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15. – 18. 3. 2016, Hustopeče

OBSAH / INDEX

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Patronem tohoto čísla je TÝDEN VÝZKUMU A INOVACÍ PRO PRAXI A ŽIVOTNÍ PROSTŘEDÍ 2016 (15. – 18. 3. 2016, Hustopeče)

Úvodní slovo šéfredaktora

Na svět přichází druhé číslo časopisu WASTE FORUM, kde v recenzované části mohou být pouze příspěvky v anglickém jazyce. Cílem je zvýšit sledovanost časopisu ze strany zahraničních návštěvníků a usnadnit tak zařazení časopisu do některé mezinárodní vědecké databáze, např. SCOPUS.

Minulé číslo nebylo zrovna číslo, kterým bychom se mohli směrem ke Scopusu chlubit neb obsahovalo pouze jeden recenzovaný článek. Proto žádost o zařazení časopisu jsme odložili.

Toto číslo vypadá dobře, hlavně díky autorům ze Stavební fakulty VUT v Brně. Takže s žádostí o zařazení do Scopusu již nebudeme váhat. Je to ale běh na dlouhou trať, oni si na vyjádření vyhrazují celý rok. A tak tedy buďme/buďte trpěliví.

Počet článků v tomto čísle mne, po chmurách, které mne obcházely koncem loňského roku a letos v létě, mi zase vrací optimismus. Ale teprve příští čísla ukážou, zda právem. Redakční uzávěrka příštího čísla je 8. 1. 2016, dalšího pak 8. 4. 2016.

Na závěr bych rád všechny čtenáře i autory příspěvků rád pozval na Týden výzkumu a inovací pro praxi a životní prostředí 2016 (TVIP 2016, 15. – 18. 3, Hustopeče). V jeho rámci se koná tradičně symposium ODPADOVÉ FÓRUM 2016, které počínaje tímto ročníkem rozšiřuje svůj odborný záběr i na odpadní vody a emise do ovzduší, obojí zaměřeno především na průmysl. Nově se pod křídla TVIP dostala i konference PRŮMYSLOVÁ EKOLOGIE, kterou pořádá VŠCHT v Praze.

Termín pro přihlášky příspěvků je 4. 1. 2016. Více informací k TVIP 2016 zde v samostatném příspěvku nebo na www.tvip.cz.

WASTE FORUM je mediálním partnerem TVIP 2016, a proto všechny prezentované příspěvky, které doporučí redakční rada, budou moci být zde uveřejněny bezplatně.

Ondřej Procházka

Editorial

The second issue of the journal WASTE FORUM is here. Its reviewed part contains only papers in English. The aim is to increase international readership and to facilitate the inclusion of the journal in international scientific databases, especially in Scopus.

Unfortunately the previous issue was not the one we could be proud of in „Scopus sense“ since it consisted only one peer-reviewed article. So a request for inclusion in Scopus database must have been postponed.

The second issue is much better, mainly thanks to authors from the Faculty of Civil Engineering of Brno University of Technology. So there is no reason to hesitate now. Nevertheless it can take a year for Scopus to satisfy the application for inclusion, so let’s be patient. The editorial deadline for the next issue is January 8th 2016 and April 4th is the deadline for the further one.

Finally, I would like to invite all readers and authors to visit the Week of Research and Innovation for practice and Environment 2016 (TVIP 2016, March 15 to 18, Hustopeče). One of the conference’s departments is traditionally Symposium WASTE FORUM 2016. Starting this year, its thematic range is expanded on waste water and air emissions, both of them are focused on industry. The new department of the conference is the Industrial ecology conference organized by University of Chemistry and Technology Prague.

The deadline for application submissions is January 4. 2016. More information on TVIP 2016 is here or here www.tvip.cz. WASTE FORUM is a media partner of TVIP 2016 and therefore all presented papers recommended by the Editorial Board will be published here for free.

Ondřej Procházka

Patronem tohoto čísla je TÝDEN VÝZKUMU A INOVACÍ PRO PRAXI A ŽIVOTNÍ PROSTŘEDÍ 2016 (15. – 18. 3. 2016, Hustopeče)

Pro autory

Časopis vychází pouze v elektronické podobě a čísla jsou zveřejňována na volně přístupných internetových stránkách www.WasteForum.cz.

Do redakce se příspěvky zasílají v kompletně zalomené podobě i se zabudovanými obrázky a tabulkami, tak zvaně ***„printer-ready“.*** Pokyny k obsahovému členění a grafické úpravě příspěvků spolu s přímo použitelnou **šablonou grafické úpravy** ve WORDu jsou uvedeny na www-stránkách časopisu v sekci **Pro autory.** Ve snaze dále rozšiřovat okruh možných recenzentů žádáme autory, aby současně s příspěvkem napsali tři tipy na možné recenzenty, samozřejmě z jiných pracovišť než je autor či spoluautory. Je vždy dobré mít rezervu.

Publikační jazyk byla zatím čeština, slovenština a angličtina. Ve snaze, aby se časopis WASTE FORUM dostal do mezinárodních databází vědeckých časopisů, což je nezbytný předpoklad, aby mohl získat časem i impakt-faktor, bude již od příštího čísla pouze angličtina. V tomto případě však bude nezbytnou součástí článku na konci název, kontakty a abstrakt v českém či slovenském jazyce, přičemž rozsah souhrnu není shora nijak omezen.

Uveřejnění příspěvků v časopisu WASTE FORUM je v zásadě bezplatné. Nicméně abychom příjmově pokryli alespoň nezbytné externí náklady spojené s vydáváním časopisu (poplatky za webhosting, softwarová podpora atd.), vybíráme symbolický poplatek za uveřejnění poděkování grantové agentuře či konstatování, že článek vznikl v rámci řešení určitého projektu. Tento poplatek činí 200 Kč za každou stránku u příspěvků v anglickém jazyce, u ostatních je 500 Kč za stránku.

Uzávěrka dalšího čísla časopisu WASTE FORUM je 8. července 2015, další pak 8. října 2015.

FOR AUTHORS

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

WASTE FORUM publishes papers in English. Articles submitted must include a longer abstract in Czech or Slovak language.

Manuscripts for publication in the journal WASTE FORUM should be sent only in **electronic form** to the e-mail address *prochazka@cemc.cz* or *wasteforum@seznam.cz*. Manuscripts must be fully formatted (i.e. printer-ready) in MS WORD. The file should have a name that begins with the surname of the first author or the surname of the corresponding author. **Due to the personal connection of the editorial staff with the editors of the professional monthly journal ODPADOVE FORUM, authors need to clearly state that their manuscripts are intended for publication in WASTE FORUM**.

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

All papers that was not subjected to a peer-review are labeled in a header of each page by the text ***Not peer-reviewed and comercial papers.*** Here are accepted papers also in Czech od Slovak language.

Publication of the articles is generally free. However, revenue to cover at least the necessary external costs associated with the issuance of the magazine, we select a symbolic fee for the publication of gratitude grant agency or a statement that the article was created as part of a project solution.. The fee is **200 CZK per each new page for articles reviewed part of issue and CZK 500 for every new page for contributions in the second part of the issue.**

The deadline of the next issue is January 8, 2016, more then April 8, 2016.

Reduction of negative impacts of road-traffic infrastructure on the surface water quality

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Summary

This study is focused on evaluation of efficiency of technologies for runoff waste water treatment from road infrastructure and carparks – typified rainwater settling tanks (DUN) and constructed wetlands (CWs) – and its impact on decreasing of negative effect of these buildings on the quality of surface and subsurface water. A monitoring of existing settling tanks was done within the project supported by Technology Agency of Czech Republic. A database of surface runoff pollution (mainly petroleum substances and toxic metals) was created during this monitoring. Other part of the project was focused on development of new technologies for surface runoff treatment and innovative ways for testing and validation of the technologies – mathematical modelling including semi-operated model validation of the model using hydraulic load tests. The research was partially focused on development of three-stage technology for surface runoff treatment consisting of mechanical pretreatment tank, combined constructed wetland (with both horizontal and vertical flow) and specially designed infiltration tanks.

The results of the three years monitoring of four selected DUN running in 2013 – 2015 (all located in Czech Republic) shows significant diversity in the capacity of DUN for retention and elimination of observed pollutants (e.g. within the range for the individual monitored parameters Cd between 5 and 100 %; Hg between -9 and 80 %; Ni between -100 and 100 %; Zn between -63 and 22 %; PAH between -174 and 59 %; total nitrogen between -2 and 32 %; total phosphorus between -13 and 27 %; suspended solids between -34 and 66 %; chlorides between -49 and 22 %).

Testing of newly developed three-stage system shows higher efficiency for elimination of monitored pollutants compared to other existing systems. Mathematical modelling also seems as a promising approach for projection of new settling tanks with special emphasis for designing of the systems regarding to specific outflow limits.

Keywords: *Constructed wetland, stormwater tanks, surface runoff, mathematic model, toxic metals*

Introduction

High amount of pollutants that can affect many elements of the environment and the human health is released by car traffic[1,2]. The origin of particular pollutants in surface run-off from roads and parking areas is summarized in detail by Lee and Touray[3] and Bäckström et al.[4] A part of the harmful substances dissolved in water flows away with the rain water and another part of noxious substances is bound to suspended particles[5]. Monitoring of the surface run-off at the control network of selected motorways and expressways was carried out between 2005 and 2009 within two research projects of the Czech Ministry of Transport[6,7]. Current situation and results of the projects leads to the pressure to provide an appropriate treatment of the surface run-off by accurate treatment facilities. Existing solutions - typified rainwater settling tank (DUN) or open settling tanks — are primarily used to capture the main portion of stormwater pollution (run-off) and reduce water pollution in rivers or other recipient. However these solutions don't represent an active stage of purification, but only mechanical pre-treatment.

Study of Aryal et al.[9] summarizes the results of a longitudinal twenty-year-long monitoring of the cleaning effect of retention and infiltration facilities where the cleaning of surface run-off from roads in the filtration bed of defined filter material was carried out. The use of chemical substances for road and parking areas maintenance (e. g. salting) has a significant impact on hydraulic characteristic changes of filtration beds and also on mobility of metals. The detailed information is summarized by Novotny et al.[8] and Bäckström et al.[4]. As a consequence of salting and presence of dust in run-off changes in granularity, porosity and thus the hydraulic conductivity of the filtration beds are observed hydraulic conductivity decrease. Changes in hydraulic conductivity are progressively leading to the clogging processes[10]. The use of the filtration beds of constructed wetlands in combination with sedimentation components described by Bulc et al. [11] shows positive influence on the run-off treatment efficiency.

Experimental part

The research was divided in to these parts: i) monitoring of existing facilities along selected parts of highway network; ii) monitoring of stormwater tanks built in commercial zones; iii) mathematical modelling of newly developed facilities; iv) pilot testing of newly developed facilities and v) study of the role of macrophytes in CWs treatment processes.

Monitoring of operating DUN and stormwater tanks was carried out in the period 2013 - 2015. Description of these facilities is provided in the project database published on Dekonta company web sites. Water samples were collected by standardized methods into pre-set sample containers for different types of pollutants. Sampling was carried out 3 - 6 times a year in relation to the rainfall periods that affect the supply of water into retention part and its delay. The physicochemical indicators (water temperature, pH, electrical conductivity) of water quality were measured in-situ using a portable device Hach Lange HQ40D. Concentrations of the following water quality parameters: turbidity, suspended solids and volatile solids, chlorides, nutrients (total nitrogen, total phosphorus), organic compounds (TC, TOC, DOC, COD), PAHs, petroleum substances (expressed as C10–C40), heavy metals (Cd, Cu, Hg, Ni, Pb, Zn) were determined in accredited laboratory. Indicators were selected on the base of literature review[1,9] and author's own findings from monitoring of surface run-off at highways and expressways[6,7].

The process of monitoring and mathematical modelling was divided into several stages. Since the beginning of the research we have used mainly Comsol Multiphysics software (CFD modules) that allows for implementation of numerical models for simulation of the mixture of two different liquids in newly designed stormwater settling tank. The mixture of two liquids was set-up by different combinations of water + gasoline and water + oil substances. The physical model of simulated pre-treatment tank is shown in Figure 1 (inflow with gray pipe, outflow in rear part of photo); numerical model of this object with rendered mesh is shown on Figure 2 (inflow in left part of the figure, outflow in right part). In order to make the simulations faster all rounded edges of the settling tank were replaced with flat walls (e. g. the circular inlet pipe is replaced by a square profile). Similarly, the rounded part in the plan view was replaced by octagon. Modelled water inflow is 0.5 l/s that means 62.5 l/s in real facility. The geometry has 106026 number of 3D elements. We assume the geometric simplification does not effect on the flow change. The high number of finite elements is a prerequisite for error elimination of simulation.

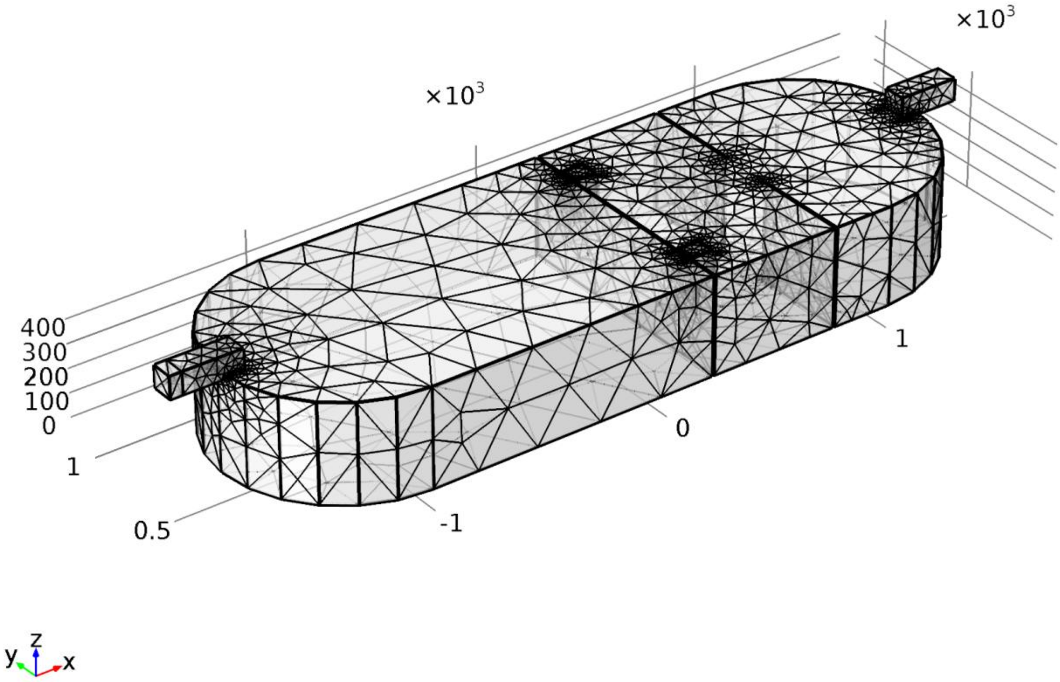

Figure 1: Finite element mesh generated for the model of DUN stormwater settling tank.

To eliminate inaccuracy of the simulations for the purposes of results applicability into practice, the model calibration and subsequent verification based on real laboratory measurements is required. Size of the real DUN usually doesn't enable performance of accurate measurements and simulations of water flow and pollution transfer. We therefore built a physical model in scale 1:5 (Figure 2a), that was used for observation of real processes (contamination transport and retention). We expected similar results of cleaning efficiency of the model analogous to real DUN during emergency situations and during standard operation conditions, when the pollutants are in trace concentrations. The validation of mathematical modelling was performed using tracer tests. For these test NaCl was used as a tracer and electrical conductivity was measured. The electrical conductivity measurement method is often used to monitor the water quality of streams and effluent from industrial sites[13] and wastewater treatment facilities[14] but also to determine the salinity, ionic strength[15] and major solute concentrations[16] of natural waters.

In the experiment physical model was initially filled with fresh water, deliberately adjusted to have an increased electrical conductivity (EC) by adding salty water. In the first step, the salt was diluted in 50 l vessels. Then the circulation of original fresh water in the model was proceeded to be mixed with the salt water. The recirculation of the water was performed until the stabilization of electrical conductivity within the entire volume of the physical model (to EC 6981.0 ± 3.2 mS/cm; n = 10). Accordingly, to verify the numerical model, we subsequently filled up the physical model with fresh water (EC 547.82 ± 0.85 mS/cm, n = 22) and observed changes of conductivity in selected profiles. For purposes of comparison with numerical model the measured values at mS/cm were expressed at % (EC of initial water 6981 mS/cm = 100 %, EC of the pumped water 547.82 mS/cm = 0% volumetric).

After calibration and adjustment of the mathematical model we performed verification of the model. Principle of the verification consists of the changes in the filling of the settling tank with different mixtures of two liquids: instead of mixing of salty water with fresh water we conducted an experiment in which oil substances were added to the pumped fresh water (Figure 2b). As a consequence, the ratio of water to oil was 99.98:0.02. Samples were taken at the outlet profile after 0-30-60-90-120-150 minutes.

Figure 2a and 2b: Semi-operated model of DUN stormwater tank (left). Accumulation of oil substances at on the water surface during validation testing (right).

During the study of the use of constructed wetlands to polish stormwater runoff after a settling tank, the uptake of toxic metals by macrophytic vegetation was also evaluated. Four constructed wetlands (two with horizontal flow, two with vertical flow) were planted by *Phalaris arundinacea* (Reed canarygrass) and *Glyceria maxima* (Mannagrass).

