparison with SF (Scheme 2) process is a maximum use of the entire adsorption capacity of the main reaction component with regard to the separated heavy metal. Unlike the SF process, the separation efficiency does not change during the entire separation process. However, as regards separation of colloid particles, it is not enough efficient, unless we want to use more efficient low-flow filters or even ultrafiltration.



Scheme 1: Colloid – sorption filtration (CS separation)

Colloidal–sorption – filtration process (CSF separation)



Scheme 2: Colloidal–sorption – filtration process (CSF separation)

Experimental

Materials

As native cellulose was used commercial cotton linter. Oxycelluloses OKCEL H-L were prepared by nitroxide-mediated oxidation of linters and bleached MgBi-sulphite wood pulp in Synthesia, Pardubice-Semtin, Czech Republic.[7]

Okcel H-L 284/051/3

DP = 35.8
x_{GA}, g/g = 0.45
P_{DP} = 0.81
x_{COOH}, % = 17,8
X_{DS}, % = 70,8
$x_{GA\text{-}PAGA}$,(mmol GA-PAGA/g oxycel.) = 0.65

Carboxymethyl cellulose (CMC) from Fisher Scientific:

DS = 0.7
M_{CMC} = 250000
M_{ACMG} = 242
M_{AG} = 162
M_{COONa} = 67

Non-active pulp

Sulphite pulp (air-dry) was defibrillated in laboratory pulper for 10 minutes, so that 3% suspensions could be obtained. The pulp (30 g of a.d. pulp) was added into the pulper vessel with 1 litre of distilled water and was left to swell for 2 minutes. Then the pulper was worked at 600 revolutions per minute.

Parameters of the pulper are: vessel volume 3L, vessel height 0.19 m, and internal diameter of the vessel 0.155 m. The mixer made from stainless steel has the diameter 9 cm with three rectangular blades situated vertically in the axis of the vessel. The vessel has 4 spiralled protrusions on its walls.

Active pulp

A sulphite pulp was activated in 3% fibrous suspension by addition of the polymer cationic agent Refaktan K (Trade mark Chemotex, Decin, CR, prepared by the reaction between dimethylamine and epichlorhydrine), which was at first activated by dissolving NaOH in Refaktan K at a weight ratio of Refaktan K: NaOH of 1:0.05. The cationization process was conducted as follows: temperature 40 – 60 ^{0}C, reaction time 30 minutes, pH 7 – 8, 10 % addition of activated Refaktan K calculated upon a.d. pulp[8].

Filter plates

For experiments, two types of filter plates were selected: filter plates SD 100N and S 80R. The both filter plates were made of special types of high-quality cellulose fibres, diatomaceous earth and perlite. However, the filter plate S 80R contained cellulose activated by cationic substance composed of quaternary oligomer epoxy-propyl-trimethylamonium chloride [9]. These ones represent three-dimensional in-depth filters with large inner surface. The filter plates were delivered by Hobra Školník s.r.o, Broumov, CR. Filter plate S 80R represents a filter sheets made of cationic-activated cellulose [8]. The main characteristics are shown in the following table 2[9].

Table 1: The of used filter plates[10]

Filter plates	Type of activation	Flow capacity $m^3\ m^{-2}\ h^{-1}$	Porosity µm	Basic weight $g\ m^{-2}$	Retentiveness µm
S 80R	active	50-90	7.0	1000-1200	8
SD 100N	non-active	90-120	9.0	900-1200	11

Hydro-colloidal mixtures of cellulose carboxyl derivatives

Suspensions of oxycelluloses were prepared by weighing 1.6 g in 100 ml of distilled water. Colloidal solutions of carboxyl methylcellulose were prepared by weighing 5 g into 500 ml of distilled water.

Calculation specific amount of flow-through filtrate SFA

SFA expresses the amount of filtrate which has flowed through a surface unit or a mass unit of the filter plate.

Experiment

Spectrophotometric determination of Cd^{2+} ions

A concentration of Cd^{2+} in the filtrate determined spectrophotometrically with the help of dithizone extract (0,005% solution of dithizone in chloroform) of alkalized filtrate (by use of 10% solution of NaOH with the ratio 1:1) at λ = 515 nm[11]. The same measurements were conducted at this wavelength against with the reference solution (solution with chemicals without Cd^{2+}). The procedure was the same as describe above. The basic cadmium solution was prepared by dissolution of 0.1 g in $CdCl_2$ and refilling with distilled water up to the 1 L volume. 1ml of the solution thus contained 61.32 µg Cd[12]. The amount of ions in the filtrate was then determined by use of spectrophotometry and standard addition method of quantitative analysis approach[12].

Colloid – sorption filtration (CS separation)

Constant specific flow-through filtrate amount; SFA = constant (88.42 L of model water per m^2 FS), c_M is changed. 4 g oxycellulose and 5 g carboxymethylcellulose were added into seven 250 ml beakers, 250 ml of $CdCl_2$ solution were added in concentrations (c_M = 1; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1 g of $CdCl_2$/L). The mixture was mixed and left to rest for 30 minutes – during which adsorption has taken place; a filtration was followed by use of Büchner funnel with filter from inactivated pulp SD 100 N and activated pulp S 80R.

Colloidal–sorption – filtration process (CSF separation)

The filters SD 100N from inactivated pulp and the S 80R prepared from activated pulp were used for experimentation.

1.6 g oxycellulose and 24 ml of 1% carboxymethyl cellulose solution were added into six 250 ml beakers. Then 100 ml of $CdCl_2$ solution was added with concentrations 1, 0.7, 0.6, 0.5, 0.4 and 0.3 g $CdCl_2$/L. The mixture was mixed with a glass stick, left to rest for 30 minutes during which a sorption took place.

Then a measuring flask was used to add 32,4 ml of active pulp to each beaker, mixed well, left to rest for 15 minutes – surface flocculation was occurred followed by filtration on Büchner funnel with use of the filters from inactivated pulp SD 100 N and activated pulp S 80R.

Result and Discussion

Triplicate samples of every experiment were assayed. The every experiment was repeated at least 3x. Data presented in Figures 1 – 4 are mean values of these experiments.

Colloid – sorption filtration (CS separation)

This is already a more complicated process, as both the sequestration reactions between cations of cadmium and strongly hydrated suspended solids (SS) and the colloid processes between hydrocolloids themselves (SS with Cd^{2+} and micro-surfaces of pores inside of filtration plate of various characters) are conducted here under dynamic conditions. The prevailing character of the filtration plates is observable here. Higher separation effects are achieved with CS separations by use of activated filtration plates, i.e. S 80 R of the cation-active character. The highest separation effects were achieved with low concentrations of cadmium, i.e. with relatively high doses of SS/M, in the system consisting of OC and filtration plate S 80 R.

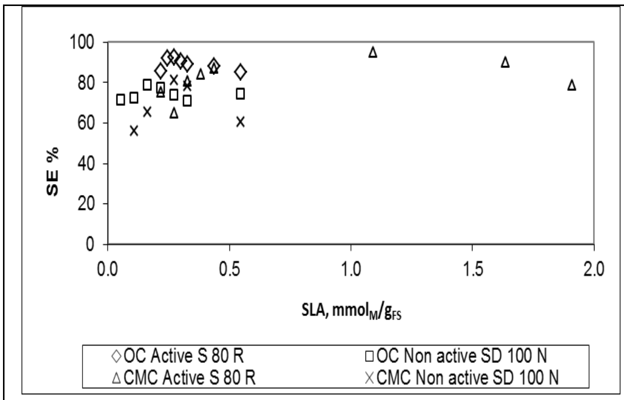


Figure 1: Dependence of SE versus SLA, mmol$_M$/g$_{FS}$

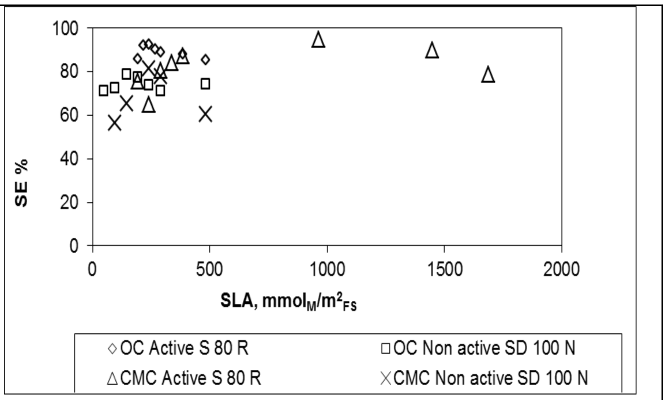


Figure 2: Dependence of SE versus SLA, mmol$_M$/m$^2_{FS}$

As it is obvious from the Figure 1-2 the dependencies of the separation effect vs. dose of sequestration agents related to the amount of cadmiums passes through their maximums. In case of CMC, however, the maximum separation effect is achieved with higher initial concentrations of cadmium. The decreasing sequestrate amount with regard to cadmium (dose SS/M^{2+}) logically leads to a decrease in its separation effect. On the other hand, this effect decreases even with higher doses of sequestration agents with regard to the content of cadmium in the model water. This process is most distinctive during filtration of such hydrocolloids through the filtration plate S 80 R which contains pores with cation-active micro-interfaces. This means that a dose of sequestrate which is higher than the optimum is counter-productive.

This behaviour shows that the capturing mechanism is somewhat more complex than the classical theory of colloid stability predicts – with an increasing dose of SS, or anion-active COOH groups with regard to cadmium, the separation effect of cation-active filtration plate S 80 R should be logically increased, and on the contrary, in case of anion-active FS SD 100 N the effect should be decrease. However, quite the opposite is true. After exceeding a certain optimum (in case of OC it is 3.7 mmol COOH/ mmol Cd and in case of CMC, which is fully soluble, 1 mmol COOH/ mmol Cd) then this leads to a smaller capturing capacity of the sequestrate with Cd on the nano-interfaces of pore-walls of FS and thereby to a decrease of the separation effect of the entire CS process. This one occurs in case of FS S 80 R with an increasing dose of SS.

What could provoke this worsening? Two colloid processes take place here:

- Drawing hydrocolloid particles into the micro-space of active centres of a cation-active character leads to their higher concentration.
- Flocculation of hydrocolloid particles in the micro-space around active centres.

In case of activated filtration plate S 80 R with an increasing dose of SS with regard to Cd, anion-active hydrocolloid particles SS with Cd are drawn by the increasingly greater electrostatic forces into the micro-space of the adjacent part of the electric double layer around cation-active nanointerfaces of the pore walls characterised by their positive Zeta potential. This leads to a higher concentration of these hydrocolloid particles in the micro-space around these centres. If suitable conditions are fulfilled, the emerging micro-colloid systems flocculate. Such suitable conditions include achieving the isoelectric point of these hydrocolloids. Originally anion-active hydrocolloid particles SS/Cd change their Zeta potential to the positive values with increase of the content of cadmium (with the reduction of the dose of SS/Cd). After achieving the isoelectric point a flocculation takes place in the maximum extent, which leads to a maximum separation effect.

Colloidal–sorption – filtration process (CSF separation)

Like in the case of a mere SF separation, the separation effect does not very change with an increasing of the filtrate specific amount (see Figure 3 – 4). Separation effect (SE) curves of CSF separation vs. SFA pass through a slight minimum with an increasing tendency at higher filtrate specific amount. Significantly higher separation effects are achieved with the application of the filter S 80 R consisting of the activated pulp. An increase in separation with higher SFA is probably caused mechanically by gradual clogging of pores of the filter bed. This increase is quite higher in case of activated FS S 80 R which supports capturing of hydrocolloid particles SS with Cd in the nano-space around active quarterly oligomer 2-hydroxy-propyl-dimethylamonium groups and controls their surface agglomeration.

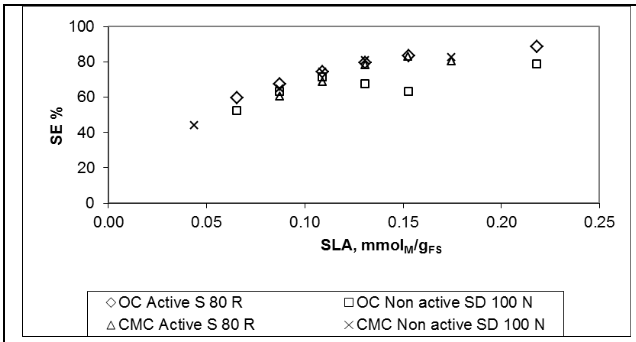


Figure 3: Dependence of SE versus SLA, $mmol_M/g_{FS}$

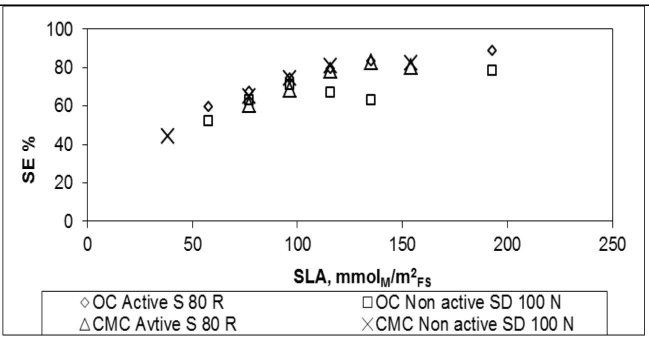


Figure 4: Dependence of SE versus SLA, $mmol_M/m^2_{FS}$

The following separation systems are the most effective from the practical perspective:

- the most suitable system in case of a high concentration of metal (e.g. cadmium > 100 mg Cd/L) is the separation system CSF consisting of hydrocolloid OC or CMC (degree of substitution > 0,7) as a sequestrate, activated pulp as the capturing agent and the activated filtration plate S 80 R with a low dose of the sequestrate in relation to M^{2+}, i.e. less than about 2 mmol COOH/mmol M^{2+}.

- in case of a low concentration of metal (e.g. in case of cadmium < 100 mg Cd/l) then it is the separation system CS consisting of hydrocolloid OC as a sequestrate and activated filtration plate S 80 R with, on the contrary, a relatively high dose of the sequestrate in relation to the metal, i.e. about 4 mmol COOH/mmol M^{2+}.

It seems that for separation of cadmium from its concentrated solutions, the optimum separation system consists of two levels. The first level is CSF consisting of hydrocolloid OC or CMC as a sequestrate and its dose is less than 2 mmol COOH/mmol Cd, moreover, activated pulp (80 % w/w from the total amount of dietary fibre and sequestrate) as the capturing agent and activated filtration plate S 80 R. The contaminated water with a low concentration of cadmium is then cleaned at the second CS separation level consisting of hydrocolloid OC as the sequestrate and activated filtration plate S 80 R with a relatively high dose of the sequestrate in relation to cadmium, i.e. about 3.7 mmol COOH/mmol Cd.

The key and joint role in all the mentioned separation processes is always reactivity, affinity of the given separated substance, heavy metal etc. to the main separating component in the separation process (sequestrate), i.e. the sorption abilities of this component. This separating component (sequestrate) may be in a colloid or rough dispersed particle or fibrous form and it is added into the polluted water in the form of a fibrous suspension, colloid mixture or solution. It may be a part of the filtration bed.

The separation effect which does not change much with the increasing specific amount of the filtrate is a typical characteristic of surface flocculation for managing supramolecular-chemical reactions and processes (see Figure 4).

Conclusion

It follows from the obtained knowledge that the practical option of an optimum cleaning process with the use of oxycelluloses, carboxymethyl celluloses, or other carboxyl derivatives of polysaccharides depend on particular conditions, composition of water, pH, temperature including efficiency and economy of such cleaning. Nevertheless, if we want to choose the most efficient separation process, it is suitable to choose a combination of a filtration and sedimentation procedure, or draining and sedimentation procedure. It was apparent from all evaluated charts that the separation of M^{2+} from the model mixture can be efficiently performed by means of sequestrates and the pulp. The efficient component in the suspension (pulp + sequestrate) is the sequestration agent. If a separation agent included only the pulp, the separation was quite small.

The recommended procedure of separation of metal cations from water.

In general, however, we can say that it is profitable to clean waste waters with a high content of cadmium and similar heavy metals by means of a two-level filtration process. First, it is suitable to filter contaminated water with the use of common filters of anion-active nature containing oxycellulose with a low level of oxidation (up to 9% COOH groups) and subsequently to complete cleaning process through filters of a cation-active character (R type filtration plates) containing up to 30 % oxycellulose with a higher level of oxidation, which can bear a higher specific load.

Symbols

AFS	activated filter sheet
c_M	original concentration of Cd^{2+}, g L^{-1}
a. d.	air-dry pulp
c_{rovn}	equilibrium concentration of Cd^{2+}, g L^{-1}
c_M	primary concentration of Cd^{2+}, g L^{-1}
CMC	carboxymethyl cellulose
CS	colloid – sorption filtration
CSF	colloidal–sorption – filtration process, g L^{-1}
DP	degree of polymerization
DS	degree of substitution PAGA
FS	filter sheet or filter plate

GA	glucuronic acid
M^{n+}	Cd^{2+}
OC	oxycellulose
PAGA	poly(1,4-D-anhydroglucuronic acid)
SE	separation efficiency, %
SFA	specific amount of filtrate, L m^{-2}_{FS}; L g_{FS}^{-1}
SLA	specific loading of filter plate, $mmol_M$ m^{-2}_{FS}; $mmol_M$ g_{FS}^{-1}
SS	suspended solids
x_{GA}	capacity of glucuronic acid , g g^{-1}
x_{COOH}	capacity of carboxyl acid, %
$x_{GA-PAGA}$	capacity of destabilizing komponent, mmol g^{-1}

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Mechanismus separace těžkých kovů z vody pomocí derivátů karboxy-celulózy

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Souhrn

Mechanismy CS (koloidní separace) a CSF (koloidně-sorpční filtrace) jsou dynamické procesy, kde se v závislosti na intenzitě média proudícího v pórech filtru účastní také smykové síly při zachycování hydrokoloidních částic. Adsorpční kapacita karboxylových derivátů celulózy se zvyšuje se zvyšujícím se obsahem skupiny COOH a je zřetelně zvýšena přítomností jiných konkurenčních iontů ve vodném roztoku.

***Klíčová slova**: koloidně-sorpční filtrace, oxycelulóza, karboxy-methyl celulóza*

Biodegradation of the synthetic Remazol Brilliant Blue R (RBBR) dye in fungal rotating biological contactor

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Abstract

Rotating biological contactor (RBC) was used for the degradation of recalcitrant textile RBBR dye by ligninolytic fungi Pleurotus ostreatus, Irpex lacteus and Trametes suaveolens F1. All three strains degraded the dye efficiently and could be used repeatedly in consequent degradation cycles. P. ostreatus decreased the growth medium pH in 1st degradation cycle. By adjusting the pH value with dimethyl succinate a more rapid and effective degradation was attained in 2nd degradation cycle. The best degradation efficiency of 100 % in 1st cycle was achieved by I. lacteus. In the two following cycles, however, the degradation process slowed down but the efficiency still was kept at 98 %. Four degradation cycles were accomplished with the fungus T. suaveolens F1. The highest degradation efficiency of 89 % was obtained in 2nd cycle after 12 days. A significant decrease of efficiency occurred in 4th cycle to reach only 49 %. The degradation was monitored by measuring the levels of the extracellular, MnP, Lac and LiP enzymes. The fungal RBC reactor is considered to be promising for remediation of wastewater contaminated with persistent textile dyes.

Keywords: *Rotating biological contactor, Remazol Brilliant Blue R, Pleurotus ostreatus, Irpex lacteus, Trametes suaveolens F1*

Introduction

The pollution of water bodies by different human activities have caused several environmental, social, economic and health problems. Synthetic dyes represent a large group of chemically different compounds whose total world production is about 800 000 ton/year[1]. The main source of water contamination by synthetic dyes is the textile industry. The elimination of synthetic dyes discharged from the textile industry is often based on physical and chemical processes that are costly and not very effective[2,3]. The textile effluents are remediated in wastewater treatment plants but the efficiency is quite poor with some types of dyes[4,5]. Conventional biological methods using activated sludge and aerated lagoons can reduce the COD load but these processes often are not able to remove the coloration[5]. The formation of toxic, mutagenic and carcinogenic residues of degradation of synthetic dyes can also be a serious problem[6,7]. By contrast, the biological methods employing white-rot fungi can significantly reduce both the color and toxicity of the contaminants[1,8,9,10]. Ligninolytic fungi have been proven to possess a significant potential for remediation of various industrial effluents including those from the textile industry[8,9].

RBBR is an anthraquinone dye used in the textile industry. It represents a class of toxic and highly resistant organopollutants. RBBR can also be used in the screening of ligninolytic activity of fungi[11,12] and was therefore chosen as a model dye for experiments in RBC.

The RBC reactor represents a prospective means for the secondary treatment of both municipal and industrial wastewaters. Although the employment of RBC includes relatively high initial capital costs, it has low costs of operation and maintenance and a relative long viability. The use of biofilm RBC reactors for wastewater treatment represents a promising technology[13].

In this study, the performance of a fungal RBC (continual mode) for the treatment of a RBBR pollution was evaluated. A comparison of the biodegradation potential of three strains of ligninolytic fungi *Pleurotus ostreatus, Irpex lacteus* and *Trametes suaveolens F1* was carried out in RBC conditions. The ability of the individual strains to form biofilms on disks from different materials under specific conditions of cultivation was investigated. Another important aim was to assess the ability of fungal biofilms to be used for degradation in multiple consecutive cycles.

Materials and methods

Chemicals

Remazol Brilliant Blue R (RBBR) (C.I. 61200; dye content 50%) was purchased from Sigma-Aldrich (USA). The chemical structure is shown in Figure 1. Malt extract and agar were purchased from Oxoid, UK.

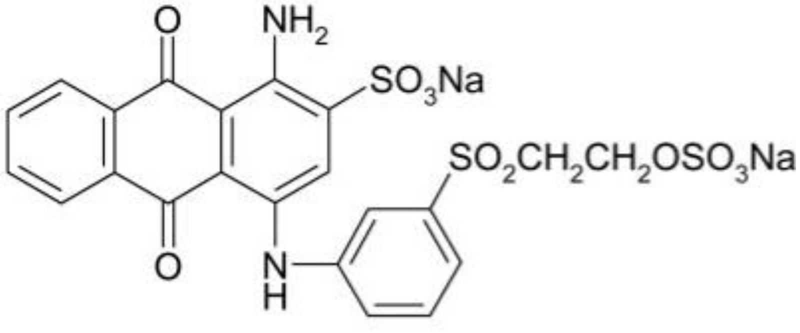

Figure 1: Chemical structure of Remazol Brilliant Blue R dye used in the study

Microorganisms

Irpex lacteus 931 and *Pleurotus ostreatus* 106 were provided by the Culture Collection of Basidiomycetes, Institute of Microbiology ASCR, Prague. *Trametes suaveolens F1* was isolated at University of Ostrava (collection no. F1, GenBank accession FJ515315 based on 18S sequence, KF573015 based on ITS sequence) and maintained on malt extract-glucose (MEG) medium containing 2 % (w/w) agar at 4 °C.

RBC reactor

The RBC reactor consisted of a polymethyl methacrylate (PMMA) vessel and a horizontal driving axis with six 1-cm-thick polyurethane foam (PUR PP145 size of pores PPI20) disks (diameter 8 cm, rotation speed 2 rpm, 40 % of the disk volume permanently immersed) (Figure 2). The experiments were carried out aseptically in MEG medium (per litre: 5 g malt extract, 10 g glucose, pH 4.5) at 22 °C under a forced aeration with air (50 l h^{-1}). Sterile foam disks were put horizontally in a volume of 1.8 l MEG medium and inoculated with a homogenate (Ultra-Turrax T25 mixer, IKA Werk, Germany, 20 s) of a 7-d-old, static fungal MEG culture grown at 28°C (10 % v/v inoculum). The disks were colonized by the fungus (7 d, 28 °C). The MEG medium was removed after 7 days and the colonized disks were mounted aseptically in the reactor containing a volume of 1.8 l of MEG medium with RBBR (concentration, 150 or 100 mg l^{-1}). The total operation volume of the medium containing the dye was 3.8 l. The decolorization was measured spectrophotometrically at 592 nm. The degradation process was stopped when the value of extinction did not have changed during last three days. The fungal biomass covering the disks was estimated gravimetrically at the end of the experiment as dry biomass.

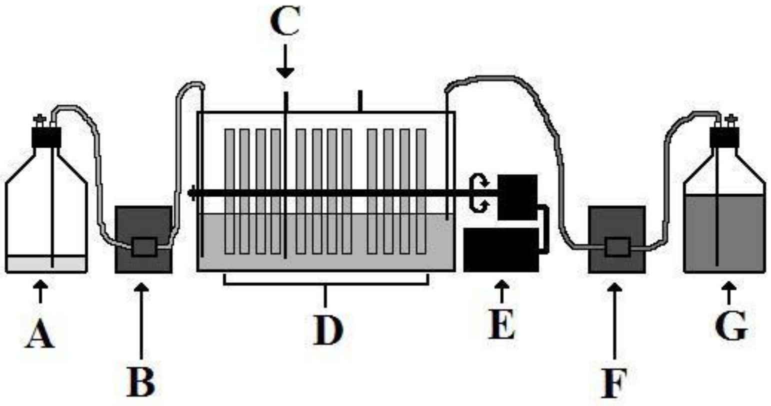

Figure 2: A scheme of the laboratory RBC: A – a bottle with polluted wastewater, B – a peristaltic pump removing the reactor content, C – an air-intake and sampling point, D – disks mounted on the rotating axis, E – a motor driving the axis, F – a peristaltic pump dosing the dye-containing growth medium into the reactor, G – a dye-containing medium reservoir

Enzyme assays and isolation

The activities of ligninolytic enzymes were determined spectrophotometrically (Epoch microplate spectrophotometer, Biotek, Vermont, USA) using standard methods: laccase (Lac) by oxidation of 2,2´-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid)[13], manganese peroxidase (MnP) by reaction with 3-(dimethylamino) benzoic acid / 3-methyl-2 benzothiazolinone-hydrazone hydrochloride[8] and lignin peroxidase (LiP) by oxidation of veratryl alcohol[12].

Results and discussion

Decolorization of RBBR dye in the RBC reactor was evaluated in three independent experiments using three different fungal strains, *P. ostreatus, I. lacteus* and *T. suaveolens F1.* Figure 3 shows the decolorization potential of the strain *P. ostreatus.* The course of decolorization of RBBR used at a concentration of 150 ppm was studied in two different regimes, i.e. in the presence and absence of dimethyl succinate (DMS), and in two consecutive cycles. DMS was used as a buffer to stabilize pH of the medium. In the situation measured in the absence of DMS, the decolorization measured after 24 days attained the value of 93.4 % and the pH dropped from a value of 5.3 to 4.0 during decolorization. When buffered by DMS (1.43 g l^{-1}) the decolorization was faster and reached a value of 97.3 %. A decrease of pH was not observed in 2nd cycle. The importance of monitoring pH during decolorization was demonstrated to ensure the maximal effectivity of the process. The change of pH that can negatively influence the decolorization process is probably caused by formation of metabolic products[14,15].

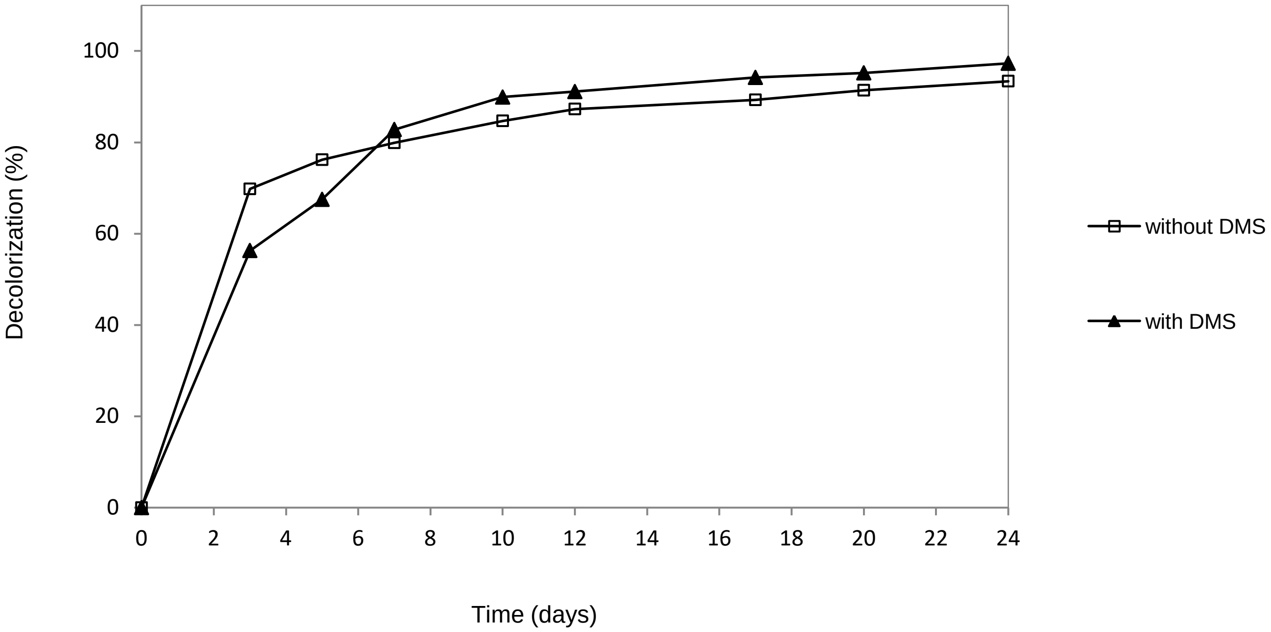

Figure 3: Decolorization efficiency of P. ostreatus measured with RBBR in 1st cycle (without DMS) and in 2nd cycle (with DMS)

Further experiments included the decolorization of RBBR (150 ppm) using the strain *I. lacteus* and were carried out in three consecutive cycles (Figure 4). In 1st cycle, a 100% decolorization was achieved within 24 h. The 2nd and 3rd cycles were slightly slower, with the respective decolorization values of 99.8 and 98.8 % reached after 6 and 14 days. No DMS was added in the medium because the pH value did not change during degradation in contrast to the degradation by *P. ostreatus*.

I. lacteus showed higher decolorization rates, 6.25 and 0.44 mg RBBR h^{-1} l^{-1} in 1st and 3rd cycle, respectively, compared to *P. ostreatus* where the maximal decolorization rate of 0.25 mg RBBR h^{-1} l^{-1} was attained in 2nd cycle in the presence of DMS. This finding is in agreement with the data published by other authors[16].

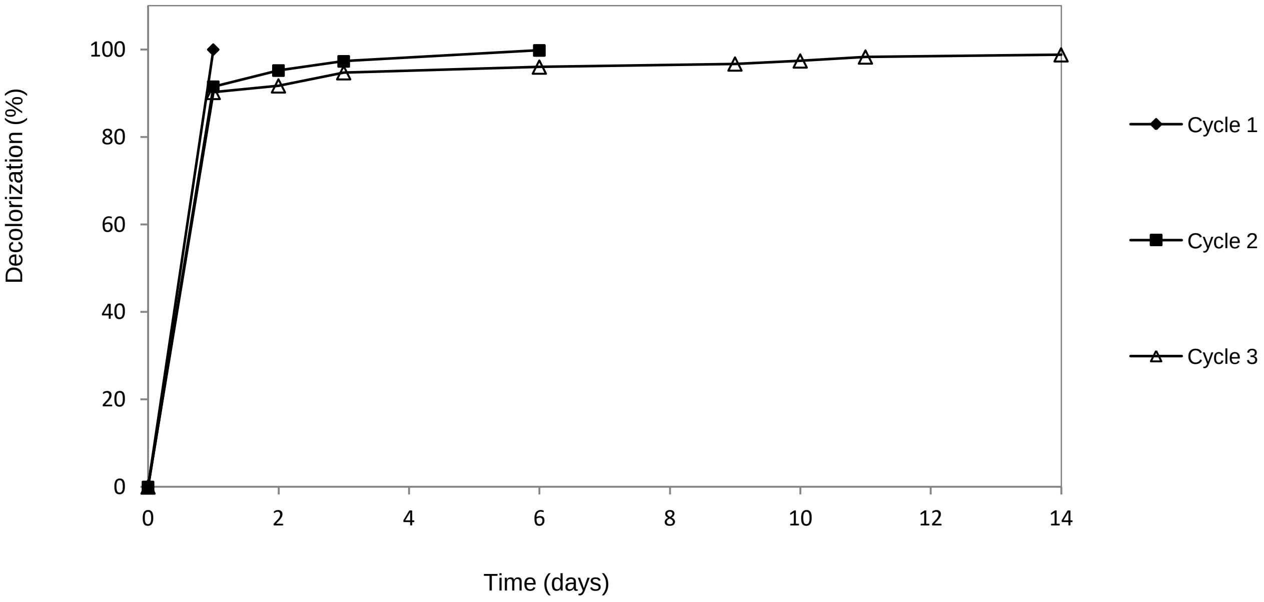

Figure 4: Decolorization of RBBR by I. lacteus carried out in three consecutive cycles

A higher efficiency of decolorization of RBBR by *I. lacteus* can result from different decolorization abilities of the two fungal strains compared but also from different conditions of decolorization. In the experiment carried out with *I. lacteus* the polyurethane disks made of PUR (T-2536), that were used in the case of *P. ostreatus*, were substituted with disks made of polyurethane PUR (PP145). The latter material is more porous and enabled us to achieve a higher biomass growth yield per the disk surface. The values of gravimetric determination of dry biomass are not shown. The findings obtained increase the knowledge of biodegradation potential of the two fungal strains employed and their applicability for bioremediation in the RBC reactor[17].

The third fungal strain tested in this study was the isolate *T. suaveolens F1* obtained in the frame of the BIOCLEAN project[18]. The experiments comprised four consecutive decolorization cycles in which RBBR dye was used at a concentration of 100 ppm. A good decolorization efficiency of 85 and 89 % after 12 days was proven in 1st and 2nd cycle, respectively. All four decolorization cycles (without pH adjustment) are documented in Figure 5. In 3rd cycle, 88 % of the dye was removed within 5 days, which represented a decolorization rate of 1.32 mg dye h^{-1} l^{-1}. In 4th cycle the fungus exhibited a lower decolorization activity of 59 % attained within 8 days.

The metabolic activity of the fungus was followed during all four cycles by measuring the activities of extracellular enzymes MnP, Lac and LiP (Figure 6, A,B,C). During the 12-d decolorization of RBBR, in the first three decolorization cycles, two enzymes were active, namely Lac and LiP. While Lac was not active in the subsequent 4th cycle, LiP activity became nondetectable from the 6th day of this cycle, which corresponded to a significant decrease of RBBR decolorization in 4th cycle (Figure 5). MnP was active during 1st and 2nd cycle but its activity was gradually decreasing. This enzyme was not active in 3rd and 4th cycle. We can thus conclude that, probably, LiP and Lac were involved in the decolorization of RBBR by *T. suaveolens F1*. However, the experiment did not allow to determine the contribution of the two enzymes to the decolorization. The degradation potential of this fungus was also studied under the conditions of static cultivation in liquid and solid media[19]. Here, *T. suaveolens F1* was capable of efficient decolorization of the anthraquinone dye Disperse Blue 3 (DB3), azo dye Reactive Black 5 (RB5), and triphenyl methane dye Bromophenol Blue (BPB). In the conditions of RBC reactor, a high decolorization capacity for RBBR was found compared to a weaker decolorization capacity in static, liquid-medium cultures where, in contrast, a high decolorization capacity was observed with DB3, RB5, and BPB dyes. We can hypothesize that continuous conditions in the RBC reactor, together with a sufficient aeration, positively influenced the vitality of the fungus, its growth yield and metabolic activity, which may support its ability to decolorize dyes.

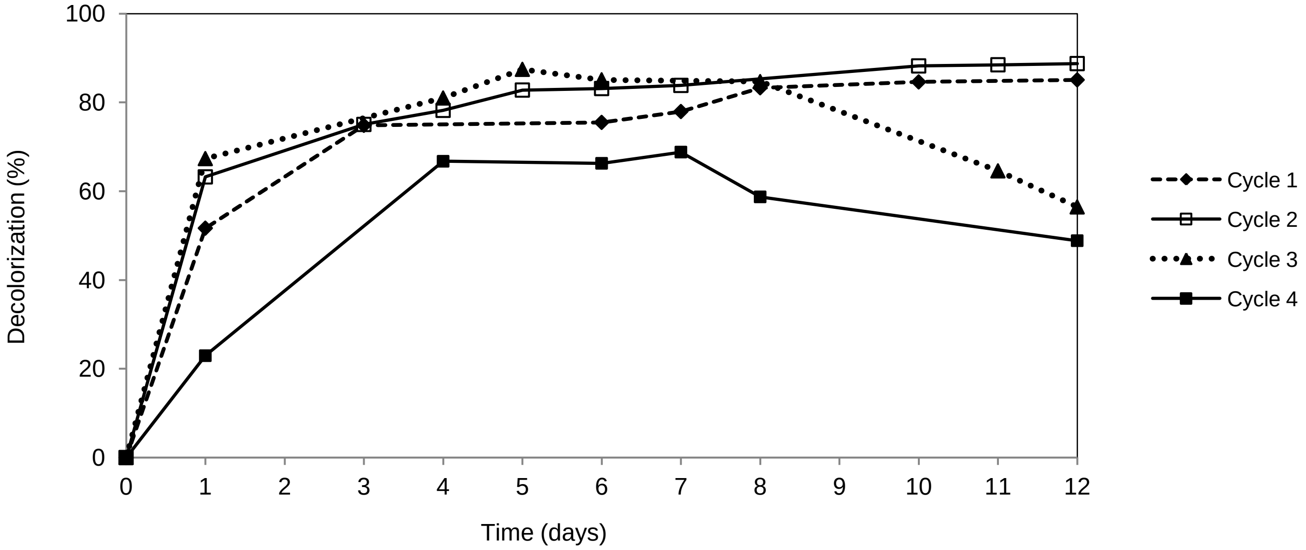

Figure 5: Decolorization of RBBR by Trametes suaveolens F1 in four consecutive cycles

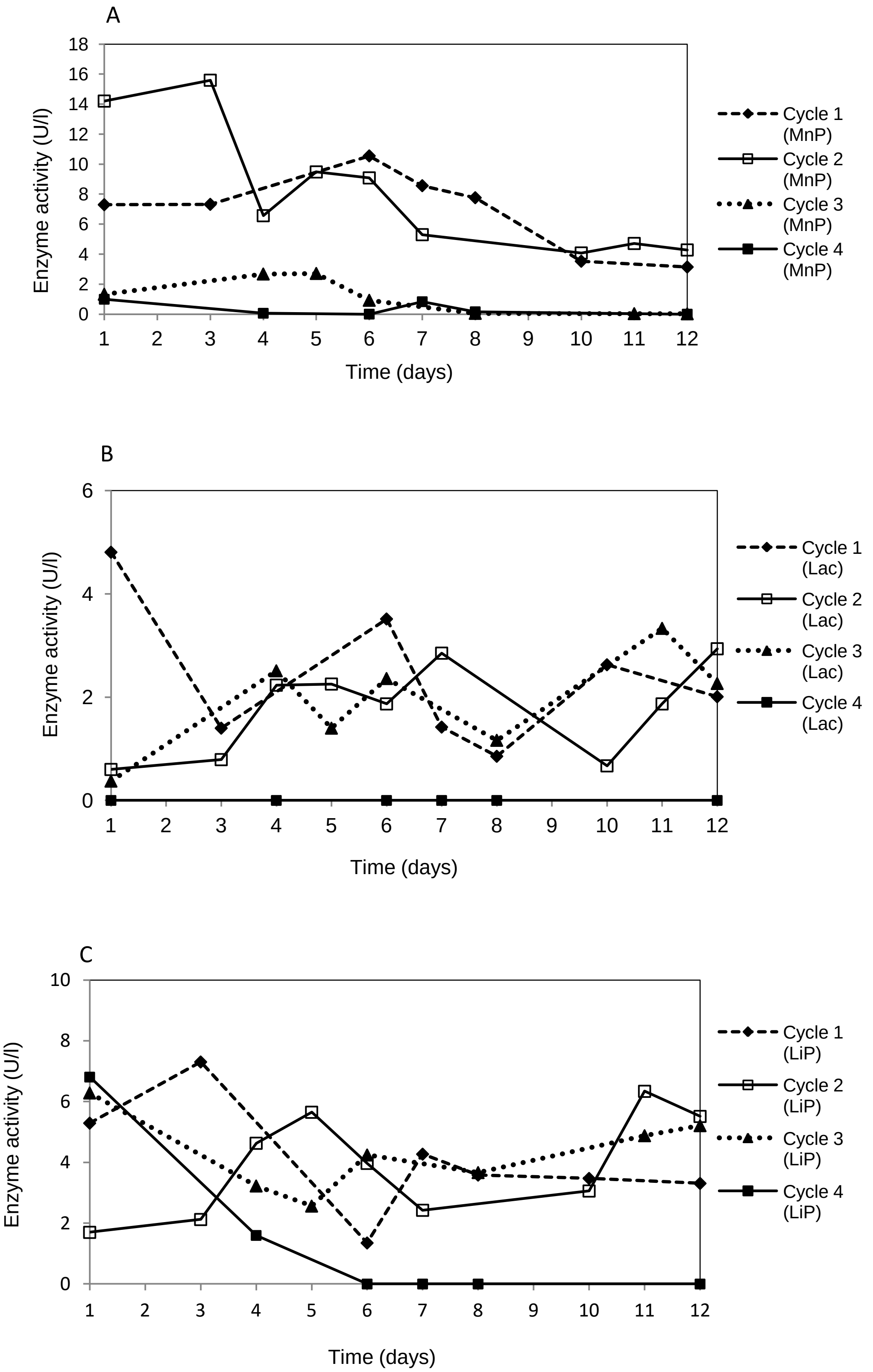

Figure 6: Activities of manganese peroxidase (MnP) (A), laccase (Lac) (B) and lignin peroxidase (LiP) (C) in T. suaveolens F1 in the course of four consecutive RBBR decolorization cycles

Conclusion

White-rot fungi *P. ostreatus*, *I. lacteus* and *T. suaveolens F1* were able to efficiently degrade the anthraquinone dye RBBR when used in the RBC reactor. The effectivity of dye degradation by *P. ostreatus* was partially inhibited by pH changes of the growth medium. The degradation process could be stabilized by using DMS to buffer the pH changes. RBC reactor was suitable for long-term applications of the immobilized fungi in consecutive decolorization cycles. *I. lacteus* decolorized RBBR with high decolorization rates in all three consecutive cycles. The efficiency of decolorization by *T. suaveolens F1* was higher in the RBC reactor compared to the static cultivation. In the first three cycles the efficiency of decolorization was high whereas in 4th cycle the extracellular enzymes Lac and LiP were losing their activities and the value of decolorization decreased. MnP was probably not involved in the decolorization of RBBR by this fungus.

The findings demonstrated that various strains of white-rot fungi can be used for bioremediation in the RBC reactor, however, their rate and efficiency of decolorization depended on the strain used. The decolorization process was shown to function over a long-term period, for instance in the form of repeated consecutive cycles, and at a low cost. The RBC reactor based on fungal biofilms was shown to be an efficient device for bioremediation of wastewater effluents contaminated with recalcitrant textile dyes.

Acknowledgment

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Biodegradace syntetického barviva Remazol Brilliant Blue R v rotačním biologickém kontaktoru využívajícím ligninolytické houby

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Souhrn

Rotační biologický kontaktor je zařízení umožňující degradaci rekalcitrantních sloučenin v delším časovém úseku za opakovaného použití disků porostlých mikrobním biofilmem. Jeho možnosti využití pro biodegradaci organopolutantů byly sledovány při použití syntetického textilního barviva Remazol Brilliant Blue R (RBBR). K posouzení degradační kapacity RBC byly použity tři kmeny ligninolytických hub Pleurotus ostreatus, Irpex lacteus a Trametes suaveolens F1. Všechny tři kmeny účinně RBBR degradovaly a byly použitelné pro opakovanou degradaci v navazujících cyklech.

V experimentech s P. ostreatus byla testována změna kultivačních podmínek po 1. cyklu. Úpravou pH dimethylsukcinátem bylo ve 2. cyklu dosaženo rychlejšího nástupu degradace RBBR a zvýšení degradační účinnosti o 4 % na 97 % za 24 dní. Degradace RBBR houbou I. lacteus byla sledována celkem ve 3 cyklech. V 1. cyklu byla účinnost degradace 100 % již za 24 hodin. Další dva cykly proběhly oproti prvnímu cyklu pomaleji. Ve 2. cyklu bylo dosaženo 99,8% dekolorizace po 6 dnech a ve 3. cyklu 98,8% po 14 dnech. Čtyři degradační cykly byly provedeny s houbou Trametes suaveolens F1. Nejvyšší degradační účinnost byla zaznamenána ve 2. cyklu, 89 % po 12 dnech. V dalších dvou cyklech nastal pokles, kdy ve 4. cyklu došlo k poklesu degradace až na 49 % za 12 dní.

Průběh degradace byl sledován pomocí extracelulárních enzymů manganperoxidázy, lakázy a ligninperoxidázy. Z hodnocení enzymatické aktivity vyplynulo, že na dekolorizaci RBBR houbou Trametes suaveolens F1 se pravděpodobně podílí LiP a v menší míře také Lac. Experimenty ukázaly, že v RBC reaktoru mohou být použity různé kmeny hub bílé hniloby, avšak rychlost a efektivita dekolorizace se liší. Bylo potvrzeno, že RBC reaktor představuje perspektivní zařízení využitelné pro remediaci odpadních vod kontaminovaných obtížně rozložitelnými textilními barvivy, v němž dekolorizace může probíhat v delším časovém intervalu s relativně nízkými náklady.

***Klíčová slova:** Rotační biologický kontaktor, Remazol Brilliant Blue R, Pleurotus ostreatus, Irpex lacteus, Trametes suaveolens F1*

Adsorption of lead ions and surfactants on sheep wool and pyrolysis material prepared from wool

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Summary

The paper deals with adsorption of lead and selected surfactants onto sheep wool and material obtained after sheep wool pyrolysis. Thermal analysis was performed for characterization of pyrolyzate surface and sheep wool. Lead adsorption on sheep wool and pyrolyzate was monitored at selected pH values ranging from 3 to 6. For the wool-lead adsorption system, the lead removal from solution ranged between 4.9 and 97.5 % in dependence of pH and initial concentration. The pyrolyzate - lead adsorption system showed a lead removal rate range of 5.5 – 94.8 %. In the case of lead ions adsorption a different adsorption mechanism can be expected. The lead ions preferably react with the carboxyl group of sheep wool keratin. The carbonaceous material, the pyrolyzate, is represented by the micropores, which are the site of immobilization of Pb^{2+} ions. Adsorption tests for surfactants were carried out without pH adjustment. The wool removed the surfactant sodium dodecyl sulfate (SDS) from the solution in a range of 23.6 – 51.7 %, for the cetyltrimethylammonium bromide surfactant (CTAB) the removal interval was 85.5 – 98.4 %. The CTAB surfactant was removed from the solution with a pyrolyzate at a range of 46.4 – 85.6 %. The differences in adsorption capacities are probably due to the mutual force effect between the dissociated functional groups of the sheep wool carboxyl groups and the hydrophilic part of the surfactants.

Keywords: *sheep wool, pyrolysis, lead, adsorption, surfactants*

Introduction

In recent years, efforts have been made to promote keratin waste from breeding. These include, for example, wool of inferior quality unsuitable for the textile industry, feathers, horns, hooves, etc. Keratin contained in these materials are among the most abundant, cheap and naturally renewable proteins. Keratin waste is mainly deposited in landfills because it has not found other uses. It is not suitable as a fuel in the incinerators because of the high sulphur content, and it is also an inefficient fuel. Keratin obtained from these waste materials is used after chemical isolation for biochemical applications such as films, fungi, fibers, degradable surfactants for fire fighting. For keratin powders, the potential of adsorbent materials for heavy metals or various organic substances is assumed[1,2].

It is well known that lead is a heavy metal and therefore toxic to human populations, aquatic animals and other forms of life. Lead is particularly problematic in wastewater from industrial dyes, car batteries, or radiation shields. Basic methods for removing heavy metals from wastewater include adsorption, ion exchange and electrochemical processes, or precipitation. In the adsorption of lead to activated carbon, which is commonly used for adsorption purposes, several negatives have been identified. Lead cations make strong interactions with activated carbon surface, resulting in poor regenereability of activated carbon and its reuse for effective adsorption. Another unfavorable fact is that active carbon is relatively expensive. These aspects lead to the search for new low-cost adsorbents for removal of heavy metals or surfactants[3].

Surfactants meet every person daily. Current waste water treatment plants are not adapted to an increasing trend in the use of surfactants in households, and so surfactants are not sufficiently removed from sewage and travel to natural waters. Here, for example, surfactants cause the destruction of protective hydrophobic shells of feathers, skin, coat of aquatic animals, the foam forming on the surface worsens the illumination of waters, the phosphates contained in surfactants stimulate the growth of cyanobacteria.

Sheep wool is very cheap and its production is more than big. It is the basic product of sheep breeding. The main component of the wool fiber is the keratin protein, which belongs to the group of fibrillar proteins in which the secondary structure prevails. Wool adsorption material can be prepared by electrostatic precipitation from a keratin extract. Subsequent adsorption tests were performed under dynamic conditions. The heavy metal solution was pumped through the membrane for 3 hours. The membrane was tested for the adsorption of copper cations. The adsorption maximum of 11.03 mg/l was reached at the initial concentration of 50 mg/l [4].

In another work, the keratin colloid solution was prepared by mixing the wool with a solution containing hydrochloric acid, thiourea, urea, and mercaptoethanol. Lead adsorption tests were performed by mixing lead solution, keratin colloid solution and distilled water. Initial concentrations of lead solution ranged from 0.3 – 2.0 mmol/l, with an adsorption peak of 43 mg/g being reached at an initial concentration of 2.0 mmol/l. The maximum removal of lead from the solution as a percentage was achieved at an initial concentration of 0.3 mmol/l and 87 % [3].

Pyrolysis of keratin waste produces new material, which has interesting properties. Practical properties include the presence of micropores in the surface structure of the material and a large surface area of material ranging from 100 – 2000 m^2/g. These properties are important for the cleaning, separation and storage of gases and liquids. That is why pyrolysis of keratin waste appears as a source of new adsorbent material.

As a source of keratin waste, chicken feathers were selected in the next case. The feather fiber itself was separated from the quill and further used for pyrolysis. The specific surface area, pore distribution and micropores volume were determined by nitrogen adsorption tests for pyrolyzate. After evaluation, a specific surface area of the micropores of pyrolyzate was determined at 436 m^2/g and the volume of micropores was 0.178 cm^3/g.[5]

The aim of the work was to prepare the adsorption material by raw sheep wool pyrolysis. Subsequently, the sheep wool pyrolyzate should be tested for the adsorption of lead, surfactants and compare with the sheep wool adsorption capability.

Experimental part

Chemicals and material

The following chemicals were used in the work: $Pb(NO_3)_2$ p.a. (Lach-Ner), Sodium dodecylsulfate / SDS p.a. (Lach-Ner), Cetyltrimethylammonium bromide / CTAB 99% (Lach-Ner), HCl 36.5% (Mach chemicals Ltd.), NaOH p.a. (Petr Švec Penta).

For all adsorption tests wool from domestic sheep intended for breeding and food purposes was used. This is not a sheep with a wool quality corresponding to the textile industry. The pyrolyzate of this wool was used as the second adsorbent. The sheep wool was adjusted for the adsorption by shredding and the pyrolyzate was triturated with subsequent sieving. For the adsorption tests, a pyrolyzate fraction of ≤ 0.15 mm was used.

Equipment

The following devices were used during the experiments: Varian AA 240FS Atomic Absorption Spectrometer with flame atomization, Orion Star A111 pH Meter, KERN ABJ analytical balance, HPServis tube pyrolysis furnace, Setsys Evolution Setaram thermogravimetric analyzer, PCTPro E & E Setaram sorption analyzer.

Workflow

Sheep wool adjustment

First, raw sheep wool was washed in clean water to get rid of plant and animal impurities. The second wash was carried out with usual detergent in hot water to remove the fatty matter (lanolin) on the wool. The washed wool was air dried. The wool thus prepared was hand-cut several times to the smallest particles. The final size of wool particles ranged between 1 and 3 mm.

Thermal analysis of sheep wool

Thermal analysis of raw sheep wool was performed on a Setsys Evolution thermogravimetric analyzer by Setaram. The loading of the raw and washed sheep wool of approximately 20 mg was pyrolyzed under next conditions: heating to 100 °C in a step of 10 °C/min, maintaining the temperature at 100 °C for 30 minutes, heating to 600° C in a step of 10° C/min, maintaining the temperature 600° C for 2 hours. This program was the same as in the preparation of sheep wool pyrolyzate.

Pyrolysis of sheep wool

The raw sheep's wool, free from impurities and fats as in the previous case, was deposited as much as possible on a pyrolysis tray. The raw wool weight was about 7.50 g. The tray was placed in a tube of the pyrolysis furnace and, after the tube was closed, nitrogen was bubbled through a volume flow of 200 ml/min. The pyrolysis program was set in steps: heating to 100 °C in 10 °C/min, keeping the temperature 100 °C for 30 minutes, heating to 600° C in 10 °C/min, keeping the temperature 600 °C for 2 hours and finally cooling at room temperature. The gain of the pyrolyzate from one pyrolysis process was then about 1.30 g. Subsequently, the pyrolyzate was ground in a mortar and sieved through a sieve with a 0.15 mm mesh.

Figure 1: Wool prepared for pyrolysis (left), sheep wool pyrolyzate (right).

Determination of pore distribution

The sheep wool pyrolysis pore distribution was performed on a PCTPro E & E Sorbam sorption analyzer by the carbon dioxide adsorption method at 30 °C. From the adsorption isotherms the following data were calculated: the volume of the micropores w_0 from the Dubinin - Radushkevich equations, the surface of the micropores S_{mi} according to Medek equation and the most recent radius of micropores r_{mic} according to Medek equation.[6]

Lead adsorption

A 100 mmol/l lead nitrate stock solution was prepared in a 1 liter volumetric flask. From this stock solution, solutions were prepared at Pb^{2+} concentrations of 50; 40; 20; 10; 5; 2.5; 1 and 0.5 mmol/l as starting solutions for adsorption. One gram of the cut wool (or pyrolyzate) was weighed into the threaded Erlenmeyer flasks and 100 ml of a solution of different concentrations were added. The adsorbent and the adsorbate were in contact for 24 hours with occasional shaking at room temperature (22 ^{o}C). With dilute solutions of HCl and NaOH (or sodium acetate), pH was adjusted. The suspension was then filtered through a KA4 filter. The concentrations of lead before and after adsorption were verified on an atomic absorption spectrometer.

Adsorption of surfactants

In this work one representative of anionic surfactants (SDS) and one representative of cationic surfactants (CTAB) were selected. For the SDS, the concentration range of the starting solutions was 0.3; 0.6; 1,2; 2.5; 5; 10 mmol/l, the concentration range of the starting solutions for CTAB was 0.3; 0.6; 1,2; 2.5; 5 mmol/l. The adsorption process itself was identical to that of lead adsorption. After contact time, the solutions were filtered through a KA4 filter into dark vials and taken to determine the concentration of surfactants after sorption in the ALS Czech Republic laboratory. Cationic surfactants were determined with bromophenol blue spectrophotometrically. Anionic surfactants were determined according to Czech technical standard ČSN EN 903 by methyl blue also spectrophotometrically.

Results and discussions

Thermal analysis

Upon heating up to 100 °C, water was released from the moisture contained in the wool. The greatest water release occurred within 10 – 15 minutes of the start of heating. When heated to this temperature, no further gas was generated.

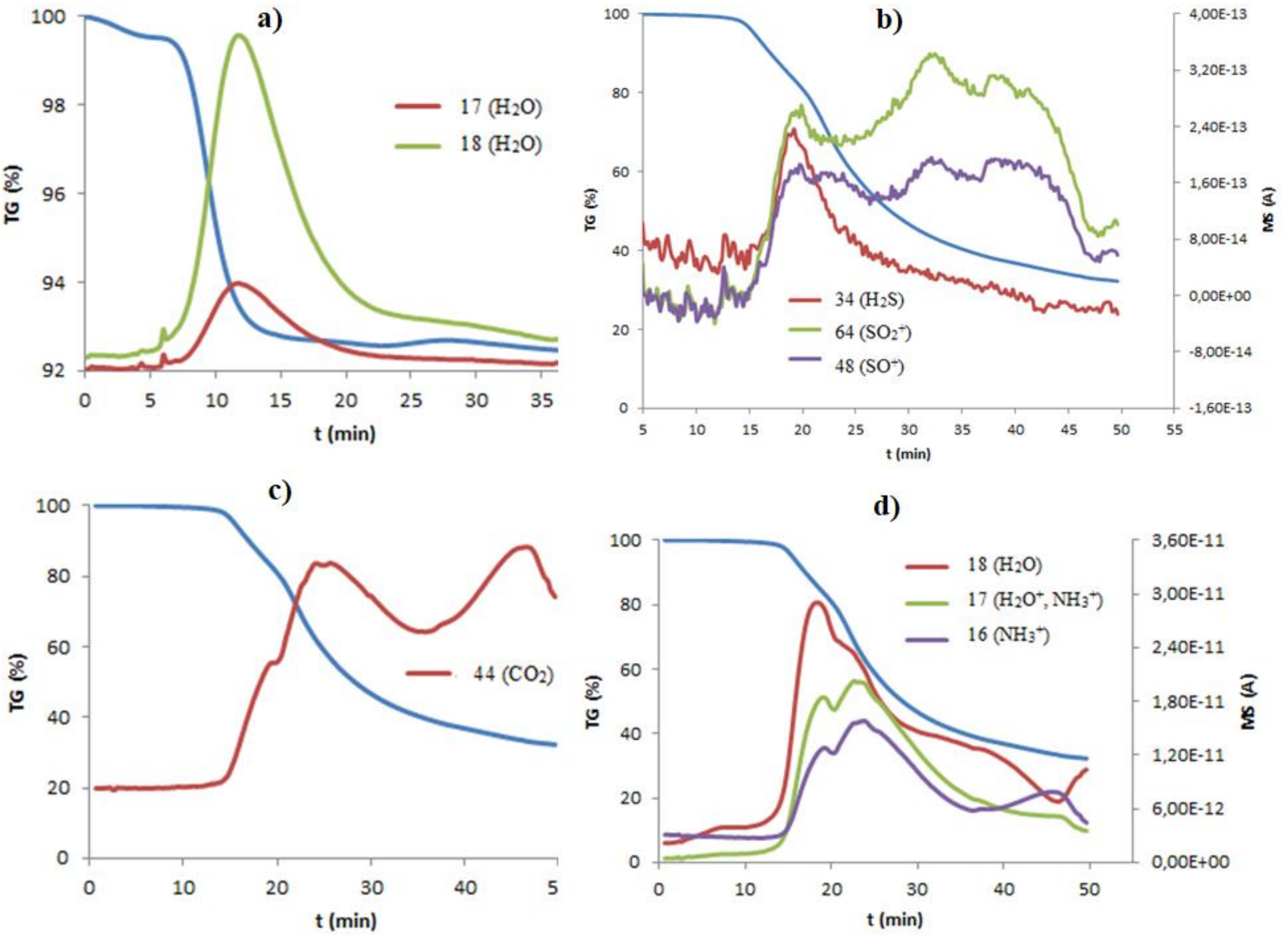

Figure 2: a) Heating up to 100 °C, blue curve shows weight loss in % at heating up to 100° C, red and green curve water development signal for molecular weights 17 and 18. b) Heating at 600° C, blue curve demonstrates weight loss in % by heating at 600° C, red, green and purple curves signals the development of gases of molecular weight 34, 48, 64. c) Heating at 600 °C, blue curve corresponds to weight loss in % when heated to 600 °C, red curve gas evolution signal with a molecular weight of 44. d) Heating at 600 °C, blue curve links to weight loss in % at heating to 600 °C, red, green and purple curve signals developing the molecular mass of 16, 17, 18

The most important gas evolution occurred when heated to 600 °C, specifically from the twenty minutes of this thermal analysis process. Released gases during heating are characteristic of amino acids formed by keratin (nitrogen and sulphur compounds). Especially sulphur compounds, which should originate from the thioaminoacids of the polypeptide chains of keratin. Upon heating to 600 °C, the largest weight loss of the sample also occurred. The isothermal thermal analysis (600 °C for 2 hours) only led to the development of the above gases and low hydrogen evolution.

Pore distribution

The volume and surface of chicken feather pyrolysis micropores were determined by nitrogen adsorption, but numerically the feather pyrolysis volume equals the volume of sheep wool pyrolysis micropores. Sheep wool pyrolyzate has got a slightly larger surface of micropores, but it is possible that pyrolysis of various keratin materials gives a product with similar surface properties. When comparing the micropore volumes and the surface area of the micropores of sheep wool pyrolysis with activated carbon, it is clear at first glance that the pyrolyzate does not reach those properties which make activated carbon an excellent adsorbent. The negative properties associated with the use of activated carbon have been mentioned above.The atomic radius of the lead cation is reported in the chemical tables as 132 μm (0.132 nm). It is suggested that lead cations can be captured by pyrolyzate in micropores having the largest radius of 0.59 nm.

Table 1: Characterization of sheep wool pyrolyzate micropores and comparison with the properties of micropores of chicken feathers and activated charcoal [5,7]

Sample	w_0 cm^3/g	S_{mi} m^2/g	r_{mi} nm
Wool pyrolyzate	0.178	541	0.59
Leather pyrolyzate [5]	0.178	436	-
Activated carbon [7]	0.510	1300	-

Lead adsorption

In adsorption experiments, the influence of pH on the sheep woole and pyrolyzate adsorption capacity was monitored. With the increasing concentration of the lead ions in the solution, of course, the amount of adsorbed on the surface of the sorbent has increased. We compared linear form of Langmuir and Freundlich adsorption equations and parameter R^2 was closer to one in the case of Freundlich theory (Table 2). The figure below shows the rate of removal of lead ions from the solution.

Table 2: Comparison of sheep wool adsorption and pyrolyzate at different pH

pH	a_{max}^{wool} mmol/g	$a_{max}^{pyrolyzate}$ mmol/g	R^2 Langmuir	R^2 Freundlich
3.0	0.19	0.52	0.92	0.98
4.2	0.27	0.62	0.90	0.97
5.4	0.43	0.71	0.93	0.97
6.0	0.51	0.80	0.93	0.99

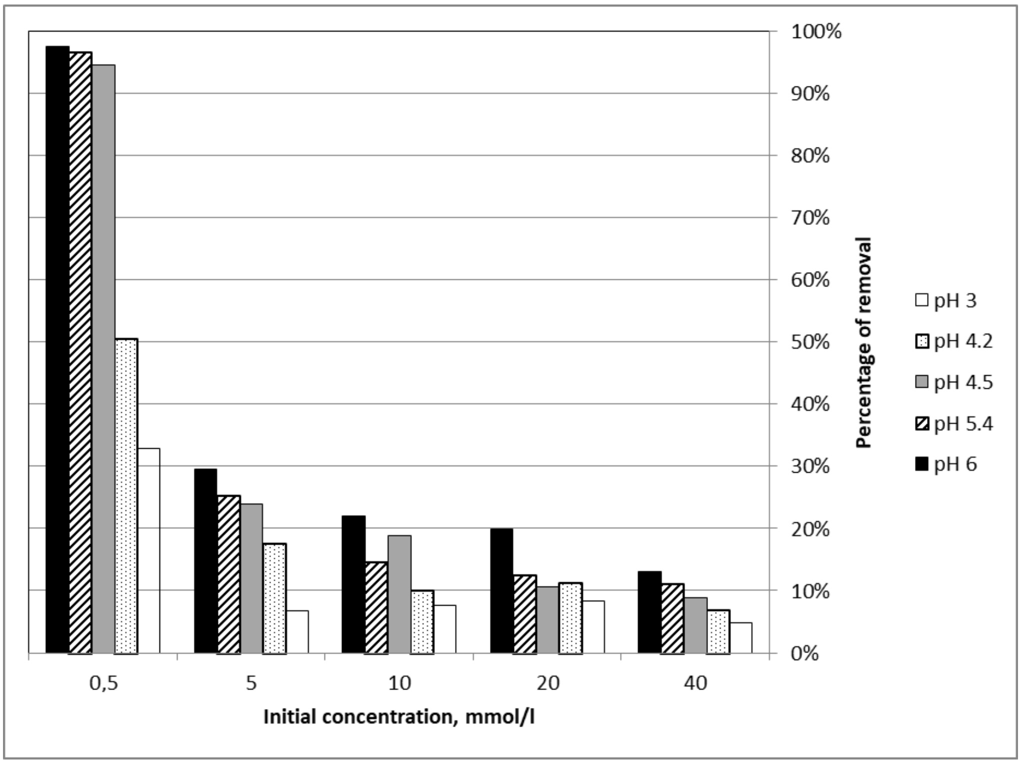

Figure 3: Effect of pH and initial concentration on removal of lead ions from solution

It is clear from the figure that increasing in pH leads to enhancement of the lead ions removal. At pH 3, the removal rate is relatively small for all starting concentrations. The carboxyl acids of the keratin amino acids at this pH dissociate very little and thus do not produce enough binding sites for the lead cations on the keratin molecule. Generally, increasing of pH and decreasing of initial concentration lead to a greater percentage removal of lead from the solution. Interesting values can be seen at an initial concentration of 0.5 mmol/l with almost 100 of lead is eliminated at pH 4.5; 5,4 and 6.

In one of the published works, a keratin colloid solution was used to remove the lead cations. The lead adsorption system with keratin colloid solution was adjusted to pH 5 and the maximum lead removal rate of 87.0 % of the keratin colloid solution was at an initial concentration of 0.3 mmol/l.[3]

The following table compares the results of adsorption of lead ions to sheep wool and pyrolyzate. The value of the adsorbed amount was calculated from the difference between the initial concentration and the lead ion concentration after adsorption. Always for an initial concentration of 40 mmol/l, the value is per gram of adsorbent.

Higher wool pyrolyzate adsorption capacity was achieved at all monitored pH values. The lowest value for the pyrolyzate is 0.52 mmol/g at pH 3.0, corresponding to the highest value obtained at sheep's wool at pH 6.0. The potential use of the pyrolyzate is therefore wider with regard to the pH range of the aqueous medium. The immobilization of lead ions is likely to have a different mechanism. In the case of sheep wool, we assume interactions between dissociated functional groups and lead ions, in the case of pyrolyzate, physical adsorption in the pores of this carbonaceous sorbent. In the previous work we have been dealing with the adsorption of heavy metal ions on various, especially natural, carbonaceous materials. For adsorption of lead ions, the highest adsorption capacity was measured on so-called oxidation-altered coal and was 0.75 mmol/g at pH 5[8] which is comparable to that obtained on the pyrolyzate. The sheep wool shows a lower adsorption capacity, however, it is necessary to consider the fact that this natural material does not require any major modifications, unlike the wrought wool.

Adsorption of surfactants

Figure 4 compares the removal of the anionic surfactant SDS and cationic surfactant CTAB with the use of the wool and its pyrolyzate.

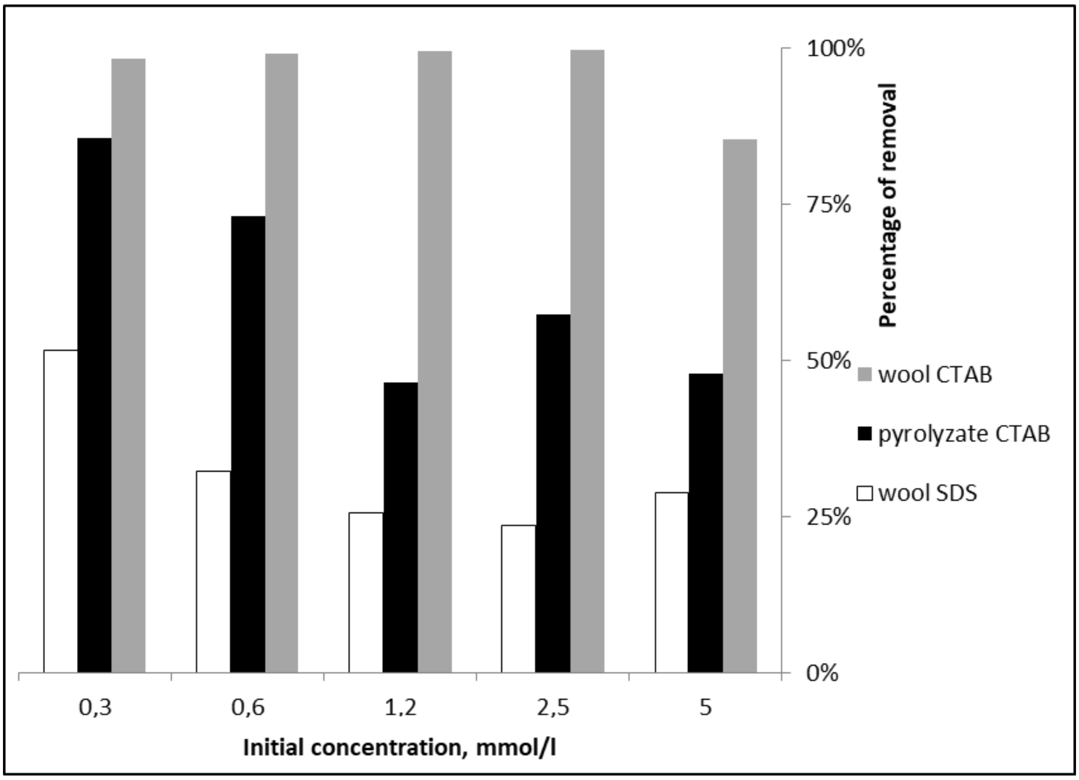

Figure 4: Percentage of removal of surfactants CTAB and SDS by sheep wool and sheep wool pyrolyzate

Dissociated functional groups on the sheep wool surface exhibit high affinity for the CTAB cationic surfactant. For all initial CTAB concentrations, a high ratio of elimination of this substance has been achieved. These values are comparable, for example, to adsorption on clay minerals and higher than to natural coal. The pyrolyzate exhibits a lower adsorption capacity than a natural wool and the rate of removal is comparable to other carbonaceous sorbents[9]. The pyrolyzate practically did not adsorb the anionic surfactant at all, the final and initial SDS concentrations were equal. The cause is probably a hydrophilic surface with negative zeta potential. Thus, the repulsive forces prevail between the negatively charged surface of the adsorbent and the negatively charged hydrophilic part of the SDS surfactant. A certain degree of SDS removal was reported by raw sheep wool. In this case, we can deduce the interactions between the positive charge amine groups on the wool surface and the negative SDS functional groups.

Conclusion

The aim of the work was to test new adsorbent materials for removal of selected heavy metal and selected surfactants from the solution. The sheep wool was selected as the starting adsorbent material from which sheep wool pyrolyzate was prepared by pyrolysis. The adsorption capacities of both test materials are quite promising in the case of lead ions and a cationic surfactant. The obtained values are comparable to adsorbents used or developed such as carbonaceous adsorbents, clay minerals, slag etc. In the absence of a "classical" application of sheep wool, its practical use as an adsorption material appears to be a more reasonable alternative to disposal in landfills.

Acknowledgment

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Adsorpce olovnatých iontů a tenzidů na ovčí vlně a jejím pyrolyzátu

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Souhrn

Práce se zabývá adsorpcí olova a vybraných tenzidů na ovčí vlnu a na pyrolyzát ovčí vlny. Byla provedena charakterizace povrchu pyrolyzátu a termická analýza ovčí vlny. Adsorpce olova na ovčí vlnu a pyrolyzát byla sledována při vybraných hodnotách pH v rozmezí 3 – 6. Pro adsorpční systém vlna – olovo docházelo v závislosti na pH a počáteční koncentraci roztoku k odstranění olova v intervalu 4,9 – 97,5 %. Adsorpční systém pyrolyzát – olovo vykazoval interval míry odstranění olova 5,5 – 94,8 %.

V případě adsorpce olovnatých iontů lze předpokládat rozdílný mechanismus adsorpce. Olovnaté ionty přednostně reagují s karboxylovou skupinou keratinu ovčí vlny. Uhlíkatý materiál, pyrolyzát vykazuje zastoupení mikropórů, které jsou místem imobilizace Pb^{2+} iontů. Adsorpční testy pro tenzidy probíhaly bez úpravy pH. Vlna odstranila tenzid dodecylsulfát sodný (SDS) z roztoku v intervalu 23,6 – 51,7 %, pro tenzid cetyltrimethylamonium bromid (CTAB) byl interval odstranění 85,5 – 98,4 %. Tenzid CTAB byl pyrolyzátem odstraněn z roztoku v intervalu 46,4 – 85,6 %. Rozdíly v adsorpčních kapacitách jsou pravděpodobně způsobeny vzájemným silovým působením mezi disociovanými funkčními skupinami karboxylových skupin ovčí vlny a hydrofilní částí tenzidů.

Klíčová slova: *ovčí vlna, pyrolýza, olovo, adsorpce, tenzidy.*

The Effect of Some Sorbents Used to the Oil Leaks Disposal

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Abstract

The aim of the study was laboratory testing effect of selected sorptive materials usually used by Fire and Rescue Services at accidents with oil leakage settlement. After clean up are environment components visually clean (especially surface water), but important is to know, if these matrixes are safe from the toxicologically and ecotoxicologically point of view. Model samples of soil and surface water were prepared, contaminated and cleaned with various sorbents. The petroleum pollution was determined by non-polar extractable substances (NES), which were determined in the samples before and after cleaning. Two petroleum products (diesel fuel and engine oil WD 40) and three sorbents (natural fibrous – CANSORB, mineral hydrophilic – EXPERLIT and mineral hydrophobic – VAPEX) were tested. The effectivity of removing of petroleum compounds from soil samples was more than 99 %, but amount of NES in all samples of soil was higher than legislative limit. The same result can be seen in the surface water testing. In all samples was determined higher amount of NES than the legislative limit. We can say that cleaning from oil pollution after an accident using tested sorbents is quite good, but further remediation is necessary to avoid undesirable impact of oil substances on environment.

Key words: *oil pollution, soil, surface water, sorbents, non-polar extractable substances (NES)*

Introduction

The life in industrial developed society is coupled with many unwilling processes, which include accidents with hazardous substances leaks, especially oil and oil products leaks. These accidents occur most often in technological processes, in the transport of petroleum substances, as well as in traffic accidents, as well as in the handling of petroleum substances. Worldwide problem is contamination of the oceans with the crude oil, but it would be escapade to omit inland countries, that are also threatened by oil pollution. Despite all preventive action taken by the industry it is impossible to remain oil pollution. Approximately 61 % of petroleum pollution is natural and more than 38 % has anthropogenic cause[1,2,3].

Accidents and leakage of petroleum substances cause environment deterioration and ecosystem instability in the affected area. To re-establish the ecological stability of the site, technically and financially demanding remediation procedures are used. A wide range of methods is available to clean up the oil pollution. Soil and water are the most affected components of the ecosystem. At present, biological, physicochemical and natural processes are used to remediate soil and water contamination (spontaneous remediation processes) [3,4,5,6].

By the average settlement is the first step to stop the leak and restrict the oil products spread. After that follow decontamination procedures to reduce the negative impacts of oil substances on environmental compartments and minimize pollution to an acceptable level. To reduce the spread of oil substances are used various sorptive materials – sorbents. Sorbents are special substances and materials that are capable to bind many liquid contaminants[5,7,8].

Various sorbent materials have been used to remove oil substances from the water, water surface and soil. Sorbents may be natural and synthetic origin. Many natural organic sorbents such as straw, cotton, wood fiber, wool, peat can be used despite its poor adsorption capacity[5,8,9,10,11]. Natural mineral sorptive materials are on the basis zeolites or natural clays, these are of hydrophilic nature and for clean-up of water can be its surface modified to adsorb oil substances[8,11,12]. Synthetic sorbents are based mostly on polypropylene and polyurethane and can be also used to clean up other liquids[5,8,13]. They can be used in pure form or can be modified, in recent years often with various nanomaterials[5,8,14,15].

The main qualities important for sorbent selection are sorption capacity, high surface area, porous structure, swelling (penetration into network structure), low degree of cross linking[8]. For the crisis situation such as car accidents or industrial accidents solution by forces of Fire and Rescue Services is very important form of sorbent (powder, granules, flakes or compact form such as various dry-goods), ability to its using on solid surface, its volume (how much place it occupy in the fire engines), good manipulation, reaction time[5,7,16].

The aim of the study was laboratory testing effect of selected sorptive materials usually used by Fire and Rescue Services at accidents with oil leakage settlement. We tested on model samples of surface water and soil, if these environmental components are after oil pollution disposal by sorbents "clean" from legislative point of view[17,18]. The petroleum pollution was representing by non-polar extractable substances (NES), which were determined in the samples before and after cleaning. Two petroleum products and three sorbents were tested.

Experimental Part

There was the accidental leak of oil products into surface water and soil simulated in laboratory conditions (constant temperature and constant humidity). The used contaminants were: diesel fuel and engine oil.

The oil products contamination was with sorbents CANSORB, EXPERLIT and VAPEX cleared. These sorbents are usually used by forces of Fire and Rescue Services. The used sorptive materials were taken from the fire station Zlaté Moravce. Sorbents after samples cleaning were rejected to fire station and processed together with its waste material. Some properties of used sorbents are listed in the Table 1.

Table 1: Properties of used sorbents[19,20,21].

	CANSORB	**EXPERLIT**	**VAPEX**
Chemical composition	Organic	Oxides of Si, Al, Fe, Ca, Mg, Na, K	Oxides of Si, Al, Fe, Ca, Mg, Na, K
Sorbent for	polar and non-polar compounds	non-polar compounds	non-polar compounds
Using at temperatures	under 200 °C	-200 °C – 900 °C	-200 °C – 900 °C
Capacity (L.m^{-3})	60 – 95	320 – 350	250 – 400

CANSORB is a fibrous organic adsorbent for hydrocarbons aimed to adsorb both oleophilic and hydrophilic compounds[19]. EXPERLIT is light porous inorganic sorbent of volcanic origin with hydrophilic properties intended to adsorption of oil compounds in dry conditions (floor of industry rooms, garages, gas stations, construction sites, asphalt and concrete, soil)[20]. VAPEX is white granulous inorganic material with hydrophobic modification aimed to adsorption of oil compounds from water and hard surfaces (floors of industry rooms, garages, gas stations, construction sites, asphalt and concrete, soil, water surface, flowing water – combination of floating barrages and VAPEX). VAPEX can be used like extinguishing powder by fires of oil compounds on hard surfaces[21].

Non-polar extractable substances (NES) were determined in the model samples like the characteristic of oil contamination by using of infrared spectral analysis.

Model Samples Preparation

The model sample of soil was prepared from garden soil (Sľažany, Zlaté Moravce). 10 part samples were taken from the top-soil in the 0 – 10 cm deep. The part samples were mixed and cleared of gross impurities (stones, roots, leaf, etc.). Amount of non-polar extractable substances was determined, result was negative (the NES amount was less than legislative limit for the risk substances in the agricultural soils 0.1 mg.kg^{-1})[17].

The model sample of surface water was taken from the natural resource – Kováčová creek. The NES amount was determined with negative result (amount of NES was less than legislative limit for the qualitative requests of surface water 0.1 mg.dm^{-3})[18].

The soil and water samples were contaminated by commonly used diesel fuel and engine oil WD 40. Some of chemical and physical properties are in the table 2.

Table 2: Physical and chemical properties of used oil products[22,23]

	Diesel fuel	**Engine oil**
State	Liquid	Liquid
Colour	Clear, colourless to yellowish	Amber
Odour	Specific	Weak
Density (g.cm^{-3})	0.820 – 0.845 at 15 °C	0.840 at 15 °C
Kinematic viscosity	2 – 4.5 mm^2.s^{-1} at 20 °C	69.9 mm^2.s^{-1} at 40 °C

Simulation of Oil Products Contamination and Disposal of Oil Products

The soil samples were situated in the plastic containers 10 x 10 cm. Samples were contaminated with diesel fuel or with engine oil. The concentration of oil products was 10 g on the surface 100 cm^2. The top of the soil was equally covered with sorbents EXPERLIT or CANSORB. The sorbent treatment of fuel contaminated soil lasted 3 min and to oil contaminated soil 10 min. Sorbents were removed out of samples after treatment and prepared to safe waste liquidation. The top part of the soil was laboratory processed, analysed by IR spectrophotometry and amount of NES was determined.

1 litre of surface water was situated in the glass container 25 x 15 x 15 cm and contaminated with 1, 5 or 10 g of oil product. The process of disposal of oil contamination was modified according to ASTM F 726 – 2006[24]. The bottom of contaminated samples was covered by coherent layer of sorbent VAPEX. The sorbent treatment of fuel contaminated water lasted 3 min and of oil contaminated water 10 min. Sorbents were removed out of samples after treatment and prepared to safe waste liquidation. Water samples were laboratory processed, analysed by IR spectrophotometry and amount of NES was determined.

Determination of Non-polar Extractable Substances

NES was determined spectrophotometrically in infrared sphere of spectrum in compliance with STN 8300530-36.[25] The method is based on extraction of petroleum substances from acidified sample using the solvent S-316 (polychlorotrifluoroethylene $(\text{-SF}_2\text{-CFCl-})_n$). Consequently the extract was dewatered by adding 5 g of anhydrous sodium sulphate (calcined before) for a period of 30 minutes. The rest of polar substances was removed by the adsorption on silica gel (silica gel for chromatography, dried and activated at 150 °C for 4 hours). The IR spectrum of samples was measured in the sphere from 3,150 cm^{-1} to 2,750 cm^{-1} after calibration and evaluation of NES using the software. We used the FTIR spectrophotometer ATI MATSON GENESIS. The measurement was performed in comparison with blank determination (use of solvent instead of sample, the procedure remains the same)[24].

Results and Discussion

There was a leak of oil products by accidents simulated in the laboratory experiment. Samples of surface water and soil were contaminated by diesel fuel and engine oil. There was amount of non-polar extractable substances in the samples after various sorbent treatment determined.

Cleaning of Soil Contamination

The experiment of soil samples cleaning was realized with two contaminants and two sorbents, each in three repeating. As a characteristic of oil contamination was amount of NES determined. The results are in the Table 3.

Table 3: Determined NES amount in the soil samples after sorbent treatment

Contaminant	Sorbent	Amount of NES after contamination ($mg.kg^{-1}$)	Amount of NES after clean up ($mg.kg^{-1}$)
Engine oil	EXPERLIT	8,450	0.318
	CANSORB	7,982	11.64
Diesel fuel	EXPERLIT	6,760	12.12
	CANSORB	6,905	18.96

The lowest amount of NES was determined after adsorption of engine oil by sorbent EXPERLIT (0.318 $mg.kg^{-1}$). EXPERLIT shows better results also for adsorption of diesel fuel (amount of NES increased from 6,760 to 12.12 $mg.kg^{-1}$).

According to the results it is possible predicate, that the most effective for sorption of petroleum compounds is EXPERLIT (expanded perlite), where results of both of contaminants were lower than in the case CANSORB. Advantage of organic fibrous adsorbents could be possibility its using on hard surfaces according to Veľková and Bubeníková[26], where CANSORB proved best results comparing EXPERLIT and JOSYP PLUS and its reusability according to research of Lim and Huang[27], who showed that natural fibrous materials can be several times reused with less than 30 % sorption capacity loss after 4 cycles.

Legislative limit[16] for amount of NES in agricultural soil is 0.10 $mg.kg^{-1}$. Despite the fact, that the effectivity of removing of petroleum compounds for both sorbents is more than 99%, amount of NES in all samples of soil is higher than legislative limit. According to the results it is obviously, that the soil cleaning from oil pollution after an accident using tested sorbents is quite good, but this soil is insufficient for its use in agriculture. When is estimated risk of contaminants impacts, chemical methods should be supplemented with biological and toxicological tests[28].

Cleaning of Water Contamination

The samples of surface water (1 litre) were contaminated with diesel fuel and engine oil in amount of 1 g, 5 g and 10 g. The layer of petroleum substance was built on the bottom of water. The oil film was stronger after application of engine oil. On the oil substances was applicated sorbent VAPEX in the way to cover entire bottom of water level, which treated on oil substance. Contaminated sorbent was removed after 3 (diesel fuel) or 10 min (engine oil) and the amount of NES was determined in the water samples. The results are in the Table 4.

Table 4: Determined NES amount in the water samples after sorbent treatment

Contaminant	Sorbent	Added amount of contaminant (g.L^{-1})	Amount of NES after contamination (mg.L^{-1})	Amount of NES after clean up (mg.L^{-1})
Engine oil	VAPEX	1	795	0.474
		5	3,980	3.569
		10	9,152	19.77
Diesel fuel		1	680	17.55
		5	4,370	24.13
		10	8,525	25.84

The comparison of the determined amounts of NES in “cleaned” water samples with legislative limits[17] demonstrate, that all water samples were still contaminated. The highest amount of NES was determined in the sample contaminated with diesel fuel (contamination with 10 g.L^{-1}). Amount of NES was in all samples higher than 0.1 mg.L^{-1}, what according to research of Hybská et al.[29,30] could lead to toxicological treat of aquatic organisms in the first step and cummulation of oil substances in other environment components.

Experiments have demonstrated higher effectivity of adsorption of engine oil on VAPEX than adsorption of diesel fuel. This is probably caused due to different viscosity of these petroleum products and affinity of VAPEX to diesel fuel is lower than the affinity to more viscous engine oil. Nevertheless, for Fire and Rescue Services VAPEX represents the best alternative of sorptive materials compared to other sorbents, thanks its sorptive capacity, its form, volume, good manipulation and reaction time and other sorbent kinds are used only like ancillary material[16,31].

Conclusions

Based on the results found experimentally in this work, we can say:

1. Soil: the single use of one sorbent does not remove the entire pollution from the surface, nor in one case the content of oil substances determined as NES has not fulfilled the legislative limit.
2. Water: determination of the NES like indicator after removal of engine oil pollution has resulted in a pronounced sorption capacity at a concentration of 1 and 5 g; in other cases the NES amount was significantly higher; the amount of NES exceeded the legislative limit.

Determined results have shown that it is very important focusing on research of new sorbents with high sorption capacity, hydrophobicity, low retention time, universal usage, reusing ability to reach higher level of decontamination.

Acknowledgement

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Účinok vybraných sorbentov pri odstraňovaní ropných látok

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Súhrn

Cieľom práce bolo testovanie účinku vybraných sorpčných materiálov používaných Hasičským a záchranným zborom pri odstraňovaní ropného znečistenia pri riešení nehôd. Po ukončení dekontaminačného procesu sa zdajú byť dané zložky životného prostredia vizuálne čisté, no je dôležité vedieť, či sú tieto matrice naozaj bezpečné aj z toxikologického a ekotoxikologického pohľadu.

V práci boli pripravené modelové vzorky pôdy a povrchovej vody, ktoré boli kontaminované a následne dekontaminované rôznymi sorbentmi. Sledovalo sa ropné znečistenie, charakterizované množstvom nepolárnych extrahovateľných látok stanoveným vo vzorkách pred a po čistení. Testované boli dva druhy ropných produktov (nafta a motorový olej WD 40) a tri druhy sorbentov (organický vláknitý materiál – CANSORB, minerálny hydrofilný sorbent – EXPERLIT a minerálny hydrofóbny – VAPEX). Účinnosť odstránenia ropného znečistenia z pôdy bola síce viac ako 99 %, ale množstvo NEL bolo vo všetkých vzorkách stanovené vyššie ako povolený limit. Podobné výsledky boli dosiahnuté aj pri testovaných vzorkách povrchovej vody, kde vo všetkých vzorkách bola prekročená povolená hodnota NEL. Na základe výsledkov môžeme tvrdiť, že sorpčné procesy dekontaminácie pri haváriách odstránia ropné znečistenie v pomerne dobrej miere, no bolo by vhodné následne použiť hlbšie remediačné postupy, aby nedochádzalo k nežiadúcim účinkom ropných látok na životné prostredie.

Keywords*: ropné znečistenie, pôda, povrchová voda, sorbenty, nepolárne extrahovateľné látky (NEL)*

Characterization of nanofiltration membrane and its practical use for separation of zinc from wastewater

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Abstract

The focus of this work is to examine the ability of a commercially available nanofiltration membrane (AFC 30) for the separation of toxic zinc sulphate from wastewater to meet the maximum contaminant level set by government regulation of countries established. In this study, two independent pore models (Donnan Steric Pore model – DSP model, and Steric Hindrance Pore model – SHP model) together with experiments with neutral solutes at various process conditions have been used. A very good agreement was found using the DSP and SHP model, which fit well with the experimental values of different neutral solutes examined. The outcome indicates that the two independent models could be used to predict and interpret the structural properties of nanofiltration (NF) membrane.

The influence of the operating variables such as feed solution concentration applied transmembrane pressure, and pH on zinc separation was studied. It has been found that metal rejection increases slightly with increasing of feed concentration in the tested range of 50 – 200 mg Zn/L. A similar trend was observed with the impact of a pressure difference. The maximum value of zinc rejection was 99.3 % for all feed concentrations. The minimum rejection was at a pressure of 5 bars and for the lowest concentration (50 mg Zn/L) was almost 98 %. In addition, rejections of zinc were very high for all pH tested (5.3 – 6.5). The results obtained show that the tested commercially available nanofiltration membrane (AFC 30) is suitable for the separation of zinc from wastewater.

***Keywords:** Nanofiltration, heavy metal, polyamide membrane, rejection, modelling*

Introduction

Nanofiltration (NF) membranes had made tremendous progress since its introduction during the late 1980s. The properties intermediate between reverse osmosis (RO) and ultrafiltration (UF). NF membranes have been used in many applications particularly in wastewater treatment as well as drinking water and process water production. The interest in the use of NF membrane can be explained by a combination of (1) growing demand for water with high quality, (2) pressure to reuse water due to rapid growing population globally (3) better dependability and integrity of the membranes (4) lower cost of membranes due to improved use and (5) more stringent water standards [1,2]. As nanofiltration application market is currently growing at a faster pace due to the rapid development in technologies, an estimation of global sales will reach $450 million by 2019 [3]. Moreover, the nanofiltration membrane has specific advantages over reverse osmosis, which makes the separation mechanism attractive. These are less energy consumption, lower operating pressure than RO, higher flux in comparison with RO, inexpensive compared to reverse osmosis and monovalent ions partly passes through the membrane whiles multivalent ions are rejected to a certain degree determined by the feed stream [4].

Characterization of NF membrane structure has a long-time history and is important to understand the fundamental principle of the separation mechanism of the process. The structural properties refer to the pore radius (r_p) and membrane thickness to porosity ratio ($\Delta x/A_k$) [5]. Over the past decades, direct measurement methods were used to characterize membrane and have several setbacks. For instance, atomic force microscopy (AFM) is used for direct measurement of the structural properties but does not give a precise reading of NF membrane. This is because it has high roughness, which may result in images that are difficult to understand and high forces that may damage the polymeric structure. In addition, the pores are very small in nature and the images of the membrane surface cannot give enough information about the structure of the pores inside the membrane[6]. There are various characteristic techniques available for NF membrane and the key is choosing the right technique, with the right resolution to have the desired result[7]. Numerous models have been employed for the prediction and performance of NF membrane due to the separation mechanism. These models are used to describe and predict flux as well as retention at different operating conditions of both uncharged and charge species by NF membrane. The mathematical models are usually divided into several classes, which are irreversible thermodynamic (IT) model, pore models and non-porous or homogeneous models[8]. A generally known method used to determine the characterization of the membrane is to carry out rejection experiments of neutral solutes and then using different mathematical models. Several authors have achieved successful studies using the rejection of inorganic solutes together with mathematical models[9-12].