Hybrid experimental constructed wetland consists of pretreatment (DUN), accumulation tank and two parallels of constructed wetlands (VF- HF, Table 1, Fig. 3).

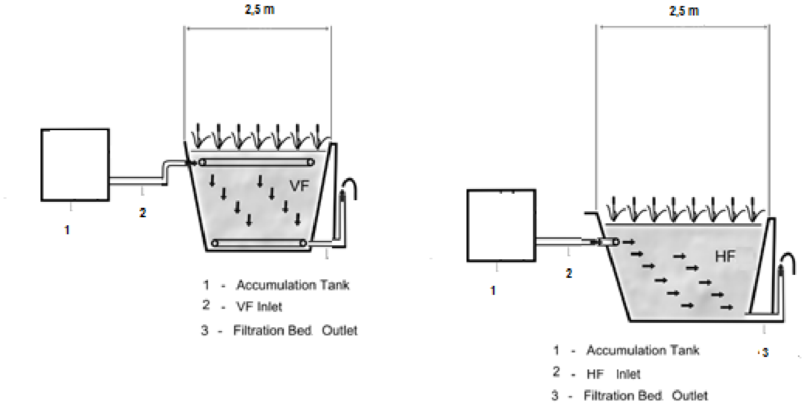

Figure 3. Layout of the experimental constructed wetland

Table 1: Major design parameters of constructed wetlands.

Parameter	Unit	VF	HF
Length	m	2.5	2.5
Effective area	m^2	5	5
Depth	m	1	0.6
Filtration material[a]		a, b, c, d	a, b, c
Effective volume	m^3	5	3

(a) Washed gravel 2–4 mm (protective material); (b) washed gravel 4–8 mm, porosity: 0.45, conductivity 16 cm s^{-1}; (c) washed gravel 8–16 mm, porosity: 0.44, conductivity 94 cm s^{-1}; (d) washed gravel 32–64 mm, porosity: 0.46, conductivity 350 cm s^{-1}.

Both plants are common wetland species that tolerate higher level of pollution, and, therefore they are used for constructed treatment wetlands. Contrary to *Phragmites australis* (Common reed) which grows very slowly, both *Phalaris* and *Glyceria* grow very fast. For the analysis of pollutant accumulation the biomass was divided into leaves (including leaf sheaths), stems, roots and rhizomes and dried at 60 °C to a constant weight and weighed. The biomass was then homogenized using a cutting mill (Pulverisette 15, FRITSCH) and mineralized in nitric acid (Ultrapur, Merck Millipore) in a microwave (Berghof, Speedwave MWS-2) under high temperature and pressure. The concentrations of toxic metals (Cu, Ni and Zn) in leaves, stems, roots and rhizomes were determined in triplicate samples using the atomic absorption spectroscopy (Agilent AAS DUO 55B/240Z). For the evaluation of measurement precision and accuracy the certified reference material (CRM) METRANAL TM3 (*Fragaria vesca*, QCM03, Analytica Ltd., Czech Republic) was used. The triplicate determinations agreed to within 5 %, and CRM recoveries were found within 90 – 105% range.

Results and discussions

Concentrations of copper, nickel and zinc in various parts *Phalaris* and *Glyceria* are presented. The highest concentrations of all toxic metals were found in roots, followed by rhizomes. On the other hand, the lowest concentrations were found in stems with higher concentrations in leaves. The ranges of values (in mg/kg) for the wetlands are presented Table 2.

Table 2: Concentrations of all toxic metals in roots, rhizomes, leaves and stems of Phalaris and Glyceria

	roots [mg/kg]	**rhizomes [mg/kg]**	**leaves [mg/kg]**	**stems [mg/kg]**
Phalaris - Cu	13-27	7-13	2-10	1-5
Glyceria- Cu	25-35	4-10	1-4	1-6
Phalaris - Ni	12-27	7-13	2-10	1-5
Glyceria - Ni	4-26	2-7	2-9	2-8
Phalaris - Zn	37-98	25-53	18-41	6-34
Glyceria - Zn	81-98	19-39	18-31	21-80

This finding is in agreement with results reported from constructed as well as natural wetlands[17,18,19,20].

The results also revealed that higher copper and nickel concentrations were found in *Phalaris* while zinc concentrations were comparable in both plants. During the harvest, only aboveground biomass could be removed, and, therefore, high concentrations in the aboveground biomass are desirable. Both plants used in the experiments could be harvested several times during the year. However, the concentration itself does not provide information about the accumulation of toxic metals in the biomass. In order to evaluate accumulation, it is necessary to take biomass into consideration.

Both plants are very productive with aboveground biomass in the range of 1000-2000 g dry matter/m^2 with 50-70% of the biomass being stems. Concentrations of all monitored heavy metals determined in the experiment varied within the range commonly found in wetland plants in natural and constructed wetlands for wastewater treatment (Table 3).

Table 3: Concentration (mg/kg) in biomass of wetland plants growing in natural and constructed wetlands

Type of wetland	**metal**	**leaves**	**stems**	**roots**	**rhizomes**	**references**
Natural	Cu	2.1-10.7	0.5-19.2	9.0-184	4.3-12.6	21,22,23,24,25,26,27,28,29
Constructed	Cu	6.1-15	5.1-25	5.3-64	6.5-33	21,23,30,31,32,33,34,35,36,37
Natural	Ni	0.5-5.8	0.2-10.3	7.7-25.5	1.6-3.8	22,24,25,26,27,28,29,34
Constructed	Ni	0.47-2.8	0.54-2.0	4.9-16.7	1.87	23,32,33,34,37,38
Natural	Zn	11-1300	10-137	1.3-588	17-66.8	21,22,24,25,26,27,28,29,30
Constructed	Zn	29-59	18-70	46-165	12.2-22	21,23,30,31,32,34,36,37

Tables 4 and 5 show the range of values found in water samples from selected DUN during monitoring in years 2013 to 2015. The ranges of values are shown for the inlet (IN) and outlet (OUT) sections of the DUN.

Table 4: Range of values of selected pollutants analysed in samples from stormwater tanks monitoring

Locality		**ENT** [CFU 1ml^{-1}]	**Cl** [mg l^{-1}]	**TSS*** [mg l^{-1}]	**VSS*** [mg l^{-1}]	**COD** [mg l^{-1}]	**TOC** [mg l^{-1}]	**TN** [mg l^{-1}]	**TP** [mg l^{-1}]
DUN1 IN	Min	0	21	3	<2	149	5.0	3.3	0.04
DUN1 IN	Max	18	3040	388	336	2230	17.6	12.5	0.60
DUN1 OUT	Min	1	11	7	3	67	5.8	2.1	0.05
DUN1 OUT	Max	12	1930	232	228	1880	15.8	12.0	0.32
DUN2 IN	Min	0	40	<2	<2	83	1.7	2.3	0.00
DUN2 IN	Max	13	760	104	90	201	11.7	8.7	0.35
DUN2 OUT	Min	0	20	<2	<2	90	2.9	2.8	0.00
DUN2 OUT	Max	18	1480	108	92	219	20.1	8.6	0.40
DUN3 IN	Min	1	3	3	<2	16	4.7	0.6	0.07
DUN3 IN	Max	8	1960	54	35	1660	16.9	3.2	0.14
DUN3 OUT	Min	0	3	<2	<2	18	2.9	0.7	0.05
DUN3 OUT	Max	5	3420	20	13	189	18.1	2.6	0.12
DUN4 IN	Min	0	15	<2	<2	132	6.0	1.0	0.00
DUN4 IN	Max	3	535	53	45	253	13.3	16.1	0.27
DUN4 OUT	Min	0	16	3	2	126	5.2	1.0	0.03
DUN4 OUT	Max	1	765	60	48	232	13.6	10.0	0.27

*ENT – Enterococci, Cl – chlorides, TSS – suspended solids, VSS – volatile suspended solids, TN – total nitrogen, TP – total phosphorus; *(ČSN 75 7350 Water quality - Determination of the loss of ignition of suspended solids; ČSN EN 872 Water quality - Determination of suspended solids - Method by filtration through glass fibre filters).*

Determination of the TSS (total suspended solids) is based on the capture of suspended solids from a homogeneous sample of a certain volume of water to a glass fiber filter and determine their weight after drying at 105°C (used analytical method is based on the ČSN EN 872 Water quality - Determination of suspended solids - Method by filtration through glass fibre filters).

Determination of the VSS (volatile suspended solids) is based on the capture of suspended solids from a homogeneous volume of water sample into a combustible filter and determine their weight after annealing at 550°C (used analytical method is based on the ČSN 75 7350 Water quality - Determination of the loss of ignition of suspended solids).

Table 5: Range of values of selected pollutants analysed in samples from stormwater tanks monitoring

Locality		**C_{10}-C_{40}** [mg l^{-1}]	**PAH** [µg l^{-1}]	**Cd** [µg l^{-1}]	**Cu** [µg l^{-1}]	**Hg** [µg l^{-1}]	**Ni** [µg l^{-1}]	**Pb** [µg l^{-1}]	**Zn** [µg l^{-1}]
DUN1 IN	Min	<0.1	<0.002	<0.1	8.5	<0.1	2.0	<0.5	7
DUN1 IN	Max	1.4	6.4	0.3	58.7	0.4	34.3	5.4	210
DUN1 OUT	Min	<0.1	<0.002	<0.1	11.0	<0.1	2.5	<0,5	33
DUN1 OUT	Max	1.6	5.8	0.1	50.5	0.2	32.3	7.0	179
DUN2 IN	Min	<0.1	<0.002	<0.1	<2	<0,1	14.3	<0.5	<5
DUN2 IN	Max	0.6	1.5	0.1	24.3	0.3	41.8	3.5	93
DUN2 OUT	Min	<0.1	<0.002	<0.1	<2	<0.1	14.5	<0.5	12
DUN2 OUT	Max	1.2	5.5	0.2	64.3	0.3	45.2	2.3	201
DUN3 IN	Min	<0.1	<0.002	<0.1	8.5	<0.1	<2	<0.5	41
DUN3 IN	Max	0.7	1.4	0.2	35.5	0.2	20.1	3.4	239
DUN3 OUT	Min	<0.1	<0.002	<0.1	5.7	<0.1	<2	<0.5	37
DUN3 OUT	Max	0.3	0.7	0.4	22.7	0.3	<2	1.5	366
DUN4 IN	Min	<0.1	<0.002	<0.1	2.4	<0.1	<2	<0.5	<5
DUN4 IN	Max	0.2	0.3	0.1	17.0	5.6	<2	2.1	73
DUN4 OUT	Min	<0.1	<0.002	<0.1	3.0	<0.1	<2	<0.5	6
DUN4 OUT	Max	0.3	0.4	<0.1	14.8	1.0	3.6	2.4	51

Recording of conductivity values during the validation experiments was performed in twelve selected profiles of the physical model at 10 minute intervals until stabilization of values after 205 minutes. Subsequent comparison of the mathematical model with physical model, which was filled with salty water and subsequently filled with fresh water (Q = 0.5 l/s), indicates that model results corresponds to the conducted experiment (Figure 4). The model was then verified using a precisely defined dose of oil with precisely defined physical characteristics (viscosity, density).

Statistical evaluation of the real experiment shows, that the portion of oil in the inflow is 0.0002 while in the outflow it is 0.000079 ± 0.00007 (median 0.000063). The mathematical simulation shows different results 0.000092 ± 0.00007 in the outflow (median 0.00008). That means 11.6% difference between mathematical simulations and real experiments.

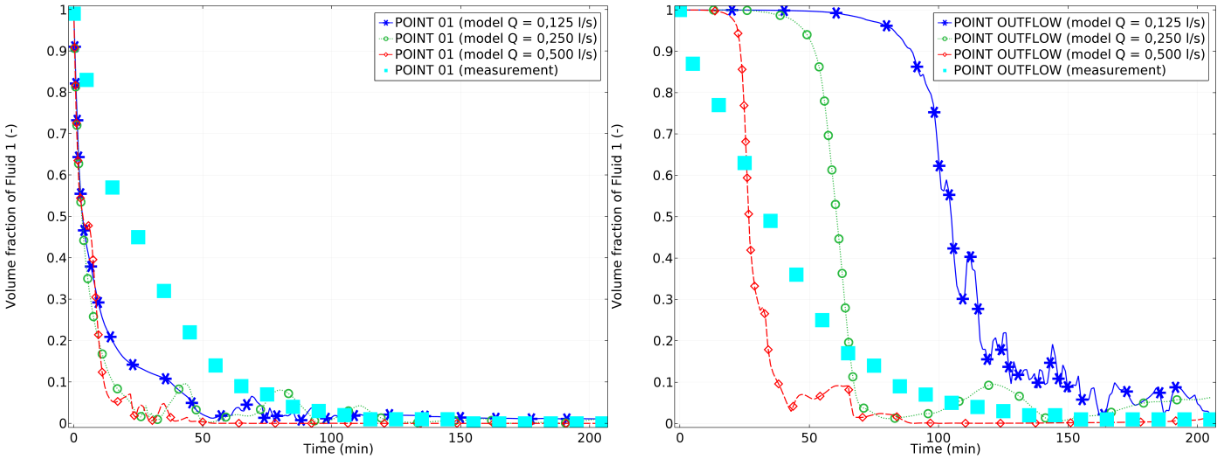

Figure 4: Correlation of measurements and mathematical modelling – course of liquid amount in the selected measurement profiles of the DUN physical model (first profile after inflow – left chart, outflow profile – right chart).

Conclusions

The retention efficiency of existing DUN settling tank was calculated from the databases of selected pollutants monitoring. It is necessary to take into account that due to a residence time dependent on the precipitation events the time samples collected from the inlet and outlet sections during each visit of subscribed objects can not exactly match each other. Efficiencies were therefore calculated for long-term average values. The results show high differences between the four presented DUN facilities in the treatment efficiency for selected metals (e.g. Cd: DUN1 46 %, DUN2 32 %, DUN3 5 %, DUN4 100 %; Hg: DUN1 33 %, DUN2 -9 %, DUN3 9 %, DUN4 80 %; Ni: DUN1 6 %, DUN2 2 %, DUN3 10 0%, DUN4 >-100 %; Zn: DUN1 -9 %, DUN2 -63 %, DUN3 -36 %, DUN4 22 %) PAH: DUN1 10 %, DUN2 -174 %, DUN3 59 %, DUN4 -11 %, but also for nutrients (TN: DUN1 18 %, DUN2 -2 %, DUN3 32 %, DUN4 27 %; TP: DUN1 23 %, DUN2 -13 %, DUN3 2 6%, DUN4 -4 %), suspended solids (between -34 % and 66%) and chlorides (between -49 % and 22 %). That can be caused by low concentrations in the samples from monitoring period in the case of metals, and by contact and exchange of pollutants between water and sediments accumulated in the monitored parts of DUN facilities.

The results of mathematical and physical modelling show that this approach can be used for designing and subsequent operation, reconstruction and maintenance of real DUN. Knowledge obtained based on the project results can be applied for designing of operation scheme of settling tanks for emergency situations (e. g. high concentrations of oil products). Mathematical modelling have 11% error compared to real experiments in this case study.

Acknowledgment

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Snížení negativního vlivu infrastrukturních staveb na kvalitu povrchových vod

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Souhrn

Tato studie se zabývá hodnocením účinností technologií pro čištění smyvů z komunikací a parkovišť - dešťových usazovacích nádrží (DUN) a umělých mokřadů - a jejich dopadu na snížení negativního vlivu dopravní infrastruktury na kvalitu povrchových a podpovrchových vod. V rámci projektu podpořeného grantem Technologické Agentury České Republiky byly monitorovány vybrané DUN a vznikla databáze výsledků monitoringu vybraných polutantů (zejména ropných látek a těžkých kovů). Dále se práce zabývá vývojem nových technologií pro čištění smyvů a inovativními způsoby jejich testování, jako je matematické modelování včetně poloprovozní validace modelu s využitím hydraulických zátěžových testů. Výzkum se částečně zabývá vývojem třístupňové technologie čištění smyvů skládající se ze systému mechanického předčištění následovaného kombinovaným umělým mokřadem (s vertikálním a horizontálním směrem proudění) a v posledním kroku se zapojením speciálně navržených infiltračních komor.

Výsledky tříletého monitoringu čtyř vybraných DUN v ČR, probíhajícího v letech 2013-2015, poukazují na velmi rozdílnou schopnost existující infrastruktury odstranit některé polutanty (např. v rozmezí pro jednotlivé sledované parametry: Cd od 5 do 100 %; Hg od -9 do 80 %; Ni od -100 do 100 %; Zn od -63 do 22 %; PAU od -174 do 59 %; celkový dusík od -2 do 32 %; celkový fosfor od -13 do 27 %; rozpuštěné látky od -34 do 66 %; chloridy od -49 do 22 %).

Výsledky testování vyvinutého třístupňového systému poukazují na navýšení účinnosti nově navrhované technologie odstraňovat zmíněné polutanty. Také lze konstatovat, že metoda matematického modelování pro navrhování těchto systémů se jeví jako vhodné řešení usnadňující projektantům verifikaci projektovaných zařízení s ohledem na požadované limity vypouštěné přečištěné splachové vody.