Toxic heavy metals of critical concerns found in wastewater are cadmium, chromium, nickel, copper, lead, arsenic, mercury and zinc. Heavy metals are usually found in wastewater from fuel industry, petroleum refining, mining, textile industry, fertilizer plants, battery manufacturing, paper industries, photographic process industry, automotive and electroplating[13]. Proper separation of heavy metal is necessary before discharging into the environment since is highly toxic, non-biodegradable and have the tendency to accumulate in living organism[14]. Nowadays, it has become crucial that regulatory measures need to be set up on the effluent limit globally as the industries realize its potential environmental impacts[15]. Apart from the environment, heavy metal beyond its permissible level poses a threat to humans as is accumulated in the body through the channel of a food chain. Such health disorders can be diseases of the kidney, damage of the fatal brain, hypertension, renal repairment, toxicity to the reproductive organs, mental retardation and many more[16,17].

The aim of this work is to investigate a commercial thin-film composite polyamide AFC 30 nanofiltration membrane. The structural characteristics of the membrane that is the effective pore radius (r_p) and thickness over porosity ratio ($\Delta x/A_k$) were determined from neutral solutes rejection. This was done by using two independent mathematical models such as Donnan Steric Pore (DSP) and Steric Hindrance Pore (SHP) to evaluate the structural parameters. The influence of the operating conditions such as applied pressure feed solution concentration, and pH to remove ions was estimated. Carrying out experimental works on these operating parameters was necessary to predict the extent of zinc that can be concentrated in the retentate.

Materials

NF tubular membrane (AFC 30) from PCI membrane system was used in this experiment. These are thin film composite membranes consisting of aromatic polyamide skin-layer on polysulfone substrate. All the reagents used were of analytical reagent grade and supplied by Penta Co., the Czech Republic. The aqueous solution was prepared by dissolving the reagents, which are zinc sulphate ($ZnSO_4$), glycerol, TEG, and glucose. Neutral solutes diffusivities and stoke radius can be found in Table 1. The solutions were prepared by dissolving the reagents in highly demineralised water (conductivity< 1 μS/cm), pH (6.0 ± 0.2).

Table 1: Diffusivities and Stokes radius of neutral solutes

Solutes	**Molecular weight** g/mol	**Diffusivity** 10^{-10} m^2/s	**Stokes radius** nm
Glycerol	92.1	9.50	0.258
TEG	150.2	7.31	0.336
Glucose	180.2	6.70	0.355

Experimental set-up and procedure

The cross-flow separation unit used in our experiment was previously published in an article [13]. The experiment temperature of the feed solution was at a constant value of 25 ± 0.5 °C by using the heat exchanger and transmembrane pressure varies in a range of 5 – 30 bars. The pure water fluxes measured at various transmembrane pressures at the same range and the membrane pure water permeability was calculated. The value obtained for pure water permeability (L_p) membrane (AFC 30) was 5.84 L/m^2 h bar at 25 ± 0.5 °C. The NF experiments were performed in total recycle mode, both permeate and retentate returned to the feed tank to maintain a constant concentration in feed. The permeate flux was determined by weighing using an electronic balance connected to a personal computer, and samples of permeate and feed were collected at each transmembrane pressure. The structural parameters of the membrane that are the effective pore radius (r_p) and membrane thickness to porosity ratio ($\Delta x/A_k$) were evaluated from the neutral solutes rejection values. The experiments were performed using 500 mg/L solutions of glycerol, glucose, and triethylene glycol (TEG) at natural pH demineralized water (6.0 ± 0.2). The neutral solutes concentration in feed and permeate was determined by the total organic carbon (TOC) technique.

Synthetic zinc polluted wastewater was prepared by adding the required amount of $ZnSO_4$ to the highly demineralized water. The pH value of the feed solutions was measured using pH meter (HI 9126 pH-meter, Hanna Instrument) then adjusted with H_2SO_4. Several experiments were performed to measure the rejection of zinc during a total circulation mode at different applied pressures, feed concentrations, feed flow velocities and pH. In NF experiment, both permeate and retentate was returned to the feed tank to maintain a constant concentration in feed. Feed and permeate samples were collected at different pressure after recirculation until the process attained a steady state. The constant composition of permeate which corresponds to the steady state was obtained by attaining a constant conductivity value in the permeate solution. By analyzing the concentration in both the feed and permeate, the transport parameters (permeate flux and observed rejections) were calculated from the experimental data.

The permeate flux was measured by weighing using an electronic balance which is connected to a personal computer. The values of the fluxes are automatically calculated by software and recorded. To assure reproducibility of the results, the experiments were performed in duplicate. The results obtained represented an average of two identical experiments; the relative standard deviation was up to 5 %.

Theory

Concentration polarization phenomena

By analyzing the solute concentration (zinc ions) in the feed side (C_f) and permeate (C_p), the observed rejection can be calculated from the following equation

$$R_o = 1 - \frac{C_p}{C_f} \tag{1}$$

The real (intrinsic) rejection is derived from the film model when taking effect of the concentration polarization and is as follows [6]

$$R = 1 - \frac{C_p}{C_m} = \frac{R_o exp\left(\frac{J}{k}\right)}{1 - R_o\left[1 - exp\left(\frac{J}{k}\right)\right]} \tag{2}$$

where C_m is the concentration of solute in the feed solution at the membrane surface (vicinity), J is the permeate volume flux and k is the mass transfer coefficient in the polarization layer which can be calculated from the well-known Sherwood relationship with Deissler correlation [18].

$$Sh = 0.023\, Re^{0.875}\, Sc^{0.25} \tag{3}$$

The Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers in equations are given by

$$Re = \frac{u\rho d_h}{\eta} \qquad Sc = \frac{\eta}{\rho D_{i,\infty}} \quad \text{and} \quad Sh = \frac{k d_h}{D_{i,\infty}} \tag{4}$$

where *u* is the fluid velocity in the channel whose hydraulic diameter is d_h (the diameter of the tubular membrane in our case), $D_{i,\infty}$is the diffusion coefficient of solute *i*, η and ρ are the dynamic viscosity and density of the aqueous solution, respectively.

The salt diffusion coefficient (D) was computed based on the diffusion coefficient (D_+, D_-) and valences (z_+, z_-) of the individual ions (cation and anions) by using the following equation [19].

$$D = \frac{(z_+ - z_-)D_+D_-}{z_+D_+ - z_-D_-} \tag{5}$$

Characterization of a membrane by using neutral solutes rejection

Donnan Steric Partitioning (DSP) model

Bowen et al. [20] originally developed the Donnan steric partitioning model based on the extended Nernst Planck equation. The NF membrane was modelled by considering the membrane as a bundle of slits with length and a half width. The structural properties, which are the effective pore size (r_p) as well as membrane thickness to porosity ratio ($\Delta x/A_k$) were estimated through independent experiments with neutral solutes rejections by considering slit-like pore geometry. In the NF membrane, rejection of neutral solutes can only be determined by a steric mechanism (size-based exclusion). The pore radius can be found by fitting the rejection using the following equation [20,21]

$$R = 1 - \frac{C_p}{C_m} = 1 - \frac{\phi_i K_{i,c}}{1 - [(1 - \phi_i\, K_{i,c})\exp(-Pe)]} \tag{6}$$

where C_p is the solute concentration in permeate, C_m is the solute concentration in feed solution at the membrane interface, $\phi_i = 1 - \lambda_i$ which is the steric partitioning coefficient of the solute *i*, and λ_i is defined as the ratio of the solute radius (r_s) to pore radius (r_p). $K_{i,c}$ and $K_{i,d}$ are the hindrance factors for convection and diffusion.

The Peclet number (*Pe*) is defined by the expression

$$Pe = \frac{K_{i,c}J}{K_{i,d}D_{i,\infty}}\,\frac{\Delta x}{A_k} \tag{7}$$

where A_k is the membrane porosity and Δx is the effective membrane thickness.

The hindrance factors for convention and diffusion (slit-like pores) can be evaluated by the following equations [22]

$$K_{i,c} = \frac{1 - 3.02\,\lambda i^2 + 5.776\,\lambda i^3 - 12.3675\,\lambda i^4 + 18.9775\,\lambda i^5 + 15.21185\,\lambda i^6 - 4.8525\,\lambda i^7}{\phi_i} \tag{8}$$

$$K_{i,d} = \frac{1 + 1.125\lambda i \ln \lambda i - 1.19358\,\lambda i + 0.4285\,\lambda i^3 - 0.3192\,\lambda i^4 + 0.08428\,\lambda i^5}{\phi_i} \tag{9}$$

Also, the Hagen–Poiseuille equation was used to determine the thickness of porosity ratio from the water flux and is as follows for slit-like pores

$$J_w = L_p\Delta P = \frac{{r_p}^2}{3\eta(\Delta x/A_k)}\,\Delta P \tag{10}$$

where J_w is the pure water flux, L_p is the pure water permeability, ΔP is the transmembrane pressure and η is the solution viscosity.

Steric Hindrance Pore (SHP) model

Transport phenomena of single solute and solvent in both NF and RO processes can be described as a well-known irreversible thermodynamic (IT) model. Kedem and Katchalsky derived transport equations for the volume flux (J_v) and solute flux (J_s) as follows [23].

$$J_v = L_p(\Delta P - \sigma.\Delta\pi) \tag{11}$$

$$J_s = P\left(C_m - C_p\right) + (1-\sigma).J_v C_s \tag{12}$$

where σ, P and L_p are the reflection coefficient, solute permeability, and water permeability respectively. The Spiegler - Kedem model is used when there exists the high concentration difference between the retentate and the permeate [24]. This can be expressed in a differential form as follow

$$J_s = -P\frac{dC_i}{dx} + (1-\sigma)\,C_i J_v \tag{13}$$

Assuming constant fluxes and constant coefficients, Eq. (13) is integrated through the membrane thickness. The real retention can be calculated by the following equation;

$$R = 1 - \frac{C_p}{C_m} = \frac{\sigma\,(1-F)}{1-\sigma F} \qquad where\ F = \exp\left(-\frac{1-\sigma}{P}\,.\,J_v\right) \tag{14}$$

Eq. (14) is the Spiegler - Kedem equation, which describes the solute retention with solvent volumetric flux and the solute permeability. This model assumes the membrane as a black box and gives no information about the transport mechanism. Several models have been introduced to interpret σ and P to estimate the structural and electrical properties of the membrane.

By using a single neutral solute and NF membrane, σ and P can be determined by the SHP model. Nakao and Kimura [25] proposed the steric hindrance pore (SHP) model that was modified from the pore model.

$$\sigma = 1 - (1 + \frac{16}{9}\,\lambda^2)\,(1-\lambda)^2\,[2 - (1-\lambda)^2] \tag{15}$$

$$P = D_s\,(1-\lambda)^2\,(A_k\,/\Delta_x) \tag{16}$$

Results and discussion

The NF experiments for evaluation of structural parameters were performed with the same concentration of 500 mg/L of neutral solutes. The pure water flux and the fluxes of the solutions used against the pressure difference are shown in Figure 1. Data from Fig. 1 indicate that the measured permeate flux as a function of the pressure difference for the neutral solutes used is similar to the flux of pure water irrespective of the solutes. It has been observed that the flux linearly increases with an increased pressure difference of membrane being considered. The water permeability is the slope of the line. This shows that the osmotic pressure of the solution is negligible and the variations of typical properties (density and viscosity) can be omitted due to low feed concentrations. It was observed (see Figure 2) that the two independent models fit well with the experimental results of all the neutral solutes tested.

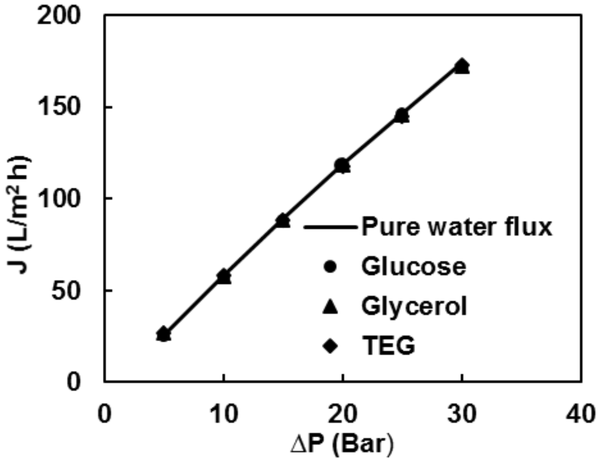

Figure 1: Permeate flux against pressure differences of neutral solutes (pure water flux - solid line, and neutral solutes - symbols)

Donnan Steric Partitioning (DSP) Model

By incorporating the expression for the thickness-to-porosity ratio into the Peclet number equation, a new expression is obtained for real rejection, depending only on the pore radius. By fitting the experimental retention value for different pressures with the real rejection from the model, the pore radius (r_p) can then be estimated. This is followed by the corresponding values for the membrane thickness to porosity ratio which is calculated from Eq. (5) and presented in Table 2. Since ($\Delta x/A_k$) is the parameter of the active layer, the application of these equations means that the pressure drop is negligible through the microporous sublayer, implying that the transmembrane pressure drop can be attributed to the active layer, which is an assumption made in most literature [26].

Steric Hindrance Pore (SHP) Model

The structural properties (r_p and $\Delta x/A_k$) were determined by using the following steps. First, the real rejection against the volume flux was used to estimate the membrane parameters (σ and P) by the χ^2-test method to get the best fit using the Spiegler - Kedem model found in Eq. (14). The membrane (AFC 30) values of the parameters can be found in Table 2. Then using Eq. (15) which was based on SHP model [25] and error function method, λ of each neutral solute is determined. Since λ is the ratio of the solute radius (r_s) to pore radius (r_p), and the solute radius is known, the pore radius of each neutral solutes can be evaluated. Furthermore, membrane porosity ($\Delta x/A_k$) of each neutral solute was calculated using Eq. (16) since, P, D_s are known.

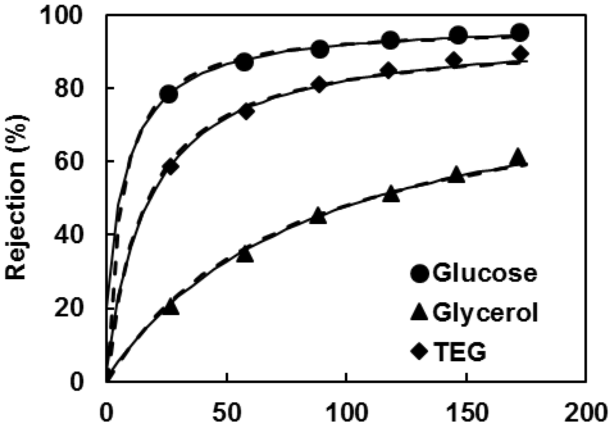

Figure 2: Rejection of neutral solutes as a function of permeate flux for AFC 30 membrane using two independent models (real rejection - symbols, DSPM - full lines, and SHP - dashed lines)

Table 2: Estimation of structural properties of NF membrane using two independent pore models

Membrane	**Solutes**	**DSP model** (Slit-like)		**SHP model**			
		r_p nm	$\Delta x/A_k$ µm	σ (-)	P 10^{-6} m/s	r_p nm	$\Delta x/A_k$ µm
AFC 30	Glycerol	0.316	2.31	0.774	19.50	0.342	2.94
	TEG	0.365	3.08	0.915	4.20	0.389	3.21
	Glucose	0.355	3.18	0.950	1.64	0.392	3.65
Average		**0.345**	**2.86**			**0.374**	**3.27**

From Table 2, the pore radius of AFC 30 membrane using two independent models was almost the same. Selection of neutral solutes for the determination the pore radius is important when considering the molecular weight of each solute. The SHP is not a good model for solutes with reflection coefficient very close to unity or highly restricted permeation. For instance, lactose has a high rejection close to unity and this model is not useful for this solute [25].

Operating parameters for heavy metals separation

To select the optimum operating parameters for the NF membrane, it is advisable to change operating conditions such as applied pressure, feed concentration, and pH. This is a useful technique used to investigate the transfer of solute Zn (II) ions as well as the separation properties of the membranes. Therefore, performing experimental works on these operating parameters is important to predict the extent of heavy metals that can be concentrated in the retentate.

Influence of applied pressure

For a better understanding of NF membrane process, the influence of different applied pressure and feed concentration on the rejection of Zn (II) ions was investigated. This was done by carrying out retention experiments with pressure difference (5 – 30 bar) over a wide concentration (50 – 200 mg Zn/L) with constant cross-flow velocity of 1.25 m/s. When operating pressures are below 20 bar, the observed rejection continuously increases with increasing pressures for all solute concentrations to reach maximum, and then start to decrease gradually. The increase in operating pressure differences increases the real rejection of all feed concentrations used as seen in Fig. 3. As observed in Fig. 3, the maximum real rejection of zinc ions was 99.3 % irrespective of the concentration range (50 – 200 mg Zn/L). At an even low pressure of 5 bar, the real rejection was greater than 97 % which indicates the membrane has a good separation property.

The separation of ions at different operating pressure condition can be explained by two phenomena. Firstly, an increase in transmembrane pressure leads to increasing of solvent flux conversely the transport of solute in the membrane is hindered by steric and charge effect. Hence, the higher flux, which leads to an increase in solute rejection, was because of permeate dilution. Secondly, an increase in the transport of the solute to the vicinity of the membrane surface is due to an increase in applied pressure, which increases concentration polarization. This, in turn, leads to a decrease in solute rejection by decreasing the charge effect [27]. The first effect leads to zinc separation of AFC 30 membrane at low applied pressure up to 20 bar, whiles the second effect occurs when the applied pressure is above 20 bar as depicted in Fig. 3, respectively. However, the metal rejection has high value, which slowly increases with increasing of applied pressure. The transport of metal by the membrane is sterically hindered. Similar studies on the difference of rejection with operating pressure have been reported by several authors [13,28,29].

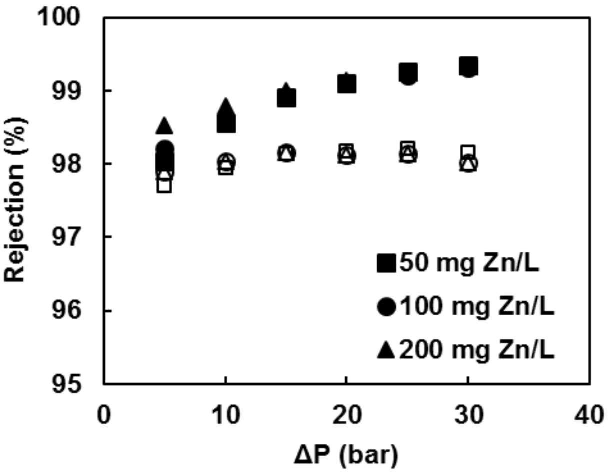

Figure 3: Rejection of zinc sulphate (AFC 30 membrane) against operating pressure with different feed concentrations (observed rejections-empty symbols, real rejection-full symbols)

Influence of feed concentration

The rejection performance of the AFC 30 membrane in the feed concentration range can be seen in Figure 4. It can be observed that the rejection is improved when the feed concentration is increased. However, at high concentration, the rejection starts to decrease due to concentration polarization and the shielding of the membrane charged. Comparable results were obtained by several authors [4,13,27-32]. Gherasim and Mikulášek [13] explained that the decrease in lead rejection when increasing the feed concentration could be mainly by the reduced solvent transport due to the increase in osmotic effects. Paugham et al. [32] attributed the decrease of nitrate retention to the characteristics of the charged membrane, which is by the shielding phenomenon. This involves increasing formation by the cations of the screen, which gradually neutralises the negative of the membrane. In addition, the retention increases at low concentration because the screen effect is very weak with the repulsion of anions playing a significant role in the process. Bouranene et al. [28] reported that the decrease of the rejection when increasing the lead and cobalt concentration of AFC 30 membrane was not strongly influenced by the ionic concentration but was mainly steric hindered.

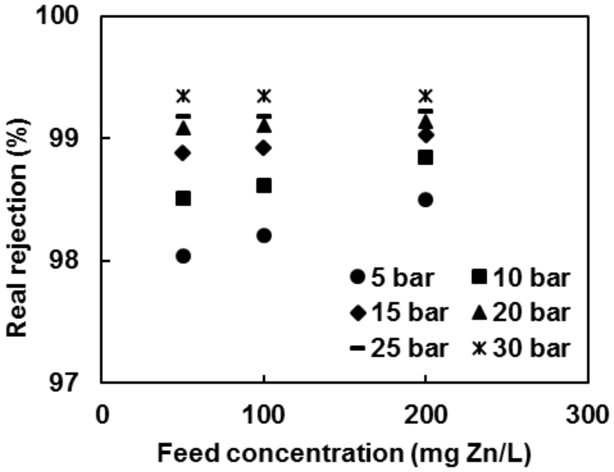

Figure 4: Effect of feed concentration on real rejection (zinc sulphate) by AFC 30 membrane

Influence of pH

One of the important parameters of the NF membrane is the pH of the solution. The pH of the feed influences the membrane charge and then the rejection properties of the NF membrane. The type of chemical structure of the membrane material determines membrane charge. Change of charge is due to dissociations of the functional group of the membrane material, or adsorption of charge polarizable solutes (cation or anions) from the solution [13]. AFC 30 membrane used has a polyamide top layer and amphoteric character. The partial hydrolysis of polyamide leads to the formation of ammonium ($-NH_3^+$) and carboxyl (-COOH) groups. The isoelectric point of AFC 30 membrane is at a pH of about 5.3 in KCl solution [28]. If the pH < IEP the membrane is positively charged as the carboxyl groups are undissociated and the amino groups are protonated. Moreover, a membrane is negatively charged at pH > IEP as the carboxyl groups are dissociated [4].

The influence of pH was considered for feed solution of 50 mg Zn/L with pH adjusted by H_2SO_4. From our result obtained (see Table 3), it was observed that rejection of zinc ion of AFC 30 membrane was very high for all pH range considered. Rejection slightly increases with increase in pH value. At isoelectric point (Table 3), the membrane is uncharged which makes a solute rejection of 96.8 % at 30 bar. At this pH, the separation is only governed by steric hindrance effect. When the pHs (6.0 and 6.5) are above IEP, the membrane becomes negatively charged which increases the rejection of zinc ions. The maximum rejection of 98.7 % was reached at the highest value of pH at 30 bar. This behaviour could be explained due to electrostatic repulsion that occurs between the negative charge (sulphate) and charged membrane, which in turn increase the rejection rate [33].

Table 3: Observed rejections at different values of pH

	ΔP (bar)		
pH (-)	**10**	**20**	**30**
5.3	95.7	96.5	96.8
6.0	97.8	98.0	98.2
6.5	98.4	98.6	98.7

Conclusions

The membrane (AFC 30) has been characterized by modelling of the respective rejection experiments of different neutral solutes. The two independent models (DSP and SHP) for neutral solutes have been confirmed useful and practical for determining the structural properties—pore radius (r_p) and membrane thickness to porosity ($\Delta x/A_k$). These models' values fit very well with the experimental data of different solutes in our case. The pore radius of DSP and SHP models for AFC 30 were 0.345 nm and 0.374 nm respectively. In addition, the membrane thickness to porosity ratio of DSP and SHP models were 2.86 µm and 3.27 µm. Based on the results, the two independent models can be used to predict and interpret the structural properties of the AFC 30 membrane.

Furthermore, the influence of operating parameters for removal of zinc ion was investigated. It was observed that the increase in operating transmembrane pressure increases observed and real rejection for different feed concentrations. In addition, it was established that the rejection starts to decrease at high concentration due to concentration polarization and shielding phenomenon. The pH of the feed was found to influence the rejection of zinc ions. From IEP to the highest pH, rejections of zinc sulphate were almost steric hindered. Therefore, we can assume that AFC 30 membrane is useful and highly recommended for the removal of zinc from wastewater.

List of symbols

A_k	membrane porosity
C_i	concentration of solute *i*, mol/m^3
C_f	concentration of solute *i* in feed solution, mol/m^3
C_m	concentration of solute *i* in feed solution at membrane surface, mol/m^3
C_p	concentration of solute *i* in permeate solution, mol/m^3
C_s	mean concentration of solute *i*, mol/m^3
$D_{i,\infty}$	bulk diffusivity of solute *i*, m^2/s
d_h	hydraulic diameter, m
J	permeate volume flux, L/m^2 h
J_w	pure water flux, L/m^2 h
K	mass transfer coefficient in polarization layer, m/s
$K_{i,c}$	hindrance factor for convection
$K_{i,d}$	hindrance factor for diffusion
L_p	pure water permeability, m/s Pa
$r_{i,s}$	Stokes radius of component *i*, m
r_p	pore radius, m
Pe	Peclet number
R	real (intrinsic) rejection
R_o	observed rejection
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
u	fluid velocity in channel, m/s

UF	ultrafiltration
NF	nanofiltration
RO	reverse osmosis

Greek symbols

ΔP	transmembrane pressure difference, bar
η	dynamic viscosity, Pa s
ρ	density, kg/m^3
ϕ_i	steric partitioning coefficient of solute *i*
λ_i	ratio of solute *i* radius to pore size

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Charakterizace nanofiltrační membrány a její praktické využití pro separaci zinku z odpadní vody

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Abstrakt

Práce je zaměřena na zjištění schopnosti komerčně dostupné nanofiltrační (NF) membrány (AFC 30) separovat z odpadní vody toxický (nebezpečný) síran zinečnatý s ohledem na maximálně přípustný legislativní limit. V práci jsou použity dva nezávislé modely popisující porézní strukturu membrány (Donnan Steric Pore model – DSP model a Steric Hindrance Pore model – SHP model) společně s experimentálními výsledky separace nenabitých látek při různých pracovních podmínkách. Oba použité modely, DSP a SHP, přesně popsaly experimentálně stanovené rejekce různých nenabitých látek. Z toho lze usuzovat, že oba dva modely lze využít pro popis strukturních parametrů NF membrány.

Byl studován vliv provozních parametrů, jako koncentrace kovu v nástřiku, tlakový rozdíl a pH, na separaci zinku. Bylo zjištěno, že rejekce kovu mírně vzrůstá s jeho rostoucí koncentrací v nástřiku v testovaném rozmezí koncentrací 50 – 200 mg Zn/L. Obdobný trend byl pozorován i u vlivu tlakového rozdílu. Maximální rejekce zinku byla 99,3 %. Minimální rejekce byla při tlaku 5 bar a nejnižší koncentraci (50 mg Zn/L) téměř 98 %. Navíc se získala vysoká rejekce zinku i při všech testovaných hodnotách pH (5,3 – 6,5). Získané výsledky ukazují, že testovaná membrána AFC 30 je vhodná pro separaci zinku z odpadní vody.

Klíčová slova: *Nanofiltrace, těžké kovy, polyamidová membrána, rejekce, modelování.*

Leaching of metals from reclaimed asphalt and their effect on living organisms

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Abstract

The article describes leaching of metals from the reclaimed asphalt (RA) repository under real conditions and laboratory leaching tests of the same material. Ecotoxicy tests have also been carried out to determine the impact of seeping water and RA material leachate on living organisms. The specific sampler was used to collect seeping water samples. Sampling was conducted in two campaigns. Seeping water collected during the first sampling campaign was typical with very high concentrations of Zn and high concentrations of Sb, Ni and Ba. The composition of the sample taken in the second campaign was different. The concentration of Zn was two orders of magnitude lower, Ba concentrations were two times lower, Cr concentrations were nearly four times lower. On the contrary, concentrations of Mn, Ni and Sb were significantly higher in the second sample. Only the concentrations of Cu, Mo, Pb, V and Cd were roughly similar in both samples. The chemical composition of RA material and rainfall were monitored as well. The RA material from the repository contained high concentrations of some metals, especially Mn, Cr, Ba and V. The results of the experiment showed that laboratory material leachate contained very low concentrations of metals while seeping waters contained the same metals in much higher concentrations. Effect of seeping water and RA material leachate on test organisms was small and limit values defined in Czech Regulation no. 387/2016 Coll. for all measured parameters were observed.

Keywords: *Reclaimed Asphalt, Leaching, Metals, Ecotoxicity*

Introduction

The construction of asphalt roads requires a large volume of aggregates used in base and subbase layers as well as in pavement[1]. To reduce costs, recycled materials are used in road construction. One of the frequently used materials is milled asphalt, known as reclaimed asphalt pavement (RAP), which originates in the reconstruction of roads. Other recycled materials used in road construction include building and demolition materials, ash, slag, municipal waste. All these materials must meet health and environmental safety requirements. Potential pollutant occurrence in water in contact with road construction materials can originate from bitumen leaching as organic material derived from petroleum containing different types of hydrocarbons and from the content of many chemicals generated from road traffic during use of the pavement including vehicle exhaust, gasoline, lubricating oils, tires and brake lining wear[2]. The major chemicals typically investigated in relation to road construction materials particularly asphalt pavement are risk elements and heavy metals like Cd, Cr, Cu, Ni, Pb and Zn and polycyclic aromatic hydrocarbons (PAHs)[3,4,2].

In order to verify the possibilities of releasing inorganic and organic substances into water, leaching tests of these materials are carried out. Leaching of volatile organic compounds (VOC), $\mathrm{PAH_S}$ and heavy metals from RAP was described[5]. Another study[6] investigated the leaching of heavy metals and anions from recycled aggregates (asphalt and concrete). The release of major and trace elements from recycled concrete aggregates used in asphalt substrates was described as well[7]. Samples of construction and demolition waste including asphalt were characterized in terms of total content and leaching of inorganic elements and the presence of persistent organic pollutants PCBs and PAHs[8]. The suitability of fly ash (FA), RAP, recycled cement material (RCM) and foundry sand (FS) mixed in with virgin aggregates as base and subbase materials was assessed[1]and the results on inorganic contaminants leaching from six mixtures of FA–RAP aggregates were reported. The most of reported tests in the text above were performed under laboratory conditions.

Experimental part

The aim of this experiment was to assess possible leaching of harmful compounds from RA under the real conditions and comparison with the results of laboratory leaching tests. The design of the experiment was to sample seeping water from the repository where the RA is stored for a limited time and which is prepared for reuse. The composition of RA is an important issue related to the possible reuse of the material in new construction. Therefore, contents of PAHs and metals in RA material, RA material leachate and seeping water were determined. These analyzes were supplemented by ecotoxicity tests that characterize the effect of the material on living organisms. Only the results of inorganic analyzes are presented in this paper. The results of PAHs analyzes were described by Jandová[9].

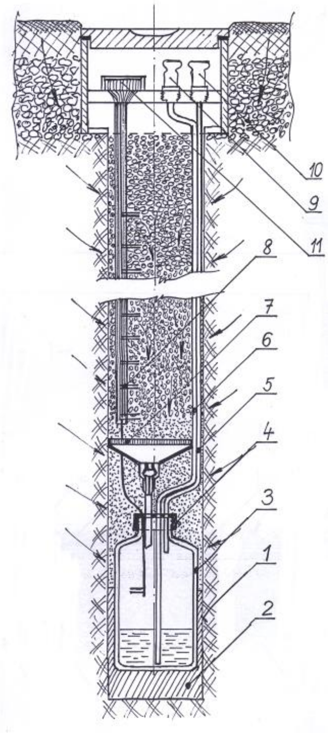
Materials

Repository of RA was chosen as the best environment for characterization of possible leaching of harmful compounds under the real conditions. Selected repository contained milled surface asphalt layer prepared for reuse in road pavement. The repository was 27 m long, 11 m wide and 2.1 m high but these dimensions changed since common activities were carried out on part of the repository. Repository contained milled material from different roads of all types. The most of the material was from 3 localities including highway, 1st class road and 3rd class road. Highway pavement was in operation 3 years and loaded by 13 201 vehicles/24hours including 4 104 heavy duty vehicles. Material from this road was represented by stone mastic asphalt from wearing course (SMA 11S) and very coarse-grained asphalt concrete (ACL 22S) from bed layer. Traffic intensity on the 1st class road was 2 706 vehicles/24hours with 775 heavy duty vehicles and material was medium-grained asphalt concrete from wearing course (ACO 11+) and coarse-grained asphalt concrete form bed layer (ACP 16+). The 3rd class road was loaded by 1 319 vehicles/24hours including 130 heavy duty vehicles and material from this road represented medium-grained asphalt concrete from wearing course (ACO 11) and medium-grained coated aggregates from bed layer (ACP 16+).

Material samples were taken from 18 sites of the repository of which 14 were taken from the part with installed samplers (7 from the lower part, 6 from the middle part, 1 from the upper part of the repository) and 4 from the upper levels in active part of the repository near the location of the samplers. The total weight of the test portion was 15 kg. This pooled sample was divided by quartering procedure into the required amount for each of subsequent test and all aliquot parts of the material were dried in the laboratory under 20 – 23°C and were sieved to contain particles less or equal to 4 mm due to the requirements of standard procedures for subsequent chemical analyses and ecotoxicity tests. Larger particles were discarded which was approx. 62 % of the material grains based on the particle size distribution analysis performed in accordance with ČSN CEN ISO/TS 17892-4[10].

Methods

The specific sampler of seeping water was used to measure possible contamination of seeping water because of leaching of pollutants contained in RA repository. The sampler represents an upgrade of the device referred to in the literature that was used for sampling water from an unsaturated zone by injecting pressure gas[11,12]. The upgrade consisting in simplification of manufacturing and assembly was designed and implemented by Krajča[13]. Special attention during the device development was paid to using inert materials with regard to observed pollutants. Polyvinyl chloride stuffed with milled basalt was used because of high rigidity and smaller adsorption of PAH_s and PCB_s, sampling bottle made of the thick-walled glass and stainless steel for construction of valve under the „square lysimeter“ (filter). The filter consists of three fine–mesh screens with siliceous sand between them with the grain diameter from 1 to 1.5 mm in the upper part and with the grain diameter from 0.5 to 1 mm in the lower part. Glass wool designed for chemical analyses is also below this filter to prevent entering of fine particles to the sample. The amount of collected water is detected with conductivity sensors. The system of sampling bottle, valve and filter need to be reinforced before installation to the bore-hole because of relatively susceptibility for damage. Sampling bottle is put into the plastic tube with plug underneath. Sand is put around the bottle in thickness layer and then the rest of free space was filled with concrete up to the filter. This sampler joins together two different approaches for soil porous water and groundwater sampling, square lysimeter and so-called Gillham principle of pneumatic sampler[14,15]. The function of this sampler can be described as follows. Water seeps from the road surface down and goes through separate layers of pavement and embankment (repository) towards a circular "funnel". Two layers of siliceous sand of different grain sizes are situated there on fine-mesh screens to prevent entrance of mechanical contamination to a sampling bottle where the seeping water is collected. When a sufficient amount of water has been collected in the sampling bottle, a gas (commonly N_2) is pressed into the bottle so as to close the valve under the funnel and water runs into the sampling bottle. A scheme and photographs of the sampler when used within the pavement are shown in Figure 1 and are also presented in[16,9].



1 = bore hole in road pavement and embankment,

2 = cement bed,

3 = sampling bottle (glass),

4 = plug (plastic),

5 = pipe for gas,

6 = pipe for water sample,

7 = sand filter,

8 = conduction sensor,

9 = quick-acting coupling (blue for water),

10 = quick-acting coupling (black for gas),

11 = connector for conduction sensor

Figure 1: Scheme of the seeping water sampler and photograph of the sampling bottle, valve and "area lysimeter"[16,9]

Two pieces of sampler were installed near the edge of the repository without any activity so the mass of the material (1.6 m) above the samplers was not changed (Figure 2). Samplers were installed at the bottom of the repository both in the same level in relation to the slope to characterize the water moving out of the whole repository body. Installation of samplers was carried out as follows. The material from the selected part of the repository was removed by loader and samplers were placed on a revealed surface. Samplers were then slowly covered with the material and quick-acting coupling devices connected with the sampling bottle underneath were placed on the top of the repository.

Figure 2: Repository and installed samplers

The sampling of seeping water was performed in two periods. Time of these periods was not equal because of meteorological conditions especially due to the amount of rainfall. The first sampling period was in summer and lasted from July to August. The second sampling period took place in the fall - September, October. Unfortunately autumn was very dry therefore the second sampling period had to be extended by November, December and half of January.

Amount of rainfall was monitored during the experiment duration. Three samplers for rainfall sampling were used. Two of them were placed next to the repository in distance of 3 m and the third one was placed circa 35 m far from the repository in shadow among the trees to minimize evaporation of rainfall from the sampler. The total amount of rainfall during the sampling periods was calculated on the basis of data received from climatological observatory operated by Czech Hydrometeorological Institute that is situated 1.5 km north of the repository.

The chemical composition of RA material, material leachate, rainfall and seeping water was determined using ICP-MS techniques. For material chemical composition determination, aliquot part of the sample was milled by using the mixer mill, digested by using microwave digestion system in closed teflon containers under high temperature and pressure. Digestion was performed in nitric acid (suprapure). Analysis of digested samples as well as material leachates, rainfall and seeping water were performed in accordance with ČSN EN ISO 17294-2[17]. Material leachate was prepared in the laboratory in accordance with SIS-CEN ISO/TS 21268-1[18].

Set of tests on 4 organisms (freshwater algae *Desmodesmus subspicatus*, higher vascular plant seeds *Sinapis alba*, water arthropod *Daphnia magna* and freshwater fish *Poecilia reticulata*) that represent all trophic levels was provided in case of evaluation of seeping water possible negative effects on living organisms (Table 1). This set of tests is used for evaluation of wastes characteristics and was in accordance with Czech Regulation no. 387/2016 Coll.[19] These ecotoxicity tests were performed in accordance with ISO standards[20,21,22] and Methodological guideline of Ministry of the Environment of the Czech Republic for waste ecotoxicity evaluation[23]. For comparison, the ecotoxicity tests were also directly performed on leachate of RA material.

Table 1: Ecotoxicity tests description

Organism	**Exposition duration**	**Measured parameters**	**Limit value**
Daphnia magna	48 hours	immobilization	Max. 30 %
Desmodesmus subspicatus	72 hours	inhibition/stimulation	Max. 30 %
Poecilia reticulata	96 hours	mortality	Max. 0 %
Sinapis alba	72 hours	inhibition/stimulation	Max. 30 %

Results and discussion

Composition of RA material and RA material leachate

Metals concentrations in RA material (Figure 3) were relatively very high especially of Mn (13 750 mg.kg^{-1}) and Cr (1 110 mg.kg^{-1}) in comparison with other analyzed metals. Also, Ba concentration (348 mg.kg^{-1}) and V concentration (236 mg.kg^{-1}) were quite high. On the contrary, the lowest concentrations were determined for Cd (0.62 mg.kg^{-1}) and Sb (0.08 mg.kg^{-1}). It is also possible to mention concentration of Pb (27.5 mg.kg^{-1}). This metal is dangerous due to negative effects on human health and as inorganic is classified by International Agency for Cancer Research as probably carcinogenic to humans (group 2A).

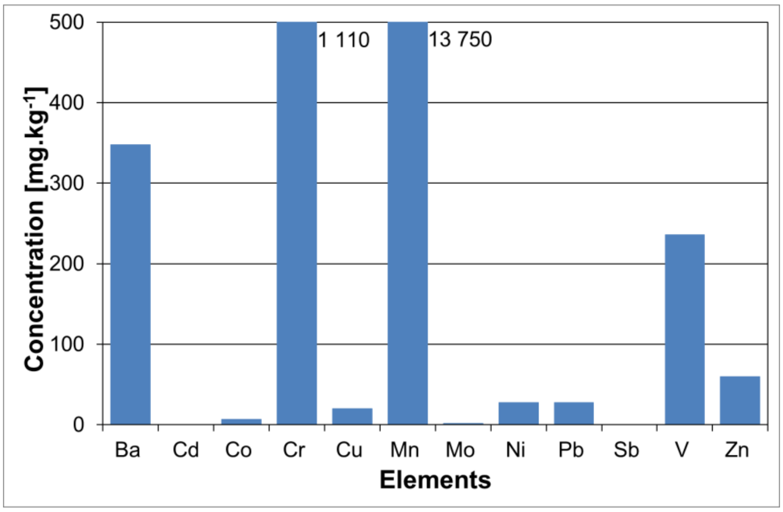


Figure 3: Selected elements content in RA material

In general, concentrations of selected metals in material leachate were relatively low even under the detection limit (Table 2). The highest concentrations were determined for V (21 μg.l^{-1}), Mo (7 μg.l^{-1}) and Ni (6 μg.l^{-1}). On the contrary, concentrations of Cd, Co, Cu, Pb, Zn, Ba and Mn were below the detection limit.

Table 2: Selected elements content in material leachate

Elements	**Concentration [μg.l^{-1}]**	**Elements**	**Concentration [μg.l^{-1}]**
Ba	<10	**Mo**	7
Cd	<0.5	**Ni**	6
Co	<1	**Pb**	<0.5
Cr	1	**Sb**	0.9
Cu	<10	**V**	21
Mn	<1	**Zn**	<10

Rainfall composition

Especially the amount of rainfall was important for the experiment because it determined the amount of water infiltrating the repository and affected the amount of sample of seeping water. Because of wet and colder summer period, the total amount of rainfall during the first sampling period was 288.4 mm. Unfortunately, autumn was very dry therefore the second sampling period had to be extended. The total amount of rainfall during the second sampling period was only 111.6 mm.

The chemical composition of rainfall was also determined to eliminate influx of observed compounds from rainfall for proper characterization of leaching processes in the repository. Most of the selected metals were below the detection limit except for Mn, Ni, Pb and Zn (Table 3) in the sample collected within the first sampling period. Sample collected within the second campaign contained higher concentrations of these metals. Particularly Mn concentration (59 μg.l^{-1} resp. 2 μg.l^{-1}) and Ni concentration (23 μg.l^{-1} resp. 2 μg.l^{-1}) were much higher and also concentration of Zn (58 μg.l^{-1} , resp. 25 μg.l^{-1}) and Pb (2.9 μg.l^{-1} resp. 0.7 μg.l^{-1}) was two resp. three times higher.

Table 3: Mean composition of rainfall during sampling periods

Elements	**Concentration [µg.l^{-1}]**	
	1st sampling period	**2nd sampling period**
Ba	<10	<10
Cd	<0.5	<0.5
Co	<1	<1
Cr	<1	1
Cu	<10	<10
Mn	2	59
Mo	<1	<1
Ni	2	23
Pb	0.7	2.9
Sb	<0.5	<0.5
V	<1	<1
Zn	25	58

Seeping water

The overall time duration of the field experiment was 26 weeks. Two sampling intervals were chosen due to meteorological conditions. It was assumed that water seeps directly down to the samplers so the catchment area was identical with the area of samplers' lysimeter that was 0.0628 m^2. During the first period of the field experiment, 874 ml of seeping water were captured in samplers. The amount of water within this sampling period was not the same in both samplers. There were 620 ml in the sampler located near the peak of the repository and 254 ml in the second sampler placed near the slope of the repository. Both samples were mixed together for subsequent analyses. Only 370 ml of seeping water was sampled during the second period. The amount of water within this sampling period was not again the same in both samplers. There were 260 ml in the sampler located near the peak of the repository and 110 ml in the second sampler placed near the slope of the repository. Both samples were mixed together for subsequent analyses.

Seeping water collected during the first sampling campaign was typical with very high concentrations of Zn (55 000 µg.l^{-1}) and high concentrations of Sb (250 µg.l^{-1}), Ni (195 µg.l^{-1}) and Ba (96 µg.l^{-1}). On the contrary, Cd concentration was under the detection limit. Seeping water from the second campaign contained in many cases different concentrations of elements compared to the first sample. Only concentrations of Cu, Mo, Pb, V and Cd were roughly similar in both samples. Ba concentrations were two times lower (96 µg.l^{-1} resp. 43 µg.l^{-1}), Cr concentrations were nearly four times lower (42 µg.l^{-1} resp. 11 µg.l^{-1}), Zn concentration was order of two magnitudes lower (55 000 µg.l^{-1} resp. 160 µg.l^{-1}). Co concentration was below the detection limit although it was 4 µg.l^{-1} in the sample from the first sampling period. On the contrary, concentrations of many metals were significantly higher in the second sample. Mn concentration (30 µg.l^{-1} resp. 465 µg.l^{-1}) was the order of magnitude higher. Ni concentration (195 µg.l^{-1} resp. 810 µg.l^{-1}) was nearly four times higher. Higher was also concentration of Sb (250 µg.l^{-1} resp. 325 µg.l^{-1}).

Concentrations of several metals were recalculated due to possible input fluxes of these metals in infiltrated rainfall. Particularly Mn concentrations were recalculated in both samples and were lower by 2 µg.l^{-1} in the first sample of seeping water resp. lower by 59 µg.l^{-1} in the second one. Also 25 µg.l^{-1} were deducted from the concentration of Zn in the first sample and 58 µg.l^{-1} in the second sample and Pb concentrations were lower by 0.7 µg.l^{-1} in the first sample of seeping water resp. lower by 2.9 µg.l^{-1} in the second one. Metals concentrations summarized in Figure 4 thereby represent concentrations released from the RA repository material and concentrations in RA material leachate prepared in the laboratory. Figure 4 shows that laboratory material leachate contained very low concentrations of metals while seeping waters contained the same metals in much higher concentrations (some of them up to two orders of magnitude). Only the V concentration is similar in seeping water and material leachate.

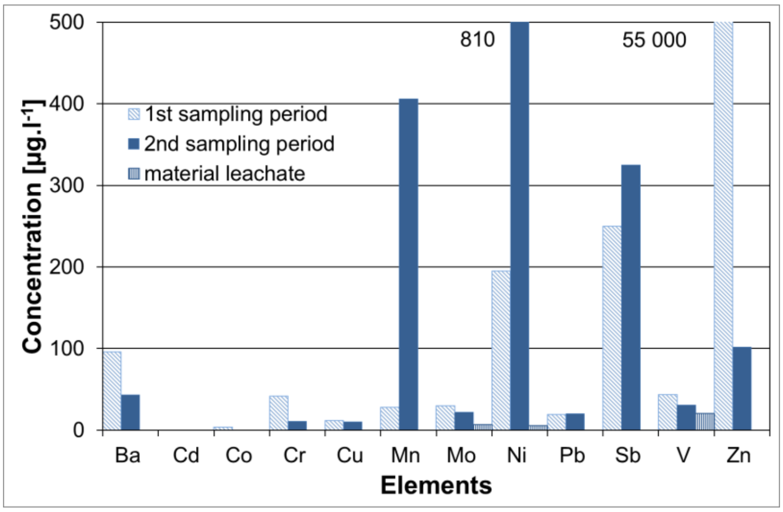


Figure 4: Elements concentration in seeping water (after recalculation to element concentrations in rainfall) and RA material leachate

Ecotoxicity tests

Results of ecotoxicological characterization of seeping water show differences in its effects on living organisms (see Table 4). Because of a very small amount of seeping water from the second sampling period, only sample from the first sampling period was tested. There was no effect on freshwater fish *Poecilia reticulata* mortality, therefore, the limit value was observed (0 % mortality). No effect was also determined on water arthropod *Daphnia magna*. The limit value represented by 30 % immobilization was also observed. Surprisingly, stimulation effect was observed for green algae *Desmodesmus subspicatus* growth (4.15 %) and also for the growth of higher vascular plant *Sinapis alba* seeds. However, limit value for this parameter (30 % inhibition/stimulation) was also observed. Seeping water was thus not dangerous and did not have significant negative effects on the freshwater ecosystem and living organisms. Although the results of the ecotoxicity tests for RA material leachate show slightly higher values for all organisms except fish compared to seeping water (Table 4), the limit values were not exceeded. There was found 10% immobilization of water arthropod *Daphnia magna* for material leachate prepared in the laboratory. Material leachate prepared in the laboratory could be more dangerous for freshwater ecosystems and living organisms compared to seeping water originated due to leaching of compounds from RA material repository under the real conditions although there were found no significant negative effects.

Table 4: Comparison of ecotoxicity test results of seeping water and RA material leachate

Organism	**Exposition**	**Value Seeping water [%]**	**Value RA Materials leachate [%]**	**Remark**	**Limit value [%]**
Daphnia magna	48 hours	0	10	Immobile	Max. 30
Desmodesmus subspicatus	72 hours	4.15	6.11	Stimulation	Max. 30
Poecilia reticulata	96 hours	0	0	Mortality	Max. 0
Sinapis alba	72 hours	3.45	8.06	Stimulation	Max. 30

Conclusions

The results of the experiment showed that RA material from the repository contained high concentrations of some metals, especially Mn, Cr, Ba and V and PAH_s[9]. In general, laboratory material leachate contained very low concentrations of harmful substances. Seeping water contained metals in much higher concentrations (some two orders of magnitude). The rainfall samples monitored during the experiment contained concentrations of most of the monitored elements below the detection limit. Excepted were the increased concentrations of Mn, Ni, Pb and Zn in rainfall, according to which the final values of the elements in the seeping water were recalculated. Seeping water contained high concentrations of Zn, Sb, Ni and Ba in the first test period and high concentrations of Ni, Mn, Sb and Zn in the second test period. As described Jandová[9], PAH_s concentrations in seeping water were higher in the sample from the first sampling period that could be due to their greater release from the "fresh" material at the beginning of the experiment.

The first sample of seeping water was relatively high polluted with selected compounds (metals and PAHs[9]) nevertheless water had almost no negative effects on living organisms. Larger negative effects on living organisms were identified in the material leachate prepared in the laboratory although concentrations of analyzed compounds were much lower. So the leachate could contain "unknown" substances originating during the leaching process in the laboratory that were not analyzed and could occur in high concentrations, responsible for toxic effects on living organisms.

Therefore this study has also demonstrated the benefits of ecotoxicity tests for evaluation of hazardousness of the materials for freshwater ecosystems, and that simple usage of chemical analyses for evaluation of possible effects on freshwater ecosystems could bring misleading information.

The presented experiment shows that in the assessment of the effects of the material used for the construction of roads on the environment is important to assess their water leachates rather than the content of harmful substances in dry matter. The reason is the contact of the material with rainwater or underground water under real conditions, in which hazardous substances are released into the environment. This experiment became the basis for the preparation of a methodology for assessing the impact of the material on the environment, which the team of authors prepares.

Acknowledgment

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Vyluhování kovů z úložiště recyklovaného asfaltu a jejich vliv na živé organismy

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Souhrn

Článek popisuje vyluhování kovů z úložiště recyklovaného asfaltu (R-materiálu) v reálných podmínkách a výsledky laboratorních testů vyluhování tohoto materiálu. Byly také realizovány ekotoxikologické testy pro stanovení dopadu průsakové vody a výluhů R-materiálu na živé organismy. Pro odběr vzorků průsakové vody byl použit specifický vzorkovač. Odběr probíhal ve dvou kampaních. Pro průsakovou vodu odebranou během první kampaně byly typické velmi vysoké koncentrace Zn a vysoké koncentrace Sb, Ni a Ba. Složení vzorku odebraného v druhé kampani bylo jiné. Koncentrace Zn byla o dva řády nižší, koncentrace Ba byla dvakrát nižší, koncentrace Cr byla téměř čtyřikrát nižší. Naopak koncentrace Mn, Ni a Sb byly v druhém vzorku výrazně vyšší. Pouze koncentrace Cu, Mo, Pb, V a Cd byly u obou vzorků přibližně podobné. Bylo sledováno chemické složení R-materiálu a srážkové vody. R-materiál z úložiště obsahoval vysoké koncentrace některých kovů, zejména Mn, Cr, Ba a V. Výsledky experimentu ukázaly, že laboratorní výluhy materiálu obsahovaly velmi nízké koncentrace kovů, zatímco průsakové vody obsahovaly stejné kovy v mnohem vyšších koncentracích. Účinek průsakové vody a výluhu R-materiálu na testované organismy byl malý a byly dodrženy limitní hodnoty pro všechny naměřené parametry.

Klíčová slova: *Recyklovaný asfalt, vyluhování, kovy, ekotoxicita*

Proposal for the combustion method of liquid radioactive ion exchange resins. Case study

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Abstract

Radioactive waste with its hazard to human health and the environment requires precisely defined regulations for handling. The liquid radioactive waste in the nuclear facilities is comprised of ion exchangers that are used for purifying of demineralized water. In case of ion exchangers used in nuclear facilities compared to ion exchangers in ordinary water treatment plants, besides their typical properties of waste, the issue of their radioactivity needs to be addressed in the process of operation and decommissioning. This is also closely associated with the choice of the most suitable technology. The best available disposal technology for ion exchangers from nuclear facilities is their controlled combustion. This paper discusses the properties of ion exchangers, their testing in terms of the input analysis and the design of solutions for the input of liquid ion exchangers into the combustion chamber.

***Key words:** ion exchangers, combustion, liquid radioactive waste*

Introduction

The final shutdown of nuclear facility (NF) operation is followed by the shutdown and final stage of its lifecycle which is safe decommissioning and disposal[1,2]. In accordance with the Slovak Atomic Act, decommissioning of the nuclear facilities is defined as post-closure activities which aim at exempting the nuclear facility from the scope of this Act[3]. The International Atomic Energy Agency (IAEA) defines decommissioning of a NF as „a set of administrative and technological activities leading to the exemption of a nuclear facility, alternatively its parts from the radiation monitoring service of the regulatory body“[4,5]. The process of nuclear facility (NF) decommissioning is challenging from the perspective of time, technical, organizational and economic aspects. For this reason, it is necessary to plan decommissioning activities well ahead and have adequate knowledge of the anticipated amount, type and category of radioactive waste (RAW), environmental releases as well as dose burden to the staff carrying out decommissioning activities and dose burden to the population[6,7].

The generation of radioactive waste varies from country to country depending on the scale of applications and range of activity associated with nuclear and radioactive material utilization in that country[8]. These wastes can affect human health and the environment, so their safe management has received considerable attention worldwide. Classification of these wastes is very helpful throughout their management phases from generation through collection, segregation, treatment, conditioning, storage, transportation to final disposal. Classifications are usually derived from different perspectives, i.e., safety perspective, the physical/chemical characteristics of the waste, process engineering demands or regulatory issues[8,9]. The radioactivity level in the waste affects the selection of its different management options owing to its shielding requirements, so the current internationally accepted classification system is based on the activity level and half-life. This system classifies the radioactive wastes to exempt (EW), low- and intermediate-level wastes (LILW), which may be subdivided into short-lived (LILW-SL) and long-lived (LILW-LL) wastes, and high-level wastes (HLW). Table 1 lists the characteristics of these waste classes [10,11].

Table 1: Radioactive waste classification[11]

Waste classes	Typical characteristics
EW	Activity levels at or below clearance levels, which are based on an annual dose to members of the public of less than 0.01 mSv
LILW	Activity levels above clearance levels] and thermal power below about kW.m^{-3}
LILW-SL	Restricted long lived radionuclide concentrations (limitation of long lived alpha emitting radionuclides to 4,000 Bq.g^{-1} in individual waste packages and to an overall average of 400 Bq.g^{-1} per waste package)
LILW-LL	Long lived radionuclide concentrations exceeding limitations for short lived waste
HLW	Thermal power above 2 kW.m^{-3} and long lived radionuclide concentrations exceeding limitations for short lived waste

Materials from the decommissioning whose excessive level of surface contamination or mass activity does not allow them to be released into the environment or reused at the site of the NF represent RAW which must be safely isolated from the environment through a set of technological processes and procedures[11,12]. The Bohunice RAW Treatment Center comprises a complex of RAW processing and treatment facilities. It treats combustible solid and liquid waste, compressible solid waste, non-combustible and non-compressible waste, concentrates, ion exchange resins (sludge) and other contaminated liquids and sludge. They are processed by a number of treatment facilities:

1. The solid RAW separation facility,
2. The solid RAW high-pressure press,
3. The solid RAW and liquid organic waste incineration facility,
4. The liquid RAW concentration facility,
5. The processing of RAW into fibre-reinforced concrete containers by cementation[13,14].

Ion exchange filters are used for the purification of water from the reactor primary and secondary system, of water from spent fuel storage pools and of condensate from evaporators[15]. Nuclear facilities use mainly organic ion exchangers, the main feature of which is the presence of active moieties on the skeleton of ion exchanger. Prior to ion exchange, liquid RAW is cleaned at mechanical filter and subsequently passed through ion filters, where certain types of radionuclides are effectively captured[16, 17].

Once ion exchange resins have been spent, they need to be further processed and modified to a state which is safe to the environment. Bitumenation and cementation are also suitable for the RAW treatment and fixing the ion exchangers[18]. In terms of waste management hierarchy, waste storage is not considered a progressive method of waste disposal, however the safety aspects of RAW are a priority. Various technologies are nowadays used to capture and fixate radioactivity along with volume reduction. Ideally, controlled combustion seems to be the most appropriate technology and some countries (e.g. Belgium, France, Germany) have relatively extensive experience with it [19].

At present, ion exchangers are burned in a BSC RAO furnace and Slovak Republic has considerable experiences with this technology. The basis of the combustion technology design is the analysis of the input data of the ion exchangers[20]. These representative input data were used to design a new process for dosing the ion exchangers into the furnace.

Experimental part

Under the influence of radioactivity in NF, the ion exchanges are subject to various changes connected in most cases with the reduction of the exchange capacity of the used ion-exchange materials, or even to their complete destruction. They are used in a wide concentration range of the processed substances – from nanogram (or even smaller) amounts of separated elements processed in columns of several cubic centimetres to large quantities of substance in columns or devices having a volume of tens of cubic centimetres. The presence of higher levels of radioactive radiation also results in different working conditions for staff and other measures compared to the treatment of non-radioactive materials.

The consequences of ionizing radiation damage can be summarized in the following points:

- loss of exchange capacity as a consequence of degradation of functional groups,
- formation of new functional groups, especially weak acids (- COOH),
- degradation of the supporting skeleton of organic ion exchangers due to the reduction in molecular weight, thereby increasing the solubility of the ion exchange material, but at the same time causing the opposite, i.e., the free-radical reactions resulting from the destruction of the ion skeleton carbon chains and a higher reinforcement of the supporting skeleton,
- all these changes are reflected in the absorption of ion exchanger,
- in case of degradation of organic ion exchangers, gaseous products are also formed.

Several ion exchangers are used in the ion exchange process, PUROLITE NRW 160, a strongly acidic cation exchange resin, was selected as the representative sample[20]. It is a macroporous polystyrene sulfonate cation exchange resin which is mechanically stable, able to withstand the conditions of considerable stress (thermal and oxidative). The high capacity and ion selectivity of Purolite NRW160 / 4491, in particular for ^{137}Cs, is due to the choice of resin to concentrate these radioactive isotopes prior to disposal (Figure 1). This resin has extremely fast kinetics compared to other macroporous strong acid cation resins. The integrity of beads with good resistance to significant changes in the osmotic pressure and high weight is crucial in order to minimize problems with loss of and decrease in pressure. The resins are expected to provide a minimal pressure drop and limit the flow rate to optimize performance and maximize efficiency[21,22].

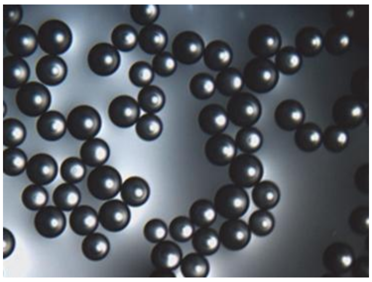

Figure 1: The structure of PUROLITE NRW 160 ion exchange resin

It must be noted that the existing input data from Table 2 were used for the purpose of data processing.

Table 2: Typical physical, chemical and operational properties of PUROLITE NRW 160

Characteristic, property	**Quantitative value**
Polymer structure	Macroporous polystyrene crosslinked with divinylbenzene
Total capacity	2.2 mval.cm^{-3}
Water content	max. 55 %
The proportion of cation exchange in H + form	99,9 %
Grains (size of beads)	425 - 1200 μm
Grain size	max. 0,5 % < 0,3 mm, max. 2 % >1,0 mm
Temperature range H$^+$	120 ^{o}C
Heavy metal levels:	
Fe	max. 50 mg.kg^{-1} of dry ion exchange resin
Cu	max. 20 mg.kg^{-1} of dry ion exchange resin
Pb	max. 20 mg.kg^{-1} of dry ion exchange resin
Na level	max. 50 mg.kg^{-1} of dry ion exchange resin
Max. operational temperature	120 °C
Density	780 – 800 g.dm^{-3}
Moisture retention	43 - 48 % (H$^+$ form)

The gravimetric method (dehydration to a constant weight at 120°C) using analytical weights was employed to determine the moisture associated with ion exchange resin in order to calculate the combustion method for ion exchange resins in the combustion furnace.

To assess the behaviour of the ion exchange resin at high temperature, samples of the original ion exchangers were subjected to thermal analysis, Thermogravimetry (TG)[23] and Differential Scanning Calorimetry (DSC)[24] using a Mettler TA 3000 Toledo. A Thermogravimetric Analysis Module with TG 50 Thermal Scale and DSC Differential Scanning Calorimetry Module with Measurement unit DSC 20 including the Grapheware TA - 72.2/5 Evaluation Software were used[25].

During thermogravimetry, the ion exchange sample was heated at a constant rate in accordance the controlled temperature programme and the weight change was measured as a function of temperature and recorded on a thermogravimetric curve. The measurement was carried out under the following conditions:

- heating rate (10 ^{o}C.min^{-1}),
- thermogravimetric analysis was carried out up to 800 ^{o}C,
- the measurement was carried out in a dynamic air atmosphere,
- the initial and final temperatures of the active decomposition, the maximum temperature for the most rapid weight loss of the sample and the combustion resistant residues at the respective temperatures were observed.

DSC is the procedure whereby the difference between the heat flow (energy) supplied to the test sample and the reference sample is measured as a function of temperature and/or time, while the test and reference samples are being exposed to the selected temperature programme. It uses an additional source in order to compensate for the temperature difference between the uniformly heated sample and the comparative substance, while measuring the energy directly consumed for this equilibration. The enthalpy change can be calculated according to the equation:

$$-\Delta H = \int_{T_1}^{T_2} c_p \, dT + i_k \tag{1}$$

where Cp is the specific heat capacity (J.kg^{-1}.K^{-1}) and i_k is the integration constant, where the area of the thermoanalytic peak (exothermic or endothermic effect) is proportional to the value of the integral. The integration constant is determined using standardized substances which exhibit an exothermic or endothermic effect in the temperature range T1 and T2 whose enthalpy (kJ.mol^{-1}) is specified. The ion exchange resin sample was tested at the same rate of heating at 10 °C. min^{-1} in an air atmosphere.

Approximate combustion heat of the ion exchange resin was determined using KALORYMETR KL-5 combustion calorimeter.

Results and discussion

The moisture level of ion exchange resin was determined by the gravimetric method to be 43.8 ± 0.8 %.

Thermal analysis was used to monitor thermolysis of ion exchangers on a laboratory scale to determine the way they behave under thermal stress. The graphical course of the thermogravimetric curve (TG and DTG) is displayed in Figure 2, the results are evaluated in Table 3. The weight of the test sample was 9.316 mg.

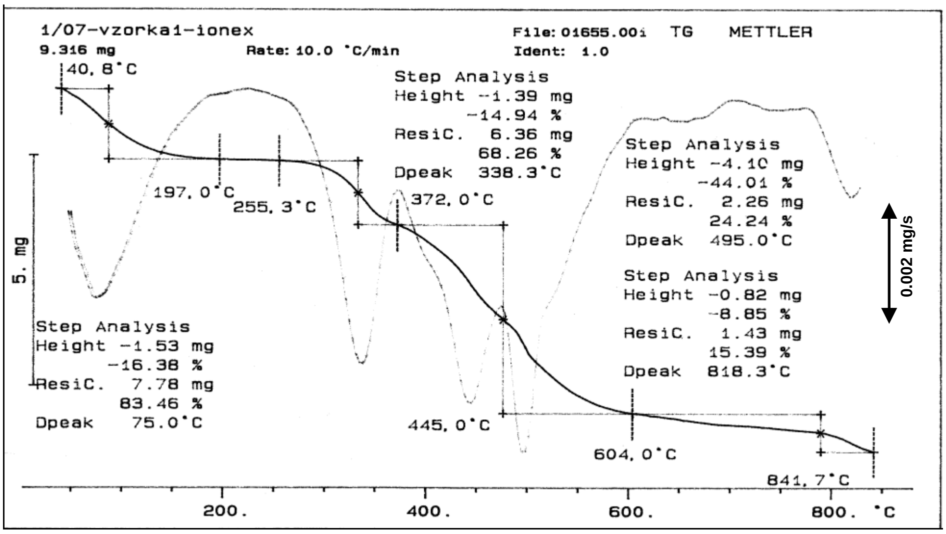

Figure 2: TG and DTG weight loss curve of the ion exchange resin sample

Table 3: Temperature characterization of individual ion exchange resin decomposition stages

Heat rate	Stages of decomposition	Heat interval	Weight loss	Temperature for the most rapid weight loss	Resistant residual
(°C.min⁻¹)		(°C)	(%)	(°C)	(%)
10	Stage I.	40.8 – 197.0	16.38	75.0	83.46
	Stage II.	255.3 – 372.0	14.94	338.3	68.26
	Stage III.	372.0 – 604.3	44.01	445.0 495.0	24.24
	Stage IV.	604.0 – 840.0	8.85	818.3	15.39

The thermogravimetric records show:

- decomposition of the ion exchange resin occurred in four stages,
- the first stage was associated with the loss of 16.38 % of the ion exchanger, with the beginning of thermal decomposition recorded at 40.8 °C, this level indicates the ongoing dehydration processes, given the assumed high water content,
- no significant changes were recorded in the temperature range of 197.0 – 255.3 °C with the selected temperature programme,
- in the second stage, the weight loss was 14.94 % in the range of 255.3 – 372.0 °C, the resistant residual value was 68.26 %,
- the third stage of thermal decomposition is decisive for the thermal decomposition of the material, since 44.01 % loss of sample weight and two maximum velocity loss rates at 445.0 and 495.0 °C are recorded on the thermogravimetric curve,
- in the last stage (the flow is recorded to exceed 800 °C) the amount of thermally decomposed material represented the smallest weight and the final value of the resistant residue was 15.39 % which indicates relatively high content of insoluble components, which must be taken into consideration during the combustion process.

The results of the thermogravimetric analysis indicate that the path of thermal decomposition of the ion exchange resin is feasible, but it is crucial to take into consideration higher energy costs associated with the evaporation of water in the initial stage and the decomposition course is shifted towards higher values compared to other tested materials burned in the given apparatus. Furthermore, the increased ash content resulting from this type of combustion process needs to be taken into account, which is in case of radioactive waste due to its cumulated radiation advisable to be in the solid residue.

Figure 3 depicts the results of the DSC and Table 4 evaluates the measurements. The weight of the test sample was 4.850 mg.

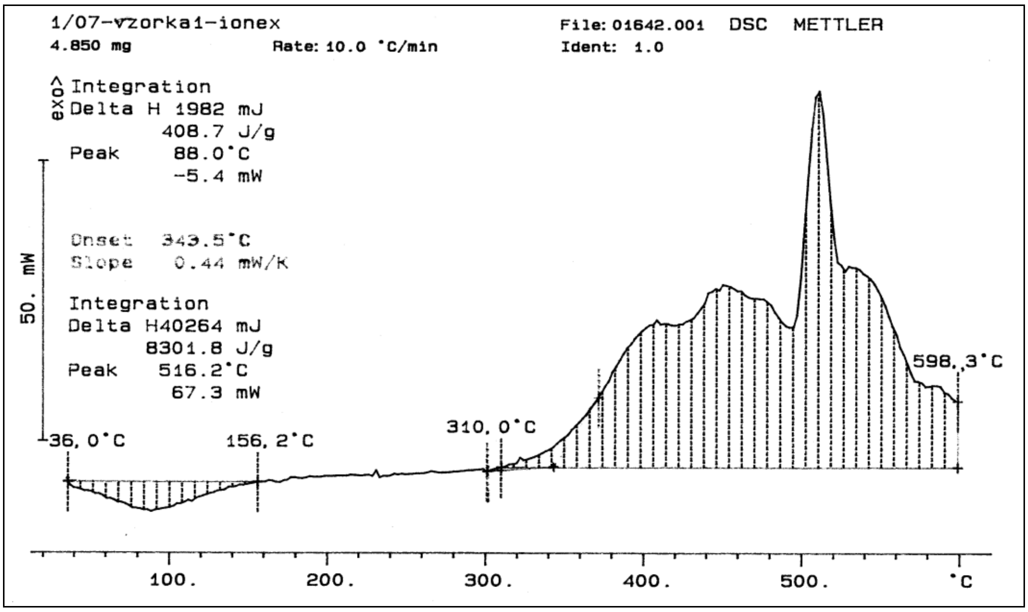

Figure 3: The DSC record of ion exchanger

Table 4: Changes in the reaction enthalpy of the ion exchanger from the DSC record

Heat rate (^{o}**C.min**$^{-1}$)	**Stages of decomposition**	**Heat interval** (^{o}**C**)	**Change in the reaction enthalpy** (**J.g**$^{-1}$)	**Maximum peak temperature** (^{o}**C**)
10	Stage I.	36.0 – 156.2	- 408.7 endo	88.0
	Stage II.	310.0 – 598.3 and more	8301.8 exo	516.2

Based on the DSC curve, the thermal decomposition of the ion exchanger practically occurred at the temperature higher than 600 °C in two stages. In the heat range of 36.0 - 156.2 °C, it is possible to determine the prevailing endo-effect of the ongoing decomposition (dehydration) mechanisms from the curve; the next stage recorded significant exothermic processes, probably related to depolymerisation, cleavage and other exothermic reaction of ion exchange resin, while this process was not completed even at 600 °C.

The results of the DSC analysis indicate that heating of the sample in the first stage, requires supply of a considerable amount of energy, which is coupled with the evaporation of water tied in the ion exchanger; in the next stage from around 300 °C, the decomposition exothermic reactions with positive thermal balance (energy release) prevail.

The combustion heat of the ion exchanger was determined by calorimeter from the total water value:

$$Q_{spal} \approx 4\ 200\ cal.g^{-1} \approx 17{,}5\ kJ.g^{-1}. \tag{2}$$

Regarding the proposal for the transport method of the ion exchanger into the combustion furnace, the feasible solution was to mix it with foam with a content of approximately 35 %. For the combustion of such ion exchanger, it is crucial to first supply the heat necessary for evaporation of the water in the first stage and subsequently release the heat upon burning of the dehydrated ion exchanger. The calculation of the energy balance of the ion exchanger combustion was based on 1 kg of foam. For the heating of 20 °C to the boiling temperature, evaporating and heating of this amount of water to the temperature of the combustion products (750 °C), the amount of heat Qv must be:

$$Q_v = m_{water} \times c_{p,l} \times \Delta T + m_{water} \times l_v + m_{water} \times c_{p,g} \times \Delta T, \tag{3}$$

$$Q_v = 2\ 552\ \text{kJ}$$

The heat released by combustion of dehydrated ion exchanger Qi:

$$Q_i = m_{ion\ exchanger} \times Q_{combustion} = 6\ 125\ \text{kJ}. \tag{4}$$

The heat Qi is released when the ion exchanger is burned, the heat Qv is consumed to heat the water, which forms the most essential part of the foam supplied to the combustion furnace. The overall energy contribution of combustion of foam and ion exchanger to the combustion process is:

$$Q = Q_i - Q_v = (6\ 125 - 2\ 552)\ \text{kJ/kg}_{\ foam} = +3\ 573\ \text{kJ/kg}_{\ foam}. \tag{5}$$

Since combustion of ion exchanger in a foam containing 35 % of the ion exchanger is energy-efficient, no further energy-rich substances need to be added to the furnace. In reality, it is obvious that the furnace processing radioactive waste will be used to burn other predominantly energy-rich substances, thereby increasing the energy balance of the combustion process.

The problem may be caused by the technical difficulty of entering the ion exchanger in the foam. Several types of equipment can be used to prepare the foam in which the ion exchanger selected for combustion is subsequently dispersed. First of all, it is the typical equipment used in the production of foam for extinguishing, the so-called whip nozzle. Water is flowing under increased pressure to the nozzle, to which a defined amount of foam compound is admixed to form a foaming substance which produces foam once the air is streamed in.

The main problem for the use of such device in the incinerator is high water and foam flows, hence the incinerator would have to be greatly oversized. The advantage of this device is that, under the right conditions, it can create light foam containing a small amount of water (unlikely to differ greatly from 43 % of the water content already present the ion exchanger). This results in higher energy intensity of combustion and greater time stability of the foam. In case of combustion of such foam, it is also necessary to increase the diameter of the duct to ensure easy dosing of the foam into the furnace.

Another device that can be designed for foam creation is a device that produces foam mechanically - mixing the foaming substance at high speed which results in formation of bubbles while these bubbles remain coated with foaming solution[26]. Disadvantage of this process is the possibility to only produce heavy foam with a high water content, which makes it unstable. This procedure will most probably require additional condensate drainage equipment. On the contrary, the advantage of this device is that it can also produce small amounts of foam with small amounts of ion exchanger.

Design of the foam forming equipment and foaming substance are shown in Figure 4.

The spiral conveyor must be used due to the ion exchanger consistency (contains 43 % of water, causing aggregation of the particles and their accumulation on the walls of the vessels). The flow of the foaming substance should be selected in such a way as to ensure transfer of the particles from the ion exchange reservoir; at the same time the amounts of the foaming substance and the supplied ion exchanger need to correspond to the weight ratio of 1:1. The mixture of the ion exchanger and the foaming substance is piped into the conic chamber and connected to the upper part by a suction nozzle to the duct which takes the produced foam into the furnace. It is necessary to place an aperture in this duct in order to regulate the supply of foam into the combustion chamber. The condensate drain pipe 9 fulfils the back flow function of the excess condensate which is led back into the chamber. The gas supply as well as the suspension of the foaming substance and the ion exchanger should be led directly on the screw of the mechanical stirrer 6. This causes the instantaneous mechanical formation of the foam when the liquid stream is mixed with the gas under the turbulent environment created by the screw. The material of the equipment must be corrosion-resistant, for example austenitic steel.

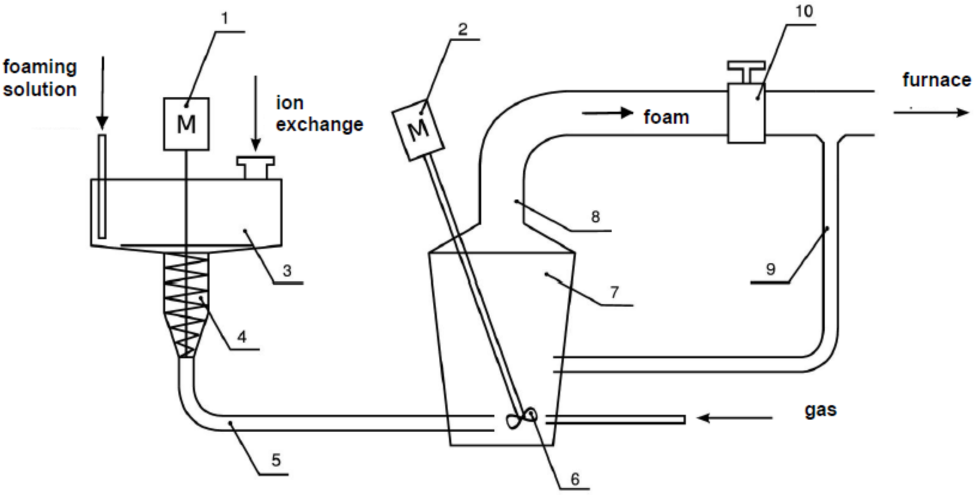

Figure 4: Proposed foam forming equipment and foaming substance

1,2 - engines, 3 – ion exchange dispenser, 4 – spiral conveyor, 5 – duct, 6 – stirrer, 7 – suction nozzle, 8 – aperture, 9 – condensate drain, 10 – combustion chamber

Conclusion

Ion exchangers as organic substances can be incinerated. Since ion exchangers as waste are fed into the combustion facility in a “wet” state, it is crucial to dispense the ion exchanger into the proposed device with water content not exceeding 50 %. Higher amount of water in the ion exchanger supplied into the device increases the energy intensity of the combustion process. Since it is most efficient to dispense the ion exchangers into the combustion chamber by means of foam, it is necessary to connect foam forming apparatus in which foam in produced and mixed with ion exchanger to a combustion device. It is possible to increase the water content of the ion exchanger supplied during production of the foam, but on the other hand, it is necessary to adjust the amount of water supplied in the foaming substance, while maintaining the optimum foam substance content in the total amount of the solution.

This is a proposal for combustion of liquid RAW with the aim to point out the possibilities of combustion of liquid waste. The paper did not address the issue of activity, but it is assumed that radioactive substances are predominantly captured in solid residues from incineration, which would be further addressed by immobilization and landfill. It is likely that the combustion of LRAW will not take place as a separate process, but rather together with other materials in different states and composition, therefore the ratios can substantially change.

List of abbreviations

C_p	Heat Capacity ($J.kg^{-1}.K^{-1}$)
DSC	Differential scanning calorimetry
IEAE	The International Atomic Energy Agency
LRAW	Liquid radioactive waste
m	Mass (kg, g)
NF	Nuclear Facility
Q	Heat (J)

RAW	Radioactive waste
TG	Thermogravimetry
ΔT	Temperature difference (^{o}C)
BSC	Bohunice RAW Treatment Center
RAW	radioactive waste
IAEA	International Atomic Energy Agency

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Návrh spôsobu spaľovania kvapalných rádioaktívnych ionexov. Prípadová štúdia

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Súhrn

Rádioaktívne odpady svojou nebezpečnosťou pre ľudské zdravie a životné prostredie vyžadujú exaktne stanovené pravidlá pre nakladanie s nimi. V jadrových zariadeniach medzi kvapalné rádioaktívne odpady patria ionexy využívaném na čistenie demineralizovanej vody. V prípade ionexov používaných v jadrových zariadeniach oproti ionexom v klasických úpravovniach vôd okrem klasických vlastností odpadu je potrebné riešiť v procese prevádzky a vyraďovania aj otázku ich rádioaktivity. K tomu smeruje aj výber najvhodnejšej technológie. Ako najlepšou dostupnou technológiou zneškodnenia ionexov z jadrových zariadení je ich riadené spaľovanie. V príspevku je pojednané o vlastnostiach ionexov, ich testovaní z hľadiska vstupnej analýzy a návrh riešenia vstupu kvapalných ionexov do spaľovacieho priestoru.

Kľúčové slova: *ionexy, spaľovanie, kvapalné rádioaktívne odpady*

Boiler performance and combusted biomass quality control improvement in an industrial biomass boiler

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Summary

Combusted biomass in steam boilers in paper mills stems mainly from internal sources but it also may be purchased from outer ones, contributing to its variable moisture, composition and lower heating value (LHV). Available process data from an industrial application were processed yielding simple biomass LHV calculation estimation to help the plant staff in online and ex post Monitoring and targeting purposes. This has not been possible in the past due to unreal LHV values obtained by laboratory analyses of biomass samples. We also paid attention to sulphuric acid dew point estimation to assess the risk of flue gas duct low temperature corrosion that has been confirmed by inspection during boiler overhaul. Measures were proposed to eliminate its occurrence after the necessary low temperature flue gas duct part repair.

***Keywords**: biomass moisture, lower heating value, thermal efficiency, stack losses, low temperature corrosion*

List of symbols and abbreviations used

AMS	Automated Monitoring System
BB	Biomass boiler
BFW	Boiler feedwater
CHTW	Chemically treated water
$\bar{c}_{p,mol,i}^{t_j-tref}$	Average molar heat capacity of i-th component in the temperature range from reference to actual temperature, [kJ.kmol^{-1}.K^{-1}]
d.b.	Dry basis (biomass composition)
ESP	Electrostatic precipitator
$\dot{H}$	Enthalpy flux, [kW, MW]
h	Molar enthalpy, [kJ.kmol^{-1}]
HX	Heat exchanger
K_1, K_2	Coefficients in material balance equations
K_p	Equilibrium constant based on partial pressures
LHV	Lower heating value, [MJ/kg, GJ/t]
M	Molar mass, [kg.mol^{-1}]
MB	Mass balance
M&T	Monitoring and targeting
$\dot{n}$	Molar flow, [mol.s^{-1}, kmol.h^{-1}]
NG	Natural gas
OMB	Overall mass balance
$\dot{Q}_{loss}$	Heat losses from surface, [MW]
P	Pressure (partial), [Pa, atm]
RES	Renewable energy source

SADP	Sulphuric acid dew point, [°C]
T	Thermodynamic temperature, [K]
t	Temperature, [°C]
$\dot{V}$	Volumetric flow, [$m^3.s^{-1}$, $m^3.h^{-1}$]
x	Molar fraction
w	Mass fraction
$\nu_{i(j)}$	Stoichiometric coefficient of i-th component in j-th chemical reaction
$\dot{\varsigma}_{(j)}$	Reaction rate of the j-th chemical reaction, [$mol.s^{-1}$, $kmol.h^{-1}$]
$\dot{\varsigma}_{(j)}^{T}$	Theoretical (maximal) reaction rate of the j-th chemical reaction, [$mol.s^{-1}$, $kmol.h^{-1}$]

Subscripts

RED	Reduced (temperature)
t	Thermal (efficiency, energy)
u	Useful (heat flux)

Introduction

Biomass continues to play an important role in heat and power production both in industrial and residential sector. Large biomass fired steam boilers are traditionally found in pulp and paper industry[1,2]. The power sector tests the possibility for biomass cofiring in coal boilers[3 - 5] or together with other kinds of fuels[2] however the economically acceptable share of cofiring does not exceed 20 % at present. Biomass can replace a part of fuel needs in other industrial sectors as well, for example as supplementary fuel in lime kilns[6], either by direct feeding of various sludges or using gas produced by biomass gasification[7].

Short and long term monitoring of boiler performance is very important when striving towards economically feasible boiler operation. Several techniques are implemented to reach this goal, but always process data represent the key to this effort. Cafaro et al.[8] apply thermoeconomic method to analyze the decay of selected power plant key components performance over time. The obtained results allow for following trends over a time period of more than 500 days. Valero and Lozano present a similar study[9] by applying fundamental approach to performance monitoring and costs assignment in a coal fired power plant located in Spain based on theory of exergetic cost. Analysis of several steady state operation data allowed them to identify the flue gas recuperator as a piece of equipment with the most significant performance decay, with exiting flue gas temperature above 200 instead of around 150 °C and leaking air. If the fuel composition varies significantly even over shorter time period, online fuel quality analysis is necessary to be conducted to proceed with any boiler or power plant performance studies. The study from Vrána and Šulc[10] indicates the possibility to deal with fuel composition and thermal efficiency using inferential sensors especially for small scale boilers where experimental data and sensors are missing. Similarly, Vrána et al.[11] successfully evaluate fuel composition based on available process variables.

SOx emissions from steam boilers and other industrial devices (furnaces…) directly impact their safe operation area regarding low temperature corrosion[12 - 14], as their flue gas content even in a few ppms rises its dewpoint by tens of °C. In order to avoid it, flue gas to stack temperature has to be sufficiently high which on the other hand impairs the boiler thermal efficiency and might be subject to discussion between engineers and managers. Verhoff[12] and Banchero[13] presented decades ago simple equations that can be used for a quick dewpoint estimation in praxis. Ibler[14] provides dewpoint charts for various fuels and air excess values. The study by Ciukaj and Pronobis[5] provides analysis of flue gas dewpoints from boilers co-combusting coal and biomass in Czech republic and Poland, the reported flue gas dewpoint rise compared to water vapor dew point reached almost 90 °C. We documented the impact of neglecting the low temperature corrosion risk in an anthracite calcination process study[15] where it led to extensive corrosion of flue gas fan and stack. For steam boilers, the study by Einstein et al.[1] recommends that "it makes more sense to preheat the feed water to close to the acid dew point before it enters the economizer. This allows the economizer to be designed so that the flue gas exiting the economizer is just barely above the acid dew point.” For situations with varying fuel quality and sulphur content preheating the water to varying temperatures may become problematic and usually “a somewhat higher flue gas temperature is acceptable to provide an extra safety margin”.

Keeping all those issues in mind a performance study of an industrial biomass fired steam boiler has been conducted, fed by biomass with variable composition to demonstrate the impact of such situation on boiler operation reliability and efficiency. The main goals of the study are as follows:

- develop a robust calculation model for online biomass moisture, flue gas mass flow and composition estimation
- provide the boiler operators with simple and easy to use tool for online estimation of boiler thermal efficiency and combusted biomass lower heating value yielding reliable results on one hour / one day basis. This tool should serve the plant technologists and managers as well in purchased and combusted biomass quality monitoring and biomass boiler thermal efficiency monitoring and benchmarking.
- assess the low temperature corrosion existence in the recuperator by calculation of sulphuric acid dew point based on measured and calculated flue gas properties, thus providing plant engineers with relevant facts in the debate with plant managers about the boiler thermal efficiency vs. boiler operation reliability

Case study: Biomass boiler and the related cogeneration unit layout

The object of our study is an industrial 100 MW_t steam boiler located in a paper mill in Slovakia, operated typically in the 80 to 95 % of nominal thermal input range. Its layout together with the RES-based cogeneration unit is depicted in Figure 1. Apart from biomass, natural gas is used in the boiler as supplementary fuel in power burners, ensuring the temperature in the combustion chamber stays above certain minimum value when combusting low quality biomass. In extreme cases the NG consumption exceeds 50 MW_t but during stable operation it is below 1 MW_t. Frequent changes in biomass quality put stress on boiler operators; boiler automation is only on moderate level so the operators have to adjust the combustion air flow and NG to power burners flow manually, often multiple times per hour, seeking both for efficient boiler operation and for keeping NO_x and CO emissions below upper environmental limits.

Biomass quality is estimated by sampling and laboratory analysis once per one or two weeks. Obtained data can thus neither be used for reliable long term boiler thermal efficiency estimation nor for operational analyses and Monitoring and targeting purposes. Applying the laboratory lower heating value data to monthly or yearly balances one gets a wide unrealistic spread of boiler thermal efficiencies, ranging from 70 up to 110 %. A simple easy to be used operational biomass lower heating value estimation procedure is thus needed to ensure reliable and economically feasible boiler operation and to help the plant technologist in balancing procedures, including correct estimation of produced steam price.

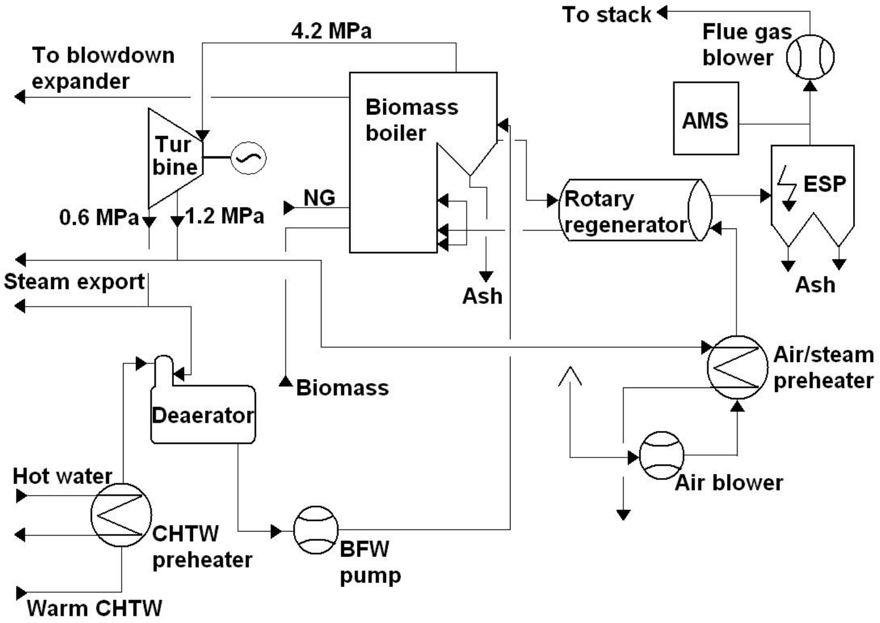

Figure 1: Schematic depiction of the RES-based cogeneration unit understudy. BFW = boiler feedwater, CHTW = chemically treated water, NG = natural gas

As a frequent measure in large steam boilers, combustion air is preheated to above 200 °C in rotary regenerator, utilizing waste heat content of flue gas leaving the boiler, thus reducing fuel consumption and increasing boiler thermal efficiency. Originally the cold ambient air should pass firstly through a steam preheater to ensure a certain minimum temperature of air entering the regenerator in order to prevent low temperature corrosion occurrence on flue gas side. The steam preheater broke down in 2012 and since then cold air passes to regenerator without preheat. Boiler operators confirmed that since then the flue gas to stack temperature dropped from around 200 to around 140 °C, thus seemingly increasing the boiler thermal efficiency (and saving steam to steam preheater which has been considered as an excellent steam saving measure at that time). However the flue gas dew point when combusting sulphur-containing fuels generally often approaches 150 °C and such situation may lead to extensive regenerator and stack corrosion if continuing for longer time. Thus the authors also concentrated on this issue, striving to verify the initial assumption of corrosion risk by flue gas sulphuric acid dew point range estimation and proposing measures to remedy this situation.

Available process data and calculation model

Outputs of process sensors incorporated in the calculation model are summed up in Table 1. Biomass mass flow is estimated by weighing the biomass surge silo content. No records are available about the last calibration date and calibration results of that weigh, thus obviously this might be a significant contributor to the current unrealistic boiler thermal efficiency values and might as well influence the accuracy of the calculation procedure described below.

Any online data characterizing biomass quality are missing. Initial estimates subject to iterative calculations thus include biomass moisture and hydrogen content. Due to the lack of any process data, fix oxygen content of 45 % wt. in biomass combustible matter has been assumed in accordance with available literature[16] and the nitrogen and sulphur content in biomass (both unknown) has been neglected. This simplification does not lead to detectable loss on calculation accuracy, as the usual nitrogen content in biomass is around 0.5 % wt. and that of sulphur below 0.08 % wt. both on dry basis.[16] Ash from boiler has been considered for simplicity as inert which, on our request, has been confirmed by its laboratory thermogravimetric analysis. Complete combustion of biomass has been assumed for simplicity, neglecting the measured 40 to 90 ppm vol. CO content in flue gas. Any other measurements regarding the other carbonaceous compounds in the flue gas are not available. All air leaks into flue gas were assumed to take place on the flue gas path outside of the boiler. Other assumptions relating to boiler mass and heat balance are listed in Table 2. All those assumptions obviously make the resulting model slightly less accurate, however they keep it thus relatively simple and easy to use.