Klíčová slova: *Kořenová čistírna odpadních vod, děšťová usazovací nádrž, povrchové smyvy, matematický model, toxické kovy*

Utilization of carbon black Chezacarb® for the treatment of water contaminated by phenols

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Summary

Partial oxidation is one of the key processes for the industrial production of hydrogen from the heaviest fractions of crude oil. Part of the raw material is transformed to "undesirable" soot, even though the reaction conditions are optimal. This soot is separated, granulated and transformed by the company Unipetrol RPA in a special production facility to a successful product – carbon black Chezacarb® which is used not only as a filler in plastics but also as an adsorbent for the adsorption of gaseous pollutants and for wastewater treatment. This paper is focused on the usage of adsorbent Chezacarb® to purify water contaminated with phenols. The adsorption of phenol and 3,4-xylenol was studied for the model samples of water containing these two substances on a granular adsorbent Chezacarb® under various reaction conditions. It was found that the adsorption capacity for phenol is between 32 to 195 g.kg^{-1} of adsorbent and increases with increasing phenol concentration in purified water. The adsorption capacity of Chezacarb® for 3,4-xylenol was 154 g.kg^{-1} of adsorbent under the given experimental conditions. The efficacy of removal of pollutants from the waste water was dependent on the water flow through the adsorber and it was decreasing with the increasing flow.

Key words: *adsorption, activated carbon Chezacarb®, water treatment, phenols.*

1. Introduction

Phenols are important basic raw material or additives in a range of industrial processes. The products of burning of organic materials (engine exhaust gases, fire or tobacco smoke, etc.) are a typical source of phenols. Occurrence of phenols in water is caused by industrial production. Phenols often penetrate into natural water streams from thermal processing of coal tar and oil industry or from pharmaceutical factories and also from the production of plastic or coke.

Table 1: Examples of limits for monovalent monocyclic non-halogenated phenols in waters under the legislation of the Czech Republic[1,2,3]

Type of water	**Concentration limit [mg.L^{-1}]**
Surface water[1]	0.005
Groundwater[2]	A = 0.0003; B = 0.75; C = 1.0 *
Waste water from the heat treatment of coal[3]	1.0

Note. * *"**A**" corresponds approximately natural levels of controlled substances in nature. "**B**" is artificially established value between the value of "A" and "C". Exceeding this value is evaluated as pollution, which can have a negative impact on human health and environmental components. "**C**" takes into account the physico-chemical, toxicological, ecotoxicological or other properties of materials. This value is exceeded pollution which may involve a significant risk to human health and other environmental elements.*

For removal of phenols from contaminated water there are used methods such as oxidation with hydrogen peroxide or wet oxidation under high pressure, ozonisation, biological treatment and adsorption. Adsorption methods are mostly used for the final refining of pre-treated water. Preferably, materials based on activated carbon are used as adsorbents.

Carbon black Chezacarb® is by-product of processing of heavy oil residues to hydrogen using an industrial process POX (partial oxidation). Carbon soot/black water is formed during cooling and cleaning of hydrogen containing gas in the process. Chezacarb® is manufactured from the carbon soot/black water in form of granules of a size up to 2 mm[4,5,6,7]. In this form it is supplied and used as filler in plastics to improve their conductivity.

Chezacarb® has unique adsorption properties that arise from its structure. Its specific surface area (estimated by N_2 adsorption at 77 K) is usually more than 800 $m^2.g^{-1}$ and its iodine adsorption number amounts 900-1250 $mg.g^{-1}$.

These properties are significant for its use in adsorption processes. Chezacarb® is used as adsorbent especially for the purification of exhaust gases from municipal and industrial waste incinerators. Its application is in the form of powder material which was obtained by the disintegration of the original product. The powdered material is then separated together with other dust particles in the bag filters[4,5,6,7].

Adsorption properties of Chezacarb® with average particle size of about 1 mm were successfully tested in the static adsorber for the wastewater treatment, including water containing phenols as contaminants[6,8]. However these real wastewaters contained in addition to phenols also various amounts of other pollutants and their concentration fluctuated. Therefore, investigation of the adsorption process using such waters seems to be difficult. For these reasons, laboratory tests were carried out with the water mixtures containing only phenols as the contaminants.

2. Materials and methods

The most common adsorption processes are based on physical adsorption and are not accompanied by a chemical reaction of the adsorbed substances with the surface of the adsorbent.

State of equilibrium (adsorption isotherm) is characterized by various mathematical equations. Langmuir, Freundlich or BET (Brunauer, Emmett, Teller) are the most famous equations. Each of the equations describes a different type of adsorption process; while the Langmuir isotherm describes monolayer adsorption, Freundlich and BET multilayer adsorption, wherein the BET combines the capacity of monolayer and multilayer adsorption and is therefore preferable to describe the physical adsorption from the gas phase at higher pressures. Freundlich isotherm is an empirical equation, which is usually used to describe the adsorption process in the liquid phase.

The mathematical form of Freundlich isotherm is as follows[9]:

$$a = k c_e^{1/n} \text{ or } a = k\sqrt[n]{c_e}$$

a – the ratio between the quantity of adsorbed substances (adsorbate) and the amount of adsorbent,
k, n – empirical constants for each pair of an adsorbate with an adsorbent and at the adsorption temperature,
c_e – the equilibrium concentration of the adsorbate in the liquid.

Two types of phenols were selected for testing, see ***Figure 1***. The first one was the most common and simplest phenol which is practically present in all phenols contaminated sites. Phenol is well soluble in water, 84 $g.L^{-1}$ at 20 °C[10].

The second tested phenol was 3,4-xylenol. Xylenols together with cresols are important class of phenols of great significance for the chemical industry. They are used for production of pesticides and antioxidants. 2,6-xylenol is used for preparing of poly(p-phenylene oxide) resins[11]. 3,4-xylenol is slightly soluble in water, 4.76 $g.L^{-1}$ at 25 °C[12].

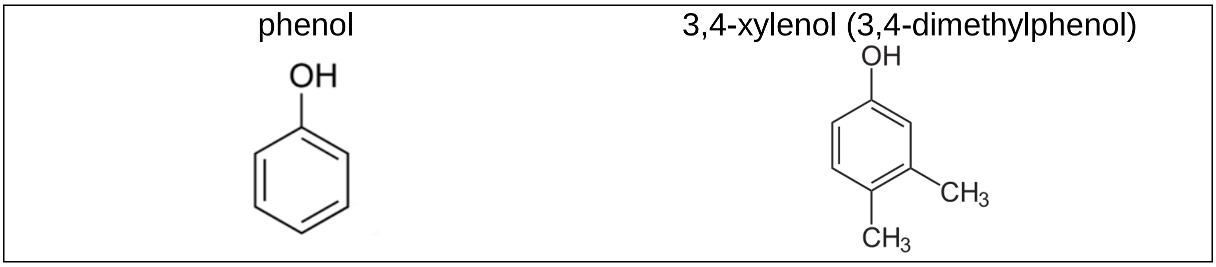


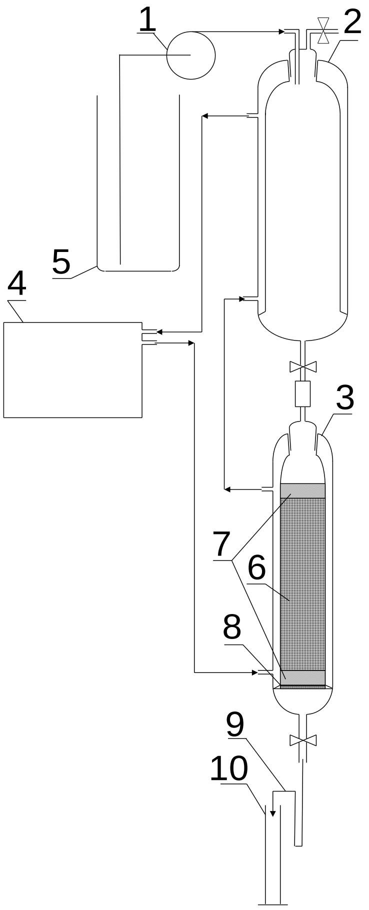
Figure 1: Tested phenols

Layout of the laboratory apparatus used for the experiments is shown in **Figure 2**. The main part of the apparatus is double wall flow adsorber (3) with an inside diameter of 25 mm, in which adsorbent Chezacarb® (6) is placed (particle diameter of about 1 mm, height of adsorbent layer approx. 170-180 mm). Adsorption layer is placed on layer of glass wool 10 mm high (7) which is positioned on the perforated glass frit (8). The top of adsorption layer is stabilized by about 20 mm glass wool (7) which has several functions:

1. to stabilize the flow of liquid through the adsorption layer
2. to hold the layer of sorbent together during manipulation with the column
3. to eliminate clogging of adsorption layer by mechanical impurities from contaminated water.

Contaminated water is dosed by a peristaltic pump (1) from the vessel (5) into a double wall tank (2) and then into a flow adsorber (3).

The tank (2) and the flow adsorber (3) are heated by the thermostat (4) on the temperature of 30 °C. Water flows through a tube water cap (9) into a graduated cylinder (10) from the adsorber (3).



Key to figure 2:

1	Peristaltic pump for contaminated water
2	Double wall tank for heating of the contaminated water
3	Double wall flow adsorber
4	Thermostat
5	Vessel with contaminated water
6	Granulated adsorbent Chezacarb®
7	Glass wool
8	Grid – perforated frit
9	Water cap
10	Graduated cylinder

Figure 2: Layout of laboratory apparatus used for the tests

Testing method

Adsorbent Chezacarb® contains air in its pore structure and is very poorly water-wettable. Therefore the adsorbent floats on the water surface after pouring into water and its correct preparation is necessary, i.e. water-saturation, before application in the liquid phase.

The adsorbent was saturated with distilled water in the bottle using vacuum pump to remove the air from the adsorbent pores. The water saturated adsorbent particles dropped from the level of water to the bottom of the flask. Some of the particles floated back to the level of water after releasing vacuum, because the granules were not fully water-saturated; so the process was repeated several times.

Water-saturated adsorbent was transferred into the adsorber, which was partially filled with distilled water to prevent adsorbent dewatering. The adsorbent was covered with water-saturated glass wool and the apparatus was rinsed with at least one liter of distilled water.

Contaminated water containing phenols was loaded in double-wall container and heated at 30 °C. The adsorption test was started by switching on the peristaltic pump and opening the valve on the adsorber exit. Contaminated water was flew through the adsorbent at a constant temperature of 30 °C and constant flow rate. The flow rate of treated water on the adsorber outlet was measured using graduated cylinder. The loading rate of the peristaltic pump was corrected according to the determined water flow rate to achieve the constant water level in the double wall tank (2).

Before each test a fresh batch of water-saturated adsorbent Chezacarb® was always prepared. Used amount of dry adsorbent for the preparation was always 11 g. Because the sorbent was water-floated with distilled water, the first 80 mL of water exiting the adsorber was not considered as the part of the first sample, and therefore not analysed. The samples of treated water were collected at regular time intervals and subsequently analysed for phenols using spectrophotometer Shimadzu UV-2600. Adsorption tests were carried out with a model mixtures of phenol (0.1 $g.L^{-1}$ and 1.7 $g.L^{-1}$) and a model solution of 3,4-xylenol (0.1 $g.L^{-1}$) in distilled water. Each test was stopped after detection of significant phenol concentration in water at the adsorber outlet.

3. Results and discussion

Four adsorption tests were carried out using phenol and 3,4-xylenol as contaminants. The conditions of all tests are summarized in ***Table 2*** and the results of the tests are shown in ***Figures 3 – 6***.

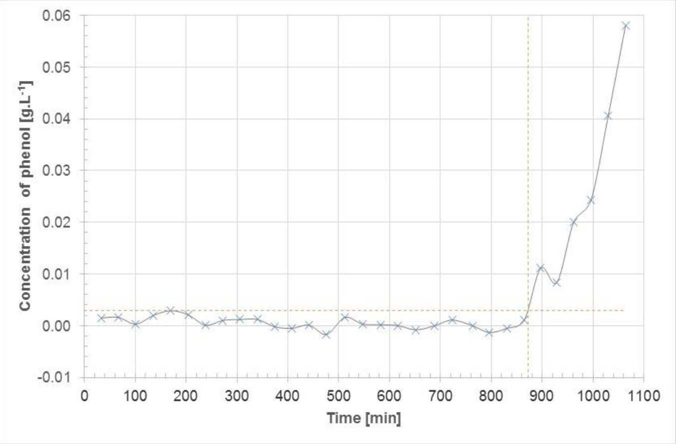


Figure 3: Test 1 – breakthrough curve for phenol measured with water flow rate 0.51 $L.h^{-1}$ and input concentration 0.1 $g.L^{-1}$

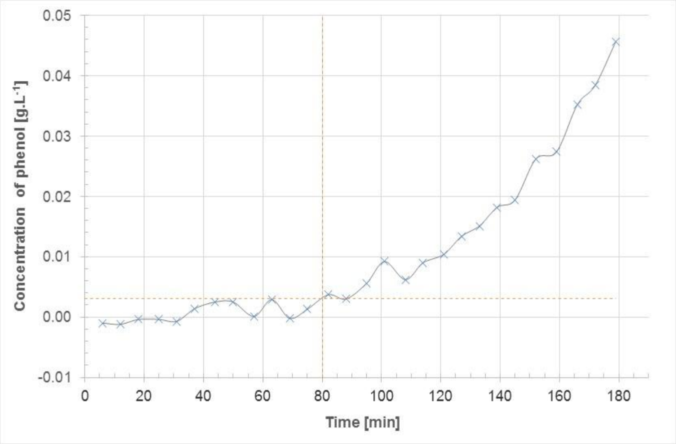


Figure 4: Test 2 – breakthrough curve for phenol measured with water flow rate 2.76 $L.h^{-1}$ and input concentration 0.1 $g.L^{-1}$

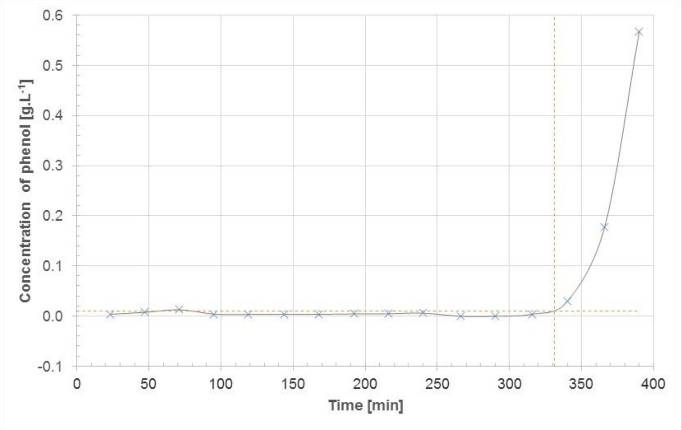


Figure 5: Test 3 – breakthrough curve for phenol measured with water flow rate 0.22 L.h^{-1} and input concentration 1.7 g.L^{-1}

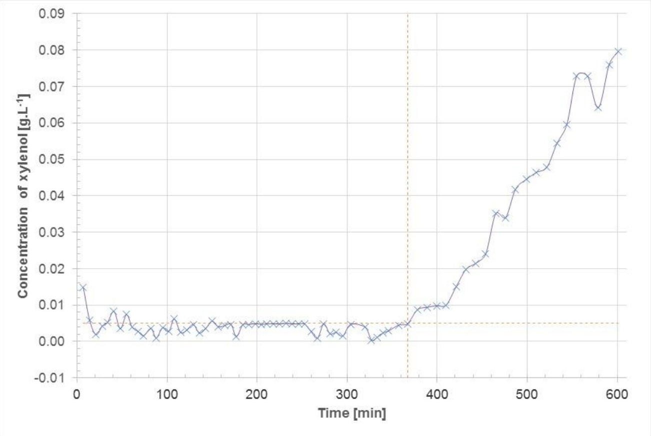


Figure 6: Test 4 – breakthrough curve for 3,4-xylenol measured with water flow rate 2.59 L.h^{-1} and input concentration 0.1 g.L^{-1}

Table 2: Summary parameters of all tests

Test	Contaminant	Penetration time	Inlet concentration		Flow rate	Volume of water	Adsorber loading	Residence time	Adsorption capacity for phenol/xylenol	
		[min]	[g.L^{-1}]	[mol.L^{-1}]	[L.h^{-1}]	[L]	[m^3.m^{-2}.h^{-1}]	[sec]	[g.kg^{-1}]	[mol.kg^{-1}]
1	phenol	897	0.0967	0.00103	0.51	7.550	1.03	595	63.71	0.68
2	phenol	82	0.0938	0.00100	2.76	3.770	5.62	109	32.05	0.34
3	phenol	340	1.7080	0.01815	0.22	1.260	0.45	1351	195.37	2.08
4	3,4-xylenol	378	0.1058	0.00087	2.59	16.340	5.28	116	154.13	1.26

Note. Mass of sorbent 11 g, volume of sorbent 0.0834 L, molar mass of phenol 94.11, molar mass of 3,4-xylenol 122.17.

The comparison of test parameters and obtained results is given in the ***Table 3***.

Table 3: Comparison of test conditions and obtained results

Number of compared tests	Contaminant	Inlet concentration	Flow rate	Residence time	Adsorption capacity
1/2	p/p	0.001/0.001	0.5/2.8	595/110	0.7/0.3
4/2	x/p	0.0009/0.001	2.6/2.8	115/110	1.3/0,3
4/1	x/p	0.0009/0.001	2.6/0.5	115/595	1.3/0.7
3/1	p/p	0.018/0.001	0.2/0.5	1350/595	2.1/0.7
3/2	p/p	0.018/0.001	0.2/2.8	1350/110	2.1/0.3
3/4	p/x	0.018/0.0009	0.2/2.6	1350/115	2.1/1.3

Note. Signification in table: p …phenol, x …3,4-xylenol

The comparison of the tests shows significant effect of the type of phenol on the adsorption capacity. The adsorption of 3,4-xylenol compared with phenol leads to a considerable increase of the adsorption capacity on adsorbent Chezacarb®. The reason of this fact is probably higher molar weight and smaller polarity and water solubility of 3,4-xylenol.