Table 1: List of process sensors considered in calculation model

Measurement	Sensor description	Physical units	Typical values
Mass flow	Biomass mass flow	t/h	20 to 50
	Boiler feedwater	t/h	95 to 120
	Steam production	t/h	90 to 110
Volumetric flow	Natural gas volumetric flow	Nm^3/h	2 to 100 (6000)
	Combustion air sum to all burners	Nm^3/s	30 to 40
	Flue gas (dry basis)	Nm^3/s	32 to 45
Temperature	Ambient air	°C	-
	Air after steam preheater	°C	30 to 60
	Flue gas to stack	°C	120 to 160
	Produced steam	°C	395 to 405
Pressure	Produced steam	MPa (g)	4.2 to 4.4
Composition	Flue gas at boiler exit	% vol. oxygen	4 to 5.5
	Flue gas to stack (AMS)	% vol. oxygen, d.b.	7 to 11
	Flue gas to stack (AMS)	ppm vol. SO_2, d.b.	2 to 30 (peaks above 200)

Balancing and calculation procedure is summed up in model equations below, comprising simultaneous solution of boiler mass and heat balance and the balance scheme is provided in Figure 2. Such balance scheme enables not only the estimation of online boiler thermal efficiency and biomass LHV and moisture, but the calculations also yield the flue gas dew point values. The mentioned calculation procedure has been applied to process data in form of one hour averages available for appr. 1.5 year period. Results for selected shorter period with stable boiler operation have been graphically processed and are shown and discussed in the next chapter.

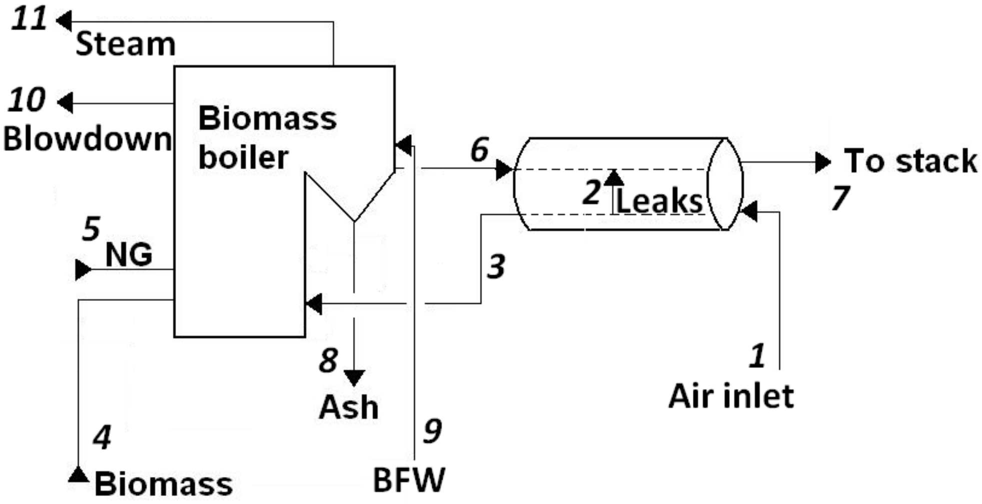

Figure 2: Balance scheme of calculation model with denoted stream numbers

Table 2: Assumed fix values employed in the calculation model

Process stream	**Parameter**	**Value**
Combustion air	Water vapour content	1 % wt. (= 1.6 % vol.)
Ash	Mass flow; Temperature	5 % of biomass mass flow; 150 °C; zero combustibles content
Blowdown	Pressure	Produced steam pressure + 200 kPa
Natural gas	Composition	94 % vol. CH_4, 3 % vol. C_2H_6, 2 % vol. C_3H_8, 1 % vol. N_2
Biomass composition	Oxygen content	45 % wt. of biomass combustible matter
Heat losses from boiler	-	1.5 MW; load independent
Biomass	Biomass lower heating value	18.95 GJ/t of dry matter
Ash	Combustibles content	Negligible (< 0.5 % wt. carbon according to laboratory analyses)

Considered chemical reactions are summed up in (1 a – e), with their reaction rates defined according to (2 – 6).

$$\begin{aligned}
&(I): C + O_2 \rightarrow CO_2 \\
&(II): H_2 + 0.5O_2 \rightarrow H_2O \\
&(III): CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\
&(IV): C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \\
&(V): C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O
\end{aligned} \qquad (1\ a – e)$$

$$\dot{\varsigma}_{(I)} = \dot{\varsigma}_{(I)}^{T} = \dot{n}_{4,C} \qquad (2)$$

$$\dot{\varsigma}_{(II)} = \dot{\varsigma}_{(II)}^{T} = \dot{n}_{4,H2} \qquad (3)$$

$$\dot{\varsigma}_{(III)} = \dot{\varsigma}_{(III)}^{T} = \dot{n}_{5,CH4} = 0.94.\dot{n}_5 \qquad (4)$$

$$\dot{\varsigma}_{(IV)} = \dot{\varsigma}_{(IV)}^{T} = \dot{n}_{5,C2H6} = 0.03.\dot{n}_5 \qquad (5)$$

$$\dot{\varsigma}_{(V)} = \dot{\varsigma}_{(V)}^{T} = \dot{n}_{5,C3H8} = 0.02.\dot{n}_5 \qquad (6)$$

The overall boiler mass balance (7a) together with the oxygen balance in the boiler (7b) defines the basis for calculation procedure. Further relations (8), (9) define the values of auxiliary coefficients while (10) and (11) provide more inputs regarding combustion air and natural gas molar flows and composition. The same, related to biomass composition, holds true for equations (12), (13). Together with (13) and (14) this represents the material balance model of the boiler. The calculation output is represented by molar flow of flue gas exiting the boiler (7a), its composition and molar flows of hydrogen and carbon in combusted biomass. As can be recognized in the used equations, the co-firing of natural gas is also dealt with. The calculation is started with initial values of biomass moisture and combustible matter composition which (except from moisture) are refined by mass balance calculation process. The biomass moisture is refined by further heat balance calculations and is returned back to mass balance equation set for iterative calculations until all three parameters are refined satisfactorily. We decided to let the hydrogen and carbon dry biomass content being subject to optimization by calculation. The reason for doing so instead of fixing the dry biomass composition lies in the very variable combusted biomass origin, with changeable share of wood chips and bark that depends on the amount, quality and origin of the wood actually processed in the paper mill. As is obvious from published data[16] the dry bark generally contains more carbon and less hydrogen compared to dry wood chips. By letting the hydrogen content being calculated instead of fixing it, this aspect can be reflected in calculation results and bring the calculation model nearer to reality in this particular case study.

$$OMB: \quad \dot{n}_6 = \dot{n}_3 + \dot{n}_{4,O2} + \dot{n}_{4,H2O} + 0.5.\dot{n}_{4,H2} + K_1.\dot{n}_5$$

$$O_2\ MB: \dot{n}_6.x_{6,O2} = \dot{n}_3.x_{3,O2} + \dot{n}_{4,O2} - \dot{n}_{4,C} - 0.5.\dot{n}_{4,H2} + K_2.\dot{n}_5 \qquad (7\ a,b)$$

$$K_1 = 1 + \sum_{(j)=(III)}^{(V)} x_{5,i}.\sum_i \nu_{i,(j)} = 1 + 0.94.0 + 0.03.0.5 + 0.02.1 = 1.035 \qquad (8)$$

$$K_2 = \sum_{(j)=(III)}^{(V)} \nu_{O2,(j)}.\dot{\varsigma}_{(j)} = (-2.0.94 - 3.5.0.03 - 5.0.02).\dot{n}_5 = -2.085 \qquad (9)$$

$$\dot{n}_3 = \dot{V}_3.(22.41\,mol.Nm^{-3});\ \dot{n}_5 = \dot{V}_5.(22.41\,mol.Nm^{-3}) \qquad (10)$$

$$x_{3,O2} = 0.21.(1 - x_{3,H2O}) = 0.21.0.984 = 0.2066 \qquad (11)$$

$$\dot{n}_{4,O2} = \frac{0.45.\dot{m}_4.(1 - w_{4,H2O} - w_{4,ash})}{M_{O2}} = \frac{0.45.\dot{m}_4.(0.95 - w_{4,H2O})}{0.032 kg.mol^{-1}} \qquad (12)$$

$$\dot{n}_{4,H_2O} = \frac{\dot{m}_4.w_{4,H2O}}{M_{H2O}} = \frac{\dot{m}_4.w_{4,H2O}}{0.01802 kg.mol^{-1}} \qquad (13)$$

$$\dot{n}_{4,H2} = \frac{w_{4,H2,dry\ matter}.\dot{m}_4.(1 - w_{4,H2O} - w_{4,ash})}{M_{H2}} = \frac{w_{4,H2,dry\ matter}.\dot{m}_4.(0.95 - w_{4,H2O})}{0.00202 kg.mol^{-1}} \qquad (14)$$

$$\dot{n}_{4,C} = \frac{(1 - 0.45 - w_{4,H2,dry\ matter}).\dot{m}_4.(1 - w_{4,H2O} - w_{4,ash})}{M_C} = \frac{(0.55 - w_{4,H2,dry\ matter}).\dot{m}_4.(0.95 - w_{4,H2O})}{0.01201 kg.mol^{-1}} \qquad (15)$$

Once the boiler material balance is solved, air leaks into flue gas system and final flue gas to stack composition and molar flow can be determined via the equation set (15 – 23), utilizing the information about oxygen content in dry flue gas to stack provided by AMS and results from previous calculations.

$$OMB: \dot{n}_7 = \dot{n}_6 + \dot{n}_2 \qquad (16)$$

$$O_2\ balance: \dot{n}_6.x_{6,O2} + \dot{n}_2.x_{2,O2} = \dot{n}_{7,d.b.}.x_{7,O2,d.b.} = \dot{n}_{7,O2} \qquad (17)$$

$$MB\ on\ dry\ basis: \dot{n}_{7,d.b.} = \dot{n}_{6,d.b.} + \dot{n}_{2,d.b.} = \dot{n}_6.(1 - x_{6,H2O}) + \dot{n}_2.0.984 \qquad (18)$$

$$\dot{n}_2 = \dot{n}_6.\frac{x_{7,O2,d.b.}.(1 - x_{6,O2}) - x_{6,H2O}}{x_{7,O2,d.b.}.(x_{2,H2O} - 1) + x_{2,O2}} = \dot{n}_6.\frac{x_{7,O2,d.b.}.(1 - x_{6,O2}) - x_{6,H2O}}{0.2066 - 0.984.x_{7,O2,d.b.}} \qquad (19)$$

$$x_{6,H2O} = \frac{\dot{n}_{6,H2O}}{\dot{n}_6} = \frac{\dot{n}_{3,H2O} + \dot{n}_{4,H2O} + \sum_{(j)} \dot{\varsigma}_{(j)}.\nu_{H2O,(j)}}{\dot{n}_6} = \frac{0.016.\dot{n}_3 + \dot{n}_{4,H2O} + \dot{\varsigma}_{(II)} + 2.\dot{\varsigma}_{(III)} + 3.\dot{\varsigma}_{(IV)} + 4.\dot{\varsigma}_{(V)}}{\dot{n}_6} \qquad (20)$$

$$\dot{n}_{7,N2} = \left(\dot{n}_2 + \dot{n}_3\right).x_{2,N2} = \left(\dot{n}_2 + \dot{n}_3\right).(1 - 0.016 - 0.2066) = 0.7774.\left(\dot{n}_2 + \dot{n}_3\right) \qquad (21)$$

$$\dot{n}_{7,H2O} = \dot{n}_6.x_{6,H2O} + \dot{n}_2.x_{2,H2O} = \dot{n}_6.x_{6,H2O} + 0.016.\dot{n}_2 \qquad (22)$$

$$\dot{n}_{7,CO2} = \dot{n}_{6,CO2} = \sum_j \dot{\varsigma}_j.\nu_{CO2,j} = \dot{\varsigma}_{(I)} + \dot{\varsigma}_{(III)} + 2.\dot{\varsigma}_{(IV)} + 3.\dot{\varsigma}_{(V)} \qquad (23)$$

Heat balance of the system understudy is formed by equation set (24 – 32) and it yields new biomass moisture estimate (27) at the first place which then is sent back to boiler material balance for calculation refining. Sensible heat flux of natural gas $\dot{H}_5$ is omitted from further calculations as the natural gas is delivered at ambient temperature. Reference temperature of 0 °C has been chosen for heat balance calculations. Lower heating values of natural gas constituents (25) as well as the average molar heat capacities of gases have been obtained from available literature[17]. Specific enthalpies of boiler feedwater, blowdown and produced steam have been correlated with the help of data published[17]. Employed average values of specific heat capacities for moisture, dry biomass and ash were 4.2; 1.5 and 1 kJ.kg^{-1}.K^{-1}. Average biomass temperature of 20 °C has been assumed.

As soon as the iterative procedure is over, final biomass lower heating value is obtained (26) and boiler thermal efficiency can be estimated (28).

$$\dot{Q}_u = \dot{H}_1 + \dot{H}_4 + \dot{H}_5 + \dot{m}_4 . LHV_4 + \dot{n}_5 . LHV_5 - \dot{H}_7 - \dot{H}_8 - \dot{Q}_{loss} = \dot{H}_{10} + \dot{H}_{11} - \dot{H}_9 \tag{24}$$

$$LHV_5 = \sum_i x_{5,i} . LHV_i \tag{25}$$

$$LHV_4 = \frac{\dot{H}_{10} + \dot{H}_{11} - \dot{H}_9 + \dot{H}_7 + \dot{H}_8 + \dot{Q}_{loss} - \dot{H}_1 - \dot{H}_4 - \dot{n}_5 . LHV_5}{\dot{m}_4} \tag{26}$$

$$w_{4,H2O} = \frac{18.95 - LHV}{18.95} \tag{27}$$

$$\eta_{t,BB} = \frac{\dot{Q}_u}{\dot{m}_4 . LHV + \dot{H}_1} \tag{28}$$

$$\begin{aligned} \dot{H}_1 &= \dot{n}_1 . \bar{h}_1 = \dot{n}_1 . (1 - x_{1,H2O}) . \bar{c}_{p,mol,dry\,air}^{\,t_1 - tref} + \dot{n}_1\, x_{1,H2O} . \bar{c}_{p,mol,H2O}^{\,t_1 - tref} = \\ &= \dot{n}_1 . \left(0.984 . 29.2 kJ.kmol^{-1}.K^{-1} + 0.016 . 33.5 kJ.kmol^{-1}.K^{-1}\right) . (t_1 - 0) \end{aligned} \tag{29}$$

$$\dot{H}_4 = \dot{m}_4 . \left(w_{4,H2O} . 4.2 kJ.kg^{-1}.K^{-1} + (1 - w_{4,H2O}) . 1.5 kJ.kg^{-1}.K^{-1}\right) . (20 - 0) K \tag{30}$$

$$\dot{H}_7 = \sum_i \dot{n}_{7,i} . \bar{c}_{p,mol,i}^{\,t_7 - tref} . (t_7 - 0) \tag{31}$$

$$\dot{H}_8 = 0.05 . \dot{m}_4 . 1 kJ.kg^{-1}.K^{-1} . (150 - 0) K \tag{32}$$

Sulphuric acid dew point (SADP) has been estimated based on the method by Okkes[13]. It employs SADP calculation using molar fractions of water vapour and sulphur trioxide in flue gas. Water vapour content in flue gas is obtained from solution of equations (16 – 23). Sulphur trioxide content is calculated by the measured sulphur dioxide content in dry flue gas, its recalculation (33) to that in wet flue gas and then assuming the reversible SO_2 oxidation to SO_3 (34).

$$x_{7,SO2} = x_{7,SO2,d.b.} . \frac{\dot{n}_7 - \dot{n}_{7,H2O}}{\dot{n}_7} \tag{33}$$

$$SO_2 + 0.5 O_2 \leftrightarrow SO_3 \tag{34}$$

Equilibrium constant of this reaction (35 a) depends on reaction temperature (35 b), where the equilibrium temperature is used in K and in reduced form (35 c). Partial pressures in (35 a) are in atm. units. Average flue gas pressure of 95 kPa which reflects the site height above sea level. A temperature of 1000 °C has been employed in calculations which is near the usual measured combustion temperature in the combustion chamber.

$$K_{p(34)} = \frac{P_{SO3}}{P_{SO2} . P_{O2}^{0.5}}$$

$$\log_{10}\left(K_{p(34)}\ (T)\right) = \frac{12.12}{T_{RED}} . \left(1 - 0.942.T_{RED} + 0.0702.T_{RED}^{2} - 0.0108.T_{RED}.\ln\left(T_{RED}\right) - 1.3T^{-1}\right) \qquad \text{(35 a - c)}$$

$$T_{RED} = \frac{T[K]}{1000}$$

By using (36) the partial pressure of SO_3 is obtained which is then recalculated to molar fraction. Lastly the sulphuric acid dew point SADP is estimated (37).

$$P_{SO3} = K_{p(34)}(T).P_{SO2} . P_{O2}^{0.5} \qquad (36)$$

$$SADP\ [°C] = 203.25 + 27.6 . \log_{10}\left(x_{7,H2O}\right) + 10.83 . \log_{10}\left(x_{7,SO3}\right) + 1.06 . \left(\log_{10}\left(x_{7,SO3}\right) + 8\right)^{2.19} \qquad (37)$$

Results and discussion

The priority of performed calculations was to formulate a simple relationship between online values of combusted biomass LHV and actual values of process variables. The relative combustion air to biomass mass low ratio has been plotted against the obtained biomass LHV and the result is shown in Figure 2 with the combustion air mass flow being recalculated to oxygen content in wet flue gas of 4.5 % vol.

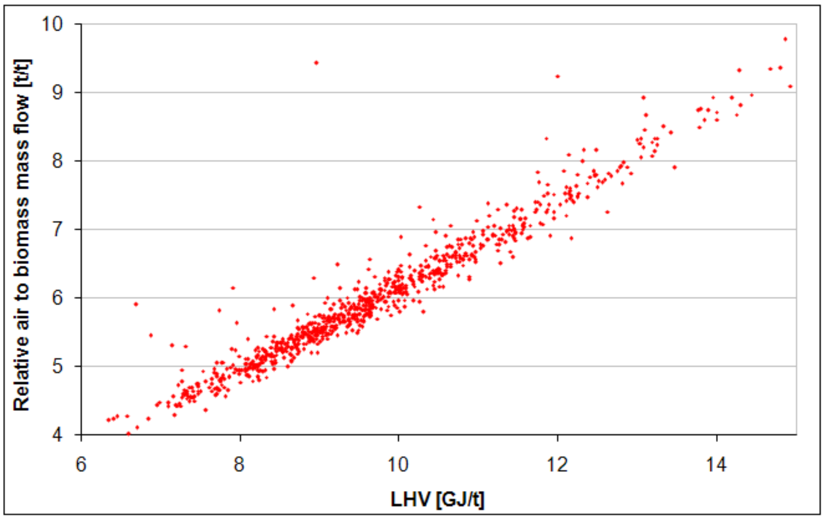

Figure 2: Specific combustion air consumption trend with rising biomass LHV

The idea behind was simple: the drier the biomass is the higher is its LHV and also more combustion air is needed to combust one ton of such biomass. As can be seen in that figure, the data trend is almost linear and can be fitted with linear relationship (38) without significant loss of accuracy.

$$\frac{\dot{m}_{air}}{\dot{m}_{biomass}} = 0.6 .\ LHV \quad [GJ/t] \qquad (38)$$

Such relationship can be used more generally, for wood based biomass that is combusted with appr. 40 % air excess (corresponding to 4.5 % oxygen content in wet flue gas). For higher or lower air excess it will deliver less correct values but via simple material balance the air mass flow can be recalculated to given range and thus correct LHV value is obtained. Moreover, it can also be used in cases when other fuel is co-fired with biomass if its share on material and heat balance is not significant. It is the case of the given biomass boiler as well with natural gas serving as fuel for pilot burners and as power fuel; the typical NG consumption of up to 100 Nm^3/h (= appr. 1 MW_t) representing less than 2 % of actual boiler thermal load.

The boiler technologist developed an alternative method for online biomass LHV estimation, based on correlation of rotational biomass feeders speed that further will be referred as "in-house correlation". Available process data included the biomass LHV resulting from the in-house correlation, so that the results of our calculations could be compared with those data as well as with (scarcely available) LHV estimated by laboratory analysis. Such comparison is shown in Figure 3. Obviously, the laboratory LHV values in the selected time period tend to lie below both our and in-house correlation data and lead to boiler thermal efficiencies around or above 100 %. Boiler thermal efficiency data resulting from the LHV in-house calculation tend to vary in a wide interval (70 to 110 %) that in our opinion makes the in-house correlation less trustworthy. In our opinion it is the result of irreproducible biomass mass flow estimated by feeders revolutions.

On the other hand, data resulting from using the relationship (38) indicate a quite narrow and reasonable boiler thermal efficiency interval of 85 to 95 %. It is believed the relationship (38) can be further improved; however it is questionable whether it would contribute to LHV estimation preciseness since there are some doubts about the correctness of biomass mass flow measurement. Thus the plant operators were recommended to stick with (38) at the moment since it represents a significant improvement in actual LHV estimation and to return to (38) and to refine it only after the biomass weigh has been calibrated.

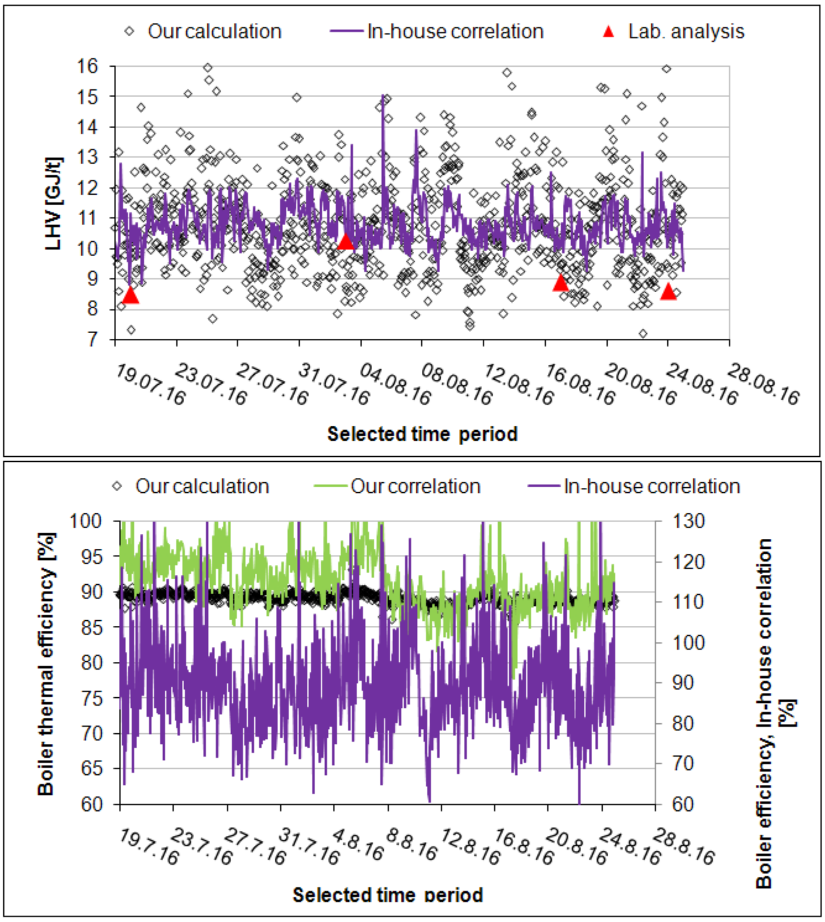

Figure 3: Comparison of biomass LHV and boiler thermal efficiency obtained by our calculation model, by model fitting with linear LHV relationship and by in-house correlation

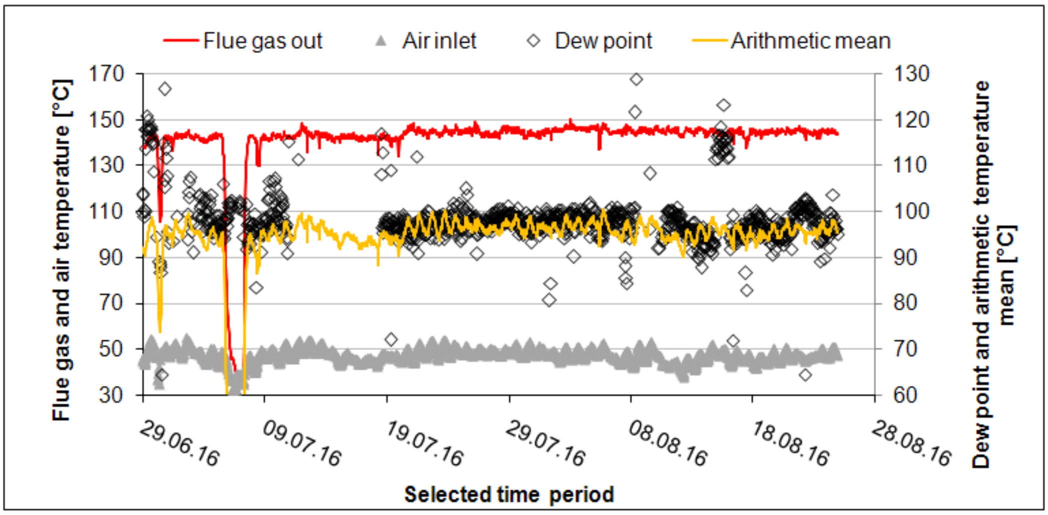

Figure 4: Calculated flue gas sulphuric acid dew point vs. flue gas to stack temperature and arithmetic mean of inlet air and flue gas to stack temperatures

Attention has been paid to flue gas dew point estimation, using process data from flue gas automated monitoring system, value calculated in boiler mass balance model and calculation procedure by Okkes[13]. Resulting data are depicted in Figure 4. Frequently appearing dew point values of 90 to 100 °C correspond to typical measured SO_x content in the flue gas of appr. 2 to 10 ppm. The depicted time period represents the trends during the analyzed 1.5 year period well – most of the time the estimated dew point is lower by around 40 °C than the flue gas to stack temperature, but short periods occur where the temperature difference is less than 25 °C. Occurrence of such periods can, according to the information from boiler staff, be attributed to occasional low quality biomass purchase from third parties that presumably has also higher sulphur content.

It must be said that even with dew points as much as 40 °C lower than flue gas to stack temperature there is risk of low temperature corrosion on the cold end of recuperator which is demonstrated in Figure 4 as well. Considering heat transfer in a flue gas - air heat exchanger, e.g. (g) – (g) system, one recognizes that the heat transfer resistances on both sides are comparable and are much higher than that of the HX wall. In such case the wall temperature is near the arithmetic mean of air and flue gas temperature. Since the air led to the recuperator has a maximum temperature of 50 °C, the corresponding wall temperature on the cold end of the recuperator ranges between 90 and 100 °C which is equal or less than the SADP. It is exactly that point where the weak acid from flue gas is likely to condense. Obviously once the liquid droplets are formed, other gases (SO_2, HCl) absorb into it, further worsening the situation. Safe boiler operation requires combustion air preheat prior to recuperator preferably to at least 80 °C – a measure that is a standard in refinery furnaces and boilers combusting sulphur containing gaseous or liquid fuel as well as in coal boilers. The existence of severe recuperator corrosion and extensive air leaks to flue gas has been later confirmed by visual inspection during boiler overhaul. In order to ensure future safe boiler operation, following measures were recommended: immediate recuperator repair / replacement by hot water heater and identification of high sulphur content biomass.

Conclusions

Analysis of the variable quality biomass fed steam boiler operation has revealed significant negative impact of such situation on boiler performance estimation possibility and operation reliability. Variable biomass moisture and lower heating value disables the online boiler M&T as laboratory LHV analyses are scarce and the in-house developed online LHV correlation does often yield unreal boiler thermal efficiencies. We successfully developed and tested calculation model based on online monitored boiler operation data and developed a reliable and simple actual biomass LHV estimation relationship Its superiority above the laboratory and in-house LHV estimation has been sufficiently proven where both approaches yielded unrealistic boiler thermal efficiency values. We recommended the staff to pay further attention to biomass surge silo weigh recalibration as its potential metering error is likely to influence the results significantly. The authors were provided with no further information about potential progress in this matter.

Another issue relates to boiler operation reliability that is threatened by existing confirmed severe low temperature corrosion of the boiler rotary regenerator, even though the sulphuric acid dew point lies well below the flue gas to stack temperature. As analyzed, current state cannot be changed and low temperature corrosion will occur again even if the regenerator undergoes repair, unless the air steam preheater is set into operation again. As an alternative, air preheater utilizing available cheap hot water instead of steam can be installed. In any case, evident facts about unsuitable boiler operation pushing the boiler efficiency beyond what can be achieved with sulphur-containing fuel have been provided to plant engineers which we hope will help in their debate on the boiler efficiency vs. operational reliability topic.

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Zefektívnenie monitoringu účinnosti priemyselného kotla na biomasu a kvality v ňom spaľovanej biomasy

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Souhrn

Parné biomasové kotle v papierenskom priemysle spaľujú biomasu pochádzajúcu najmä z výrobného procesu (kôra, nekondičné štiepky, piliny...), avšak v menšej miere sa palivová biomasa môže nakupovať zvonka, čo prispieva k jej premenlivému zloženiu, vlhkosti a výhrevnosti. Analyzovali sme prevádzkové údaje z priemyselného biomasového parného kotla s cieľom získať jednoduchú koreláciu medzi nimi a aktuálnou dolnou výhrevnosťou biomasy. Získaná korelácia pomôže obsluhe aj technológom pri vyhodnocovaní aktuálnej tepelnej účinnosti kotla a na účely online aj ex-post monitoringu a targetingu, čo vzhľadom na nereálne hodnoty účinnosti po použití výhrevností zistených laboratórne nebolo doteraz možné. Merané zloženie spalín vykazuje nezanedbateľný obsah oxidov síry a teda aj rosného bodu kyseliny sírovej, práve kvôli meniacej sa kvalite spaľovanej biomasy, čo komplikuje prevádzku kotla s cieľom vyhnúť sa nízkoteplotnej korózii spalinového traktu. Táto bola pri obhliadke počas odstávky kotla potvrdená a navrhli sme opatrenia na jej spomalenie, resp. minimalizáciu jej opätovného výskytu po nutnej oprave nízkoteplotnej časti spalinového traktu kotla.

Klíčová slova: *vlhkosť biomasy, dolná výhrevnosť, tepelná účinnosť, komínové straty, nízkoteplotná korózia*

Development of parameters of slags from ladle metallurgy during their primary treatment

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Summary

Slags from steel production represent a significant high volume waste. More than 0.5 mil tons of slags is produced in steelmaking in The Czech Republic per year. A considerable amount of these waste products is uselessly deposited. Knowledge of slag properties leads to higher rate of its use. A high variability in quality of produced steel, as well as various type of aggregates, where the steel is produced in, contribute to fact, that steel slags show varied parameters.

An introduced paper tries to describe development of the chemical and the phase composition of slag from a ladle metallurgy in process of their primary treatment with regard to possibilities of further material use of this type of slag. An essential discovered fact is that, the slag taken from metallurgical ladle shows different parameters as the same slag, which is taken in specific points of its primary treatment. It was discovered, that slag becoming from melting aggregate changes in the process of its following treatment. This change is obvious in a chemical and a phase composition of slag. The changes of a chemical composition are caused by a contamination of slag, particularly by a steel contamination. The changes in phase composition of a slag are the result of a thermal history of slag.

Keywords: *Slag, material use of slag, chemical and phase composition*

Introduction

Metallurgy is a significant indicator of economic and particularly technology advanced level of state. Today in The Czech Republic, as well as in the past, metallurgy is a traditional and significant branch of national economy. Metallurgy, as an industrial sector focusing on an iron and steelmaking, represents sector with amount of produced wastes. Production of slag, related to volume, is the most significant.

Potential of using possibilities of metallurgical slags, as a by-product, is high. Knowledge of its properties is essential for a possible further application of slag. These properties could be limiting criteria in specific cases.

Slags from iron and steel

Iron and steelmaking plays the dominant role in metallurgy. Figure 1 shows volume of production of pig iron and steel in The Czech Republic and in the world in period 1992 – 2016[1].

Iron and steelmaking is essentially accompanied by forming slag by-product. Forming of slag is caused by addition of slag forming ingredients, corrosion and erosion of working lining of melting aggregate, content of waste rock in metal bearing ores, ash in coke and other impurities[2].

Creation of slag in a metallurgical process has required and unrequired consequences. An active participation on metal refining, slag as an insulating material on melt surface, where blocks transport of thermal energy, decrease losing radiation of thermal energy and so slows down cooling of metal in melting aggregate, these can be considered like required consequences. On the contrary, the costs of energy needed to melting, costs of slag treatment and if it does not exist, also costs of its storage in a dump can be considered like unrequired consequences from the plant point of view[3].

Slags can be divided into two basic categories according to type of production, blast furnaces slag and steel slag.

Chemical composition of blast furnace slag (BFS) depends on composition of metal bearing charge, slag forming additives, purity of coke, etc. BFS contains mainly (CaO, SiO_2, Al_2O_3, MgO, MnO, FeO, TiO_2), also sulphides get into slag (CaS, MgS, BaS, MnS, Na_2S, K_2S), alternatively some nitrides and carbides. Table 1 introduce typical composition of BFS[4].

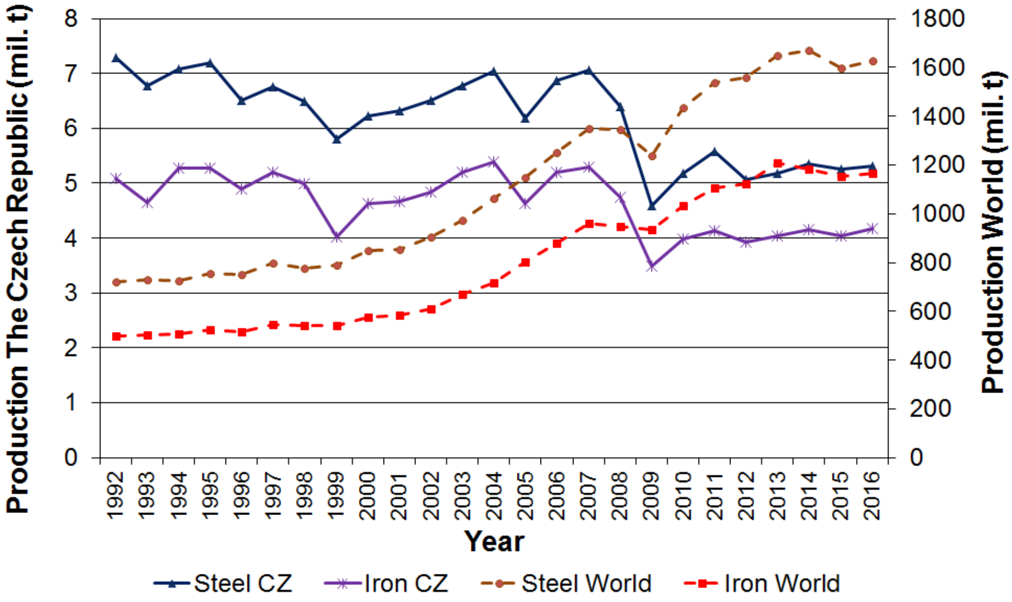

Figure 1: Iron and steel production in the Czech Republic and in the World in period 1992 – 2016[1]

Table 1: Typical composition of BFS[4]

Component	**Wt. %**
SiO_2	34 – 38
MgO	10 – 14
Al_2O_3	6 – 9
CaO	35 – 38
MnO	0,5 – 2
$FeO + Fe_2O_3$	0,5 – 1

Steel slag can be classified according to the type of melting aggregate, where they are formed, on furnace slag (forms in steelmaking furnace) and ladle slag (forms in ladles). Slag becoming from steelmaking aggregate shows, related to variability of aggregates, where it forms, and various quality of steel, variability in its chemical composition. Table 2 introduce a typical chemical composition of steel slag[5]. Mineralogical composition of steel slag is, equally to its chemical composition, very variable. Acidic, basic and neutral oxides create in slag in solid state string of compounds. From the phase point of view, it is heterogeneous system, where can be attended minerals like merwinite, gehlenite, cristobalite, brownmillerite, tricalciumsilicate (C_3S), dicalciumsilicate (C_2S), periclase, CaO and so on, very often that ones with non-stoichiometric composition.

The phase composition is essential for further use of slag. Phase composition depends on a chemical composition and cooling conditions of slag. In ideal conditions, slag should in molten state create only one glassy phase. This glassy phase is characterized by its chemical composition and temperature. At fast cooling process of molten slag, the glassy state is maintained and so solid amorphous state can form. This fast cooling is usually taken by spoiling of water, or by rapid cooling by air flow. Glass-forming of slag is supported by presence of SiO_2. On the contrary, at slow cooling process atoms arrange into regular crystalline structure[6].

Table 2: Typical composition of steel slag[5]

	EAF – carbon steel	**EAF – alloy steel**	**Converter**	**Ladle**
Component	**Wt. %**	**Wt. %**	**Wt. %**	**Wt. %**
SiO_2	9-20	24-32	8-20	2-35
MgO	5-15	8-15	5-15	1-10
Al_2O_3	2-9	3-8	1-6	5-35
CaO	35-60	39-45	30-55	30-60
MnO	3-8	0,4-2	2-8	0-5
$FeO + Fe_2O_3$	15-30	1-6	10-35	0,1-15

Nowadays, material use of BFS is very well solved. BFS is treated in liquid state by the method of granulation, which is fast cooling. Resulting amorphous product, so called a granule BFS, is used mainly as an active ingredient to cement. Another possible use slowly cooled BFS is its treatment to so called artificial dense aggregate. Product is characterized by its volume stability; thanks to that wide possibility of use of this by-product from production of pig iron exist.

Situation in the case of steel slag is more difficult. At first, chemism of this type of slag is much strongly various, than in the case of BFS. Part of steel slag, which does not succumb to volume changes, is used as dense heavy aggregate for less demanding applications. Slag from ladle metallurgy is partly recycled in aggregate of its primary forming; considerable part is stored on slag heap. The reason is its inappropriate composition and volume instability.

A granule BFS as well as some other steel slag can be used by the method of alkali activation. Condition is that it must be in amorphous state, which ensures its latent hydraulicity. A latent hydraulic substance does not react with water, suitable activator has to be added for its setting and solidification. These activators are solutions of salts of alkali metals. As an available and verified activator seems to be sodium silicate, of which addition ensure alkali activation. Products from activated slag commonly achieve value of compressive strength over 100 MPa [4].

Experimental part

Evidence system of metallurgical slags is nor simple nor definite. Dispersion of data from the point of view of amount of produced slag and also its composition occurs. Slag assembled with remains of steel in the place of its primary occurrence. Consequently, the slag is cooled down, present steel oxidizes, then the steel is magnetically separated. Slag is often treated in places, where can be contaminated by other wastes from metallurgy, for example by crashed lining from thermal aggregates. A significant fact for forming of slag phase composition is its different speed of cooling. These aspects resulting in amount of slag which depends on place, where this parameter is investigated, whereas this amount can differ on next stand or after next operation of slag treatment, and simultaneously slag composition changes. Stated paper tries to describe the change of ladle slag composition during technological cycle of its primary treatment (cooling, separation of metal remains, granulometry sorting), which has direct consequence with possibilities of its use.

Ladle slag was separated in chosen steel plant. For this type of slag, there is not discovered optimal material use in producing plant. The slag excellent in a negative property, which is its volume instability. Modificatory transformation of dicalcium silicate is the reason in this case. This mineral transforms from the form β to form γ during cooling. Unlike balanced conditions, this change does not take place immediately, but products become partly unstable and change can occur much more later. Next cause of volume instability is presence of free lime CaO and MgO, which are oxides easily hydrating and forming phases succumb to a strong volume change[2].

In this plant, slag is, at ordinary circumstances, transported from steelmaking hall to next treatment on to a slag field, after steel casting out of ladle. Already in this moment different type of slags are mixed.

The reason is a fact, that quality of manufactured steel changes with high frequency, thereby also slag composition changes. An operating system of chosen plant allowed to ensure separate gathering of two type of slag for the purpose of this work. It is possible to concentrate "blended" slags by the system commonly used in steel plants and additionally it is also possible to concentrate slags from specific melt ages. For the purpose of this work from a blended slag was divided the slag with high SiO_2 content and it can be considered, that this slag can behave similarly to well exploitable BFS.

A chemical composition of slags was evaluated by the method of XRFA (spectrometer SPECTRO XEPOS equipped with 50 W Pd X – ray tube) and the phase composition of slags was determined by the method of XRD Bruker D8 Advance type (theta/2theta). Source of X-Ray was Cobalt lamp. For determination of diffract positions on registered diffract records PC software Diffrac.eva and COD crystallographic database were used.

Slags with high SiO_2 content

An experiment, in which a ladle slag was separated from 9 melt ages took place in a mentioned sense. Slag with higher content of SiO_2 was chosen for an experiment. The reason for the use was its suitable chemical composition for application in bonding systems. High SiO_2 content ensures good glassy state forming. More over 30 tons of slag was taken by experiment realization. It was confirmed, that increasing effort can provide for the separation of slag in operating conditions.

Treatment of taken slag took place by common way. Slag was transported on slag field, where final wet cooling proved and also magnetic separation of metal parts of slag run. Consequently, the slag was transported into mill plant, where fractions between 0 – 8 mm and 8 – 64 mm were separated. These grain fractions were chosen purposely related to common operation condition of mill plant. Sample of slag was taken in each step, four in total. Sample 1 – taken directly from ladle in liquid state. Sample was taken in each of 9 following melt ages. Sample 2 – taken on workplace of slag field, sample 3 – fraction 0 – 8 mm after treatment, sample 4 – fraction 8 – 64 mm. Chemical composition introduces Table 3 and Figure 2. The table asserts only presence of most important components, minors are excluded.

Table 3: Chemical composition of slags, in wt. %

Sample	Specification	Fe_{metal}	Fe_{total}	FeO	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	S	TiO_2	Total ∑
1	Ladle slag – higher SiO_2 content, sampling from ladle (liquid state)	0,45	2,2	1,7	0,61	37,5	6,9	38,3	12,7	0,019	0,496	98,675
2	Ladle slag – higher SiO_2 content, sampling from slag field after cooling (soild state)	0,51	14,8	11,9	7,54	27,5	4,2	36,5	10,2	0,074	0,413	98,837
3	Ladle slag – higher SiO_2 content, sampling from mill plant 0-8 mm	0,56	13,9	10,1	8,20	27,6	4,4	37,3	10,1	0,124	0,430	98,814
4	Ladle slag – higher SiO_2 content, sampling from mill plant 8-64 mm	0,34	14,0	11,4	7,06	27,7	4,2	35,8	11,6	0,083	0,387	98,570
5	Ladle slag (mixture of various types) – mill plant after arrival from slag field	0,43	18,3	15,9	8,10	16,1	6,1	46,6	4,9	0,240	0,287	98,657
6	Blended ladle slag (mixture of various types) – mill plant 0-8 mm	0,27	12,7	9,3	8,09	18,1	8,0	44,8	7,9	0,390	0,404	97,254
7	Ladle slag (mixture of various types) – mill plant 8-64 mm	0,24	15,3	13,5	7,26	18,2	7,2	40,9	8,7	0,254	0,452	96,706
8	Slag waste dust from mill plant	0,19	10,9	4,8	10,70	16,0	3,8	54,1	7,2	0,419	0,324	97,533
9	Ladle slag – heap	0,47	21,3	15,9	12,48	14,5	4,1	40,3	10,7	0,184	0,207	98,841

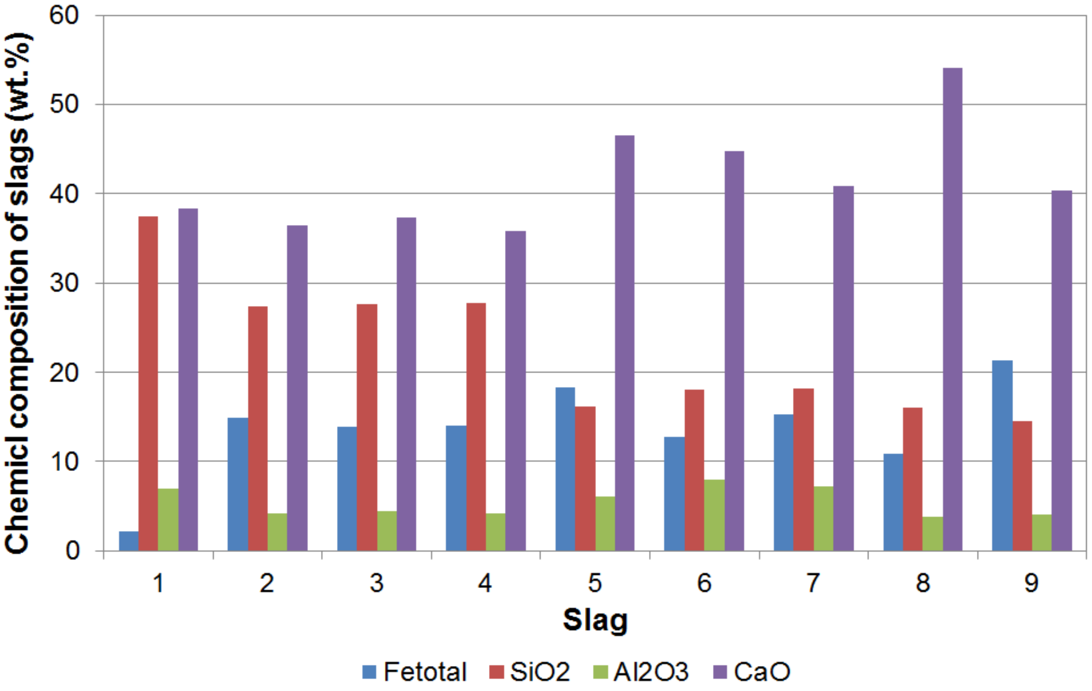

Figure 2: Chemical composition of slag (main chemical components)

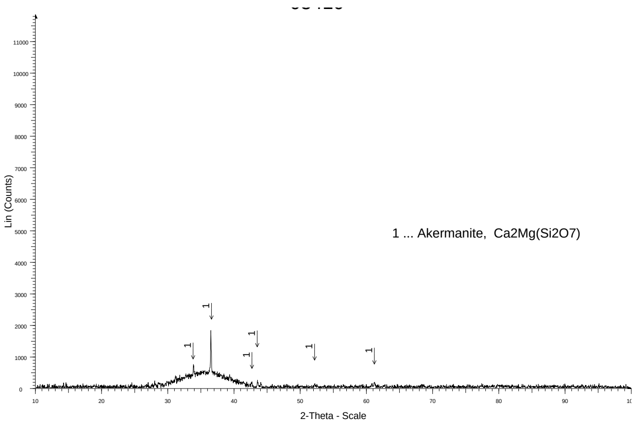

Figure 3: X-Ray difractogram of sample 1

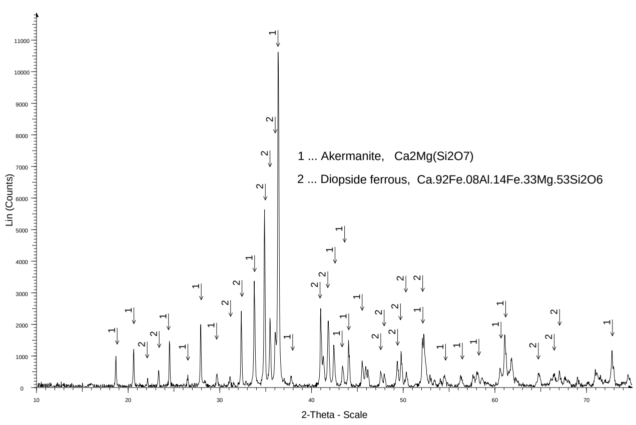

Figure 4: X-Ray difractogram of sample 2

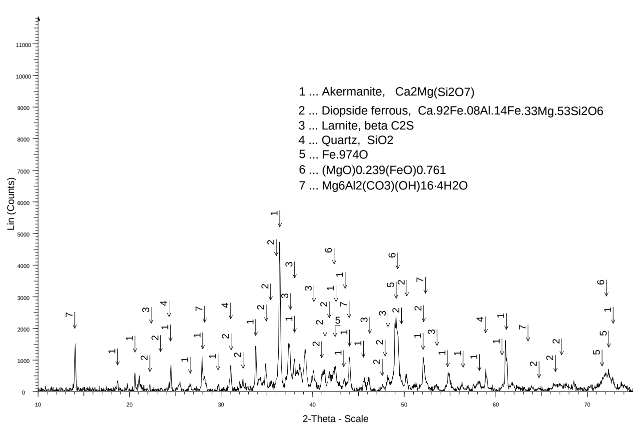

Figure 5: X-Ray difractogram of sample 3

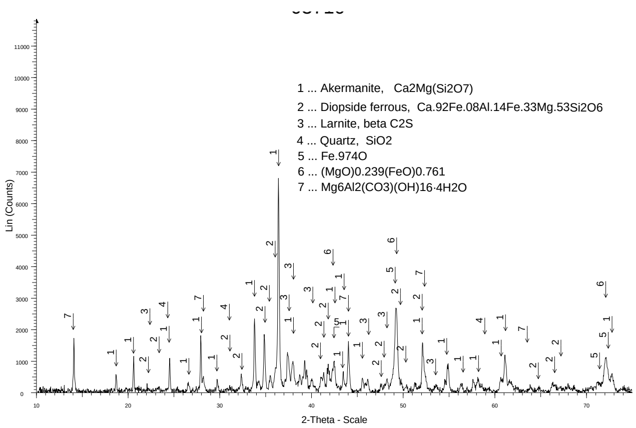

Figure 6: X-Ray difractogram of sample 4

Different chemical composition of slags with higher SiO_2 content taken from different stands reflected also in their phase composition, Figures 3 – 6.