Also the flow rate and pollutant concentration have impact on adsorption capacity. These effects have not so significant influence on the adsorption capacity as the effect of the chemical properties of adsorbed substances. However, the impact of change of input concentration has more significant impact on the adsorption capacity than the change of flow rate.

The dependence of adsorption capacity of Chezacarb® on phenol concentration in the water indicates binding of phenol on adsorbent according to the mechanism of physical adsorption.

Change of the water flow rate has no significant effect on the adsorption capacity but influences the adsorption efficiency.

Conclusions

Adsorbent Chezacarb® seems to be very good adsorbent for removal of phenols from contaminated water. The phenol adsorption takes place as physical adsorption, no chemical reaction between adsorbent and adsorptive occurs. The adsorption capacity for phenols on Chezacarb® grows according to the molecular weight of the adsorbed phenols and decreases with growing polarity and water-solubility of the phenols.

The flow rate (residence time) of the purified water has no significant influence on the adsorption capacity, but influenced the efficiency of phenol removal from water. The kinetics of phenol adsorption at Chezacarb® is relatively slow.

Using optimal condition the adsorption capacity of phenol on Chezacarb® ranged from 64 to 195 $g.kg^{-1}$ adsorbent depending strongly on its concentration in water. The adsorption capacity of Chezacarb® for 3,4-xylenol is higher than for phenol under similar conditions.

Acknowledgement

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Využití sazí Chezacarb® při čištění vod kontaminovaných fenoly

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Souhrn

Jedním z postupů používaných pro průmyslovou výrobu vodíku je parciální oxidace nejtěžších ropných frakcí. I při optimálních reakčních podmínkách se část suroviny zpracovávané v tomto procesu transformuje na saze. V Unipetrolu RPA se tyto saze ve speciálním výrobním zařízení separují, granulují a transformují se tak na další výrobek – Chezacarb®, který se využívá nejen jako plnivo do plastů ale i jako sorbent jak v oblasti adsorpce plynných škodlivin, tak k čištění odpadních vod. Článek je zaměřen na využití adsorbentu Chezacarb® k čištění vod kontaminovaných fenoly. V laboratorní aparatuře s průtočným reaktorem byla sledována adsorpce fenolu a 3,4-xylenolu z modelových vzorků vody obsahující tyto látky na granulovaném adsorbentu Chezacarb® za různých reakčních podmínek. Bylo zjištěno, že adsorpční kapacity pro fenol se pohybují v rozmezí od 32 do 195 g.kg^{-1} adsorbentu a zvyšují se s rostoucí koncentrací fenolu v čištěné vodě. Adsorpční kapacita Chezacarbu® pro 3,4-xylenol činila za daných experimentálních podmínek 154 g.kg^{-1} adsorbentu. Účinnost odstranění polutantu z odpadní vody je závislá na průtoku vody adsorbérem a s rostoucím průtokem klesá.

Klíčová slova: *adsorpce, Chezacarb®, čištění vod, fenoly*

Experimental verification of utilization of solidification product containing galvanic neutralisation sludges in building industry

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Summary

Due to undesirable production of huge amount of hazardous waste - neutralization sludges from galvanic metal plating it is necessary to find new technology enabling transformation of these wastes with strongly negative impact on the environment into some usable product. Solidification technology appears to be the right one for this purpose. On that ground this paper is involved in experimental research of material application possibilities of solidification products (SPs). The main aim is to find such a solidification way (solidification formula and technology) using which it would be possible to obtain such physical and mechanical properties of SPs providing future safe and effective utilization of these materials in civil engineering for various earthworks and base layers of road construction. On that ground physical and mechanical properties are examined within this work by determination of compaction (Proctor test), unconfined compressive strength (UCS) and California bearing ratio (CBR). Considering the long-term durability the test of frost and water resistance is carried out and within environmental requirements also leaching test is performed.

Key words: *stabilisation and solidification, solidification product, fly ash, neutralisation sludge, compaction, compressive strength, leachability, durability.*

Introduction

The permanent production of galvanic neutralisation sludge (NS) as waste products during galvanic metal plating and metal surface treatment burdens environment especially with extension of inconvenient and unsecured dumping grounds. These sludges contain big amounts of heavy metals and it is difficult to find a technology using which these contaminants would firmly incorporate into a new and further efficiently usable product[1]. Stabilisation and solidification (S/S) technology appears as the most convenient way of heavy metal containing sludge treatment[2]. If it is possible to find out and verify such a solidification technology and formula using which it will be possible to produce solidification product (SP) with required physical and mechanical properties and secure in a way that the contaminants could not leach into the environment; they might be efficiently applied in civil engineering primarily as substitution of raw material primary resources at earthworks - backfills and mounds[3]. Cement, ground-granulated blast-furnace slag, fly ash from circulating fluidized bed combustion (CFBC fly ash) and fly ash from pulverized coal combustion (PCC fly ash), lime and in particular their combinations belong among the most commonly used solidification agents used at S/S process of hazardous inorganic wastes[4]. From economic and ecological point of view it is important that suitable solidification formulas contain highest amount of NS and lowest content of binders and admixtures while meeting all the requirements. The selection of the most suitable formulas is carried out on the basis of the results of physical and mechanical and ecological testing performed with solidification products (SPs). For future safe use of SPs in building industry it is necessary to deal also with their long durability. After a thorough examination of SPs in laboratory conditions it is possible to verify the technology on pilot solidification line then to certification and subsequent application of this new material in practice. For the purpose of SP safe use it is therefore essential to monitor also its durability (long-term stability of all parameters of SP at given place of use).

Input hazardous waste

As input hazardous waste (HW) two different neutralisation sludges (NS) were selected from two different producers with marking NS1 and NS2 (Figure 1, Figure 2). Both of the neutralisation sludges (NS1, NS2) are generated due to galvanic metal plating in the sulfate electroplating bath. In both cases they are sulphate electroplating baths consequently neutralized with lime, therefore the essence of sludge are metal sulphates. They are sludges coming from physical and chemical processing containing dangerous substances (according to Czech waste catalogue they belong to the group HW 19 02 05). These sludges were selected as input HW, especially due to their permanently high annual production and accumulation on the unsecured landfills and also in connection with distance from the technological solidification lines and producers of solidification agents. Neutralisation sludge (NS) can generally be characterised as a waste, generated after waste acid neutralisation from various industrial fields which contain dangerous substances[5].

Figure 1: Neutralisation sludge NS1

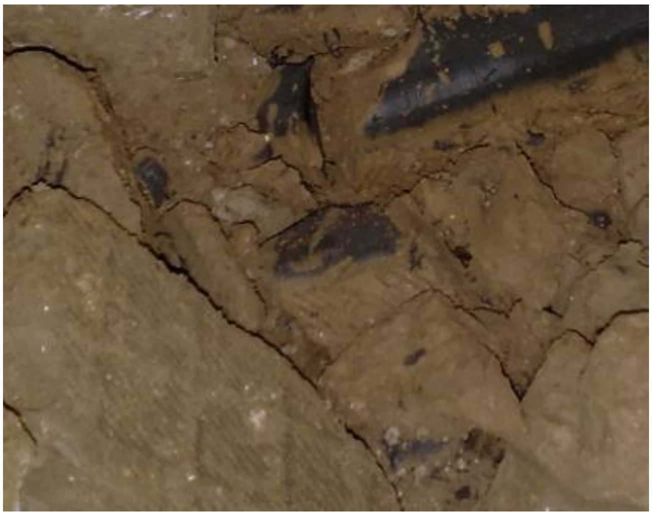

Figure 2: Neutralisation sludge NS2

Solidification agents

Under the term "solidification agents", binders and admixtures are within this work understood that are used for the purpose of solidification of NS and therefore production of materially applicable product –solidification product (SP). Main principle of heavy metals incorporation into cement matrix is mostly chemical reaction of heavy metals with cement hydration products to form poorly soluble metal compounds[8]. The mixture of fly ashes and cement showed as successful solidification binder even for solidification of soils contaminated by mostly heavy metals, while contaminant leachability was kept under set terms for a long time[9]. Cement (CEM II/B-M (S-LL) 32.5R), fly ash from circulating fluidized bed combustion (CFBC fly ash), fly ash from pulverized coal combustion (PCC fly ash) and carbide lime which is a by-product originating during acetylene production were used as solidification agents for the solidification of the neutralisation sludges.

Experimental part

Characterization of input hazardous waste

As input hazardous waste (HW) two different galvanic neutralisation sludges (NS) were selected and their identification was carried out mainly for the purpose of clarification of their negative impacts on the environment. On that ground the leachability test, determination of contaminant concentration in dry matter and also determination of content of contaminants in the dry matter were carried out[6]. The leachability test and the determination of concentration of contaminants in NS dry matter was carried out in accredited laboratory Labtech in Brno.

Laboratory preparation of test samples

Solidification formulas. After laboratory examination of basic solidification formulas five suitable ones with highest solidification effect were selected and were further tested according to effectively proposed methodology of solidification product (SP) testing. The selected solidification formulas are shown in the Table 1 while the formulas with designation NS1-D and NS2-E contain even 15 % of cement. All the formulas contain also CFBC fly ash and PCC fly ash as binders and NS2-C formula contains 10% amount of carbide lime instead of cement. All the samples were prepared using electric manual mixer in 10 l vessel while water was added considering required consistency or to obtain required solidification mixture moisture.

Table 1: Composition of examined solidification formulas in wt.[%]

Component	*NS1-A*	*NS2-B*	*NS2-C*	*NS1-D*	*NS2-E*
NS	50	50	50	40	40
CFBC fly ash	25	25	25	25	25
PCC fly ash	20	20	15	20	20
*CEM**	5	5	-	15	15
Carbide lime	-	-	10	-	-

**Cement CEM II/B-M (S-LL) 32.5R*

Examination of physical and mechanical properties of solidification products

The methodology of testing of solidification products (SPs) was prepared on the basis of future optimal use of SPs. Most possible applications result from technical specifications elaborated primarily for fly ashes group and fly ashes mixtures while the herewith stated application is closest to suitable application of SPs^{5}. Within this paper only several tests drawing from advanced testing methodology of SPs were selected. SPs application possibilities closely relate to the technology of its production. SP is generally produced on solidification lines in form of granulate from which the possibility of its application in building industry implies, for various mounds, fills, road base layers and especially as substitution for materials used at present for landfills recultivation and rehabilitation of old ecological burdens. Application of SPs as building materials with common earthwork is hardly plausible due to high content of contaminants in dry matter not allowed by strict standards and national legislation.

Compaction. The Proctor compaction test was carried out according to EN 13286-2. Using this test optimal moisture is verified with which maximum bulk density of dry compacted mixture (ρ_{dmax}) is obtained. From each solidification formula, approximately 2 kg of damp mixture was prepared using determined amount of water. In all the cases it was Standard Proctor compaction test using Proctor mortar type A, diameter 100 mm and height 120 mm, determined for mixtures with maximum grain size 16 mm. As compaction device Proctor rammer was used (weight 2.5 kg, Ø 50 mm, fall impact height 305 mm). The mixture mixed according to NS2-C formula showed high adhesion to metal mortar and therefore the specimen of SP was loosing its consistency at mortar removal. On that ground only three assessments were performed with this solidification formula.

Formed specimens of SPs were stored for 28 days in laboratory conditions for subsequent determination of unconfined compressive strength (UCS) and frost resistance. ČSN 736133 (Design and realisation of earthwork element for roads) determines for material intended for earthwork ρ_{dmax} < 1500 kg/m^3.

In the figures bellow we can see the mixture with optimum moisture (Figure 3), which was subsequently filled and compacted in three layers in Proctor mortar (Figure 4) and after mould removal cylindrical specimens were formed for further testing (Figure 5).

***Figure 3:* Solidification mixture with optimal moisture (NS1-A)**

***Figure 4:* Proctor rammer and mortar fulfilled with mixture NS1-A**

***Figure 5:* Cylindrical specimens from Proctor compaction test**

Unconfined compressive strength (UCS). Mechanical properties of SPs were tested by unconfined compressive strength (UCS) according to EN 14227-3 with cylindrical specimen with height 120 ± 0.5 mm and width 100 ± 0.5 mm with optimal moisture which were produced within Proctor compaction test. The cylinders were stored for 28 days in damp conditions in order the hydration reaction might better occur and subsequently loaded on hydraulic press for verification of UCS values. For road bottom/base layers and for objects fillings, backfills and earthwork UCS is required within 1.0 to 1.8 MPa for design and realisation of road construction with application of fly ashes and ashes according to Technical specifications (TS93). Before the determining of UCS bulk density (BD) of the samples was also determined.

Frost resistance. When SPs application possibilities are being solved, for instance for various mounds, backfilling, earthwork or as technological material applicable at landfills, they must also be checked for frost and water resistance in respect of long-term durability[11]. The frost resistance was tested with specimens - cylinders produced according to formulas NS2-B, NS1-D and NS2-E using Proctor mortar at 28-day age. Frosting and defrosting of samples and subsequent strength examination were carried out in accordance with instruction stated in EN 14227-3, while values for bottom base layer were considered therefore with freezing temperature -15 ± 2 °C and number of cycles 10. According to TC93 UCS values after performed freezing cycles are considered for frost and water resistances as parameters for bottom/protection road layers and for backfilling and mounds of objects while the required value here is 1.2 MPa.

California Bearing ratio (CBR). CBR test principle based on mixture compacting to maximum bulk density with optimal moisture and pressing cylindrical penetration stud with 50 mm diameter into cylinder sample surface. From the working diagram of the recording force depending on the pressing stud CBR value expressed in percentage is then calculated according to EN 13286-47. Measuring of CBR was carried out with SPs with optimum moisture in the laboratory specialised for earth mechanics. The national standard ČSN 73 6133 requires minimum CBR value 10 % for materials with high fly ash content intended for mounds, backfilling and other earthwork compacted at optimal moisture after four-day storage.

Assessment the impact of SP on the environment

Leachability. The leaching test was carried out according to the standard EN 12457-4 - Compliance test for leaching of granular waste materials and sludges - Part 4 which is required by the Czech and Slovak legislations. Test of this type belongs to static (extraction) leaching tests setting amount of extraction medium for given time in contact with set waste amount with fluid renewal. Water leachate is prepared by leaching crushed sample of SP mixed with water in ratio 1: 10.

Results and discussion

Characterization of input hazardous waste – neutralisation sludges (NS)

Results of concentration of the contaminants in NS1 and NS2 dry matter are stated in the Table 2, while the limits for waste application on terrain surface were according to the Regulation no. 294/2005 exceeded in lead and chrome with both of the sludges. The results are average values of three determinations. Multiple exceeding of limits for carbohydrates C_{10} – C_{40} was registered with NS2.

Table 2: ***Results of concentration of contaminants (Labtech, s.r.o.)***

Parameter	Neutralisation sludge		Limits for waste application on surface[10]
	NS1	NS2	
Dry matter [%]	42.9	44.1	-
Cadmium (Cd) [mg/ kg dry]	0.38	0.15	1
Lead (Pb) [mg/ kg dry]	1870	247	100
Chromium (Cr) [mg/ kg dry]	159	854	200
Arsenic (As) [mg/ kg dry]	1.49	6.41	10
Nickel (Ni) [mg/ kg dry]	77.8	55.2	80
Carbohydrates C_{10} – C_{40} [mg/ kg dry]	23.1	2530	300

Further the leaching test according to EN 12457-4 (water leachate) was carried out with used NS. Table 3 shows pH of water leachate, amount of dissolved substances (DS), sulphates, chlorides, total dissolved organic carbon (DOC) and heavy metals in NS water leachate. On the basis of test results both NS can be classified in the leachability class IIa[10]. High DS concentration in the water leachate means relatively high dissolubility of some organic and inorganic substances contained in both NS. On the basis of leachate pH value showed in the Table 3 we can assume that both NS have alkaline character[5].

Table 3: ***Results of leaching test***

Parameter	Neutralisation sludge		Limits for leachability class IIa[10]
	NS1	NS2	
pH [-]	11.4	9.2	≥ 6
Dissolved substances (DS) [mg/l]	5250	3480	8000
Sulphates [mg/l]	15.9	1820	3000
Chlorides [mg/l]	2760	121	1500
DOC [mg/l]	11.9	57	80
Cd [mg/l]	<0.005	<0.005	0.5
Pb [mg/l]	<0.005	<0.005	5
Cr [mg/l]	<0.03	<0.03	7
As [mg/l]	<0.001	<0.001	2.5
Ni [mg/l]	0.0328	<0.02	4

Note: If the value of DS (dissolved substances) indicator is set, according to the Regulation no. 294/2005 it is not necessary to determine values of sulphates and chlorides and conversely => both NS meet IIa leachability class requirements[10].

Physical and mechanical properties of solidification products (SP)

Compaction. In the Figure 6 we can see dependence of bulk density of the compacted dry solidification mixture to a total moisture of the mixture. From this graphic chart value of maximum bulk density (ρ_{dmax}) with optimal moisture w_{opt} were determined. These values, results of Proctor test are rounded in accordance with EN 13286-2 and stated in Table 4.

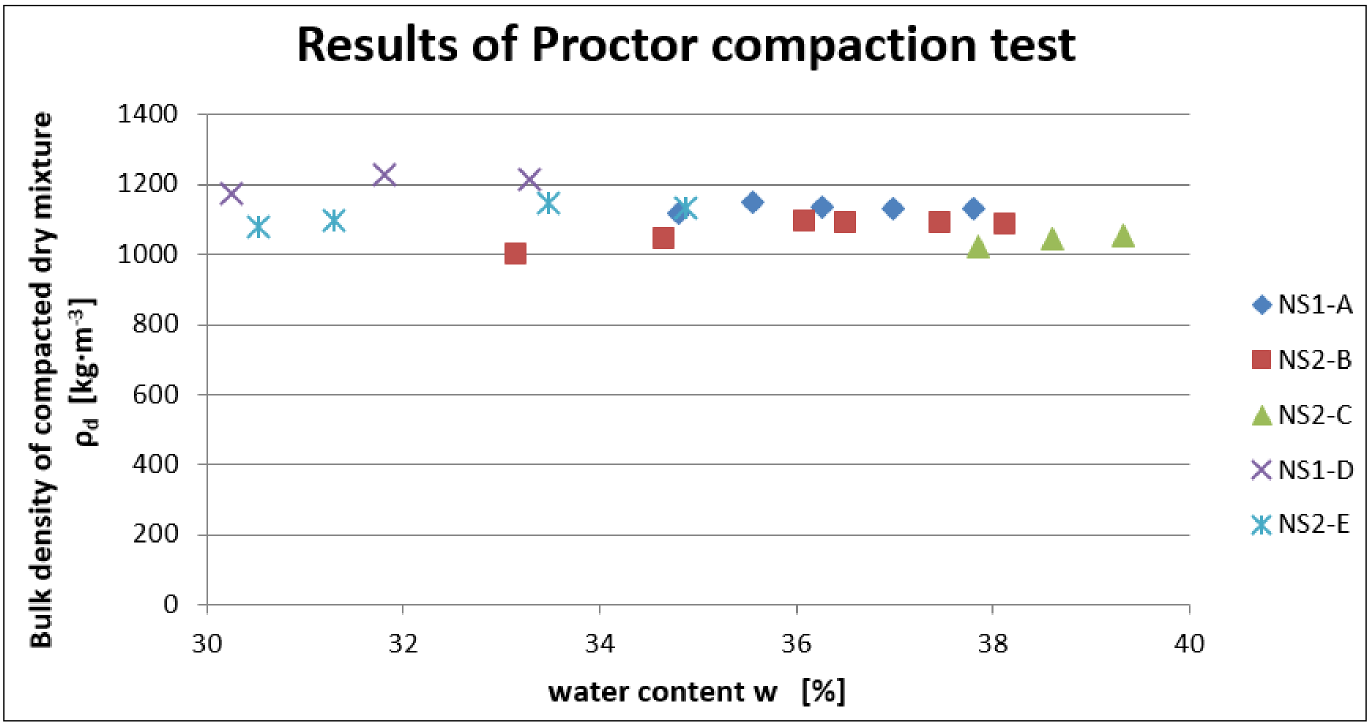

Figure 6:* *Graph of the dependence of bulk density of the compacted dry solidification mixture to the total moisture of the mixture

Table 4:* *Final rounded results of Proctor compaction test

parameter	*NS1-A*	*NS2-B*	*NS2-C*	*NS1-D*	*NS2-E*
ρ_{dmax} [kg·m^{-3}]	1150	1100	1060	1230	1150
w_{opt} [%]	36	38	39	32	34

Unconfined compressive strength (UCS). The results of UCS and bulk density (BD) are stated in Table 5. Values of UCS required according to TS93 were met with all the formulas except NS2-C where SP did not contain cement, but only carbide lime and fly ash as binder. The highest UCS showed a sample NS1-D in which the highest bulk density (BD) was also recorded.

Table 5:* *Bulk density (BD) and unconfined compressive strength (UCS) of SPs after 28 days of curing

parameter	*NS1-A*	*NS2-B*	*NS2-C*	*NS1-D*	*NS2-E*
UCS [MPa]	1.0	1.3	0.9	2.0	1.7
BD [kg·m^{-3}]	1210	1110	1100	1500	1380

Frost resistance. Only the specimens produced according to formulas NS2-B, NS1-D and NS2-E containing also cement in the matrix did not crumble after 10 cycles of frosting and defrosting, therefore they only were subsequent carried out strength examination in accordance with instruction.

The requirement resulting from TC93 (1.2 MPa) was achieved by solidification product (SP) marked NS2-E (Figure 8) and NS1-D (Figure 7) which contain up to 15 % cement in its matrix from which also better resistance to climatic condition results as it was demonstrated. By comparison of UCS results of cylinders not tested for frost resistance (Table 5) with UCS values of tested ones (Table 6) even small UCS value growth can be noted.

Table 6: Results of the frost resistance test

Designation of SP	*Weight change Δ m [%]*	*Number of cycles*	*UCS after frost resistance test [MPa]*
NS2-E	3.4	10	**2.0**
NS1-D	1.9	10	**2.2**
NS2-B	7.7	10	**0.8**

Figure 7: Solidification product NS1-D after frost resistance test

Figure 8: Crushed solidification product NS2-E at UCS test (subjected frost resistance test)

California Bearing Ratio (CBR). The results of CBR test rounded in accordance with EN 13286-47 are shown in Table 7. NS2-C formula showed the lowest Californian bearing ratio (CBR) value, therefore the lowest resistance to stud penetration probably due to cement absent in SP matrix. From the results it is obvious that all tested SPs met the minimum require value of CBR 10 % for materials with high fly ash content intended for mounds, backfilling and other earthwork compacted at optimal moisture after four-day storage. Figure 9 and figure 10 shows also the diagram of force depending on penetration for solidification products NS2-C and NS1-D as the result of the test and related diagrams showed another tested SPs.

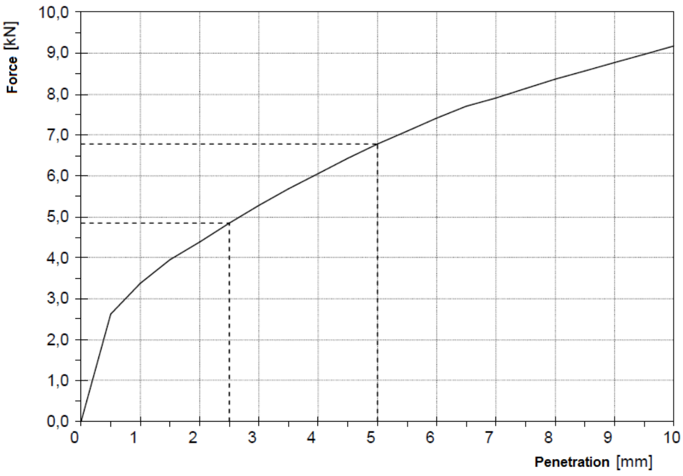

***Figure 9:* Graph of the force depending on penetration – NS2-C**

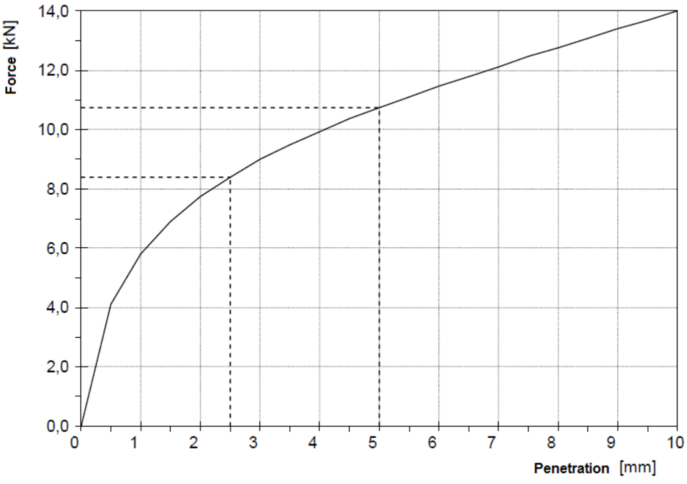

***Figure 10:*Graph of the force depending on penetration – NS1-D**

***Table 7:* Results of CBR at the penetration 5 mm**

Parameter	*NS1-A*	*NS2-B*	*NS2-C*	*NS1-D*	*NS2-E*
Force [kN]	13.68	10.01	6.78	10.74	12.31
CBR [%]	70	50	35	55	60

Assessment the impact of SP on the environment

Leachabilty. The results of leaching test carried out according to EN 12457-4 are stated in Table 8. By evaluation of the water leachate analysis of examined SPs it can be assumed that the ecological limits stated in TS93 were met with all SPs except NS2-C where cadmium (Cd) limit was exceeded. Also all the tested SPs met the requirements for the classification in leachability class IIa according Regulation no. 294/2005.

***Table 8:* Analysis of the water leachate of SPs**

parameter	*NS1-A*	*NS2-B*	*NS2-C*	*NS1-D*	*NS2-E*	*limits according TS93* [12]
pH [-]	11.3	9.8	9.7	11.5	11.6	-
Dissolved substances [mg/l]	2450	2980	2990	1840	866	-
Ag [mg/l]	<0.01	0.014	0.026	<0.01	<0.01	0.1
As [mg/l]	<0.001	0.0041	0.0067	0.0025	<0.001	0.1
Ba [mg/l]	0.152	0.127	0.081	0.122	0.0077	1.0
Be [mg/l]	<0.005	<0.005	<0.005	<0.005	<0.005	0.005
Pb [mg/l]	<0.001	<0.001	<0.001	<0.001	<0.001	0.1
Cd [mg/l]	0.00017	0.00013	**0.0105**	<0001	<0001	0.005
Cr total [mg/l]	<0.03	<0.03	<0.03	<0.03	0.1	0.1
Co [mg/l]	<0.03	<0.03	<0.03	<0.03	<0.03	0.1

Cu [mg/l]	0.025	0.111	0.374	0.023	0.14	1.0
Ni [mg/l]	<0.02	<0.02	<0.02	<0.02	<0.02	0.1
Hg [mg/l]	<0001	0.0002	<0001	0.0001	0.0003	0.005
Se [mg/l]	0.0019	0.0067	0.0069	0.0038	<0.001	0.05
V [mg/l]	<0.01	0.015	<0.01	<0.01	0.039	0.2
Zn [mg/l]	<0.02	<0.02	<0.02	<0.02	<0.02	3.0

Conclusion

Upon the evaluation of performed test results it can be assumed, that solidification products (SPs) prepared according to formulas NS1-D and NS2-E in granulated form with optimum moisture can be used as material for various mounds, backfilling, sub-bases and for such road parts (protection and base layers) where they meet technical criteria for particular construction element and general requirements for utilisation. At the same time, other conditions must also be met - provision of safety under condition of permanently stabile earthwork body and at provision of health and safety at work including protection of the environment during construction works and permanent operation subject to legislation in force.

Granulated solidification products (SPs) can be applied in backfilling only above the underground water level. The SPs layer must be protected from capillarity using sealing and or interrupting layer. To separate the SPs in a mound from watered subsoil a sealing layer or change of subsoil must be done to prevent excessive subsoil settlement in case of occurrence of unsuitable soil in the subsoil. Nevertheless this material containing in its structure immobilised and inbuilt heavy metals may be used for above stated purposes only after determination of pollutant concentrations and comparison of the results with the limits set in the Regulation no.294/2005 - Highest admissible concentrations of pollutant in waste dry matter applied on terrain surface.

Due to the high amount of pollutants in input NS and high amount of NS in SPs it can be assumed that these limits might be exceeded with the verified formulas. The solidification formulas where the limits will be exceeded can be then used as recultivation material at solution of old ecological burdens or as technological and recultivation materials at landfills. SPs can be applied as technological materials on dumping ground only if they meet the parameters for landfills, they must not be in liquid form and must be approved in landfill operating rules.

Compacted filling materials made from neutralisation sludges (NS) for mounds and backfilling, the most suitable alternative of application of laboratory verified SPs can be used for covering and levelling of waste layers under landfill sealing layer of groups L-OW (landfill for other waste) and L-HW (landfill for hazardous waste) according to § 6 of the Regulation no. 294/2005 and clause 7.2. of the national standard ČSN 83 8035 at closing of its surface. However, considering environmental and economic point of view SPs prepared according to formulas NS1-A, NS2-B, NS2-C are the most efficient because they contain none (NS2-C) or minimum amount – 5 % of cement (NS1-A, NS2-B) in their matrices and at the same time they meet the required parameters for specified purpose.

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Experimentální prověření možnosti využití solidifikátu obsahujícího neutralizační kaly po galvanickém pokovování ve stavebnictví

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Souhrn

Z důvodu nežádoucí produkce velkého množství nebezpečného odpadu – neutralizačních kalů po galvanickém pokovování je potřeba najít takovou technologii, která by umožnila transformaci těchto odpadů s výrazně negativním vlivem na životní prostředí na využitelný produkt. Jednou z technologií, která se zdá být pro tento účel velice vhodná je technologie solidifikace. Tento příspěvek se proto zabývá experimentálním prozkoumáním možnosti materiálového využití produktů solidifikace-solidifikátů. Cílem je nalézt takovou solidifikační cestu - recepturu a technologii pomocí níž by se dosáhlo takových fyzikálně-mechanických vlastností solidifikátů, které by zaručily bezpečné a efektivní využití tohoto materiálu v oblasti stavebnictví pro různé násypy, zásypy a při stavbě pozemních komunikací. Aby se dal solidifikát efektivně využít je potřeba nejprve podrobně prozkoumat jeho fyzikálně-mechanické vlastnosti. V rámci této práce se jedná o stanovení stlačitelnosti (Proctorova zkouška), pevnosti v prostém tlaku a Kalifornského poměru únosnosti. S ohledem na dlouhodobou trvanlivost posuzovaných solidifikátů je prováděna i zkouška mrazuvzdornosti a pro posouzení vlivu na životní prostředí budou na závěr práce uvedeny i výsledky zkoušky vyluhovatelnosti.

Klíčová slova: *stabilizace a solidifikace, solidifikát, popílek, neutralizačný kal, stlačitelnost, pevnost v tlaku, vyluhovatelnost, trvanlivost*

Influence of fly ash and binders on designing a grouting mix

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Abstract

Sand and gravel sealing by chemical injection has been known and used for a long time. Chemical grouting can be expensive. Not even the use of cement sometimes brings the desired effect. Thus, there is an effort to seek new materials and methodologies of grouting. Clay and cement are added in mixtures to limit the use of chemicals. Clay-cement grouts are of better quality and tend to better enter incoherent sediments which require sealing by means of chemical injection. In order to reduce costs, there is an effort to replace traditional clay. Secondary raw materials are a suitable alternative to clay to an extent. One such material is especially fly ash. The paper deals with the suitability of using fly ash and its performance in mixtures. It was found that the use of fly ash brings an improvement of fresh mixture consistency, reduction of w/c ratio and shrinkage. On the other hand, the use of fly ash brought an increase of decantation, permeability, etc. The goal was to design an optimal grouting mixture for additional sealing of embankment dams.

Keywords: *embankment dam, grouting, clay, lime, cement, fly ash.*

Introduction

According to [1], embankments are among the simplest types of dams. They are the most frequent type in the Czech Republic. In most cases they are smaller pieces of water infrastructure such as ponds, reservoirs, etc. They were constructed most often between 1960s and 1990s. For this reason, they often suffer from leaks and loss of stability. This was well observable in 1997 and 2002 during the severe floods in the country. Leaking embankment dams can have devastating consequences which may only become apparent in weeks or months. It is therefore advisable to address their inspection and, if necessary, rehabilitation. Since they are only small dams, the optimal remedial technology was decided to be traditional injection grout. The choice of technology was made based on optimisation calculation. The actual method of rehabilitation must not cause further damage to the embankment.

This paper builds upon the findings about the application technology and choice of material suitable for rehabilitation [2]. The use of secondary products from the power industry is emphasised when making the choice of a suitable material composition. The production of these materials increases constantly and their landfilling is becoming more difficult as time progresses. For this reason there is the effort to apply them in the design of injection ground mixes. The material in question is primarily fly ash. These materials can be used as partial replacement of traditional clay. The most important requirement the materials must meet is their fineness. The reason being the ease of entry into the newly formed discontinuities (caverns, cracks, voids, etc.) in the embankment. Another requirement is their mineral composition. The content of binders is also important during the design of a mix. Binders improve strength and mixture stability [2].

After the choice of raw material, the mixtures must be well designed and tested in a number of ways. The tests correspond to the requirements for the injection grouting mix. An examination of the test results will determine the choice of optimal composition of the mixtures for additional sealing of embankment dams.

Experimental Unit

As suggested above, the technology of traditional grouting is optimal during embankment dam rehabilitation. This technology improves the properties of the foundation soils. In Building Foundation [3], the process of grouting is described as pressure pumping an injection mixture into the dam. This seals discontinuities which are the cause of leakages. Filling of these spaces improves the physical-mechanical properties of the soils forming the embankment. Verfel, J. claims in [2] that grouting always starts with drilling a bore. In case of cohesive rocks, this bore is used for fitting a double obturator. In case of incoherent soils, filling is applied into the bore which is then fitted with a cuffed pipe. Cuffed pipe is perforated at the depth of grouting and covered with cuffs.

Mixes such as clay fillings or stabilised cement mixes [2] can be used for the technology of traditional injections. Clay-cement mixtures are used for sealing purposes which was one of the basic points of the research. In order to reduce or prevent permeability, the general principle is that the grain size should be at least 3 times smaller than the pores of the area being grouted. The reason being the ease of entry into voids, caverns, etc. Larger particles prevent entry and in case of build-up, barriers can form which block out the mixture. For this reason the correct choice of materials is very important [4].

The main raw material for grouting is therefore clay. This is due to its mineral composition. Mixture consumption is high during grouting for which reason it is appropriate to use widely available materials. According to [5], such materials can be divided into three main categories:

- sealants – high swelling pressure, low filtration coefficient,
- binders – high compressive strength,
- fillers – optimal maximum bulk density at a given water content.