Blended slags

Consequently, next four ladle slags were taken from mill plant. These slags become from common occurrence, in this case any separation did not carry out. These slags can be considered as blended slags, their composition depends on actual producing programme of steel plant. So that sample of blended slag was taken, no. 5 – after suppling from slag field, just before separation of metal part. After that sample 6 was taken – fraction 0 – 8 mm and sample 7 – fraction 8 – 64 mm after a granulometric treatment on milling line. These samples were already magnetically separated from metal remains. Finally, it was taken sample 8 – slag waste dust from milling line. Chemical composition introduces Table 3. Phase composition is documented on attached difractogrames below, Figures 7 – 10. On these difractogrames, as well as further in this paper, a chemical formulas of substances are simplified according to common practise used in silicate industry. It means, that C means CaO, S - SiO_2, F - Fe_2O_3, A - Al_2O_3. Then for example C_2S is dicalcium silicate $2CaO{\cdot}SiO_2$.

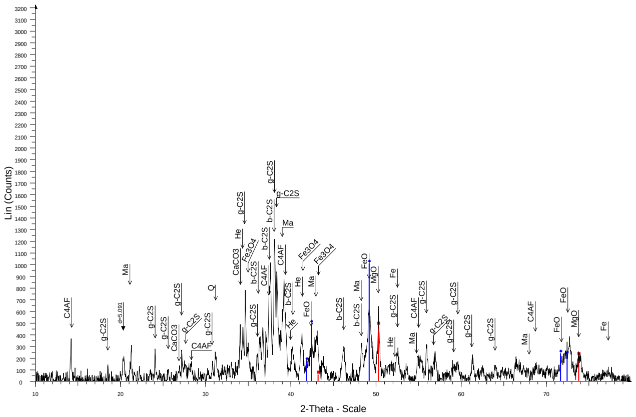

Figure 7: X-Ray difractogram of sample 5

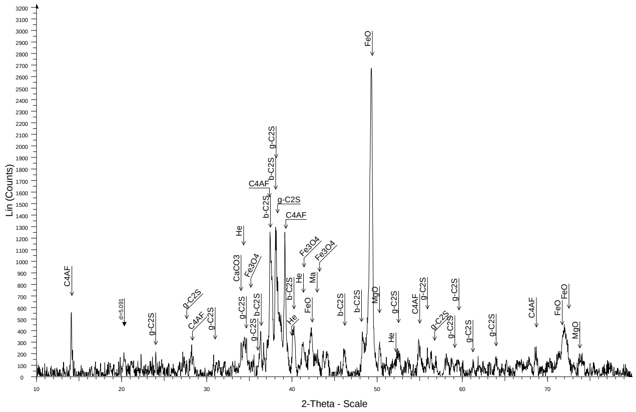

Figure 8: X-Ray difractogram of sample 6

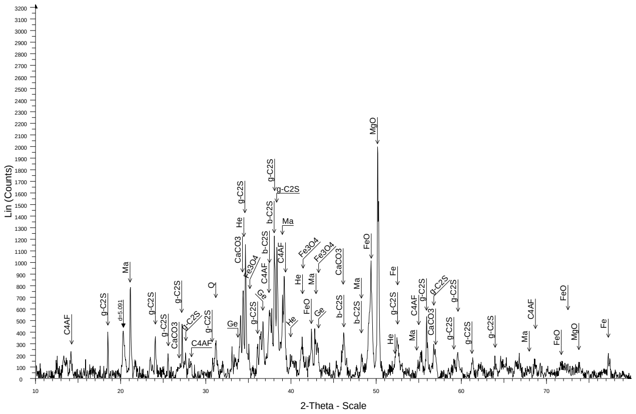

Figure 9: X-Ray difractogram of sample 7

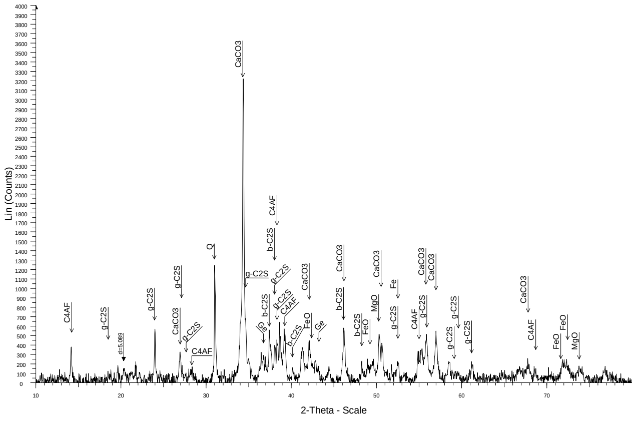

Figure 10: X-Ray difractogram of sample 8

Photos of taken slags are given on Figures 11 – 18.

Figure 11: Ladle slag, sample 1

Figure 12: Ladle slag, sample 2

Figure 13: Ladle slag, sample 3

Figure 14: Ladle slag, sample 4

Figure 15: Blended Ladle slag, sample 5

Figure 16: Blended Ladle slag, sample 6

Figure 17: Blended Ladle slag, sample 7

Figure 18: Slag waste dust, sample 8

Results and discussion

Slags from ladle metallurgy were taken and evaluated. Selectively chosen slag with a higher SiO_2 content was taken in a various treatment stands. All analyses were carried out on the same slag batch. A physical transport of slag over whole plant was observed, it means from it's primarily occurrence in steel plant (sample 1), over slag field (sample 2) to mill plant, the slag was divided into grain classes, samples 3 and 4. Furthermore, composition of blended ladle slag was observed too, i.e. mixes of slag, which formed according to actual producing plan in steel plant. It was observed composition of blended slag after its arrival to mill plant (sample 5) and consequently composition of separated grain classes from mentioned slag (sample 6 and 7). An elder slag randomly chosen from storage on heap was analysed (sample 8) and so slag waste dust was analysed, which formed during slag separation into particular grain fractions (sample 9).

Chemical composition of studied slags

The first evaluated group was group of slag with a higher SiO_2 content. While sample 2 and 4 show very similar chemical composition, sample 1 shows difference, where all samples (1 – 4) present one type of slag which only differ in a stand where they were taken. The main difference in chemical composition lies in their iron content. Slag 1 was taken as a liquid, directly from the steel ladle. Clean sample of slag is achieved at precious taking of slag sample without metal content (total amount of Fe 2.2 wt. %). Content of iron oxide in samples 2 – 4 (average total content of Fe 14.2 wt. %) can be explained like, slag, in operating conditions, is poured into slag ladle with included remain of non-casted steel. This slag is after that cooled by water, thereby conditions for oxidation of metal iron, are created. This oxidized iron becomes part of slag due to this phenomenon.

During the experiment does not occur a stronger contamination of observed slag by polluting components in manipulation at slag field plant and mill plant. Prevention of pollution was priority of whole experiment. Assumption of additional oxidation of iron, which is presented in slag, confirms also another experience, when next sample of randomly chosen ladle slag no. 9 taken from heap at mill plant, contains 21 wt. % of total iron. The same like blended slag, which analysis was carried out till its treatment on slag field, contains in an average 15.4 wt. %. To this conception, from which can be concluded, that ladle slag gains its metal part thanks to the way of its treatment, perfectly fits also composition of waste slag dust, which were taken from long term grain separation from mill plant, when sample of waste slag dust (sample 8) contain 11 wt. % of total iron. Declared finding explains causes of different composition of ladle slag, which is given in literature. When slag contains insignificant amount of iron, it means, that analysis belong to slag taken from metallurgical aggregate, when slag contains iron, it means, that the sample from so called "occurrence" was analysed.

Difference in SiO_2 content is also significant. Representation of this component in slags 1 – 4 is between 28 and 38 wt. %, thereby 15 – 18 Wt. % in slags from group 5 – 9. Decrease of SiO_2 content in case of slag 2 – 4 comparing to sample 1 is given by the fact, that melt ages, from which slags become, require basic character, which ensure presence of CaO, resp. MgO.

Phase composition of studied slags

Resulting phase composition is affected partly by a chemical composition and also significantly by a speed of cooling, which differed in a particular taking. Thereby sample 1 cooled down quickly after taking, its structure is typically amorphous, containing akermanite. Its high speed of cooling was ensured by spoiling of taken sample on steel plate, which takes away the slag heat quickly. Forming of amorphous character of slag was supported by the presence of higher SiO_2 content. Samples 2 - 4 have completely different thermal history, they were taken from slag, of which weight achieved a few dozen tons, and thereby by significantly slower cooling was given. Under these conditions, crystalline phases crystallised from slag. Presence of akermanite and diopside is obvious in sample 2. Samples treated at mill plant (sample 3 and 4) also contained phase of lime, quartz, wüstite and other oxide phases containing MgO and FeO.

In the case of blended slags 6 - 9, their phase composition is similar. Part of β-C_2S and C_4AF phases seems to be interesting. These phases are hydraulic, which means, that they react with water and products of this reaction set and solidify. Listed minerals occur also in Portland clinker, which is used for cement production. Forming of these phases is caused by the presence of CaO, which is represented in observed slags in big enough amount, overwhelm 40 wt. %. Next presented phase of γ-C_2S is non-hydraulic. The presence of CaO and MgO cause volume instability of this type of slag, when appropriate hydroxides create by the reaction with water and so strong volume change occurs.

Possible application of observed slags

Pictures of slags illustrate their various morphology. Completely different is slag 1. From its picture it is obvious its amorphous character. Other slags are crystalline, grain size is caused by the way of their treatment at specific technology stand, where it was taken.

This work proves, that it is possible to ensure separately take chosen quality of slag, which significantly differs from commonly produced blended slag, in operating conditions. The importance of finding is raised by the fact, that slag 1 shows excellent bonding ability. Introduced slag was tested for determination of efficiency index according to standard[7]. Principle of the method lies on comparing of strength parameters gained on body prepared from mix of standard sand and Portland cement, class CEM I 42.5R and body, which is prepared by the same way differs only in that 50 Wt. % of cement is replaced with slag. After 28 days of hydration it was found out, that tested bodies containing slag1 achieved flexural strength on level 121 % and compressive strength on level 104 % comparing to body without slag. The strength was ensured by activation of latent hydraulic glassy components of this slag. In this case the activator was $Ca(OH)_2$, which creates during cement hydration. Slags 2 – 4, even though the same type, they already did not show such strength. The reason is absence of glassy phase, because crystalline phases are inert against alkali activation.

Other slags, which were taken from mill plant (samples 5, 6 and 7), is possible to recycle back in steelmaking process, where slag partly step slag forming components commonly used during melt ages. This way of use of ladle slags is hopeful and effective. It is limited by the fact, that slag before its application into melting aggregate decompose to fine grain powder, which is later manipulated with difficulties. The reason of slag decomposition is very briefly mentioned in previous part of text, this work does not interest in it. Phase composition of observed slag 5 – 7 contains mentioned parts of β-C_2S and C_4AF phases, which can be used for the purpose of slag solidification. Solidification can be achieved by milling of slag and its following briquette solidification at the use of bonding ability of slag gained by water addition. Authors of paper are long term interested in this topic and briquette process of slags is successfully implemented in steel plants. The example of this successful application is utility model with no. of record 23992[8] or works[9,10].

Conclusion

Presented work documented changes of a chemical and phase composition of a ladle slag from steelmaking during its primal treatment. Slags enriches with iron in conditions of their occurrence. Iron gets into material during gathering of slags in steel plant operating stands. Part of elementary iron remains in slag over the effort of magnetic separation, but particularly as iron oxides or more complex compounds. Further was found, that comparing to common practise, it is technically possible gathering of separated slag from individual melt ages according to their similarity. This arrangement allows to gain slags, which related to their specific parameters is possible purposefully material use. Ladle slags show bonding ability, which can be activated by adding of water or by alkali activation. Considering this property, the slags can be used into stabilizing mixtures, for example in the process of restoration. It is also possible to use them because of their bonding ability for compaction of disintegrated slags in process of their recycling in melting aggregates. The correct choice of a concrete use of slag is conditioned by a chemical and a phase composition of slag.

Acknowledgment

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Vývoj parametrů strusek z pánvové metalurgie v průběhu jejích primárního zpracování

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Souhrn

Strusky z výroby oceli představují významný velkoobjemový odpad. V České republice vzniká při výrobě oceli více než 0,5 mil. tun strusek ročně. Značná část těchto odpadních produktů se materiálově nevyužívá a je deponovaná. K větší míře využití přispívá znalost jejich vlastností. Vysoká variabilita jakostí vyráběných ocelí, stejně jako variabilita zařízení, ve kterých je ocel produkovaná, přispívají ke skutečnosti, že ocelárenské strusky vykazují různorodé parametry.

Uvedená práce se snaží popsat vývoj chemického a fázového složení strusek z pánvové metalurgie v procesu jejich primárního zpracování s ohledem na možnosti dalšího materiálového vyžití těchto strusek. Zásadní zjištěná skutečnost je, že struska odebraná z metalurgické pánve vykazuje odlišné parametry jako tatáž struska, která se odebírá v uzlech jejího primárního zpracování.

Klíčová slova: *Struska, materiálové využití strusek, chemické a fázové složení.*

Properties of alkali-activated systems and the possibilities of their application in the decorating elements of the facades

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Abstract

Alkali-activated systems represent inorganic substances resulting from alkali activation of suitable precursors and subsequent polycondensation. They offer great energy and environmental potential.

The goal of the experiment is to research the impact of various types of applied activators on the final properties of prepared composites prepared on the base of granulated blast furnace slag. The properties were verified with respect to the intended application in construction practice as decorating elements of the facades.

We verified the possibility of substance preparation through a common construction practice method and the suitability of formulas for decorating elements of the facades production. During our experiment, we observed the degradation changes of body surfaces over the course of one year from preparation, and we also observed the impact of deposit methods on decreasing pH values and strength development. During our experiment, we observed the sample degradation during exposure on a common facade composition and the impact of exposure to environmental impacts on the strength characteristics of loosely located samples compared to samples stored in a laboratory environment.

The main contribution of this work is the implementation of scientific-research activity results in the actual conditions of a specific area of the construction industry.

Keywords: *Alkali-activated, blast furnace slag, activator, decorating elements of the facades.*

Introduction

Alkali-activated materials are compounds of two or more components prepared through alkaline activation of latently hydraulic substances or pozzolans using an alkaline activator (carbonate, silicate or hydroxide). The activator initiates the splitting of bonds of aluminium silicate and subsequent polymerisation, during which new phases are created. These reactions take place in the presence of water. Currently, alkali-activated systems are most often divided according to the content of CaO in their binding components. Based on the contents, the form and crystal phases of calcium in the original binding component, the final alkaline activation products differ.[1 - 4, 6, 7, 8]

Substances with high CaO contents (blast furnace slag) are expected to show similar hydrating process products similar to the products of hydration of Portland cement with water; therefore, generation of C-S-H gel. Compared to cements, slag does not generate portlandite and ettringite. [1, 3, 6, 7]

Alkali-activated materials have great potential not only in the construction industry. Their wide application in construction is mainly complicated by the need for significant technological discipline during the alkaline activation proces. If it is not applied, the monitored parameter values will significantly fluctuate.[5] Practical use is also complicated by the use of highly alkaline compounds, often in the form of solutions, which is a health risk for workers.

It is quite possible to use these materials first in non-supporting, filling, or decorative construction elements, which may be, if necessary, easily replaced. They may be used in supporting structures only when they meet the condition of declaration of resulting product sustainable quality. That is why the goal of our experiment is the preparation and verification of the long-term properties of alkali-activated substances integrated into common facade compositions.

Experimental part

Used Materials

During the experiment, the following items were used: mixing water, finely ground granulated blast furnace slag, 0/4 mm Tovačov fraction mined sand, the activator types described in detail below - DESIL AL, sodium and potassium water glass, and disodium metasilicate with the composition specified in Table 1.

Table 1: Activator properties

Activator Type	K_2O [% wt.]	SiO_2 [% wt.]	Na_2O [% wt.]	Al [% wt.]	SiO_2/Na_2O [-]	Density [kg/m^3]
DVS2	26.0 - 26.5	28.2 - 29.0	–	–	1.7*	1650
Desil AL	–	31.0 - 45.0	15.0	0.1 - 2.0	2.1 - 3.0	1470
MKS	–	44.0	44.0	–	1.0	950**
NaVS1,5	–	15.8	10.8	–	1.5	1352

** SiO_2/K_2O, **bulk density*

The specific surface of the slag used during the experiment is 420 m^2/kg. Measured through the BET analysis. The percentages of the individual oxides are described in Table 2.

Table 2: Oxide percentages in the slag

Oxide	Percentage [%]
CaO	40.0
MgO	8.9
SiO_2	39.9
Al_2O_3	6.9
Fe_2O_3	0.4
SO_3	0.6
$(CaO + MgO)/ SiO_2$	1.2

Sample Preparation and Testing

During our experiment, we strove to imitate the actual body production as much as possible; therefore, we prepared our mixtures in a bucket using a traditional construction mixer. Due to the specific needs of the given material, we selected the following procedure.

Finely ground blast furnace slag, activator and water were mixed in a smaller bucket. Our formulas were based on previously completed research works - see [5]. The only difference was that our mixture had 4-5% more mixing water due to improved workability, and we also changed the sand type used. Ordinary construction sand (due the czech standards) was put into a larger bucket. We mixed our binder mixture with the construction mixer until everything was properly mixed. It took 120 s.

After that, the binder mixture was mixed into the filler, where it was mixed until a homogeneous mixture was produced. At the time of pouring, the identified mixture consistency due the standard

ČSN EN 1015-3 was 130 ± 10 mm. The mixtures were poured into moulds and vibrated. We find out behaviour of the mixtures which is similar to thixotrophic mixtures, since during vibrations the alkali-activated systems became very liquid and perfectly filled the mixture moulds even when their original consistencies were quite solid before the vibrations. These findings are very important for the practical use of alkali-activated mixtures.

For the tests, we produced both standardized samples meeting the requirements of the Czech technical norms guiding the tests, as well as samples resembling facade components.

As suitable items, we selected rosette facade components with a diameter of 150 mm and tiles (dimensions 300 x 300 x 30 mm) for visual observation. For our mechanical properties tests, we produced prismatic samples with dimensions 160 x 40 x 40 mm. For pH value identification – the items left over from the tensile strength and cut-off point tests were used.

Before practical application, it is necessary to observe the long-term properties of these materials, both when they are exposed to environmental loads on the exterior and regular interior conditions. The goal of our experiment was therefore to observe the visual changes of our facade components over time during their exposure to the external environment for a period of 360 days.

Tested tiles (with larger areas in order to observe their surface) and rosettes (to observe a more complex shape item) were integrated into a regular uncovered facade composition located in the structure of a brick garden alcove in the Ostrava Mariánské Hory locality. This quarter borders with industrial operations and is therefore exposed to emissions. Prismatic samples were located there as well. We established their contact with soil.

An old brick wall was used that was splashed with a thin mixture of mortar to ensure a perfect fit and further painted with a Salith limestone mortar layer to level the surface. After its maturing, the mortar was penetrated with a single-component penetration based on acrylic resins to improve the properties of the surface. According to the manufacturer's recommendation penetration was applied with a brush and left for 24 hours. The facade glue Mapei was then applied to the wall imposing facade elements of rosettes and tiles.

Results and discussion

At the end of the intended experiment period, we determined the properties of the samples exposed to the exterior (EXT) and compared them with the reference sample set kept in our interior (INT) laboratory environment during the whole experiment period.

The samples were observed at approximately monthly intervals. Our documented visual checks were always conducted after approximately three months.

After about six months, the facade components changed colour, indicating the completion of hydration processes and the unification of the colours in the individual mixtures.[9] The body based on disodium metasilicate showed the greatest colour change, since its binder processes mainly feature dark green to blue sample colours that eventually disappear. Also, there was the obvious efflorescence on the edges of the potassium water glass based sample. This behaviour may have been caused by an excess of alkali metal in the artificial stone structure, colour changes are the subject of further research.

During our check completed after 11 months, we identified potassium water glass element separation. The lack of cohesion with the common facade composition was demonstrated in the contact between glue and the alkali-activated element. The body was partially not cohesive with the glue (about 70 %) and its lower edge was partially chipped off in the glue due to the static impact of its own weight (about 30 %). The causes of the break will be studied. In practice, facade components are further mechanically anchored through nail joints; therefore, their poor cohesion would not make the use of the given component unsafe.

During a check completed after a year-long exposure, the tile with disodium metasilicate had a dusty surface, indicating onset surface layer degradation. However, the rosette sample did not have this type of surface. During the whole period, the tile sample with disodium metasilicate most significantly changed its colours from dark green-blue through dark grey with clear light efflorescence to dark grey after 360 days.

The rosettes only unified their colours (see Figure 1.). They showed no obvious degradation processes, their surface was not damaged, and none of their elements broke off (Figure 2. and 3.).

Figure 1: Comparison of rosette appearances after 360 days on the facade

Figure 2: Detail views of the Desil AL (left) and DVS2 rosettes (right) after 360 days on the facade

Figure 3: Detail views of the NaVS1.5 (left) and MKS rosettes (right) after 360 days on the facade

The prepared prismatic samples were subjected to tensile strength tests under bending after 1, 7, 28, 90, and 360 days of ageing. One test mixture comprised of three samples was tested at a single time. Average tensile strength under bending are specified in Table 3. and graphically indicated in Figure 4.

Table 3: Tensile strength under bending

Age (days)	EXT-DVS2	EXT-NaVS1.5	EXT-Desil AL	EXT-MKS	INT-DVS2	INT-NaVS1.5	INT-Desil AL	INT-MKS
1	2.7	0.3	0.7	3.2	2.5	0.2	0.5	3.0
7	7.7	0.3	6.5	7.1	7.5	0.3	6.0	7.0
28	10.0	3.0	8.3	7.4	9.7	2.7	8.2	7.0
90	9.2	4.1	8.5	6.9	9.2	4.0	8.4	6.9
360	7.7	6.2	7.8	6.5	4.8	5.8	4.9	4.2

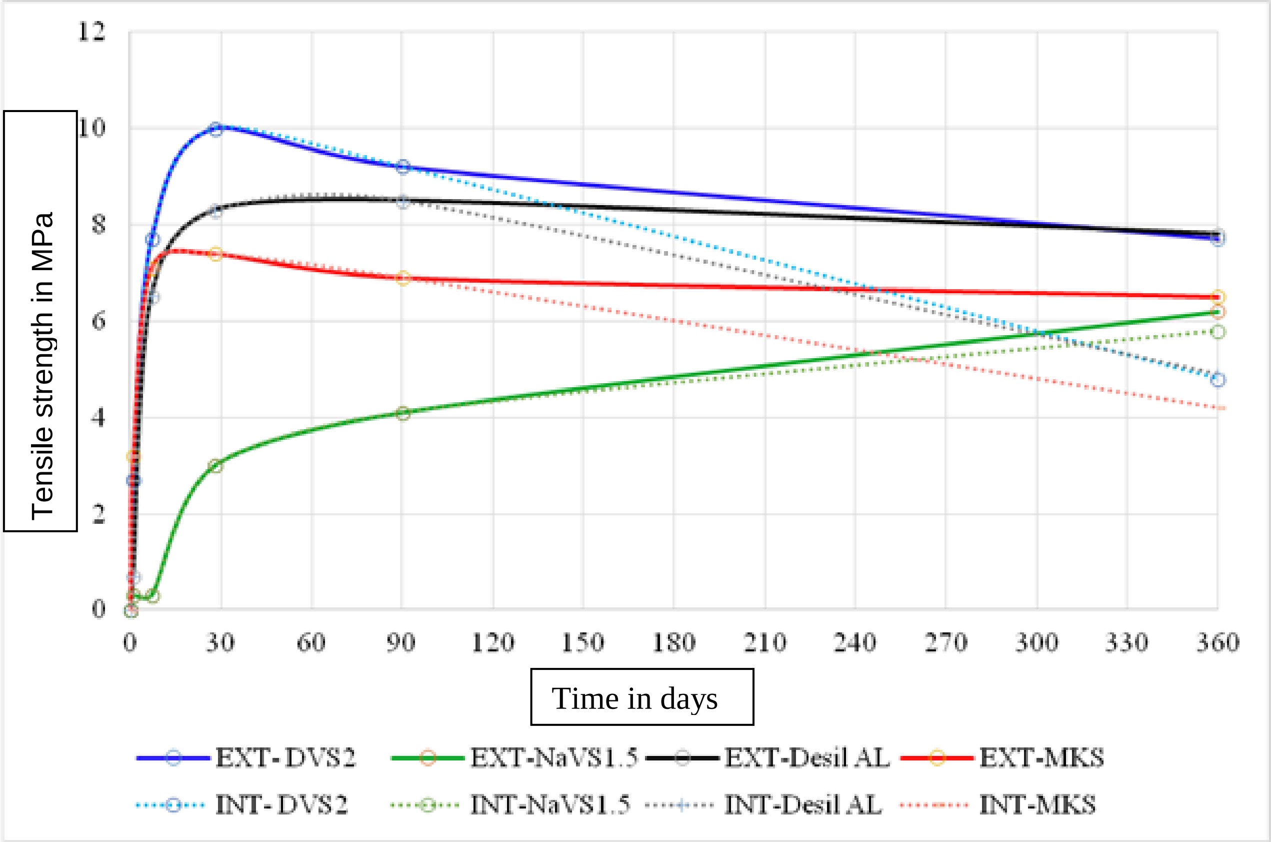

Figure 4: Tensile strength under bending

During the observed period, all the examined samples, except for NaVS1.5, had reduced tensile strength under bending. In the case of the samples stored on the exterior, the decrease of their tensile strength under bending is not that significant. It approximately corresponds to a 30% loss of the original strength when, after 30-90 days, the body shifts from its values of 8-10 MPa to about 6 - 8 MPa after 360 days. This development of values indicates processes occurring in the artificial stone structure. They occur in alkali-activated systems based on their surrounding environment, even 28 days after production.

After the tensile strength under bending test, body fragments were subject to compressive strength determination after 1, 7, 28, 90, and 360 days of ageing. The average values are available in Table 4. and graphically indicated in Figure 5.

Table 4: Compressive strength of the samples

Age (days)	EXT-DVS2	EXT-NaVS1.5	EXT-Desil AL	EXT-MKS	INT-DVS2	INT-NaVS1.5	INT-Desil AL	INT-MKS
1	20.2	2.3	3.6	19.2	20.2	2.3	3.6	19.2
7	68.6	2.3	54.2	68.1	68.6	2.3	54.2	68.1
28	71.0	16.8	63.1	71.7	71.0	16.8	63.1	71.7
90	91.5	-	71.0	63.1	91.5	23.1	71.0	63.1
360	98.4	61.0	82.3	89.8	56.4	41.0	52.4	69.7

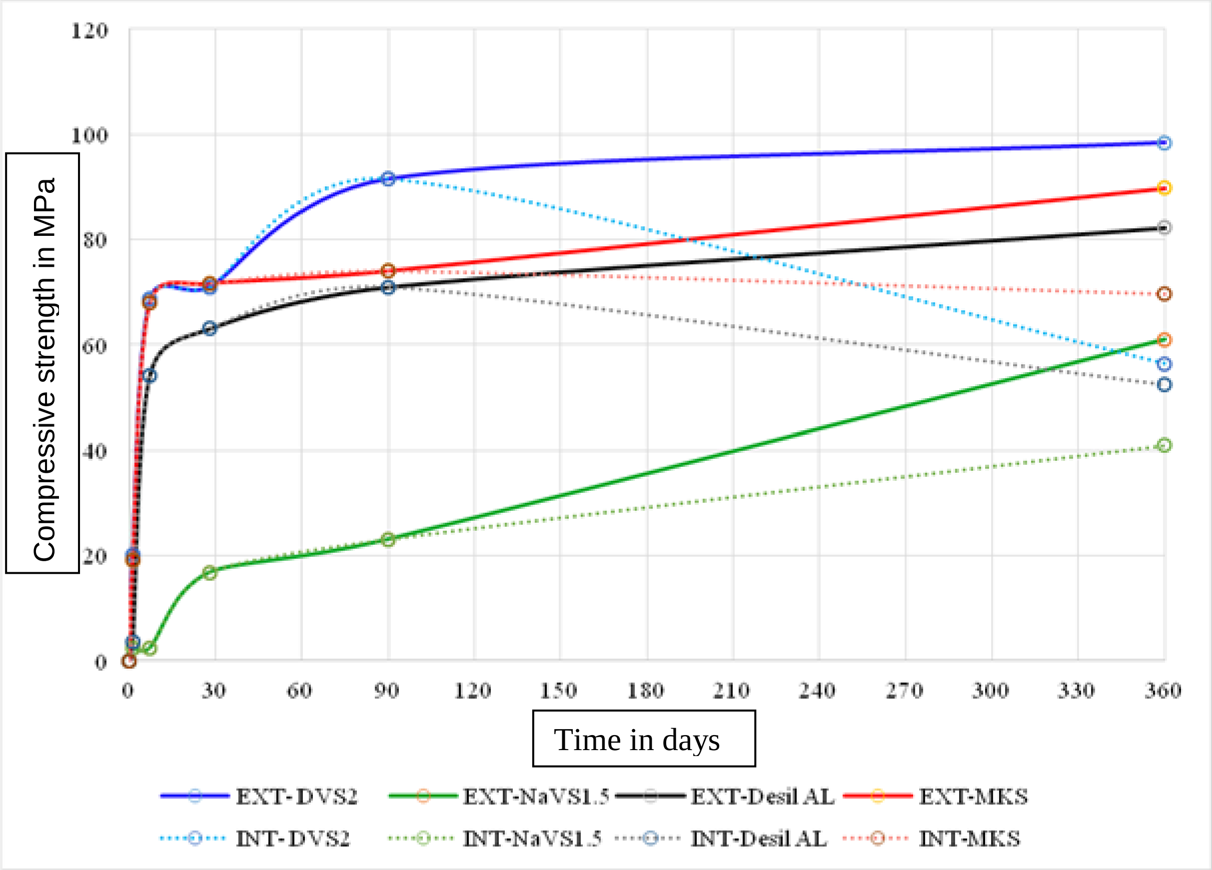

Figure 5: Compressive strength of the samples

The compressive strength of the samples stored on the exterior reach their maximum values after 360 days of ageing. Therefore, it indicates an ongoing hydration processes. The formula with DVS2 reached a compressive strength of over 98 MPa. The final compressive strength reached after 360 days is 80 – 100 MPa.

The pH value was identified at the constant laboratory temperature of 24.4 ± 1 °C due the standard ČSN EN ISO 787-9 , always after value stabilization according to the pH meter value reading requirements. The pH value was measured on the damaged body parts after compressive strength identification for which the interior and exterior samples were used. After 1 day, all the mixtures had a pH of 12.5 ± 0.1 (Table 5.). Based on the measured values, degradation of the alkali-activated system samples can be observed. It is generally problematic when the pH value falls below 9.5, when the material loses its steel reinforcement passivation ability.

Table 5: pH values after 1 and 360 days

pH		**DVS2**	**NaVS1.5**	**DESIL AL**	**MKS**
After 1 day in interior	Temperature [°C]	24.1	24.4	24.3	24.6
	pH	12.6	12.6	12.6	12.6
After 360 days in interior	Temperature [°C]	23.8	23.9	24.4	24.1
	pH	11.7	11.8	12.0	12.0
After 360 days on exterior	Temperature [°C]	23.0	23.0	23.4	23.6
	pH	11.7	11.3	11.7	12.6

Based on the measured values, we may conclude that at least during the first year of the sample's age, alkali-activated systems lose their alkaline pH quicker than cement-based binders. In the case of alkali-activated substances, their significant decrease of pH levels is caused by the loss of unbound Na or K ions, which initiate reactions. They are not firmly bound in the structure. However, a certain number of these ions stay in the structure. Regarding the tested mixtures, their annual average pH loss is about 0.9.

Conclusion

The goal of the experiment was to verify the activator's impact on the selected properties of alkali-activated systems based on finely ground granulated slag in relation to their usability in decorating elements of the facades field.

We prepared alkali-activated materials based on activators like DESIL AL, disodium metasilicate, and sodium and potassium water glass. Under laboratory conditions, we verified the possibility of preparing mixtures in the way applied in construction and evaluated the usability of production formulas of the decorating elements. It is possible to conclude that substances may be prepared in the manner common in construction.

The prepared samples of the individual formulas were integrated into a common facade composition masonry, malt, glue, element - without any final layer exposed to environmental impacts and Ostrava's aggressive climate. During our visual check completed after six months, the samples did not show any significant degradation signs. Their colours became unified in their white to grey shades.

During our visual check of the samples exposed to environmental impacts for 10 months, we identified minimum degradation signs. The body based on disodium metasilicate had a slightly dusty surface.

Our observation of strength development in time revealed that after 28 days, which is the regular ageing period of cement-based substances, the processes occurring in the alkali-activated systems were far from being over. Therefore, the subsequent development of the material properties evolves from the subsequent way of storing the samples. While after 28 days, the compressive strength values of the exterior samples continue to grow significantly, the samples located in the interior stagnate or possibly lose compressive strength. The tensile strength under bending values gradually decrease in the case of both storage methods. However, the exterior samples only show a slight decrease, compared to the decrease demonstrated by the interior samples. It was up to 50%. The exception rests in the NaVS1.5 samples. During the whole period, their strength kept increasing. However, their initial strengths are relatively low: after 28 days, only 16.8 MPa under compression, after 360 days reaches 61 MPa.

Based on the pH measurements, one may conclude that the pH value decreases after one year of age by 0.5 to 1.2 a year. Future research should show determine whether the pH values will decrease at the same speed during the subsequent years as well or whether it will slow down or completely stop.

Based on the achieved results, the prepared MKS, DESIL AL, and NaVS1.5 alkaline mixtures may be recommended for exterior applications, e.g. as cast decorating elements of the facades. The DVS2 mixture must be, in terms of its integration into common facades, further tested with an emphasis on the thermal expansion of the whole system or other factors that could cause the loss of adhesive strength.

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Vlastnosti alkalicky aktivovaných systémů a možnosti jejich použití jako fasádních prvků

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Souhrn

Alkalicky aktivované systémy představují anorganické hmoty vzniklé alkalickou aktivací vhodných prekurzorů a následnou polykondenzací. Vyznačují se velkým energetickým a ekologickým potenciálem.

Podstatou experimentu je výzkum vlivu použití různých typů aktivátorů na konečné vlastnosti připravených kompozitů, které jsou připraveny na bázi vysokopecní granulované strusky. Vlastnosti byly ověřovány s ohledem na zamýšlené použití ve stavební praxi jako prvky fasád.

Byla ověřena možnost přípravy směsí způsobem běžným ve stavební praxi a vhodnost receptur pro výrobu fasádních prvků. V experimentu byly sledovány degradační změny povrchu těles v průběhu jednoho roku od přípravy, byl sledován vliv způsobu uložení na pokles pH a vývoj pevností. V rámci experimentu byla sledována degradace vzorků během expozice na běžné fasádní skladbě a vliv expozice povětrnostním vlivům na pevnostní charakteristiky volně uložených těles, ve srovnání s tělesy uskladněnými v laboratorním prostředí.

Hlavním přínosem této práce je implementace výsledků vědecko-výzkumné činnosti do reálných podmínek konkrétní oblasti stavebního průmyslu.

Klíčová slova: *Alkalická aktivace, vysokopecní struska, aktivátor, fasádní prvky*

Mercury emissions from brown coal-fired power plants

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Summary

In present contribution, natural and anthropogenic mercury sources are summarized, new European Union legislation for Hg emissions from combustion plants is introduced and mechanisms of different Hg forms formation (elementary mercury, oxidized mercury and mercury bound to particles) together with the possibilities of Hg emissions control in coal-fired power plants are showed. The calculated estimation of mercury emissions from coal combustion showed that the efficiency of mercury capture in the existing flue gas treatment system is probably not sufficient.

Keywords: *mercury, air pollution, coal-fired power plants, legislation.*

Introduction

Mercury is a rare element in the earth's crust and it is classified as heavy metal. It is contained in many minerals e.g. its main source is cinnabar and it is also found in trace quantities in fossil fuels, soil and vegetation.[1, 2] The natural mercury level background is caused by the mercury migration between the atmosphere, the ocean, the terrestrial environments and its deep reservoirs. The cycle includes processes such as volcanic and geothermal activity, emissions and re-emissions from the ocean surface and the land into the atmosphere, deposition into the soil and the ocean by wet or dry way and through ocean sediments back into the deep reservoirs. This natural mercury cycle has been in balance and stabilized the amount of mercury in the environment at the same level as show analysis of mercury concentration in lake sediments cores and glacial ice cores. Here is also clearly seen the increase of mercury level in the environment after the start of the industrial period in the end of 19th century.[3] This increase is due to human activity which increases the transfer of mercury from deep reservoirs to environment. Processes that release mercury into the environment are primarily gold mining, fossil fuels burning and other high-temperature processes such as metallurgy and cement production. During the mercury cycle, there are various chemical transformations and one of them is the biosynthesis of methyl mercury and dimethyl mercury. These extremely toxic compounds produce bacteria in the aquatic environment where they are also easily absorbed by the organisms e.g. plankton. It occurs to bioaccumulation along the food chain and in the end it has a negative impact on animals and human health.[3, 4] With regard to the global environmental impact of mercury pollution, there is an effort to regulate anthropogenic sources of mercury in recent years.

The aim of present contribution is to introduce new European Union legislation for Hg emissions from combustion plants, formation of Hg emissions and its forms and possibilities of Hg emissions control.

New European Union legislation for Hg emissions

The main source of mercury emissions in the EU is coal burning.[1] For this reason, the Best Available Techniques (BAT) Reference Document for the Large Combustion Plants with thermal input equal or greater than 50 MW was approved in 2017. This document sets new limits of known pollutants and introduces new ones that also include mercury. The new limits for mercury shall enter into force since 2021 are listed in Tab. 1.

Table 1 New emission levels for mercury emissions to air from the combustion of coal and lignite[5]

Combustion plant total rated thermal Input (MW)	BAT-AELs* (µg/Nm³)			
	Yearly average or average of samples obtained during one year			
	New plant		Existing plant	
	black coal	brown coal	black coal	brown coal
< 300 MW	1-3	1-5	1-9	2-10
≥ 300 MW	1-2	1-4	1-4	1-7

**BAT-AELs – Emission levels associated with the best available techniques*

These new limits will have a significant impact on energy sources in the Czech Republic, since coal combustion, especially brown coal combustion, is the main source of electrical energy and heat production, as is shown in the Figure 1 and Figure 2.

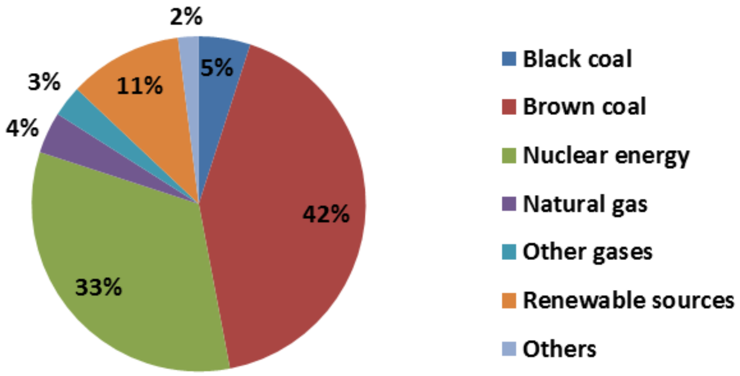

Figure 1: Sources of electricity production in the Czech Republic in 2017 [6]

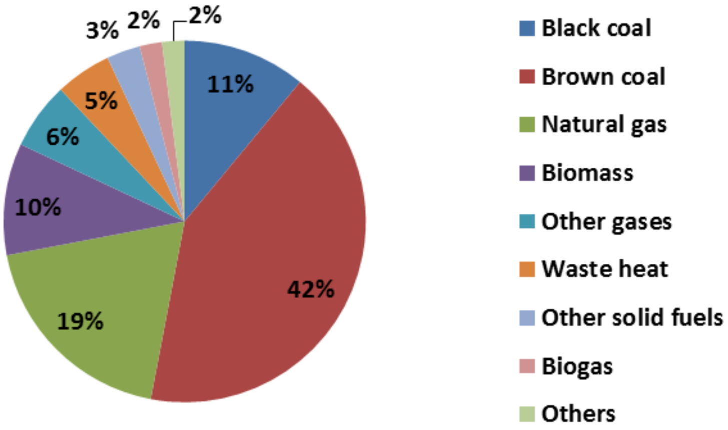

Figure 2: Sources of heat production in the Czech Republic in 2017 [7]

Aspects of mercury control in combustion plants

There are three forms of mercury in the flue gas: elemental mercury Hg^0, oxidized mercury Hg^{+2} and mercury bound to particles Hg^P. During the combustion process at temperatures 1200 – 1600 °C, nearly all mercury gets into the gas phase as Hg^0, due to its high volatility.[8] Hg^0 is practically insoluble in water and therefore remains in the gas phase and easily passes through the flue gas cleaning system.[3, 9] After the flue gas is cooled to about 700 °C, the Hg^0 begins to oxidize to Hg^{+2}.[9] This oxidation can be homogeneous in the gaseous phase or heterogeneous on the surface of the flue-gas particles. Heterogeneous oxidation of Hg^0 involves reactions of all the acid components of the flue gas.[10] According to the several authors Pavlish[10] Livengood[11] Niksa[12] Galbreath[13], oxidation of mercury is influenced by many factors such as thermodynamic conditions, kinetic conditions relative to residence time, concentration of other components and the content of the key component of chlorine. Depending on the operating conditions, the selective catalytic reduction of NOx by ammonia or urea (SCR) can also participate in the oxidation of mercury.[14] Hg^{+2} forms are more soluble in water and therefore can be captured in wet FGD (Flue gas desulphurization). After the flue gas is cooled down, part of gaseous mercury is condensed on the fly ash surface and produces Hg_P. Hg_P can be easily removed by ESP (electrostatic precipitators) or FF (fabric filter). Therefore, the maximum conversion of Hg^0 to Hg^{+2} and Hg_P forms is preferred to capture maximum amount of mercury by existing flue gas cleaning system.