Plasticity is important for the resulting mixtures. According to French experts [6], only clay with yield value at least 60 % can be considered suitable for mixture production. Based on this information, clay was used together with fly ash and lime as binder.

Clay

The design of a grouting mix must take into account the choice of a suitable kind of clay. In [7], Hobst et al. state that in terms of granulometry, clay should not exceed 0.02 mm grain diameter in more than 5 % of its particles. The chosen clay is a typical representative of montomillonite-illite-kaolinite clay. Its yield value is around 85 %. The presence of Iillite determines the plastic properties of the clay. According to ČSN 75 2410 [8], the clay can be categorised as one with (extremely) high plasticity. For its good properties (especially plasticity and swelling), the clay was chosen as the main material during mixture design. The clay properties are in Tab. 1 and Tab. 2.

Table 1: The main characteristics of clay

Montmorillonite	Illite	Kaolinite	Quartz	Feldspar	Others
29 %	27 %	11 %	20 %	1 %	12 %

Table 2: Chemical composition of clay

Sample	Al_2O_3 [%]	Fe_2O_3 [%]	TiO_2 [%]	SiO_2 [%]	MgO [%]	CaO [%]	Na_2O [%]	K_2O [%]
Clay	24.37	6.53	0.87	54.79	0.72	0.68	0.09	1.44

Fly ash

The financial aspect is very important in mixture design. It is mainly due to the fact that grouting consumes a great amount of mixture. For this reason, there is an effort to replace the traditional raw material, i.e. clay, with an alternative one. Alternative raw materials must perform similar functions as clay and must not reduce the parameters of the mix. Fly ash appears to be the most suitable. It has very low particle size (0 – 1 mm). Fly ash can be divided into common fly ash and FBC ash. When fly ash is being utilised, its physical, chemical and mineral composition must be understood. The properties of the fly ashes are in Tab. 3. The experiment tested common fly ash (CA) and FBC ash (FA).

Table 3: Chemical composition of fly ash

Ash	SiO_2 [%]	Al_2O_3 [%]	Fe_2O_3 [%]	SO_3 [%]	CaO [%]	MgO [%]	K_2O [%]	Na_2O [%]	P_2O_5 [%]
FA	48,3	22,8	16,6	0,5	3,7	1,73	1,163	0,447	0,177
FBCA	27,6	17,5	5,63	7,57	30,4	0,84	0,46	0,33	0,25

Binders

Igles, O. and Metcalf, J. [9] list the five most important properties that the mix must meet. They are strength, volume stability, permeability, resistance and variability. Suitable mixture stabilisers are those which can be broadly applied in different types of soils and are inexpensive. Materials meeting these requirements are lime and cement. During the stabilisation of clay with lime, fast chemical reactions occur on the surface of clay particles. The stabilisation of clay soils with lime has a tendency towards changing their strength and water tightness. Soils stabilised with lime exhibit greater strength, erosion resistance, volume stability and greater permeability. Despite the advantages of using lime it is necessary to note that the stabilised soils do not reach strength as high as ones stabilised using cement. The experiment used white, airy, sharply burnt lime.

Testing procedure

A number of laboratory tests need to be performed when designing the correct grout composition. Based on the obtained results, the amount, interaction and suitability of material use are determined. The formula needs to be determined for each structure individually as even a small change in water or clay chemistry can change the composition of the grout. The mixtures are tested for consistency, viscosity, decantation, unconfined compressive strength, etc.

First, the properties of materials for the grout design are determined. For instance, it is *grain size measurement*. Next, tests are performed with the mixture in fresh state. In this case it is *yield value, consistency, viscosity, decantation* and *bulk density*. Finally tests with mixtures in hardened state are performed. These are the determination of *compressive strength, bulk density, contraction, permeability - i.e. filtration coefficient, ecotoxicity* and *leachability.* The most important tests are the determination of *viscosity* and *compressive strength*; the results of these tests are discussed in the following chapter.

Results and discussion

The grouting process requires the formation of a broad enough grout curtain which prevents leaks. The formation of such curtain is possible by means of selecting the appropriate materials comprising the grout mix and the technology of application. The optimal technology appears to be traditional grout. It is a simple technology which does not cause damage to the embankment. The grout mix is chosen according to the permeability of the environment. There are many types of mixes which are suitable for sealing embankment dams. They range from clay-cement suspensions to chemical mixtures. Grout design is mostly based on grain-size curves [7]. Due to this, the main raw material was clay.

Financial aspects are also important during grout design. For this reason there is an effort to substitute clay with an alternative material such as fly ash. The fly ash must have suitable granulometry, mineral and chemical composition. Fly ash is a very fine grained powder suitable for grout design. It is given by its good properties which improve the properties of the mixture. Thus, the first mixture was based on traditional clay and fly ash. The amount of fly ash added ranged from 0 % to 50 %. The use of fly ash brought a reduction in the amount of water necessary for determining consistency using Marsh cone. The use of common fly ash (CA) reduced the amount of water in the mixture. This way, the mixture hydrates faster and has lower decantation. However, this only applied up to a certain value. The optimal amount of common fly ash appears to be 25 % of clay mass. Higher amounts of fly ash increases decantation and reduces yield value. Overall, the presence of common fly ash improves rheological properties. Results illustrating the influence of fly ashes on the properties of the mixture are in Fig. 1. The presence of FBC ash (FA) caused a slight increase in strength and reduction of plasticity of the clay. The amount of FBC ash above 25 % reduced decantation and contraction of the mixture. The results of the tests performed with the newly designed mixtures are in Fig. 1 and Fig. 2.

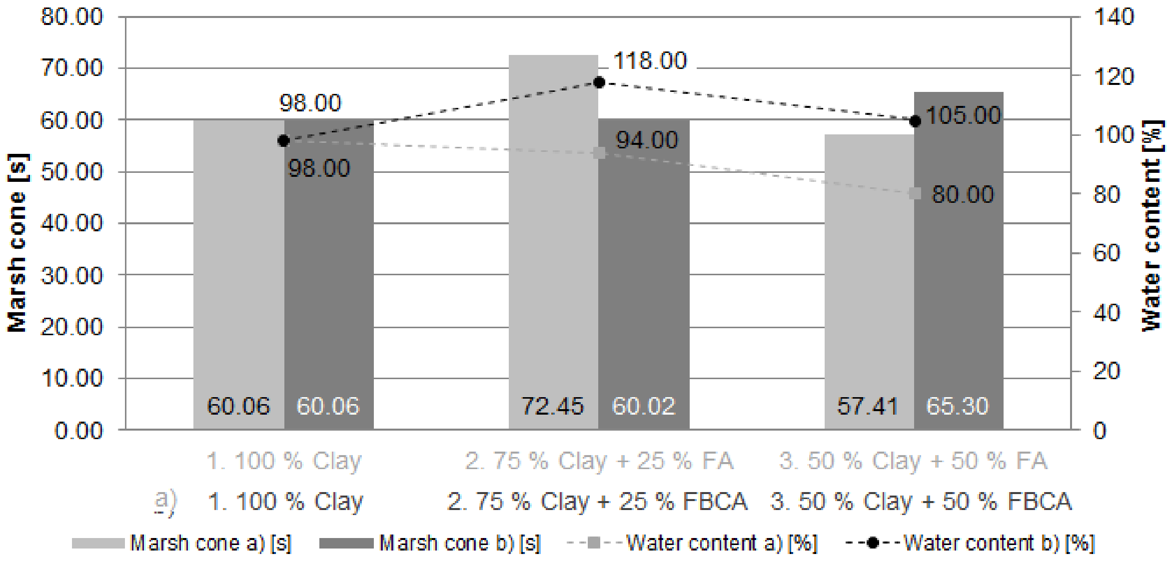

Figure 1: Dependence of viscosity on water content of a suspension based on clay, ash and fly ash

Fig. 1 shows that as the amount of fly ash increased, the necessary amount of water decreased. A higher yield value of the clay caused the high values of necessary water. This had an effect on consistency. Comparing FBC ash with common fly ash, we can see that the addition of FBC ash increased the amount of required water. Fly ash improved rheological properties but simultaneously increased decantation. For this reason, it was suitable to dose the amount of fly ash no higher than 25 %. An amount of FBC ash above 50 % limited the rheological properties of the mixture in raw state. At the same time, the required amount of water increased. This was caused by an increased content of CaO in comparison with common fly ash. CaO in a mixture causes an immediate reaction in contact with water. The addition of fly ash above 50 % was ineffective as the mixture parameters deteriorated.

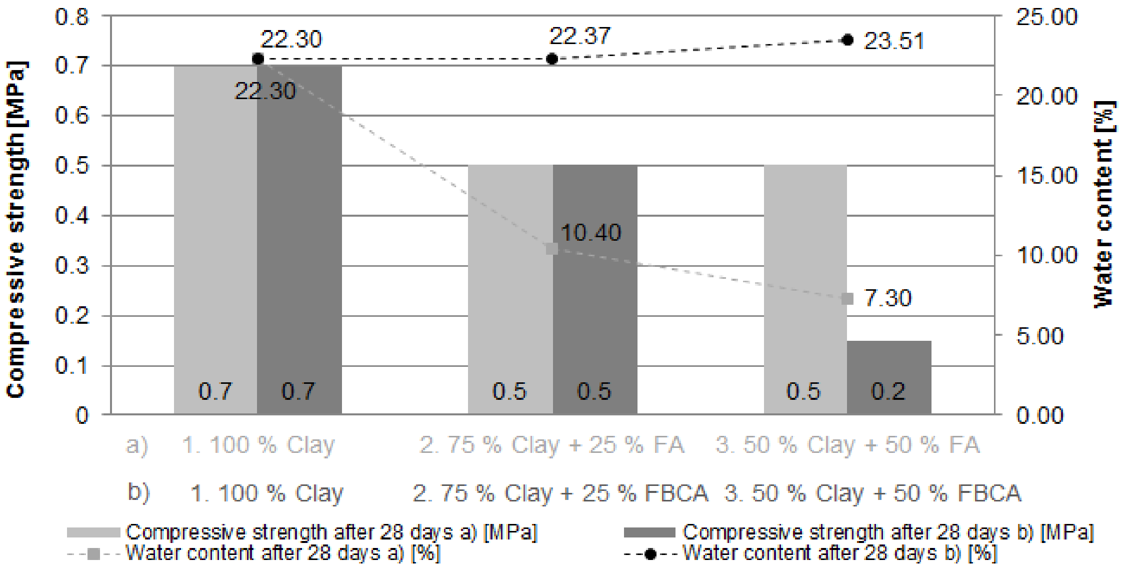

Figure 2: Results of compressive strength determination and water content of specimens based on clay, common fly ash and FBC ash

Fig. 2 shows that as the amount of fly ash increased, strength decreased. Clay forms less strong bonds with fly ash which led to the decrease. It is apparent that the optimal amount of fly ash was around 25 %. A slight increase in strength in case of use of FBC ash can be caused by a higher amount of CaO.

According to their rheological behaviour, grouts are divided into stable suspensions, unstable suspensions, colloidal solutions, clear solutions and gaseous emulsions. In sealing of embankment dams, mainly stable suspensions are used. One kind of stable suspension are clay-cement mixtures which is what the experiment was based on. These mixtures must not exhibit particle sedimentation during injection. The mixture must set in the same form in which it was made [9]. If this is fact is observed, the strength is higher. Thus, the use of binders brings mixture stabilisation. This was another determining fact for the experiment. Clay stabilisers operate mainly by means of ion exchange. Clay loses cations which are replaced by native soluble cations (e.g. sodium). Cement, contrary to lime, does not chemically attack the clay part of the soil. For this reason lime was used as the main stabilisation component. Another type of mixtures were ones based on clay, fly ash and lime. The optimal amount of lime was 2 %. This percentage brought a slight increase in the amount of water needed for the determination of viscosity. Yield value also increased. However, a disadvantage brought by the use of lime was a reduction of clay plasticity. The test results for the mixtures containing lime are in Fig. 3 and Fig. 4.

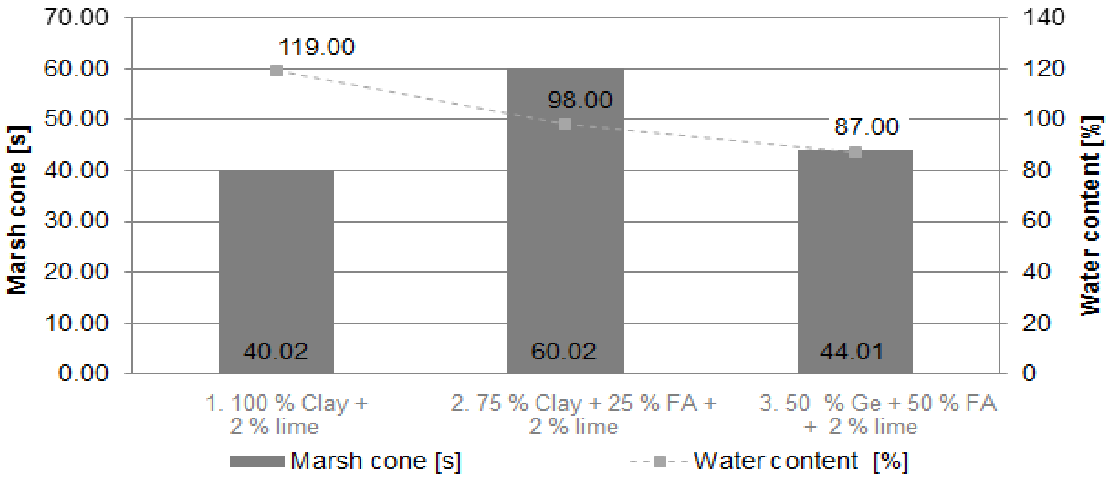

Figure 3: Dependence of viscosity on water content of a suspension based on clay, fly ash and lime

Fig. 3 shows the dependence of viscosity on water content. After the determination of mixture consistency, there was an observable decrease in workability. There was also a slight decrease of decantation. This was due to the content of lime which immediately reacted once in contact with water. Lime thus influenced value of necessary water content which was increased due to its presence. Conversely, with increasing amount of fly ash, this value decreased slightly.

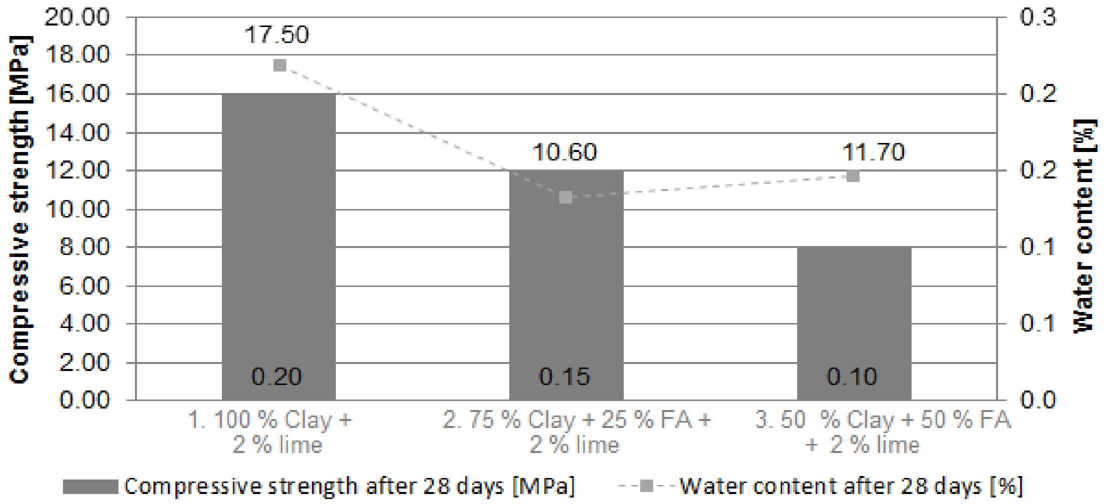

Figure 4: Results of compressive strength determination and water content of specimens based on clay, ash and lime

Fig. 4 shows the influence of lime on compressive strength (after 28 days of curing). The specimens exhibited no significant changes compared with previous specimens. The lime chemically attacked the clay which led to a decrease of its properties. It was especially a slight reduction of its strength after 28 days of curing. The figure shows that an increase of the amount of fly ash and the presence lime did not affect the compressive strength values very significantly.

Conclusion

The dominant embankment dam rehabilitation grouts are clay suspensions. Clay suspensions are made of clay, water, suitable alternative raw materials (fly ashes) and binders. After injection into pores, the mixture has virtually no strength but is able to resist water pressure. In terms of the condition of embankment dams, there are some requirements that the dam must meet. An important parameter which is observed in the raw materials is their granulometry and mineral composition. In common practice, it is clay which meets these requirements. Fly ashes are suitable alternative raw materials. They can partially replace clay and, more importantly, they reduce the costs of mixture production.

The granulometry of the components may affect their sedimentation that can lead to segregation which must be prevented. In other words, the mixture must be stabilised. A suitable stabiliser is lime. The laboratory measurement has revealed that an optimal amount of lime for stabilisation is 2 %.

Currently, a specific embankment dam is being selected for application of these grouts. After further optimisation, they can be expected to be used in specific structures in the catchment area of the river Labe.