Estimation of the current situation in the Czech coal-fired power plants

At most large power plants (> 300 MW) in the Czech Republic, the cleaning system consists of ESP and wet FGD. These coal-fired power plants usually burn coal from local sources. Details of local coal characteristics and mercury content are given by Pilař[15] and Pešek[16]. The effectiveness of mercury capture for the ESP + wet FGD configuration is 21 – 56 % for brown coal as reported Srivastava[17]. By combining this data, it is possible to obtain an approximate estimation of mercury emissions from given plants. It is possible to obtain a theoretical volume of dry flue gas (V_{FGTD}) and theoretical volume of required dry air (V_{ATD}) from the elemental composition of the fuel and stoichiometry of oxidation reactions. The amount of dry flue gas for a reference oxygen content of 6% (V_{FGRD}) is obtained by the Eq. 1.

$$V_{FGRD} = V_{FGTD} + \left(\frac{21}{21-6} - 1\right) * V_{ATD} \qquad (1)$$

P Estimation of Hg emissions (HgE) can be obtained by Eq. 2 using the value of mercury content in coal (Hg_C) and the efficiency of the Hg capture ε given by Srivastava[17].

$$Hg_E = \frac{Hg_C * \frac{(100-\varepsilon)}{100}}{V_{FGRD}} \qquad (2)$$

Estimation of Hg emissions from combustion of different coals are shown in Table 2 where the characteristics of coal from individual mines are given by Pilař[15] and Pešek[16].

Table 2: Coal composition and estimated Hg emissions from its combustion

Name of mine	Water content	The values given for dry coal						Estimated Hg emissions
		Ash	S	H	C	O	Hg_C	
	%	%	%	%	%	%	mg/kg	µg/Nm^3
Libouš	34.0	35.5	2.5	3.6	42.6	16.1	0.236	18 - 31
Bílina	25.4	39.7	1.0	3.6	40.2	15.0	0.207	16 - 29
Jiří	35.0	24.5	1.0	4.7	53.2	18.8	0.469	28 - 50
Vršany	28.2	39.0	0.8	3.7	37.5	15.2	0.244	20 - 37
ČSA	28.5	18.3	1.2	4.9	47.9	20.3	0.243	16 -28

Here we can see that mercury emissions significantly exceed the approved limit of 7 µg/m^3 given for combustion of brown coal in large power plants even in the case of the highest efficiency of mercury capture, given by Srivastava[17].

Conclusion

As can be seen from the estimation of mercury emissions from coal combustion, the efficiency of mercury capture in the existing flue gas treatment system in coal-fired power plants is probably not sufficient. As described above, the capture of mercury affects many factors. There may help to add a SCR system if it is not already installed, mixing fuels to obtain mixture with less mercury content and/or higher chlorine content. The installation of a catalyst for mercury oxidation or a special sorbent injection for the capture of mercury are the other options. There is necessary to determine the mercury concentration and its form distribution at each power plant to verify the most efficient and economical solution.

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Emise rtuti z hnědouhelných elektráren

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Souhrn

V prezentovaném příspěvku jsou shrnuty přírodní a antropogenní zdroje rtuti. Dále nastiňuje nové právní předpisy Evropské unie pro emise rtuti ze spalovacích zařízení a jejich předpokládaný dopad na výrobu energie v České republice. Jsou zde uvedeny mechanismy vzniku různých forem rtuti (elementární rtuť, oxidovaná rtuť a rtuť vázaná na částice) a jejich možnosti odstranění v systému čištění spalin. Vypočítaný odhad emisí rtuti ze spalování hnědého uhlí ukázal, že účinnost zachytávání rtuti na stávajících zařízeních pravděpodobně není dostačující.

Klíčová slova: *rtuť, znečištění ovzduší, uhelné elektrárny, legislativa*

Economically profitable waste treatment within the concept biorefinery: fiction or reality?

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Abstract

There is generally known that nowadays designing and operating pilot plant or industrial technologies, in which waste is transformed to biofuels and biochemicals are not economically profitable without subsidies. The paper discuss results of fundamental techno-economic studies of waste treatment using biorefinery approach, i.e. fibre based biorefinery, lignocellulosic bioethanol biorefinery and algal biorefinery. The results showed that there is a potential to reach economic feasibility of waste conversion to bioethanol, and attractivity of waste CO_2 *to algal lipids conversion, i.e. to reach simple payback time up to 6 – 8 years without any subsidies. Nevertheless, low process efficiency, technologic maturity, policy, trade demand and pricing are still the main limiting factors that affect their realization in industrial scale.*

Keywords: *biorefinery, biogas, algae, ethanol, lignocellulosic waste*

Introduction

In Europe, more than $1.8{\cdot}10^9$ t of dry waste is produced each year[1], including agricultural waste from plant and animal products, waste from the food and processing industry, municipal waste, green waste, sewage sludge, separately collected municipal biodegradable waste from households and gardens, and waste from restaurants and canteens, quarries and surface mining, and energy production. The goal of EU policy is to substantially reduce the volume of waste produced and minimize its adverse impact on the environment and human health. For example, up to 80 % of biodegradable waste is currently deposited in landfills; however, according to the EU “Landfill Directive” 99/31/EC, 65 % less biodegradable waste than in 1995 must be deposited by 2020. Waste biomass is therefore one of the most energy-rich and unutilized renewable raw materials, not only for the production of alternative energy sources (biomethane, biohydrogen, bioethanol, pyrolysis oil, synthetic gas), but also for the preparation of valuable chemicals (oligosaccharides, furans, polyhydric alcohols, organic acids, cellulose fibers, natural antioxidants, essential substances, oils), which are applied in the production of eco-innovating materials (bioplastics, biocomposites). By using waste to produce biofuels and bioproducts, it is possible to partially reduce fossil fuel burning, reduce dependence on oil and petrochemical products, reduce carbon dioxide production, contribute to mitigating global warning and improve the quality of the environment. However, technology for efficient transformation of waste into biofuels or valuable chemical substances is still undergoing development. Today it can be seen that the professional public and the industrial sphere are increasingly oriented towards the processing of waste within the concept of a biorefinery.

A biorefinery is a flexible multi-technology facility in which waste biomass is converted in parallel to biomaterials, biochemicals and biofuels, along with the production of electricity or heat. The technological process of waste biomass processing in a biorefinery can be divided into several basic steps – storage; primary processing *(sorting, pretreatment, extraction, separation)*, secondary processing *(thermochemical, biochemical methods)* and tertiary processing *(separation, purification and refining of the products)*, see Figure 1. Typical bioproducts that can be obtained from waste biomass are bioalcohols, biohydrogen, elastomers, fibers, resins, carbohydrates, antibiotics, flavors, dyes, polyols, surfactants, oils, dextrins, ethyl esters, organic acids and solvents. Depending on the purity of products, they can be used in the transport, energy, textile, construction, cosmetics, pharmaceutical, chemical, plastics, paper and food industry to produce food flavors and nutritional products. When designing technology and particularly when selecting a suitable portfolio of products that can be obtained by processing the waste, it is necessary to pay attention to its production costs and especially the purchase price of the product in relation to demand. The output of waste treatment technology in a biorefinery must therefore be a combination of primary products of high economic value and secondary products of lower economic value, see Figure 2. Products with a high economic value include commodities for the food industry, the production of biocomposite materials and bioplastic.

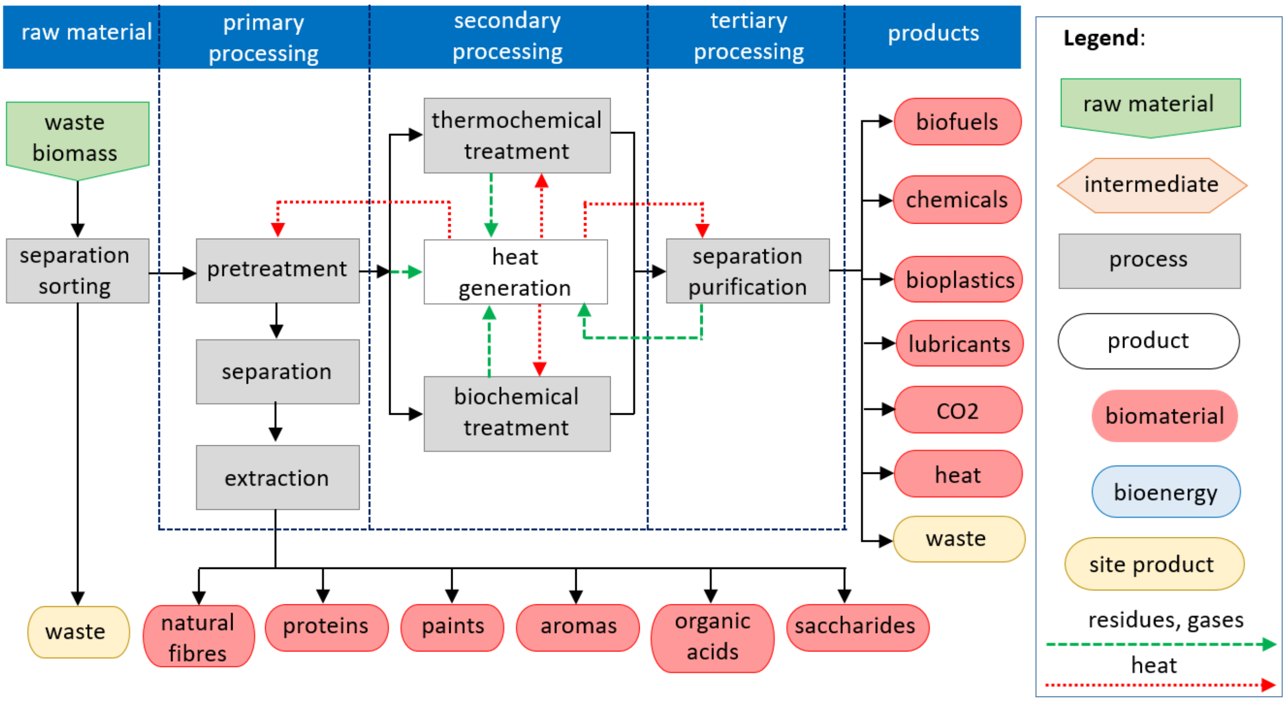

Figure 1: Waste treatment possibilities in biorefinery concept*[2]*.

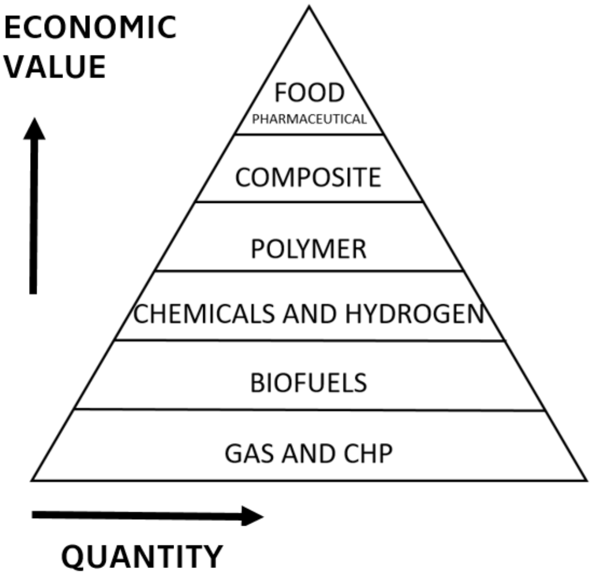

Figure 2: Economic value of product*[2]*.

There is plenty of research and studies of conventional, lignocellulosic, oil crop, lignocellulosic or algal biorefineries[2]. Based on the results, it is well known that biofuels and bioproducts are currently not able to compete with conventional fuels or petrochemical products, especially in terms of production costs subsidies excluded. The main task for the professional public is therefore to do engineering studies and to find promising technology for the transformation of waste biomass into bioproducts that will be produced simultaneously with alternative energy sources. The aims of the paper were therefore to overview the results of fundamental technical and economic studies on waste treatment within the concept of a biorefinery[3,4,5]. All studies were evaluated without the impact of subsidies in order to define crucial technological steps, machines or apparatuses, technology pricing that significantly affect economic feasibility and impede industrial realization.

Methods

Three waste treatment studies within the concept of biorefinery are discussed in the paper, i.e. (1) fibre based biorefinery[3], (2) lignocellulosic bioethanol biorefinery[4], and (3) algal biorefinery[5]. The technical and economic elaboration of presented studies was based on uniform approach, i.e. on the design of detailed current technological schemes (PFD diagrams). Defining model mass and energy balances with consideration of heat regeneration, basic design of the installed machines and apparatuses was created, and economic studies evaluating investment and operating cost were done.

- The total investment costs (CAPEX) were estimated as the sum of ISBL, OSBL, DE and EaE[6]. ISBL represents the sum of individual prices of installed machines and equipment. OSBL are investment costs for the installation of equipment, i.e. installation, piping, measurement and control, power distribution, construction, load-bearing elements, protection and coatings, and they usually amount to 40 % of ISBL costs. DE represents investment costs for technology planning, construction and implementation of construction, and it is recommended that it be defined as 0.1·(ISBL +OSBL). The last investment cost item is EeE, which is a reserve for price fluctuations of materials and labor; its value is defined as 0.1·ISBL. The error in determining the total investment costs is ± 15 – 30 % of the total amount.
- Technology operating costs (OPEX) were determined based on partial estimates of costs of raw materials, energy, staff costs, professional supervision, service and maintenance, consumables, laboratory analysis, insurance, overhead costs, transport costs and the reserve. Operating cost items were set as follows - three employees with average brutto wage 630 Eur per month, supervision being 15 % of personal cost, maintenance being 2 % of CAPEX, consumables 0.5 % of CAPEX, laboratories 15 % of personal cost, reserve as 3 % of direct operational cost, and insurance as 0.7 % of CAPEX, corporate directions as sum of personal and supervision cost and 60 % of maintenance cost. The following prices of conventional consumable, i.e. electricity 35 Eur MWh^{-1}, water steam 20 Eur t^{-1}, process water 2.2 Eur t^{-1} and cooling water 0.1 Eur t^{-1} were used in the model. Another prices of raw material, products and consumables are discussed in relation to individual technologies.

Results and Discussion

(1) Fibre based biorefinery[3]

Figure 3 presents a biorefinery that processes fibrous waste. The lignocellulosic waste rich in cellulosic fibers first passes through a crusher in order to reduce the particle size and intensify the subsequent hydrothermal boiling process followed by the sudden decompression of the batch[7]. The crushed waste is mixed with recycled water in a homogenization tank in a mass ratio of 1:10; the prepared batch is then subjected to hydrothermal decomposition without the addition of chemicals, and it is treated at a working temperature of 200 °C for a residence time 20-40 min. After the required time, the batch is suddenly decompressed into an expansion vessel, from where it is led to the separator. The separated cellulose fibers are dried to the desired moisture by drying air, which is indirectly preheated by combustion gases from the cogeneration unit. The liquid phase, which is rich in dissolved and unseparated, undissolved organic and inorganic compounds, is anaerobically fermented in under mesophilic temperature conditions, and the resulting biogas is combusted in a cogeneration unit. All generated electricity and some heat are used to meet the energy demands of the technology itself. The primary product of a biorefinery are cellulose fibers, which are used in insulation materials, electrotechnics, pharmacy, cosmetics, and especially as reinforcements to increase the strength of bioplastics and composite materials with a biocomponent. Secondary products include heat, sludge, cogeneration emission gases, and waste vapor from the dryer. Detailed information about the PFD diagrams, balances, total investment costs, operating costs and ROI are available in the work by Azivov[3].

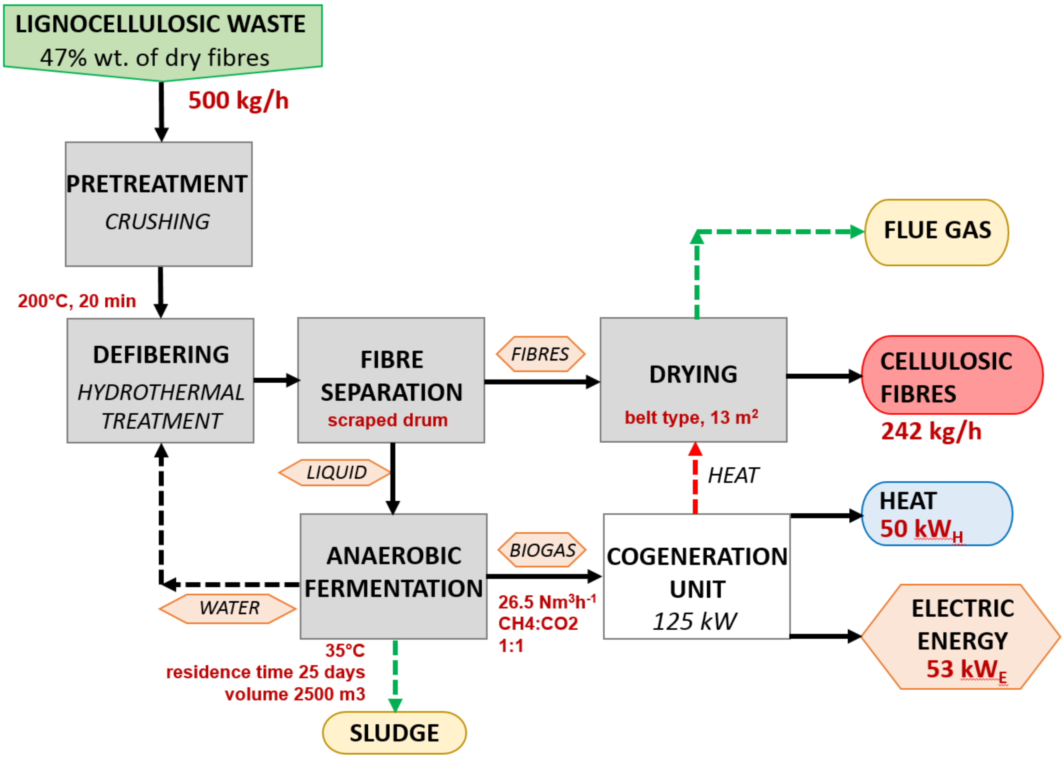

Figure 3: Block diagram of fibre based biorefinery

As for a technical point of view, the presented technology is easier to implement because its own technical solution for the production of cellulose fibers is based on the use of devices that are common in today's facilities. An economic assessment of the technology has shown, see Table 1, that for the given model case, the total investment costs are equal to 2 200 000 Eur, and technology operating costs amount to 3,000,000 Eur y^{-1}. The purchase price of cellulosic fibres 1.7 Eur kg^{-1} was used for model set-up, the average buying price of wooden chips 20 Eur t^{-1}. Operating cost of raw materials was 0.04 \$ kg^{-1} with the cost of transport being 2 % of the raw material price. When considering the purchase price for cellulose fibers of 1.7 Eur kg^{-1}, the income from their sale is 3 300 000 Eur, i.e. a taxable profit of 300,000 Eur y^{-1} can be achieved. When considering a depreciation period of 20 years, the simple return period of the investment is 22.3 years, i.e. at the end of the lifecycle of the technology itself, which is expected to be 20 – 30 years. A sensitivity analysis was performed for this technology, which showed that especially the purchase price of cellulose fibers has a dominant effect on the economy of the technology operation. The aforementioned 1.7 Eur kg^{-1} is considered by the authors to be the minimum purchase price of the product in order to achieve a reasonable payback period for the technology.

Lignocellulosic waste is an affordable raw material that is normally processed by composting, combustion, pyrolysis, gasification or anaerobic fermentation, i.e. CO_2 is always emitted. However, the present technology is based on material-energy recycling of lignocellulosic waste rich in cellulosic fibers, i.e. waste from agriculture, the woodworking industry, the maintenance of communal greenery, etc. The main benefits of this technology include environmentally friendly waste treatment in a closed system with heat recovery, material and energy recycling of lignocellulosic biomass, minimized waste production, and the reduction of CO_2 emissions compared to combustion. Based on the mass balances of the presented technology, it is estimated that thanks to hydrothermal processing about 50 % of the feedstock is dissolved in liquid, which is further anaerobically fermented, and the remaining extracted cellulose fibers go for subsequent processing in an oven. The anaerobic fermentation of the liquid residue therefore reduces the volume of produced CO_2 by about 50 % in comparison with anaerobic fermentation of the entire feedstock. Nevertheless, despite these benefits, it is necessary to state that the actual implementation and operation of this technology cannot do without the demand for cellulosic fibers and without an appropriate economic policy taking into account the benefits discussed.

Table 1: Techno-economic analysis of fibre based biorefinery.

Capital Investment Costs CAPEX		**2,200,000 Eur**
Investment to equipment		1,220,000 Eur
Investment to constructions, site machinery, measurement and control		460,000 Eur
Projection, production, realisation		340,000 Eur
Financial reserve		160,000 Eur
Operational Costs OPEX		**3,000,000 Eur y^{-1}**
Direct operational costs		1,720,000 Eur y^{-1}
raw material, consumables, energies		*1,480,000 Eur y^{-1}*
service and maintenance		*130,000 Eur y^{-1}*
others	*salary, laboratory, supervision*	*110,000 Eur y^{-1}*
Indirect operational costs	*overheads, insurance*	30,000 Eur y^{-1}
Transportation fees	*raw material, products, wastes*	1,250,000 Eur y^{-1}
Economic evaluation		
cellulosic fibre production	*operation 8000 hours*	1,936,400 kg y^{-1}
estimated purchase price of fibres		1.7 Eur kg^{-1}
annual income from fibre sale		3,300,000 Eur y^{-1}
taxable income		300,000 Eur y^{-1}
depreciation with a period of 20 years		220,000 Eur y^{-1}
simple payback time		22.3 y

Critical areas that strongly affect the technical and economic side of the whole technology include the pretreatment of the raw material with lignocellulosic fiber pulping technology and the refining of cellulosic fiber. The actual anaerobic fermentation and drying are technologically advanced. Therefore, scientific research needs to focus especially on improving the efficiency of pretreatment technology, i.e. research and development of intensive, energy-saving and environmentally friendly technologies for pulping biomass waste in order to reduce investment and operating costs. Cellulose fiber refining technology is not considered in the technology described, but it is necessary to have a defined product quality, i.e. the customer must define his requirement for the purity of cellulose fibers and chemical stability with respect to their subsequent application.

(2) Lignocellulosic bioethanol biorefinery[4]

Figure 4 presents a block diagram of technology for the production of lignocellulosic ethanol from corn stover[5] within the concept of a biorefinery. The raw material is rid of impurities (dirt, stones, metals) and crushed to a size suitable for its subsequent processing. The disintegrated raw material is then subjected to pretreatment with steam expansion. During the pretreatment, the saturated steam at a working temperature of 235 °C comes into direct contact with the raw material, dissolving a portion of the hemicellulose and lignin, thereby greatly improving the accessibility of cellulosic bundles to the following microbial decomposition. After the expiration of the required time at the working temperature, which is several seconds, the batch is suddenly decompressed, resulting in an intense breakdown of the material's structure. This prepared batch must be neutralized and detoxified. It is therefore led to a separator, where the solid and liquid phases are separated. The solid phase proceeds directly to the subsequent processing step, which is the continuous simultaneous saccharification and fermentation (SSF) in bioreactors connected in series. The liquid phase is first led into neutralizing tanks prior to its entry into SSF bioreactors, where it is cleansed and detoxified by adding a suitable chemical agent. The batch is then pumped through the filter press into a homogenization tank, where it is mixed with the solid phase, yeast and enzymes to a quality suitable for SSF technology. The fermentation tanks operate in a temperature range of 41-65°C depending on the stage of the SSF process. After the total required time, which is about 6 days, the batch is pumped into a hopper, from which it is fed into the product separation and cleaning section. The first stage of SSF fermentation product separation takes places in a column still heated with saturated steam. The column produces vapors rich in ethanol and water, and the residue containing all insoluble substances (silage residues, yeast) and water. The vapors from the head of the column still pass through a condenser to the rectifying column, the products of which are ethanol vapors with a composition corresponding to the azeotropic point, i.e. 95 % w/w ethanol and water, and fusel oil, i.e. a mixture of heavier alcohols and other organic substances. To refine the ethanol to 99% w/w, moisture absorption on molecular sieves is used. The waste product from the column still is first centrifuged. The solid residues are separated, and they are used as feed or dried to be used as fuel in the energy section of the bio distillery. The liquid phase is thickened on the evaporator, and the resulting vapor steam is used in heat recovery; the condensed product, lignin syrup, is another biorefinery product.

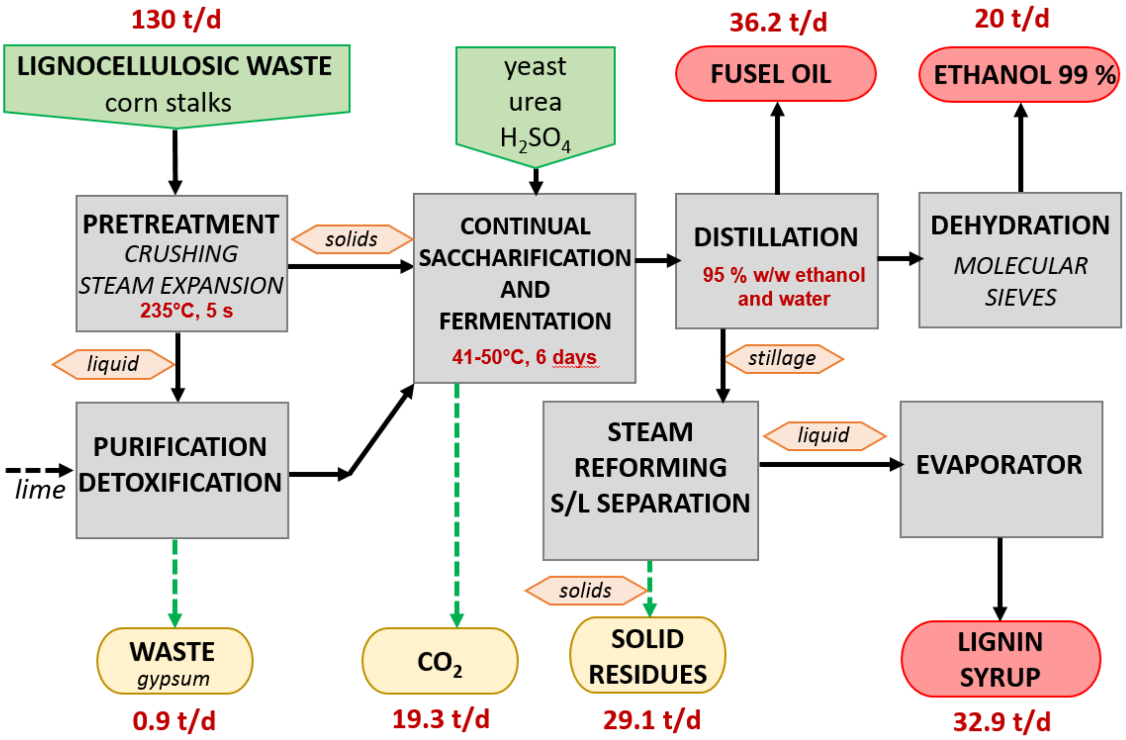

Figure 4: Block diagram of lignocellulosic bioethanol biorefinery

The industrial technology for producing classic ethanol from starch-based raw materials is an old and technically very sophisticated process. The raw material does not need to be pretreated in a complicated way; its biodegradability is close to 90%. The technology for producing bioethanol from lignocellulosic waste differs from classic ethanol production in that it also contains a raw material pretreatment section and different batch saccharification technology; the other technological units are almost the same. An economic assessment of the technology has shown, see Table 2, that for the given model case, the total investment costs are equal to 9,050,000 Eur, and technology operating costs amount to 10,130,000 Eur y^{-1}. The following buying prices were used for modelling: corn silage 18.5 Eur t^{-1}, sulphuric acid 1,600 Eur t^{-1}, lime 148 Eur t^{-1}, yeast 148 Eur kg^{-1}, enzymes 1,600 Eur t^{-1}, urea 240 Eur t^{-1}, and following purchase prices for gypsum 370 Eur t^{-1}.The purchase price of cellulosic fibres 1.7 Eur kg^{-1} was used for model set-up, the average buying price of wooden chips 20 Eur t^{-1}. When considering a purchase price for 99 % w/w bioethanol of 1,150 Eur t^{-1}, a price of 110 Eur t^{-1} for solid residues, and a price of 370 Eur t^{-1} for lignin syrup, the annual income from their sale is 12,850,000 Eur y^{-1}, i.e. a taxable profit of 2,650,000 Eur y^{-1} can be achieved. When considering a depreciation period of 10 years, the simple return period of the investment is 5.2, with the expectation of a 30-year lifecycle of the technology. A sensitivity analysis revealed that the predominant parameter affecting the economy of operation is the purchase price of bioethanol and lignin syrup. It was found that at a purchase price of 1,000 Eur t^{-1}, the payback period begins to grow rapidly. The price of 1,000 Eur t^{-1} is the approximate price of first generation bioethanol. If the purchase price of bioethanol was the regular price, i.e. 330 Eur t^{-1}, the biorefinery would suffer a loss and the payback period of the project would be near its lifetime. The limit purchase price of ethanol with a payback period of up to 9 years is 1,110 Eur t^{-1}. The production of lignin syrup is about 50 % higher than the production of ethanol, so its price also has a significant effect on the economics of the process. The greatest degree of uncertainty lies in the very determination of the price of lignin syrup. Lignin is widely used in the chemical industry and its price depends on several parameters (purity, water content, origin). However, the technological section of lignin syrup production is only profitable at purchase prices higher than 340 Eur t^{-1}. If its purchase price is lower, the application of an evaporator and its operation increases costs more than what the yield from the sales of the thickened syrup would be.

Table 2: Techno-economic analysis of lignocellulosic bioethanol biorefinery

Capital Investment Costs CAPEX		**9,050,000 Eur**
Investment to equipment		5,400,000 Eur
Investment to constructions, site machinery, measurement and control		2,100,000 Eur
Projection, production, realisation		1,050,000 Eur
Financial reserve		500,000 Eur
Operational Costs OPEX		**10,130,000 Eur y^{-1}**
Direct operational costs		8,800,000 Eur y^{-1}
raw material, consumables, energies		*8,700,000 Eur y^{-1}*
service and maintenance		*480,000 Eur y^{-1}*
others	*salary, laboratory, supervision*	*520,000 Eur y^{-1}*
Indirect operational costs	*overheads, insurance*	290,000 Eur y^{-1}
Transportation fees	*raw material, products, wastes*	1,040,000 Eur y^{-1}
Economic evaluation		
annual production of ethanol 99 %	*operation 8000 hours*	6,660 t y^{-1}
purchase price of ethanol 99 %		1,150 Eur t^{-1}
annual income of ethanol 99 % purchase		7,659,000 Eur y^{-1}
annual production of gypsum	*operation 8000 hours*	302 t y^{-1}
purchase price of gypsum		0.4 Eur kg^{-1}
annual income of gypsum purchase		120,000 Eur y^{-1}
annual production of solid residues	*operation 8000 hours*	9,690 t y^{-1}
purchase price of solid residues	*feed*	110 Eur t^{-1}
annual income of solid res. purchase		1,070,000 Eur y^{-1}
annual production of lignin syrup	*operation 8000 hours*	10,800 t y^{-1}
purchase price of lignin syrup		370 Eur t^{-1}
annual income of lignin syrup purchase		4,000,000 y^{-1}
taxable income		2,650,000 Eur y^{-1}
depreciation with a period of 10 years		905,000 Eur y^{-1}
simple payback time		5.2 y

The technology for producing bioethanol from lignocellulosic waste is not a technologically or technically advanced process. However, the presented technical and economic study showed that the technology of lignocellulosic ethanol production has a future, and it can be used in decentralized waste treatment technology. Nevertheless, in order to make this technology effective, it is very important to direct research and development into these areas of raw material pretreatment, the transfer of momentum, mass and heat in mechanically mixed fermenters and tanks, and the SSF process. The pretreatment of the raw material is a key operation necessary to increase the biodegradability of waste, both cellulose and hemicellulose enzymatic hydrolysis and fermentation to bioethanol especially. Despite the application of various pretreatment methods, the biodegradability of the raw material currently ranges from 30 % to 50 %, and only cellulose is a saccharide source for SSF process. It is therefore necessary to focus primarily on finding efficient, energy-saving and economically profitable technologies for the pretreatment of lignocellulosic waste, as well as the SSF process, pumpability and mixability of the batch with lignocellulosic feedstock, which tends to cling to the working parts of the device, settle at the bottom of the vessel or float on the surface of the batch. The optimization of the transfer of momentum, mass and heat in mechanically mixed fermenters and tanks is also necessary. This is the only way to increase the biodegradability of the raw material, increase the production of primary products, reduce operating costs with appropriate heat recovery and chemicals used, and thus improve the economy of operation with a low sensitivity of biofuel purchase prices.

(3) Algal biorefinery[5]

In recent years, there has been increasing emphasis on the global reduction of CO_2 emissions, so research is focused on the potential for its use in the production of third and fourth generation biochemicals or biofuels. One possibility is the photosynthetic transformation of CO_2 waste into lipid-rich microalgae. In available literature, many publications on the subject of photobioreactors, algae harvesting and the extraction of valuable substances from algae can be found. However, all these technological steps are dealt with completely separately. There is no comprehensive idea of complex technology for microalgae processing, i.e. how to design and implement complex production technology. This paper presents technology for the production of cellulose fiber as well as technology for the production of lignocellulosic ethanol. Both technologies are the source of CO_2 as a secondary product. For this reason, a technical and economic study of the biochemical transformation of CO_2 waste into lipids was performed[6] in order to obtain a concept of a zero emission biorefinery.

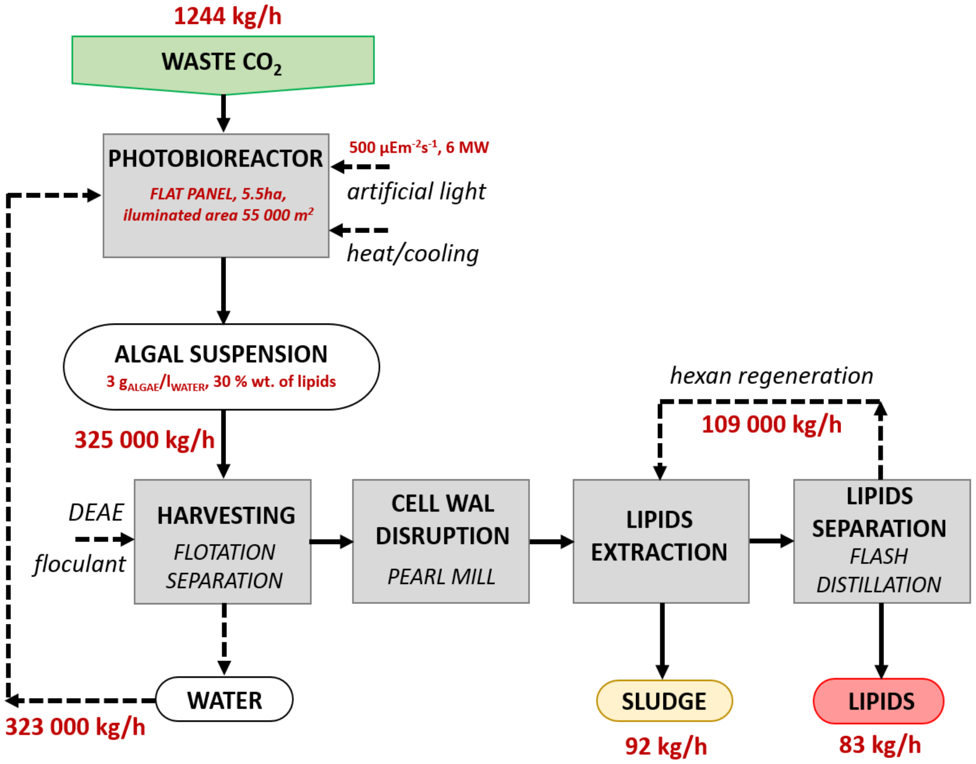

Figure 5: Block diagram of algal biorefinery

Figure 5 shows a block diagram of a continuous technology for the production of lipids from waste CO_2. Waste CO_2 is fed into a vessel in which it is dissolved and mixed with algae inoculated with liquid. From there, the suspension is led by a pump into flat-plate photobioreactors[8], where the heat and light interact causing the photosynthetic transformation of CO_2 waste into Chlorella microalgae. The output of the photobioreactor is a water-microalgae suspension with a characteristic content of 30 % w/w lipids and a typical concentration of 3 g of algae per liter. The suspension is stored in a tank, from where it is pumped into the technological harvest block. The suspension first flows through a static mixer to which a floculant is continuously added. Flocculation occurs in the hopper, and the suspension then enters a flotation apparatus where the microalgae are primarily thickened. From the flotation apparatus, the primarily thickened algae are pumped into a decanter centrifuge, where they are ultimately drained to the value desired in the subsequent processing step. The separated water goes back to the microalgae production technology, and the thickened microalgae are pumped into a bead mill that breaks the cell walls of the microalgae and releases the contents of the algal cell into the carrier fluid-water. The disintegrated microalgae pass into an extractor, where they are mixed with a solvent, hexane, in a ratio of 200 ml g^{-1} dry algae with a treatment time of 2 hrs. The technology requires the installation of several extractors connected in parallel and the continuous operation of the line. After the necessary time, the batch from the extractor is pumped into a continuous drum centrifuge, in which solid impurities (flocs, biomass) are separated. This is followed by the hopper in which the remaining water is set off. The solvent and lipids are separated in the next step by means of two-stage expansion distillation. The proposed technology considers heat and solvent recovery.

Table 3: Techno-economic analysis of algal lipids production technology

Capital Investment Costs CAPEX		**20,226,000 Eur**
Investments to algae cultivation technology		7,520,000 Eur
Investments to harvest, cell wall disruption, extraction and separation		4,036,000 Eur
Investment to constructions, site machinery, measurement and control		4,623,000 Eur
Projection, production, realisation		2,430,000 Eur
Financial reserve		1,617,000 Eur
Operational Costs OPEX		**24,934,000 Eur y^{-1}**
Direct operational costs		24,664,000 Eur y^{-1}
raw material, consumables, energies for algae cultivation without light		*11,968,000 Eur y^{-1}*
energy price for artificial illumination of photobiorector		*6,252,000 Eur y^{-1}*
raw material, consumables, energies		*5,186,000 Eur y^{-1}*
service and maintenance		*61,000 Eur y^{-1}*
others	*salary, laboratory, supervision*	*1,197,000 Eur y^{-1}*
Indirect operational costs	*overheads, insurance*	270,000 Eur y^{-1}
Transportation fees		0 Eur y^{-1}
Economic evaluation		
annual lipids production	*operation 8000 hours*	666,667 Eur y^{-1}
purchase price of lipids		41 Eur kg^{-1}
annual income of lipids purchase		27,350,000 Eur y^{-1}
taxable income		3,629,000 Eur y^{-1}
depreciation with a period of 10 years		2,022,600 Eur y^{-1}
simple payback time		8.0 y

An economic assessment of the technology has shown, see Tab. 3, that in the given model case the total investment costs for the construction of a photobioreactors amount to 7,520,000 Eur, and 4,036,000 Eur for the remaining part of algae processing, of which 22 % is for the harvesting technology, 12 % for the disintegration technology, 42 % for the extraction technology, and 24 % for the lipid separation technology The operating costs of the technology were estimated at 24,934,000 Eur y^{-1} using prices of hexane 9 Eur l^{-1} and flocculant 3.5 Eur kg^{-1}. When considering the purchase price for extracted lipids of 41 Eur kg^{-1}, the income from their sale is 27,350,000 Eur, i.e. a taxable profit of 3,629,000 Eur y^{-1} can be achieved. When considering a depreciation period of 10 years, the simple return period of the investment is 8.0 years, with the expectation of a 30-year lifecycle of the technology. However, a technical and economic assessment has shown that the economy is extremely sensitive to the investment and operating costs of photobioreactors, the type and efficiency of extraction, and the purchase prices.

- The technology is only profitable in the considered concept at a lipid purchase price that is higher than 30 Eur kg^{-1}.
- Photobioreactors – From the perspective of the theoretical production of algae in the irradiated volume, the flat plate photobioreactor achieves the highest algal yield of 297 g m^{-2} d^{-1} and 2,970 kg algae d^{-1} ha^{-1}. 1 liter of culture medium contains 3 g of algae with 30 wt. % lipid content, i.e. 1 g of lipids per 1 liter of water. Therefore, 1 t of culture medium is required to produce 1 kg of lipids, i.e. water with algae, at 100% extraction efficiency. The reason for the high investment and operating costs is the very low concentration of lipids in algae, as well as the concentration of algae in the feedstock.
- From the perspective of algae cultivation in photobioreactors, it is suitable to focus on the possibility of increasing the lipid concentration in microalgae, or increasing the concentration of microalgae in the culture medium. Therefore, the photosynthetic transformation of CO_2 into microalgae should be resolved as a decentralized microalgae cultivation technology with subsequent harvesting, where the output product would be thickened microalgae. The algae would then be transported to centralized algae extraction technologies. This solution would substantially reduce the investment and operating costs of both technologies.
- Extraction efficiency - The efficiency of lipid extraction from microalgae in most studies is defined as the yield of lipid mass out of the total microalgae mass. The present study considered 10 % w/w of the total microalgae mass, which, at a concentration of 30% w/w lipids in the algae, means that no more than 1/3 of the lipids can be extracted. It is therefore necessary to perform research and development of effective extraction technologies.

The whole technology consists of conventional machines and apparatuses that are easily accessible in the market today. The critical points of the technology include algae cultivation and technology for the collection and separation of algae from an aquatic environment, where it is necessary to intensify separation techniques with respect to the design limits of flotation units and decanter centrifuges. The disintegration of cell walls in a bead mill is energy-intensive and there is a risk of the thermal degradation of lipids due to the inhomogeneity of the temperature field in the mill's workspace. Extraction and extractors are ineffective according to current scientific knowledge; there is a risk of thermal degradation of the product even during expansion distillation, which is why it is necessary to focus research and development on the mentioned areas in order to achieve intensified processes.

Conclusions

Waste treatment technology in the concept of a biorefinery is currently a not very economically interesting solution for material and energy waste recycling. Due to the very high investment costs of the technology and product production prices, they are not able to compete with conventional petrochemicals. However, it is important to realize that these technologies have a positive impact on the environment. Waste treatment in a biorefinery can reduce the amount of landfilled or incinerated waste;

the transformation of waste can result in products that can become substitutes or admixtures for petrochemicals, reduce the production of emission gases and achieve a zero emission technology.

Technical and economic studies have shown the prospects of economically profitable processing of lignocellulosic waste in second generation bio-distilleries, as well as the attractiveness of the biochemical transformation of CO_2 waste into lipids. Research and development in all areas of environmentally friendly waste treatment is therefore still necessary, with an emphasis on the potential of industrial applications, see Table 4. It is necessary to find such technical solutions that will ensure efficient, energy-saving, economically favorable and environmentally friendly transformation of waste into alternative energy sources and chemicals. However, without favorable legislation and economic policy *(affordable raw materials, strict environmental protection, funds to support the development of new technologies for processing waste materials, efficient layout of industrial technologies with regard to raw material availability, a plan for the use and promotion of biofuels, provision of financial support for the production of biofuels from waste materials, tax incentives for industrial plants and consumers of biofuels)*, it is not possible to realize this concept with a vision of immediately economically profitable operation.

Table 4: SWOT analysis of the prospects of a biorefinery[9]

Strengths	**Weaknesses**
• Possibility of achieving maximum conversion of large-scale biomass waste processing. • Production of a large number of different products for different sectors (agriculture, food, chemicals, energy). • New technology based on well-known and industrially operating facilities (production of paper, alcohol and food). • Possibility of efficient decentralized waste treatment.	• Effort to break through into a closed market with new products (chemical, energy, consumer and food industry, transport). • Competitiveness with traditional products due to quality. • Economic profitability (especially for more sophisticated products). • The development of bulk processing technology requires testing on a laboratory, bench and semi-industrial scale. • Strong dependence on the quantity and composition of waste.
Opportunities	**Dangers**
• Minimizing the amount of landfill waste. • Production of eco-innovating materials. • Reducing the burden on the environment. • Making a significant contribution to sustainable development. • Compliance with global policy goals to limit the use of fossil energy sources.	• Demand versus supply of products and their quality. • Uneven distribution of waste quantity and composition (possibility of political and logistics changes). • High initial investment costs (trouble finding investors). • Strong dependence on legislation.

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Ekonomicky rentabilní zpracování odpadů v konceptu biorafinerie: fikce nebo skutečnost?

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Souhrn

Je známo, že projektované i provozované poloprovozní i průmyslové technologie výroby biochemikálií a biopaliv z odpadní biomasy jsou bez dotací ekonomicky nevýhodné. Článek seznamuje čtenáře s výsledky základních technicko-ekonomických studií zpracování odpadu v konceptu biorafinerie, a to s (1) biorafinerií s výrobou vláken, (2) s lignocelulózovou bioetanolovou biorafinerií a s (3) mikrořasovou biorafinerií.

Technicko-ekonomické studie prokázaly perspektivitu ekonomicky rentabilního zpracování lignocelulózových odpadů v biolihovarech druhé generace, a i atraktivitu technologie biochemické transformace odpadního CO_2 *na lipidy, tj. možnosti dosáhnout rozumné návratnosti investice do 6 – 8 let s výstavbou a provozem bez dotací. K tomu, aby toho bylo dosaženo, je však stále nutný výzkum a vývoj ve všech oblastech ekologicky šetrného zpracování, a to zejména v oblastech zvýšení účinnosti dílčích technologických procesů, zvýšení technické úrovně instalovaných strojů a zařízení, v oblastech tržního hospodářství a cenové politiky.*

Klíčová slova: *biorafinerie, bioplyn, mikrořasy, etanol, lignocelulózový odpad*

Působnost zákona o odpadech ve vztahu k odpadním vodám

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Souhrn

V roce 2015 zúžila novela zákona o odpadech dosavadní úplné vyloučení odpadních vod z působnosti tohoto zákona ve vztahu k odpadním vodám. Nově se zákon o odpadech nevztahuje na odpadní vody v rozsahu, v jakém se na nakládání s nimi vztahují vodní zákon a zákon o vodovodech a kanalizacích. Článek se zabývá vývojem této otázky v právních předpisech. Stěžejní část článku je věnována posouzení aplikace zákona o odpadech na některé vybrané činnosti ve vztahu k odpadním vodám. Vymezuje nakládání s odpadními vodami, na které se zákon o odpadech nadále nevztahuje, a činnosti ve vztahu k odpadním vodám, které nově spadají do působnosti zákona o odpadech. Článek zároveň upozorňuje na hraniční případy, kde není při stávajícím znění právních předpisů řešení otázky uplatnění zákona o odpadech na odpadní vody zcela zřejmé. Článek se rovněž zabývá otázkou aplikace odpadových předpisů na velmi aktuální problematiku využívání případně recyklace odpadních vod.

Klíčová slova: *odpadní voda, odpad, působnost zákona o odpadech*

Úvod

S účinností od 1. října 2015 byl v návaznosti na infringementové řízení vedené proti České republice kvůli nedostatečnému provedení směrnice Evropské Rady a Parlamentu č. 2008/98/ES o odpadech novelizován zákon č. 185/2001 Sb., o odpadech (dále jen „zákon o odpadech“). S ohledem na namítaná pochybení upravil novelizační zákon č. 223/2015 Sb. mimo jiné ustanovení o působnosti zákona o odpadech vztahující se na odpadní vody. Zatímco do října 2015 se zákon o odpadech podle svého § 2 odst. 1 písm. a) na odpadní vody nevztahoval vůbec, nově se podle novelizovaného ustanovení nevztahuje na nakládání s odpadními vodami pouze v rozsahu, v jakém se na nakládání s nimi vztahují jiné právní předpisy. Poznámka pod čarou pak odkazuje na zákon č. 254/2001 Sb., o vodách, ve znění pozdějších předpisů a zákon č. 274/2001 Sb., o vodovodech a kanalizacích pro veřejnou potřebu a o změně některých zákonů (zákon o vodovodech a kanalizacích), ve znění pozdějších předpisů. Působnost zákona o odpadech ve vztahu k odpadním vodám je tedy nezbytné nové posuzovat s ohledem na výklad jiných právních předpisů.

Zde je třeba uvést, že jsem se podílel na zpracování výše uvedené novely zákona o odpadech, a i nadále působím na Ministerstvu životního prostředí (dále jen „MŽP“). Téma tohoto článku jsem však zpracoval v rámci svého studia na Masarykově univerzitě. Závěry tohoto článku jsou odlišné od dosavadního postoje MŽP a nevyjadřují tak v tuto chvíli oficiální postoj MŽP. Zpracování tohoto článku mě zároveň dovedlo k názoru, že bude nezbytné se touto otázkou na úrovni státní správy dále zabývat.

Základní postoj MŽP jako předkladatele novelizačního zákona je vyjádřen v odůvodnění tohoto zákona, kde je uvedeno: *„S ohledem na širokou úpravu nakládání s odpadními vodami v ostatních předpisech se bude zákon vztahovat na nakládání s odpadními vodami velmi okrajově.“*[1] V současné době se domnívám, že stávající text ustanovení o působnosti zákona o odpadech vyžaduje mnohem širší aplikaci zákona o odpadech na odpadní vody, než předpokládá důvodová zpráva.

V článku nejprve představím vývoj této problematiky v právních předpisech na národní i evropské úrovni. V hlavní části článku pak popíši některé způsoby nakládání s odpadním vodami, na které se nadále zákon o odpadech nevztahuje a pokusím se identifikovat činnosti ve vztahu k odpadním vodám, na které se nově zákon o odpadech vztahuje.

Na závěr se zaměřím na jednu z oblastí, která rovněž může nově spadat do působnosti zákona o odpadech, a tou je recyklace odpadních vod. Tato stále aktuálnější otázka nemá doposud uspokojivé legislativní řešení a ani aplikace zákona o odpadech, který má pravidla pro recyklaci odpadů nastavena, problémy s recyklací odpadních vod neřeší. A jak se pokusím vysvětlit, ani do budoucna nejvhodnější cestu pro nastavení řešení nepředstavuje.

Vývoj právní úpravy

Působnost odpadových předpisů na odpadní vody upravoval již první zákon o odpadech. Zákon č. 238/1991 Sb., o odpadech, ze dne 22. května 1991, odpadní vody ze své působnosti nevylučoval. Ustanovení o působnosti vztahující se na odpadní vody § 2 písm. a) bylo formulováno pozitivně: *„pokud zvláštní předpisy nestanoví jinak, vztahuje se tento zákon též na nakládání a) s odpadními a zvláštními vodami“*[2], toto ustanovení odkazovalo na zákon č. 138/1973 Sb., o vodách. Důvodová zpráva uváděla k tomuto ustanovení o působnosti následující: *„Cílem tohoto ustanovení je vztáhnout působnost zákona na maximální počet subjektů a maximální šíři jednotlivých druhů, popřípadě skupin odpadů a pouze tam, kde zvláštní charakter odpadů vyžaduje specificky přístup, ponechat úpravu zvláštním předpisům.“*[3]

Ve sledovaném cíli takováto formulace odpovídá přístupu současného znění zákona o odpadech. Šíře aplikace zákona č. 238/1991 Sb. byla odvislá od toho, co vše ostatní právní předpisy upravovaly. Stejně jako současný zákon o odpadech umožňovala tato formulace plné uplatnění pravidel pro nakládání s odpady kdekoliv, kde nebyla zvláštní právní úprava dostatečná. Pro ochranu životního prostředí je takový přístup velmi vhodný, protože zajišťuje ochranu životního prostředí i v případě, že právní režim upravený zvláštními právními předpisy není nastaven důsledně.

Tehdejší zákon č. 138/1973 Sb., vodní zákon, již obsahoval pravidla pro zneškodňování odpadních vod. Ve vztahu k odpadním vodám byl nastaven velmi obdobně současnému vodnímu zákonu. Existoval zde požadavek na povolení vypouštění do podzemních a povrchových vod a upravoval jejich odvádění kanalizací. Co tento zákon například oproti současnému vodnímu zákonu neupravoval, bylo akumulování odpadních vod v bezodtokých jímkách.

Zajímavé je, že ustanovení zákona č. 238/1991 Sb. o působnosti ve vztahu k odpadním vodám odpovídalo v té době účinnému znění směrnice 75/442/EHS o odpadech. Zde bych se chtěl pozastavit nad pozdějším rozdílem české jazykové verze směrnice doplněné zvláštním vydáním Úředního věstníku k 1. květnu 2004 v souvislosti se vstupem České republiky do Evropské unie oproti ostatním jazykovým verzím směrnice.

Článek 2 odst. 1 české jazykové verze směrnice 75/442/EHS ve znění směrnice 91/156/EHS zní: *„1. Z oblasti působnosti této směrnice jsou vyňaty:*

a) plynné emise vypouštěné do ovzduší;

b) oblasti již upravené jinými předpisy:

... iv) odpadní vody s výjimkou odpadů v kapalné formě; ...“

Podle české verze by bylo rozdělení do písmen a) a b) zbytečné. Z jazykového výkladu vyplývá, že rozsah vyloučení pro plynné emise vypouštěné do ovzduší a položky uvedené pod písmenem b) je stejný, protože všechny položky jsou fakticky vyloučeny zcela, pouze u písmene b) je vysvětleno, proč byly tyto oblasti z působnosti vyloučeny.

Při pohledu do jiných jazykových verzí, je zřejmé, že písmeno b) nebylo přeloženo do českého jazyka správně. V jiných jazykových verzích začíná písmeno b) odlišně zde například v angličtině a francouzštině: *„where they are already covered by other legislation“, „lorsqu'ils sont déjà couverts par une autre législation“*.

Druhý odpadový zákon č. 125/1997 Sb., o odpadech, pak v § 1 odst. 2 písm. a) vyloučil ze své působnosti odpadní vody zcela*: „Zákon se nevztahuje na nakládání a) s odpadními a zvláštními* *vodami“*[5] Důvodová zpráva k tomu uvádí: *„Zákon má velmi široký záběr a v podstatě se podle něj řídí režim nakládání se všemi odpady. Výslovně jsou vyloučeny jen takové případy, kdy režim nakládání je natolik specifický, že je upraven zvláštní právní normou.“*[6]

V případě druhého zákona o odpadech tedy došlo ke změně přístupu, přičemž se tato změna dotkla i dalších zvláštních odpadů. K dnešnímu dni se mi nepodařilo dohledat, jaký byl důvod této změny. Důvodová zpráva ji nevysvětluje. Předkladatel mohl být přesvědčen, že oblast odpadních vod je jinými předpisy dostatečně pokryta. Takový přístup by odpovídal právě oficiální české jazykové verzi tehdy účinného znění směrnice 75/442/EHS. Oficiálně byl však tento překlad zveřejněn až k 1. květnu 2004, nicméně nelze vyloučit, že z jeho dřívější verze případně stejné chyby v jiném překladu vycházel předkladatel již při přípravě zákona v roce 1996.

Úplné vyloučení z působnosti přejal do svého § 2 odst. 1 písm. a) i současný zákon č. 185/2001 Sb., o odpadech a zrušení některých zákonů, ve svém původním znění, ač bylo formulováno jinak než v předchozím zákoně: *„Zákon se vztahuje na nakládání se všemi odpady, s výjimkou a) odpadních vod.“*[7] Tato formulace zůstala nezměněna až do 1. října 2015, tedy účinnosti zákona č. 223/2015 Sb. Vyloučení z působnosti bylo rovněž v souladu s výše zmiňovanou českou jazykovou verzí evropské odpadové směrnice, nicméně bylo v rozporu s ostatními jazykovými verzemi.

V roce 2006 byla přijata nová Směrnice Evropského parlamentu a Rady 2006/12/ES ze dne 5. dubna 2006 o odpadech, která nahradila směrnici 75/442/EHS. Nastavení vyloučení z působnosti bylo v této směrnici zachováno téměř stejné jako ve směrnici předchozí. Zachována byla nicméně rovněž odlišnost českého znění ustanovení upravujícího působnost.[8]

V roce 2008 byla přijata Směrnice Evropského parlamentu a Rady 2008/98/ES ze dne 19. listopadu 2008 o odpadech a o zrušení některých směrnic (dále jen „rámcová směrnice o odpadech“). V nové směrnici bylo vyloučení formulováno lépe než ve směrnici předchozí při zachování stejného významu. Česká jazyková verze v tomto případě odpovídá jiným verzím a ve svém čl. 2 odst. 2 písm. a) ze své působnosti vylučuje odpadní vody *„v rozsahu, v jakém se na ně vztahují jiné právní předpisy Společenství“*.[9]

Z důvodové zprávy k novelizačnímu zákonu č. 154/2010 Sb., kterým byla transpozice nové směrnice provedena, není zřejmé, proč nebylo vyloučení odpadních vod z působnosti zákona o odpadech uvedeno do souladu s novou rámcovou směrnicí o odpadech.

Ke změně došlo až novelizačním zákonem č. 223/2015 Sb., a to podle důvodové zprávy až na základě procedury EU-Pilot a infringementového řízení. Z hlediska působnosti zákona o odpadech ve vztahu k odpadním vodám je velmi zajímavý i průběh přípravy této novely. V návrhu předloženém do meziresortního připomínkového řízení se MŽP pokusilo oproti znění směrnice upřesnit, na jaké konkrétní způsoby nakládání s odpadními vodami se zákon o odpadech nevztahuje. Návrh novelizovaného § 2 odst. 1 písm. a), zněl: *„Tento zákon se vztahuje na nakládání se všemi odpady s výjimkou a) odpadních vod, pokud jde o nakládání dle povolení k vypouštění odpadních vod do vod povrchových nebo podzemních nebo jejich odvádění kanalizací“*.[10] Taková formulace sice jednoznačně vymezovala činnosti, které jsou plně upraveny jinými předpisy, ale řada připomínkových míst v rámci meziresortního připomínkového řízení[11] namítala, že takový přístup ponechává některé činnosti v působnosti jak zvláštních předpisů, tak zákona o odpadech.

Typickým příkladem jsou odpadní vody akumulované v bezodtokých jímkách. Přesto, že mají svůj režim nastaven v § 38 odst. 6 vodního zákona, by při výše uvedené formulaci plně podléhaly rovněž právnímu režimu zákona o odpadech. To znamená, že osoby takto akumulující odpadní vody by byly původci odpadu ve smyslu zákona o odpadech a všechny čistírny odpadních vod, které by zpracovávaly takovéto odpadní vody, by musely disponovat souhlasem s provozem zařízení určeného k odstraňování odpadů. Zároveň by se s ohledem na infekčnost těchto odpadních vod jednalo o nebezpečný odpad, na který se vztahuje celá řada dalších povinností.

Kompromisním výstupem z meziresortního připomínkového řízení pak bylo navržení a přijetí textu odpovídajícího rámcové směrnici obsahující pouze částečné omezení působnosti zákona o odpadech.

Možnosti transpozice rámcové směrnice o odpadech

Text ustanovení o působnosti v rámcové směrnici byl uveden již výše. Chtěl bych se k němu nicméně ještě jednou vrátit a zhodnotit, jaké jsou možnosti transpozice takto formulovaného omezení působnosti. Základním požadavkem na transpozici samozřejmě je, že na odpadní vody, na které se směrnice vztahuje, musí být na národní úrovni uplatněny požadavky, které na ně směrnice klade.

To může pro zákon o odpadech znamenat užší omezení působnosti, pokud by například rovněž transponoval požadavky směrnice o čištění městských odpadních vod. Nebo naopak nastavení třeba i úplného vyloučení z působnosti pro odpadní vody v případě, že by například zákon o vodách fakticky kladl na nakládání s odpadními vodami v působnosti rámcové směrnice o odpadech stejné požadavky jako tato směrnice.

Takovému závěru odpovídá i rozsudek Soudního dvora Evropské unie C-252/05.[12] Jednalo se o případ, kdy došlo k úniku odpadní vody z potrubí, přičemž postup v takové situaci nebyl upraven ve směrnici o čištění městských odpadních vod. Soud konstatoval, že na takovou situaci je nezbytné aplikovat tehdejší směrnici o odpadech, respektive zákon, kterým byla do vnitrostátního práva Spojeného království provedena. Tento rozsudek je kromě výše uvedeného důležitý z důvodu, že vymezuje, a to poměrně přísně, co znamená, že se na odpadní vody vztahují jiné předpisy. Takovým případem je podle Soudního dvora pouze případ, když jiné předpisy zajišťují stejnou míru ochrany životního prostředí jako tehdejší směrnice o odpadech. Jednalo se o směrnici 75/442/ES, jejíž anglický text odpovídal vyloučení v současné rámcové směrnici o odpadech.

Ze tří výše uvedených odstavců vyplývají následující závěry pro výklad vnitrostátní právní úpravy, která má vyloučení z působnosti formulováno stejně jako rámcová směrnice o odpadech. Za prvé transpoziční předpis se nevztahuje na odpadní vody pouze, pokud zvláštní právní předpis zajišťuje v konkrétní situaci stejnou míru ochrany životního prostředí jako rámcová směrnice o odpadech. Za druhé s ohledem na obsah jiných právních předpisů a to, zda zajišťují stejnou míru ochrany životního prostředí při nakládání s odpadními vody, jakou požaduje rámcová směrnice o odpadech, se může faktický rozsah působnosti zákona o odpadech ve vztahu k odpadním vodám v průběhu času měnit, pokud je zachován první uvedený princip.

Zajímavou otázkou z hlediska souladu s evropskou úpravou je definice odpadní vody. Zákon o odpadech odkazuje na definici odpadní vody použitou v zákoně o vodách. Na evropské úrovni však definice odpadních vod neexistuje. Rozpor by proto mohl nastat v tom, jak je odpadní voda definována na národní úrovni, a jaký význam má v rámcové směrnici o odpadech. Otázkou je, zda by odpadní voda neměla být v kontextu rámcové směrnice o odpadech s ohledem na použití slova „odpadní“ vymezena jako voda, která naplní definici odpadu. Na tuto otázku nejsem schopen v tomto článku odpovědět, přesto se k této otázce v další kapitole ještě dostanu, protože může mít na posouzení některých případů a případného uplatnění zákona o odpadech výrazný vliv.

Nakládání s odpadem a odpadní vody

Pokud se chci zaměřit na otázku, v jakém rozsahu se na odpadní vodu vztahuje zákon o odpadech, musím začít u vymezení obecné působnosti zákona o odpadech.

Podle návětí § 2 odst. 1 se zákon o odpadech vztahuje na nakládání se všemi odpady. Pojem nakládání s odpady je definován v § 4 odst. 1 písm. e) zákona o odpadech a je poměrně široký, spadá sem obchodování s odpady, shromažďování, sběr, výkup, přeprava, doprava, skladování, úprava, využití a odstranění odpadů. Řadu činností vykonávaných s odpadní vodou je možné pod některý z těchto pojmů podřadit. Naopak mě nenapadá, jaká činnost pod některý z těchto pojmů nespadá. Jako příklad je možné uvést již zmiňované akumulování odpadních vod v bezodtoké jímce. Z hlediska zákona o odpadech jde buď o shromažďování, případně skladování odpadu podle dalších okolností.

Klíčovou otázkou pro uplatnění zákona o odpadech je samozřejmě naplnění definice odpadu. Odpad je definován v § 3 odst. 1 zákona o odpadech jako *„movitá věc, které se osoba zbavuje, má úmysl nebo povinnost zbavit se“*. Všemi aspekty naplnění definice odpadu není možné se zabývat a taková otázka přesahuje problematiku řešenou tímto článkem.

Chtěl bych zmínit pouze otázku vedlejšího produktu vymezeného v § 3 odst. 5, který není při splnění podmínek v tomto ustanovením stanovených odpadem. Domnívám se, že celá řada odpadních vod by mohla definici vedlejšího produktu naplnit. V podstatě by tomu tak mohlo být v případě všech průmyslových vod, které budou v budoucnosti nějakým způsobem využívány, aniž by musely být před takovým využitím vyčištěny. K problematice vedlejšího produktu více například v Guidance on the interpretation of key provisions of Directive 2008/98/EC on waste.[13]

Z hlediska uplatnění zákona o odpadech na odpadní vody a na vody obecně je zajímavý odlišný rozsah definice odpadní vody podle zákona o vodách a definice odpadu.

Odpadní vody jsou definovány v § 38 vodního zákona. První odstavec obsahuje pozitivní vymezení odpadních vod, když definuje, co je možné za odpadní vody považovat: *„Odpadní vody jsou vody použité v obytných, průmyslových, zemědělských, zdravotnických a jiných stavbách, zařízeních nebo dopravních prostředcích, pokud mají po použití změněnou jakost (složení nebo teplotu), jakož i jiné vody z těchto staveb, zařízení nebo dopravních prostředků odtékající, pokud mohou ohrozit jakost povrchových nebo podzemních vod. Odpadní vody jsou i průsakové vody z odkališť, s výjimkou vod, které jsou zpětně využívány pro vlastní potřebu organizace, a vod, které odtékají do vod důlních, a dále jsou odpadními vodami průsakové vody ze skládek odpadu.“*)[14]

Druhý odstavec obsahuje negativní[15] vymezení odpadních vod, protože vymezuje výčet vod, které nemají být považovány za odpadní vody přesto, že naplní definici podle odstavce prvního. *„Vody z drenážních systémů odvodňovaných zemědělských pozemků, chladící vody užité na plavidlech a pro vodní turbíny, u nichž došlo pouze ke zvýšení teploty, a nepoužité minerální vody z přírodního léčivého zdroje nebo zdroje přírodní minerální vody nejsou odpadními vodami podle tohoto zákona. Za odpadní vody se dále nepovažují srážkové vody z dešťových oddělovačů, pokud oddělovač splňuje podmínky, které stanoví vodoprávní úřad v povolení. Odpadními vodami nejsou ani srážkové vody z pozemních komunikací, pokud je znečištění těchto vod závadnými látkami řešeno technickými opatřeními podle vyhlášky, kterou se provádí zákon o pozemních komunikacích.“*

Z porovnání obou definic vyplývá, že definice odpadní vody zahrne více vod než definice odpadu. To, že voda naplní definici odpadní vody, nutně neznamená, že se zároveň stane odpadem. I pokud má voda po použití změněnou jakost, neznamená to, že se jí někdo zbavuje, má úmysl nebo povinnost se jí zbavit.

Mnohem zajímavější je však případ, kdy vody naplní definici odpadu a nenaplní definici odpadní vody. V takovém případě není možné uplatnit ustanovení omezující působnost zákona o odpadech ve vztahu k odpadním vodám. Myslím si, že takovýto problém by se mohl týkat některých vod z negativního vymezení odpadních vod. Jak u vod odváděných drenážním systémem nebo nepoužitých minerálních vod může totiž docházet a dochází ke zbavování.

Tento problém souvisí s již výše naznačeným rozdílem mezi definicí odpadní vody podle zákona o vodách a jejím možným významem z hlediska rámcové směrnice o odpadech. Kdyby byla odpadní voda vymezena tak, že se jedná o vodu, která naplní definici odpadu, k výše uvedenému problému by nedošlo. Tímto rozporem by bylo vhodné se v rámci budoucích změn právní úpravy zabývat. Myslím si, že hlediska ochrany životního prostředí je aplikace zákona o odpadech na vody z odvodňování zemědělských pozemků nebo nepoužité minerální vody zbytečná.

Nakládání s odpadními vodami, na které se vztahuje zákon o vodách nebo zákon o vodovodech a kanalizacích

Pokud odpadní voda v konkrétním případě naplní definici odpadu a činnost s ní vykonávaná definici nakládání s odpady, je nezbytné pro zodpovězení otázky uplatnění zákona o odpadech posoudit, zda se v takovém případě na odpadní vody vztahuje jiný právní předpis, přičemž v úvahu přichází zejména zákon o vodách nebo zákon o vodovodech a kanalizacích.

Zvolená formulace neúplného vyloučení odpadních vod z působnosti zákona o odpadech není ideální. Čistě jazykový výklad by v tomto případě mohl vést k závěru, že odpadní vody jsou vyloučeny z působnosti zákona o odpadech zcela, protože uvedené jiné zákony se na odpadní vody obecně vztahují. Zákon o vodách nijak nevylučuje ze své působnosti žádné odpadní vody. To však nebylo záměrem zákonodárce, takový výklad by byl v rozporu se smyslem předmětného ustanovení a rovněž s již uvedeným rozsudkem Soudního dvora Evropské unie. Proto by bylo vhodnější, aby § 2 odst. 1 písm. a) zněl například takto: *„v rozsahu, v jakém je nakládání s nimi upraveno jinými právními předpisy“*. S ohledem na důvod novelizace ustanovení a jeho smysl je stávající znění nezbytné takto alespoň vykládat.

Zákon o odpadech se podle mého názoru jednoznačně nevztahuje na vypouštění odpadních vod do vod povrchových nebo podzemních. Zákon o vodách reguluje tyto činnosti v § 38. Z hlediska zákona o odpadech by se jednalo o odstraňování odpadu, protože je ale tato činnost zákonem o vodách plně upravena, včetně požadavku na povolení takové činnosti v § 8 odst. 1 písm. c), povinností podle § 38 odst. 7 a 8 a řady dalších povinností, zákon o odpadech se na ni nevztahuje.

Další činností, kterou zákon o vodách upravuje v § 38 odst. 6 a na kterou se podle mého názoru zákon o odpadech nevztahuje, je již několikrát zmíněné akumulování odpadních vod v bezodtokých jímkách. Odstavec 6 stanovuje každému, kdo akumuluje odpadní vody v bezodtoké jímce, povinnost akumulovat je tak, aby nedocházelo k ohrožení životního prostředí, a pravidelně je zneškodňovat, včetně povinnosti prokázat takové zneškodnění na výzvu kontrolního orgánu. Zneškodňováním se zde myslí likvidace odpadní vody na čistírně odpadních vod. To potvrzuje rovněž přijatá a doposud neúčinná novela vodního zákona (zákon č. 138/2018 Sb)., která mimo jiné upravuje text § 38 odst. 6 do podoby nového § 38 odst. 8 tak, aby bylo jednoznačné, že jediným způsobem zneškodňování odpadních vod akumulovaných v bezodtoké jímce je jejich odvoz na čistírnu odpadních vod, a dále s účinností posunutou na rok 2020 ještě zpřísňuje způsob prokazování toho, že byla odpadní voda skutečně na čistírnu odpadních vod dopravena a zlikvidována. Otázkou, která není podle mého názoru dostatečně pokryta, je samotná přeprava odpadní vody. Otázce přepravy odpadních vod se budu věnovat podrobněji v další části.

V tomto místě je nezbytné zastavit se u § 4 vyhlášky č. 268/2009 Sb., o technických požadavcích na stavby, která ve vztahu k bezodtokým jímkám stanoví mimo jiné, že *„s obsahem žumpy musí být nakládáno v souladu s jiným právním předpisem.“* Přičemž poznámka pod čarou odkazuje na zákon o odpadech. Toto ustanovení podle mého názoru nemůže stanovit povinnou aplikaci zákona o odpadech na odpadní vody akumulované v bezodtokých jímkách. Z hlediska právní síly se jedná vyhlášku, která je v rozporu s ustanovením zákona o odpadech o jeho působnosti. Navíc vyhláška sama o sobě by nemohla stanovit takovouto povinnost, i kdyby v přímém rozporu s ustanovením o působnosti nebyla.

Zajímavou otázkou je, nakolik se zákon o vodách a zákon o vodovodech a kanalizacích vztahují na provoz čistíren odpadních vod. I když v zákoně o vodách a v zákoně o vodovodech a kanalizacích není nikde přesně vymezeno fungování čistírny odpadních vod, není možné říci, že by tyto zákony na provoz čistíren odpadních vod nedopadaly. Ať už se jedná o otázku výstavby čistíren jako vodního díla, spadajících do působnosti vodoprávního úřadu jako speciálního stavebního úřadu, požadavky na provozní řád vyplývající ze zákona o vodách nebo nastavení podmínek pro čistírnu v kanalizačním řádu podle zákona o vodovodech a kanalizacích. Lze předpokládat, že výše uvedená právní úprava představuje dostatečnou ochranu životního prostředí, kvůli tomu byla ostatně přijata, a zákon o odpadech se proto na provoz čistírny odpadních vod nevztahuje.

Otázka zůstává otevřená v případě dalších technologií úpravy kalů provozovaných v rámci čistíren odpadních vod. V současné době čistírny odpadních vod většinou nedisponují souhlasem k provozu zařízení podle zákona o odpadech, pokud upravují vlastní kaly a je třeba uvést, že ani v případě, kdy upravují kaly z jiných čistíren odpadních vod. K této otázce se vrátím později. Běžné kalové hospodářství, kde dochází k úpravě kalů tak, aby mohly být v souladu s § 32 a § 33 zákona o odpadech použity na zemědělské půdě, je součástí provozu čistírny odpadních vod a rovněž se na něj zákon o odpadech nevztahuje. S ohledem na novou vyhlášku č. 437/2015 Sb., která od roku 2020 výrazným způsobem zpřísňuje podmínky pro používání kalů na zemědělské půdě, budou čistírny odpadních vod v budoucnu hledat nové způsoby nakládání s kaly vystupujícími z čistíren odpadních vod[16], od sušení kalů až po jejich spalování a bude velmi důležité rozlišit, kdy se bude na takové technologie provozované v rámci čistírny odpadních vod aplikovat zákon o odpadech a kdy nikoliv.

To je možné posoudit ze dvou hledisek. Jedním je nalezení rozdílu mezi odpadní vodou a kalem. Současná právní úprava nedává žádné vodítko, kdy by bylo možné říci, že kal z čistírny odpadních vod již není odpadní vodou. Pokud by taková jasná hranice existovala, bylo by zřejmé, že technologie, která zpracovává kal, který již není odpadní vodou, musí být provozována v režimu zákona o odpadech.

Druhým hlediskem pak může být již vícekrát zmiňovaný princip stejné míry ochrany životního prostředí, který je možné uplatnit i v případě, že by byl kal vstupující do technologie zpracování stále považován za odpadní vodu. Z tohoto pohledu by pak například spalování kalů v rámci čistírny odpadních vod jednoznačně podléhalo zákonu o odpadech a rovněž režimu tepelného zpracování odpadů podle zákona č. 201/2012 Sb., o ochraně ovzduší. Protože obsahují velmi přísné podmínky. Složitější otázku představují například technologie sušení kalů nebo provoz vyhnívacích nádrží jako bioplynových stanic. Myslím si, že tato otázka si v budoucnosti vyžádá jednoznačné rozlišení v podobě úpravy ustanovení o působnosti ve vztahu k odpadním vodám, nebo úpravu definic a jednoznačné vymezení toho, co je součástí čistírny odpadních vod jako vodního díla a co nikoliv.

Nyní zpět k předávání kalů mezi čistírnami odpadních vod. Malé čistírny odpadních vod často nedisponují technologií zajišťující úpravu kalů, která by umožňovala jejich použití na zemědělské půdě. Nejčastěji je proto předávají k úpravě do čistíren, které takovou technologii mají. V současné době toto předání provádějí mimo režim zákona o odpadech.

Takový přístup vyplývá ze stanoviska MŽP[17], které uvádí, že předávání výstupu z čistíren odpadních vod bez kalové koncovky v podobě řídké suspenze pevných a koloidních částic, organických i anorganických, do čistíren odpadních vod s kalovou koncovkou nespadá do působnosti zákona o odpadech. V tomto stanovisku není používán pojem kal. Jak jsem již uváděl, pojem kal není v právních předpisech nikde definován a ani pojem řídká suspenze nestanoví jasnou hranici. Opět se zde nabízí, že by bylo do budoucna vhodné na základě nějakého kritéria odpadní vodu a kal, který již není odpadní vodou, v právních předpisech odlišit.

Stanovisko se nezbývá tím, jaká ustanovení zákona o vodách se na takovéto odpadní vody vztahují. Domnívám se však, že uvedený přístup je v souladu s výše uvedeným principy, jakými by měl být vztah zákona o odpadech k odpadním vodám vykládán. Akumulaci odpadních vod vystupujících z jedné čistírny odpadních vod na této čistírně lze považovat za akumulaci v odpadní jímce v režimu § 38 odst. 6 vodního zákona. Odvoz odpadů na jinou čistírnu odpadních vod je pak s tímto ustanovením v souladu a následná likvidace kalů, které jsou odpadní vodou, na jiné čistírně odpadních vod, která je vodním dílem, rovněž podléhá vodnímu zákonu. Otázkou zůstává, do jaké fáze technologie čistírny odpadních vod takový kal vstupuje. To pak otevírá již výše naznačené otázky ve vtahu k jednotlivým následným technologiím provozovaným v rámci čistírny odpadních vod. Problémem stanoviska MŽP je opět již výše uvedená otázka přepravy odpadních vod.

Posledním ze způsobů nakládání s odpadními vodami, na které se nevztahuje zákon o odpadech, které jsem dokázal identifikovat, je zcela jistě s ohledem na komplexní úpravu v zákoně o vodovodech a kanalizacích odvádění odpadních vod kanalizací.

Nakládání s odpadními vodami, na které se vztahuje zákon o odpadech

V této části bych chtěl identifikovat činnosti, na které se zákon o odpadech nově vztahuje.

Nejprve bych se chtěl vrátit k výše zmíněné problematice přepravy odpadních vod. Přeprava odpadů spadá do definice nakládání s odpady. V tomto ohledu představuje nakládání, které zákon o vodách ani zákon o vodovodech a kanalizacích nepokrývají. Myslím si proto, že na přepravu odpadních vod by se měly podmínky zákona o odpadech vztahovat. To by bylo z hlediska běžné praxe velmi zajímavé. Mimo jiné by to znamenalo, že na přepravu odpadních vod z domácností akumulovaných v bezodtokých jímkách by se vztahovala povinnost ohlašování přepravy nebezpečných odpadů. Nelegální vyvážení těchto odpadních vod a jejich rozlévání například na polích je stálým problémem. Kontrolní orány by díky tomuto výkladu získaly účinný nástroj, který by umožnil kontrolu takového jednání.

Otázkou je, zda by se měl režim přepravy odpadů vztahovat i na odpadní vody akumulované v bezodtokých jímkách. Po již zmíněném upřesnění a zpřísnění vodního zákona ve vztahu k odpadním vodám akumulovaným v bezodtokých jímkách, představuje nová úprava poměrně výraznou ochranu životního prostředí, která zajišťuje vysledovatelnost odpadních vod při případné kontrole. Nicméně pokud jde o odpadní vody, které mají nějakou odpadovou nebezpečnou vlastnost, nejsou splněny všechny požadavky čl. 36 rámcové směrnice.

Novelizovaný § 38 odst. 8 zákona o vodách bude stanovovat osobě, která akumuluje odpadní vodu v bezodtoké jímce povinnost uchovávat doklady o odvozu odpadních vod po dobu dvou let, přičemž rámcová směrnice o odpadech požaduje v případě nebezpečných odpadů roky tři. V případě osoby přepravující odpadní vody pak novelizovaný § 38 odst. 8 zákona o vodách nepožaduje uchovávání dokladů vůbec, zatímco rámcová směrnice o odpadech požaduje uchovávání po dobu 12 měsíců. Zůstává otázkou, jak by k této otázce přistoupil Evropský soudní dvůr. Zda by vyžadoval uplatnění stejných požadavků jako v rámcové směrnici o odpadech, nebo by považoval za dostačující, že je zajištěna přibližně odpovídající míra ochrany životního prostředí.

Zajímavou související otázkou je problematika přeshraniční přepravy odpadů. Základním předpisem upravujícím přeshraniční přepravu odpadů je Nařízení Evropského parlamentu a Rady č. 1013/2006 ze dne 14. června 2006 o přepravě odpadů (dále jen „nařízení o přepravě“), které v čl. 3 písm. e) ze své působnosti vylučuje mimo jiné přepravu odpadních vod, „pokud se na ni vztahují jiné právní předpisy společenství obsahující obdobná ustanovení“.

S ohledem na přímou použitelnost evropského nařízení, vyloučení z působnosti pro odpadní vody v zákoně o odpadech ve znění účinném před novelizací související s infringementovým řízením nevylučovalo odpadní vody z působnosti nařízení o přepravě. Nicméně je vylučovalo z působnosti zákona o odpadech, který provádí adaptaci českého práva na nařízení o přepravě, a dále stanoví omezení a zákazy, které nařízení umožňuje nastavit na vnitrostátní úrovni.

Zákon o odpadech tak v § 54 odst. 2 zakazuje přepravu odpadů do České republiky za účelem odstranění. Výjimku představují pouze odpady vzniklé v sousedních státech v důsledku živelních pohrom nebo za stavu nouze. Pomineme-li možnost uplatnění těchto výjimek, je přeprava odpadních vod do České republiky za účelem jejich likvidace v čistírně odpadních vod zakázaná, protože likvidaci odpadních vod v čistírně odpadních vod a jejich následné vypuštění do vod povrchových je z hlediska způsobů nakládání s odpady nezbytné považovat za odstranění odpadů.

S ohledem na formulaci sankčních ustanovení v zákoně o vodách a v zákoně o vodovodech a kanalizacích může nově dojít k uplatnění sankce podle § 66 odst. 4 písm. b) zákona o odpadech na odpadní vody. Bude tomu tak v případě, kdy osoba nebude vypouštět odpadní vody do vod povrchových nebo podzemních, ani se nebude jednat o jejich akumulaci v bezodtoké jímce a zároveň takovým jednáním nedojde k ohrožení podzemních nebo povrchových vod. Pro takové jednání neexistuje v zákoně o vodách ani v zákonech o vodovodech a kanalizacích sankční ustanovení. To znamená, že se na takové nakládání s odpadními vodami zákon o vodách ani zákon o vodovodech a kanalizacích nevztahují. Takové jednání pak bude téměř vždy možné podřadit pod povinnost stanovenou v § 12 odst. 3 zákona o odpadech nakládat s odpady v zařízeních k tomu určených s nastavenou odpovídající sankcí právě v § 66 odst. 4 písm. b) zákona o odpadech. Příkladem takového jednání může být právě vývoz odpadních vod na pole, ale také cílené zavlažování odpadní vodou.

Recyklace odpadních vod

Tím jsem se dostal i k další činnosti, na níž se nově vztahuje zákon o odpadech, a tou je využívání nebo recyklace odpadních vod. Jedná se o činnost, která není v současné době v zákoně o vodách upravena, zřejmě proto, že se doposud odpadní vody v České republice nevyužívaly. To bude nicméně v blízké době s ohledem na klimatickou změnu a související nárůst sucha nutné změnit a zareagovat by na to měla i právní úprava.

Ač je zákon o odpadech zákonem, který recyklaci odpadů upravuje, nejedná se o zákon, který by problematiku recyklace odpadních vod uspokojivě řešil. Pokud někdo využívá odpadní vody účelným způsobem, může se z hlediska zákona o odpadech jednat o tři různé režimy.

Prvním režimem jsou případy, kdy nedojde k naplnění definice odpadu. To může být jednak v případě, pokud osoba využívá odpadní vodu, která ji vzniká v rámci její vlastní činnosti. V takovém případě totiž nemusí jít o zbavování se odpadní vody. Dále v případě, pokud je odpadní voda využívána znovu ke stejnému účelu a jedná se opětovné použití, anebo v případě, kdy naplní definici vedlejšího produktu podle § 3 odst. 5 zákona o odpadech.

Za druhé, odpadní voda může být využívána jako odpad v zařízení na využití odpadu. Posledním možným režimem využití odpadních vod z hlediska zákona o odpadech je uplatnění konce odpadu podle § 3 odst. 6 tohoto zákona. V rámci tohoto přístupu může být odpadní voda po úpravě vyvedena z odpadového režimu a využita již mimo pravidla pro nakládání s odpady.

Možnost uplatnění výše uvedených režimů komplikuje nastavení jednotných kvalitativních kritérií, které by zajišťovaly, že voda při svém opětovném použití bez úpravy nebo po úpravě nebude ohrožovat životní prostředí nebo zdraví lidí. V případě, že nedojde k naplnění definice odpadu, nemůžou odpadové předpisy nastavovat jakékoliv požadavky na kvalitu něčeho, co není odpadem. Takové požadavky mohou být pro vedlejší produkty a odpady, které přestanou být odpadem, nastaveny vyhláškou § 3 odst. 8 zákona odpadech.

Podmínky využívání odpadních vod jako odpadu může MŽP rovněž nastavit vyhláškou. V takovém případě by ale každé místo použití muselo být provozováno jako zařízení na využití odpadů.

Dalším problémem je, že při uplatnění jakéhokoliv z výše uvedených režimů podle zákona o odpadech nepřestane být odpadní voda odpadní vodou podle vodního zákona. A v takovém případě se uplatní omezení, která zákona o vodách na používání odpadní vody klade. Zde myslím hlavně omezení jak ve vztahu k odpadním vodám akumulovaným v bezodtokých jímkách, které mohou být odváženy pouze na čistírnu odpadních vod, tak pravidla pro vypouštění odpadních vod do vod povrchových nebo podzemních.

Zajímavá je v tomto ohledu aktuální praxe, kdy si zemědělci nechávají zaregistrovat oplachové vody z mytí potravin Ústředním kontrolním a zkušebním ústavem zemědělským jako pomocnou půdní látku a následně je využívají na polích k závlahám. Z hlediska zákona o odpadech v takovém případě nedojde k naplnění definice odpadu nebo půjde případně o vedlejší produkt. Nicméně z hlediska zákona o vodách půjde stále o odpadní vodu. Otázkou, na kterou neumím s jistotou odpovědět, je, který zákon je v tomto případě zákonem zvláštním, zda zákon o hnojivech nebo zákon o vodách. Bylo by možné konstatovat, že to spíše bude zákon o hnojivech a takovýto postup je s ohledem na účinné právo legální, o ideální řešení se však nejedná.

S ohledem na výše uvedené se domnívám, že nejvhodnějším řešením pro umožnění využívání nebo recyklace odpadních vod by bylo nastavení mechanismu využívání odpadních vod nebo podmínek jejich recyklace do zákona o vodách. Vedle nějakého nastavení administrativního mechanismu by mělo jít o nastavení požadavků na kvalitu odpadních vod v podobě limitů obsahu škodlivých látek a mikroorganismů, které by umožnily buď přímé využití odpadních vod, nebo by umožnily nepovažovat vody, které taková kritéria splní, nadále za odpadní vody. Druhá možnost by však neumožňovala využít stávající ustanovení o působnosti v zákoně o odpadech a hrozilo by uplatnění pravidel zákona o odpadech, včetně povinnosti využívat odpady pouze v zařízeních k tomu určených. Vhodnější by proto bylo považovat odpadní vody nadále za odpadní vody a pouze nastavit pravidla pro jejich využívání zajišťující obdobnou ochranu životního prostředí, jakou požaduje pro recyklované odpady rámcová směrnice o odpadech.

Závěry

V článku jsem se pokusil vymezit nakládání s odpadními vodami, které je i po změně působnosti zákona o odpadech z působnosti tohoto zákona vyloučeno. Jedná se o vypouštění odpadních vod do vod povrchových a podzemních, o akumulaci odpadních vod v bezodtokých jímkách a také o provozování čistíren odpadních vod. Dále jsem se pokusil identifikovat případy, kdy nově dojde k uplatnění zákona odpadech na činnosti vykonávané s odpadními vodami. Zde se jedná o přepravu odpadních vod a zejména o jejich přeshraniční přepravu, a dále o možné uplatnění povinnosti nakládat s odpady výhradně v zařízení k tomu určeném v případě některých nelegálních způsobů nakládání s odpadními vodami, ale také při snaze o využívání odpadních vod za stávajícího znění právních předpisů.

Nemyslím si, že by výčet případů, kdy dojde k uplatnění zákona o odpadech na odpadní vody uvedený v tomto článku byl vyčerpávající, další příklady se časem objeví v aplikační praxi a později rovněž v rozhodnutích správních soudů. Cílem tohoto článku bylo primárně upozornit, že uplatnění zákona o odpadech na odpadní vody bude širší, než předpokládala v důvodová zpráva k novele zákona o odpadech, kterou byla změna působnosti zákona o odpadech ve vztahu k nakládání s odpadními vodami provedena.

V článku jsem se rovněž pokusil popsat několik hraničních případů, které by bylo podle mého názoru vhodné řešit doplněním právních předpisů. Jedná se jednak o otázku, kdy je kal z čištění odpadních vod odpadní vodou, a kdy nikoliv. Další otázkou je nejasná povaha některých technologií upravujících nebo zpracovávajících kaly v rámci čistírny odpadních vod a související otázka uplatnění podmínek zákona o odpadech na tyto technologie. Další nejasnou otázkou je uplatnění požadavků odpadových předpisů na přepravu odpadních vod akumulovaných v bezodtokých jímkách.

Posledním cílem tohoto článku bylo zdůraznit nevhodnost uplatnění stávají právní úpravy jak zákona o odpadech, tak zákona o vodách na využívání nebo recyklaci odpadních vod. Myslím si, že je nezbytné zahájit diskuzi o tom, pro jaký typ odpadních vod přichází využití případně recyklace v úvahu, a jak by měly být podmínky pro jejich využívání nastaveny v právních předpisech.

Takové podmínky by bylo možné nastavit jak do zákona o odpadech, tak do zákona o vodách. Případné nastavení v zákoně o odpadech by se vztahovalo pouze na odpadní vody, které naplní definici odpadu nebo vedlejšího produktu, a vyžadovalo by omezení působnosti zákona o vodách ve vztahu k odpadním vodám využívaným podle zákona o odpadech.

Vhodnější by proto podle mého názoru bylo nastavení komplexních podmínek pro využívání odpadních vod v zákoně o vodách, zajišťujících ochranu životního prostředí srovnatelnou s rámcovou směrnicí o odpadech, což by automaticky s ohledem na znění ustanovení o působnosti zákona o odpadech omezovalo působnost zákona o odpadech ve vztahu k takto využívaným odpadním vodám.

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Scope of the Act on Waste in Relation to Waste water

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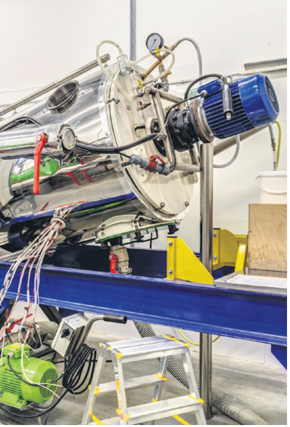
Summary

In 2015, the amendment to the Act on Waste narrowed the exclusion of the waste water from application of the Act on waste. The Act on Waste does not apply to waste water to the extent to which the Act on Water and the Act on the Water and Sewerage Systems are applicable. The article deals with the development of related legislation. The main part of the article is devoted to the assessment of the applicability of the Act on Waste to certain selected activities in relation to waste water. It defines the treatment of waste water that remains excluded from the scope of the Act on Waste on the one hand and on the other hand it defines activities in relation to waste water which are newly covered by the Act on Waste. The article also focuses onto borderline cases where, the applicability of the Act on Waste is unclear. The article also deals with the currently important topic of the application of the Act on Waste to the reuse or recycling of waste water.

Key words: *wastewater, waste, scope of the Act on Waste*



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