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Klasifikace vlivu popílků a pojiv při návrhu injektážní směsi

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Shrnutí

Těsnění písků a štěrkopísků chemickými injektážemi je známo a používáno už dlouhou dobu. Chemické injektáže bývají finančně nákladné. Také použití cementu někdy nevede k žádoucím účinkům. Proto je snahou hledat nové hmoty a metodiky uspořádání injekčních prací. Pro úsporu chemických produktů se do směsí přidává jíl a cement. Jílocementové injekční směsi jsou kvalitnější a mají tendenci lépe vnikat do nesoudržných náplavů, které je potřeba dotěsnit chemickou injekcí. Pro snížení ekonomického hlediska je snahou nahradit klasický jíl. Vhodnou alternativou jílu jsou do určité míry druhotné suroviny. Především se jedná o elektrárenský popílek. Příspěvek se zabývá vhodnosti použití popílků a pojiv a jejich vlastností ve směsi. Bylo zjištěno, že při použití popílků docházelo ke zlepšení konzistence čerstvé směsi, snížil se vodní součinitel a smrštění směsi. Na druhé straně docházelo při použití popílku ke zvýšení dekantace, propustnosti atd. Cílem bylo navrhnout optimální injektážní směs pro dodatečné těsnění sypaných hrází.

***Klíčová slova**: sypaná hráz, injektování, jíl, vápno, popílek.*

Recycled glass as a filler for screeds and other materials

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Summary

Recently, the use of a variety of recycled materials is a live issue. A whole range of different materials, from recycled materials from the rubble to the materials industrially produced from waste is available and used. This contribution is dedicated to the development of floor screeds with aggregates of expanded waste glass. The aggregate is usually spherical in shape and it is therefore very suitable for use in concrete, materials on silicate basis and other composites. Other important properties of aggregates of expanded glass are low density, excellent thermal insulation, good sound absorption, high resistance to pressure, etc. The aggregate of expanded glass was proved to be a suitable substitute for the classical aggregate in lightweight floor screeds.

Keywords: *screed, foam glass, expanded glass aggregate, floor.*

Introduction

As it is generally known, nowadays there is a lot of pressure on the production to be ecological and economic. The construction industry is a great producer but also processor of waste. Besides commonly and long-term used waste materials such as recycled concrete, brick and rubble and by-products like fly-ash, slag and others, there is always a need to include into the production new recycled materials such as various types of wastes on the organic basis (PE, PTFE, PET and rubber granulates etc.) and new types of recycled materials from other industries such as treatment of municipal waste, paper and glass production.

A lot of the named materials are not very suitable for the production of silicate-based materials, mainly due to the high content of organic substances. However, those materials can be included in polymer and polymercement based materials, where the negative impacts on the properties of cement are not compromised.

Recently, there is an expansion in the use of various kinds of recycled glass in both silicate and polymer based building materials. The use of glass in cement based material can be a little delicate, especially when raw recycled glass is used only in its crushed or grounded form, as the alkali-silica reaction may occur. This can be prevented with use of more processed recycled glass.

Recycled glass as a filler and aggregate

As mentioned earlier, there are three basic types of recycled glass filler/aggregate. The first type is a simple glass from various sources, which is only crushed or grounded. This type of glass is not a focus of this paper and it is mentioned only for the sake of completeness.

Foamed glass

The production of foam glass is an effective method for low-cost recycling of waste glass. The foam glass is mainly used in the construction industry, where high compressive strength and thermal insulation are important. Therefore, many studies focus on understanding the relation between structural properties and mechanical and thermal properties. The compressive strength of foam glass is strongly dependent on foam density and pore morphology. The thermal conductivity is also strongly related to the foam glass density; often in a linear fashion. [1]

On the market in the Czech Republic, there are two types of recycled foamed glass available Refaglass and Geocell. Those are almost similar materials with only minor differences between them and are almost interchangeable. Those are available in form of coarse gravel and also crushed into required fractions for the applications, which may be insulation of foundations, embankments, concrete aggregate, base layers and so on.

Expanded glass aggregate

On the market are available two basic aggregate from expanded glass of German origin. Those materials are Poraver and Liaver. There are the differences larger than with the foam glass, but both are successfully used in the building industry. There are spheres with almost closed porosity on the surface produced in common grain sizes.

The Poraver is a creamy-white lightweight aggregate with bulk density from 190 kg.m^{-3} and it is available in grain sizes from 0.04 mm to 4 mm. [2]

The Liaver is a yellowish gray lightweight aggregate with bulk density from 200 kg.m^{-3} and it is available in grain sizes from 0.1 mm to 8 mm. [3]

The Liaver is more commonly used in the Czech Republic than the Poraver.

The composition of lightweight screed with expanded glass aggregate

The composition of screeds was based on previous research on the university. Next to the expanded glass aggregate, the sand in the grain size 0 mm – 4 mm, cement CEM I 42,5R, fly ash, crushed and grounded calcium carbonate, super plasticizer, and a setting retarder were used. The proposed mixtures are in the table below.

Table 1: The proposed mixtures – composition per 100 g

Materials		**Mixtures [g]**									
		REF	K1	K2	K3	K4	K5	K3+	V1	V2	V3
Sand 0-4 mm		40.4	36.4	32.4	28.4	24.4	20.4	28.1	42.4	34.9	27.4
CEM I 42.5 R		28.6	28.6	28.6	28.6	28.6	28.6	28.6	30.0	30.0	30.0
Fly ash		9.5	9.5	9.5	9.5	9.5	9.5	9.5	10.0	10.0	10.0
Crushed calcium carbonate		14.3	14.3	14.3	14.3	14.3	14.3	14.3	5.0	10.0	15.0
Grounded calcium carbonate		4.8	4.8	4.8	4.8	4.8	4.8	4.8	0.0	2.5	5.0
Super plasticizer		0.5	0.5	0.5	0.5	0.5	0.5	0.8	0.5	0.5	0.5
Setting retarder		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Liaver	0.25-0.5 mm	0.0	2.0	3.0	4.0	5.0	3.0	6.0	6.0	6.0	7.0
	0.5-1 mm	0.0	2.0	3.0	4.0	5.0	3.0	6.0	6.0	6.0	7.0
	1-2 mm	0.0	2.0	3.0	4.0	5.0	3.0	0.0	0.0	0.0	2.0
	2-4 mm	0.0	2.0	3.0	4.0	5.0	3.0	0.0	0.0	0.0	0.0

Results

In the table 2, the measured physic-mechanical properties are introduced.

Table 2: Physic-mechanical propeties

Mixture	Bulk density [kg.m^{-3}]	Flexural strength [N.mm^{-2}]	Compressive strength [N.mm^{-2}]	Surface microhardness [N.mm^{-2}]	Constructiveness coefficient [-]
REF	1970	5.3	31.3	6.96	1.6
K1	1690	5.2	23.9	2.24	1.4
K2	1440	3.9	18	2.05	1.3
K3	1340	4.3	16.7	2.92	1.2
K4	1160	3.1	12.9	2.49	1.1
K5	1020	2.9	9.2	1.96	0.9
K3+	1210	2.9	10.7	3.00	0.9
V1	1370	1.5	12	2.18	0.9
V2	1390	2.9	14.2	2.37	1.0
V3	1420	2.1	14.7	2.36	1.0

As it is visible from figure 1, the bulk density has assumable sunken with increased amount of expanded aggregate. The reference mixture has bulk density of 1970 kg.m^{-3} and the mixture K5 with the highest amount of Liaver is almost half the measure, namely 1400 kg.m^{-3}.

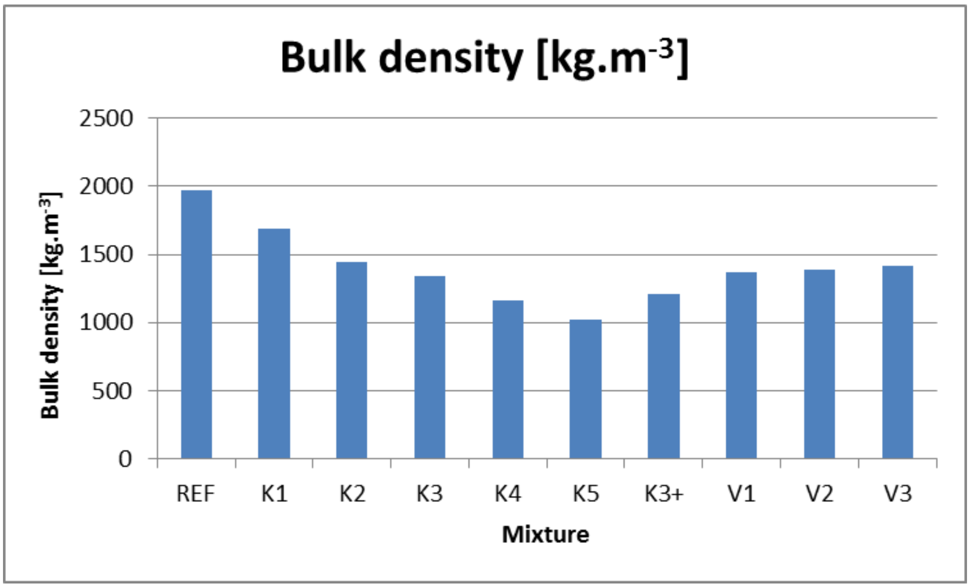

Figure 1: The bulk density of mixtures

From the figure 2 it is visible, that the compressive strength precisely corresponds to the bulk density. With decreased bulk density, the compressive strength is also decreasing. The reference mixture has compressive strength of 31.3 N.mm^{-2}, the mixture K5 is about a third of the value of the reference mixture, therefore 9.2 N.mm^{-2}. With the addition of calcium carbonate, there is a slight increase in the values of compressive strength.

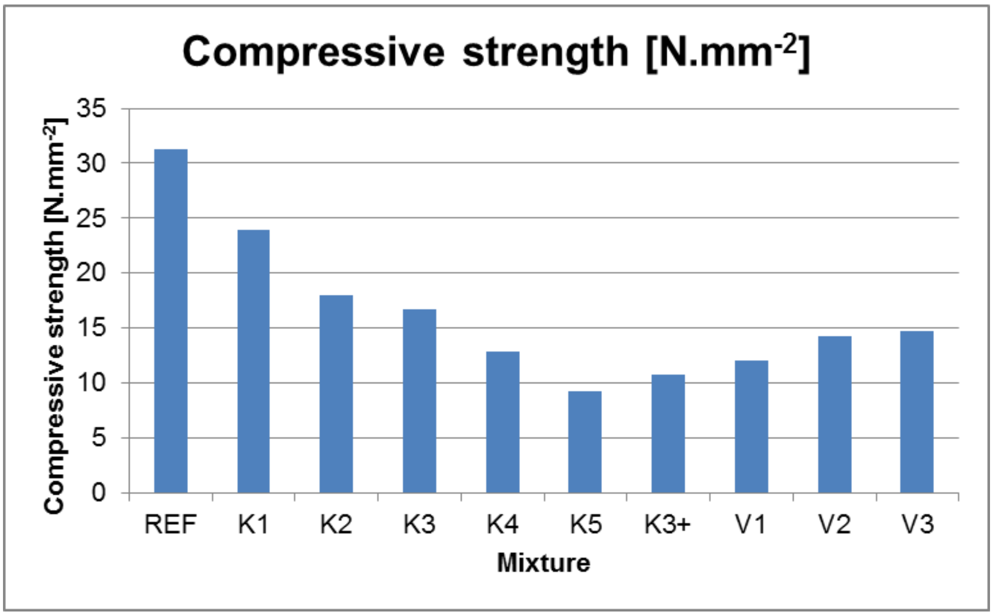

Figure 2: The compressive strength of the mixtures

Another indicator of the properties of proposed screeds is a surface micro hardness which is shown in the figure 3 This is especially important for the flooring screeds, which are there developed. By far the highest value of surface micro hardness has the reference mixture, almost 7 N.mm^{-2}. All other mixtures fluctuate around 2 – 3 N.mm^{-2} and there is no apparent pattern with those values, so it can be concluded, that the addition of expanded aggregate has overall effect on the surface micro hardness and this does not depend entirely on the amount added or other additives and ingredients added.

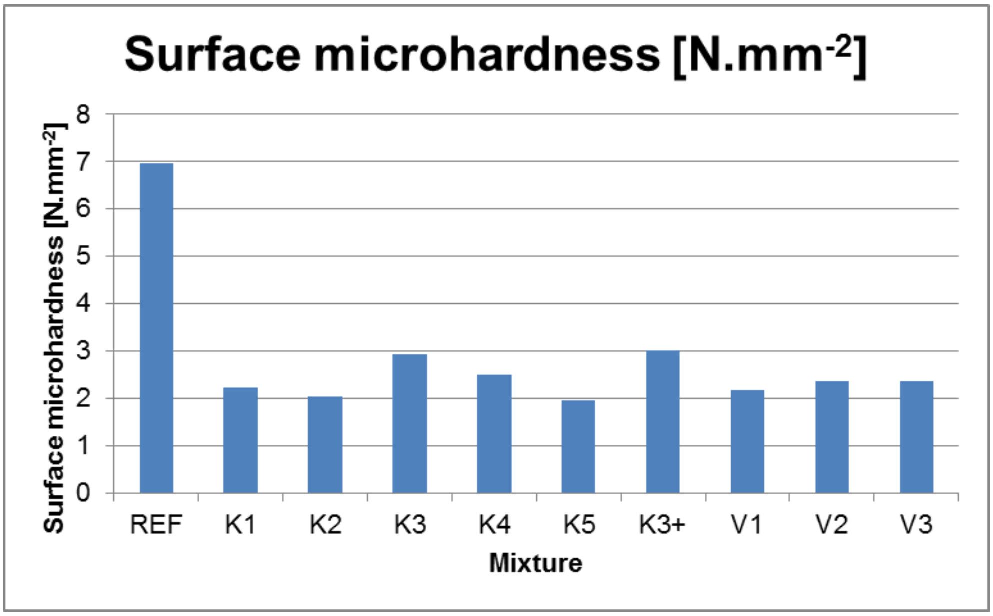

Figure 3: Surface micro hardness

Conclusion

At present, the use of recycled materials in the construction industry is a very alive topic. All kinds of recycled materials, from construction site rubble to various types of products made from recycled materials are available and used.

This contribution is dedicated to the development of flooring screeds with expanded glass aggregate made of recycled glass. As a material for concrete, silicate based materials and composites and there proposed screed, it is a very suitable for its unique spherical shape, which is the most appropriate as well as for the other properties such as low bulk density, excellent thermal insulating and sound absorption properties, high pressure resistance etc.

The expanded glass aggregate was proved to be a suitable addition to the mixture of lightweight flooring screeds. It has a lowering effect for both compressive strength and bulk density. Because of this, the more appropriate mixtures for further research are those with smaller amount of this aggregate, such as mixtures K1 and K2. However, this lightweight screed is not suitable for use as an industrial floor and should never be let as a top wear layer of floor, as it must be always be protected with e.g. tiles or similar top coat or treatment.

Acknowledgement

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Skelné recykláty jako plnivo pro potěrové a jiné hmoty

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Souhrn

V poslední době je používání recyklátů a různých recyklovaných materiálů ve stavebnictví velmi živé téma. Celá škála nejrůznějších materiálů, od recyklátů ze stavební suti po materiály již průmyslově vyráběné z odpadů je dostupná a používaná.

Tento příspěvek je věnován vývoji podlahových potěrů s kamenivem z expandovaného odpadního skla. Toto kamenivo má zpravidla kulovitý tvar a je tedy velice vhodné pro použití v betonu, silikátových materiálech a dalších kompozitech. Dalšími vlastnostmi kameniva expandovaného skla, které je vhodné vyzdvihnout, jsou např. nízká objemová hmotnost, vynikající tepelně-izolační vlastnosti, dobrá absorpce zvuku, vysoká odolnost proti tlaku atd.

Jako plnivo se kamenivo z expandovaného skla osvědčilo jako vhodná náhrada klasického kameniva v lehčených podlahových potěrech.

Klíčová slova: *potěr, pěnové sklo, kamenivo z expandovaného skla, podlaha.*

Poděkování

Příspěvek byl vytvořen v rámci řešení projektu č. LO1408 "AdMaS UP - Pokročilé stavební materiály, konstrukce a technologie" podporovaného Ministerstvem školství, mládeže a tělovýchovy v rámci účelové podpory programu „Národní program udržitelnosti I"."

Possibilities of Using By-product Organic Fibres for Manufacturing Thermal Insulation Materials to Be Used in Civil Engineering

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Summary

The consumption of thermal insulation materials worldwide has been increasing every year together with greater demands on improving the energy performance of buildings – EPB (within Europe in accordance with directive 2010/31/EU of the European Parliament and the Council on the energy performance of buildings). This brings a greater need of raw materials for the production of thermal insulation materials and an increase in the consumption of energy necessary for the manufacturing process (primary energy intensity – PEI). In connection with this, there may be some reduction in CO_2 *emissions in terms of EPB, however, the overall amount of* CO_2 *produced (GWP) is increasing in the area of thermal insulation material production, especially in the case of energy-demanding materials such as mineral wool, etc.*

In terms of sustainable development and with regard to global strategies of reducing greenhouse gas emissions and the consumption of non-renewable raw material resources [1, 2], the use of organic fibres as secondary raw materials for the manufacture of thermal insulation materials appears to have good potential.

Keywords: *by-products, organic fibres, insulation materials, thermal conductivity*

Utilization of organic fibers for the production of advanced thermal insulation materials

Organic fibres are suitable for manufacturing thermal insulation for civil engineering for the reason of their low thermal conductivity and relatively simple technology involved enabling the incorporation of the fibres in a structure or making insulation materials in the shape of a mat or composite. The advantage of natural fibres is their worldwide availability and in most cases the fact they are an easily renewable raw material resource [1, 2]. Conversely, a great disadvantage is often the high price of the input fibres as some types of fibres need to be treated (both mechanically and chemically) prior being used in an insulation mat. Often, the fibres must also be treated in order to attain the required properties of the insulation; especially in terms of fireproofing, moisture and biotic resistance and degradation.

Due to these facts, it often happens that insulation made of raw natural fibres is relatively expensive and does not compete well with other insulation on the market. Its use is therefore more common in special environmentally friendly wooden buildings; however, it is not abundant throughout Central Europe.

Research focused on the application of natural fibres in thermal insulation materials has been carried out at the Faculty of Civil Engineering of Brno University of Technology for more than ten years. The results of the research indicate that raw natural fibres are expensive in Central Europe and often the availability of some types of natural fibres can be unpredictable (especially in the Czech Republic). The most promising fibres appear secondary organic fibres of natural origin produced as waste in agriculture, textile industry or obtained by recycling fabrics. Their advantages are mainly:

- low price,
- mostly pure fibres (e.g. sheep wool, cotton, etc.),
- local availability,
- low impact in terms of PEI and GWP in connection with fibre recycling (in some cases, waste fibres can be used with no treatment).

When using waste organic fibres it is always necessary to choose the optimal treatment technology of the material so as to minimise the extent of the treatment during recycling and maintain minimal increase in PEI and GWP. All technological treatment also has an influence on the price of the fibres and by extension the insulation as a whole. Secondary fibres suitable for producing building thermal insulation are especially:

- **bast fibres of agricultural origin** – fibres extracted from the stalks of hemp, flax; from plants grown primarily for seeds. In case of these plants, the stalk is usually not suitable for fibre extraction (among others due to a higher lignin content) and therefore the use of these stalks in civil engineering is only limited to a curious option,
- **keratin fibres** (fibres obtained from livestock), mainly sheep wool. Raw sheep wool must be washed to rid it of grease and other dirt which greatly increases its price. However, if the fibres are available as a waste from yarn spinning and weaving, it is no longer necessary to treat the fibres and the price of the fibres is much more reasonable,
- **seed fibres** – these include mainly cotton. These fibres can be obtained by recycling old fabric with high content of cotton. Cotton fabrics typically have more than 95 % of cotton. To recycle the fabrics, they must be shredded and afterwards defibrated.

The technology of producing thermal insulation mats from organic natural fibres can be different; however, in the Czech Republic the dominant method is thermal bonding in to insulation mats or composites (Strutto technology).

Development of thermal insulation materials based on organic fibres

During the research, prototype samples of insulation were made. They contained secondary fibres from the livestock, plants and waste textile. In all cases, the specimens were made by means of thermal bonding using polyester fibres making up 15 % of the specimen mass. The properties of the input fibres are in the table below:

Tab. 1: Overview of the thickness of the secondary fibres

Raw material	Fiber thickness [mm]	Fiber length [mm]
Flax	0.115	39
Sheep wool	0.028	95
Cotton fibers	0.039	42

Lofty mat specimens of varied bulk density were made from the fibres. Their thermal conductivity in dependence on bulk density was determined as the optimal choice of bulk density in relation to the properties and the material costs and with regard to the final properties is key for fibre insulations. Thermal conductivity was determined with the specimens at laboratory humidity (at equilibrium humidity corresponding to the environment with temperature +23 °C and relative humidity 50 %) according to ČSN EN 12667 [3] using a method according to ISO 8301 [4] at mean temperature +10 °C and temperature gradient 10 K. The determination of bulk density was performed in accordance with ČSN EN 1602 [5] and the determination of thickness according to ČSN EN 823 [6]. The measurement results are in the charts below:

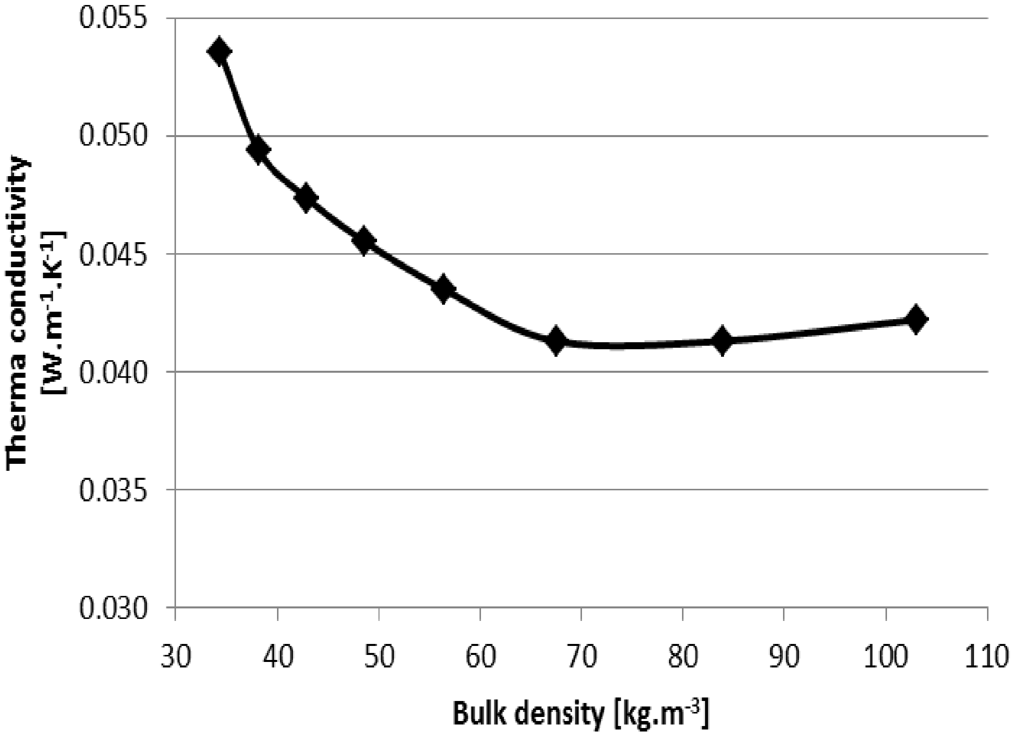

Fig. 1: Determination of the dependency of thermal conductivity for flax insulation specimens

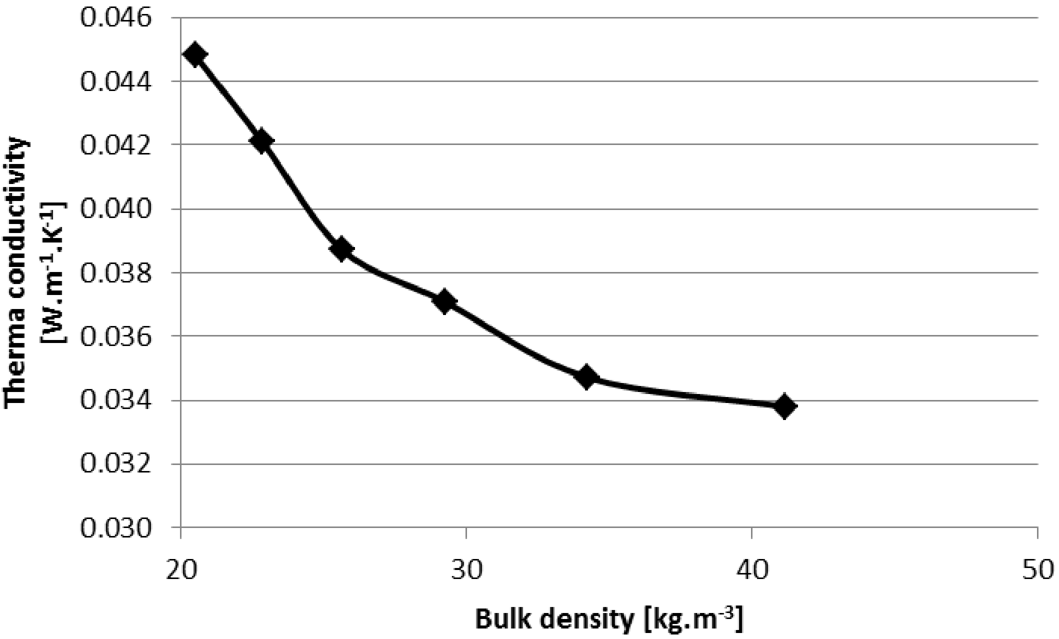

Fig. 2: Determination of the dependency of thermal conductivity for sheep wool insulation specimens

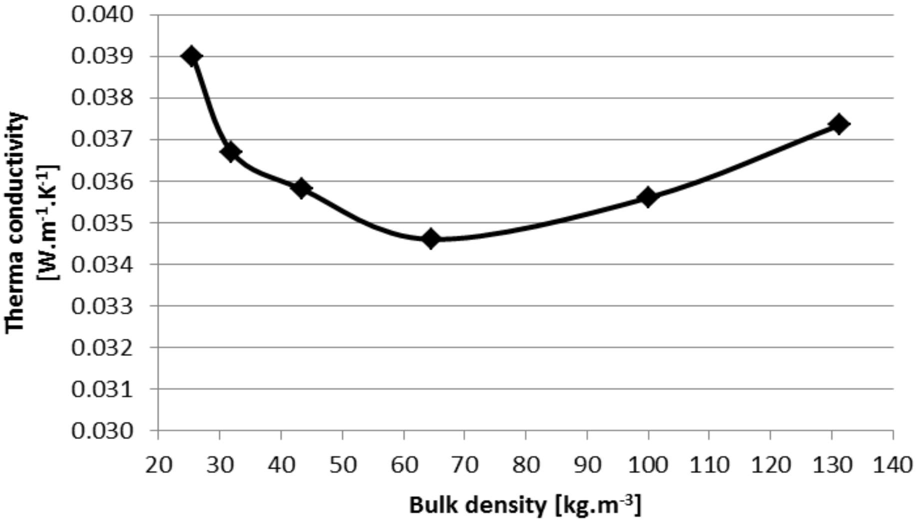

Fig. 3: Determination of the dependency of thermal conductivity for insulation specimens made of secondary fibres from waste fabrics with high cotton content (over 95 %)

Evaluation of results

The results indicate that for each material there is an interval of optimum bulk density in relation to the lowest value of thermal conductivity; i.e. 60 – 80 kg.m^{-3} (in the case of sheep wool, the measurement was performed only up to bulk density of 41 kg.m^{-3}, however a similar progression of thermal conductivity in dependence on bulk density can be expected as in the other specimens).This interval is typical for each type of fibres and is dependent on the quality of their treatment and purity. In case of bast fibres, which are treated to a lesser degree and the material contains a greater amount of shives and is not defibrated enough, higher bulk density is required if good thermal insulation properties are to be attained. Sheep wool and recycled textile fibres can reach good thermal insulation properties at lower bulk density as these materials possess overall better thermal insulation properties compared with bast fibre specimens.

Financial assessment was performed where the approximate manufacturing costs of each insulation material was determined and calculated per unit of thermal resistance R = 1 m^2.K.W^{-1}. The results are in the chart below.

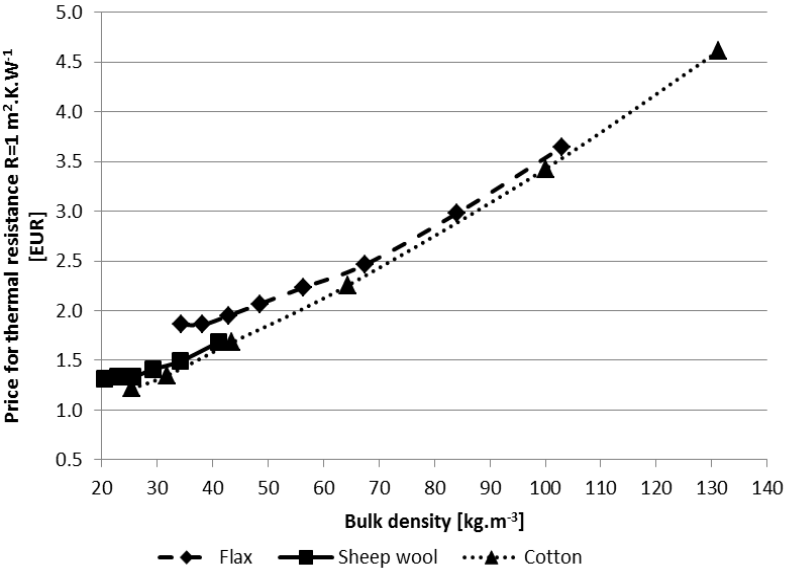

Fig. 4: Overview of the calculated manufacturing costs for the insulation materials in order to achieve thermal resistance R = 1 m^2.K.W^{-1}

Fig. 4 indicates that the most cost-efficient insulation materials are those from recycled textile; conversely, the least cost-efficient ones are the bast fibre ones. However the differences are not too substantial and they dissipate as bulk density increases and as the thermal insulation properties of the bast fibre specimens improve.

Conclusion

Based on the experiments performed with the prototype specimens, the thermal insulation mats based on secondary organic fibres can exhibit very good thermal insulation properties with suitable bulk density. In all cases the optimum interval of bulk density was proven to be 60 – 80 kg.m^{-3}.

In case of bast fibres at a lower degree of treatment (less defibration and greater content of shives) it is necessary to achieve higher bulk density in order for the material to have good thermal insulation properties. Generally speaking, insulation materials form sheep wool have better thermal insulation properties compared with flax insulation. In terms of manufacturing costs, the most efficient is the secondary fibre insulation from recycled fabrics; conversely, the least cost-efficient one is the flax insulation.

It can be stated that, generally, the use of secondary organic fibres can bring a reduction in the energy consumption of manufacturing thermal insulation materials and the resulting insulation can have properties comparable to other thermal insulation materials on the market.

Acknowledgment

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Možnosti využití druhotných organických vláken pro výrobu tepelně izolačních materiálů s použitím ve stavebnictví

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Souhrn

Spotřeba tepelně izolačních materiálů celosvětově každým rokem stoupá, spolu se zvyšujícími se nároky v oblasti snižování energetické náročnosti budov - ENB (v rámci Evropy v souladu se směrnicí Evropského parlamentu a výboru 2010/31/EU). Proto také roste potřeba surovin pro výrobu tepelně izolačních materiálů a spotřeba energie nutné k jejich výrobě (primární vázané energie – PEI). V souvislosti s touto skutečností dochází sice k úsporám v oblasti emisí CO_2 *v oblasti ENB, ale roste množství produkovaných emisí* CO_2 *(GWP) v oblasti výroby tepelně izolačních materiálů, především u energeticky náročných materiálů, jako je například minerální vlna apod.*

Z pohledu trvale udržitelného rozvoje a také z pohledu celosvětových strategií v oblasti snižování emisí skleníkových plynů a snižování zátěže materiálové základny v oblasti neobnovitelných surovinových zdrojů se jeví jako potenciálně velmi zajímavé využití organických vláken v podobě druhotných surovin pro výrobu tepelně izolačních materiálů.

Příspěvek popisuje vývoj a studium tepelně technických vlastností perspektivních izolačních materiálů na bázi organických vláken.

Klíčová slova: *druhotné suroviny, organická vlákna, izolační materiály, tepelná vodivost*

Properties of cement mortar with addition of mineral wool waste

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Summary

This experiment is about options of utilization of the mineral wool waste in cement mortar. Nowadays, mineral wool waste doesn´t have any wider utilization in building materials. Mineral fibres can improve some utility properties of the cement mortar. In this experiment were mineral wool boards defibrated on clump of mineral fibres and it was tested the addition of these fibres in different quantity to cement mortar. In cement mortar with addition of mineral fibres was detected compressive strength, tensile strength, thermal conductivity coefficient and density. Results of these experiments are interesting, because mineral wool fibres can improve some properties of cement mortar.

Keywords: *Cement mortar, waste, mineral wool*

Introduction

Mineral wool waste is primarily produced during production of mineral wool. Waste from production can be reused and recycled directly in manufactory. In construction, especially in building insulation, mineral fibres are widely used for their thermal insulation properties. Mineral wool waste is created when insulating boards are cut and when the old ETICS are demolished. It is not possible to use this material during production of new mineral fibres, because it is mixed with other building waste and we do not know the origin of this material. The material is inert and it is permitted to make landfills, but it remains unused by the high amount of energy that is necessary for its production. Nowadays, for economic reasons, the possibilities of industrial recycling of mineral fibres are not developed. One possible re-use of this material is its defibration, and then adding to suitable matrix, which may improve some of its certain properties [1].

Experimental part

As one of the variants was used cement mortar, to cement mortar was added various amount of fibres. Due to the impossibility shredded mineral insulation board mechanically, board was only "torn" into clumps using a sieve with a mesh size of 8 mm. These clumps were prior to the preparation of cement mortar mixed with aggregate fraction 0-4 mm and thoroughly mixed by hand mixer. Larger clumps of mineral wool were torn by aggregate into individual fibers. To this mixture was added water and cement, after mixing the mixture has been stored into forms of dimensions 40 x 40 x 160 mm and its subsequent compacting using a vibrating table. Samples were stored in a laboratory environment at 22°C and relative humidity of air 65%. On the hardened samples it was performed to measure the coefficient of thermal conductivity λ by the hot wire method, and then the samples were dried to constant weight at 105 (+/- 5) °C and it was performed again to measure the coefficient of thermal conductivity λ. Samples were measured in each condition, weighed and calculated the bulk density ρ. After 28 days was determined tensile strength R_f and compressive strength R_c. All measured and calculated values were recorded in tables and graphs.

Figure 1: Clumps of mineral fibers

Results and discussion

Table 1: Composition of tested mortars

Composition of mortars					
	REF	**1**	**2**	**3**	**4**
CEM I 42,5 R Mokrá m_c [g]	450	450	450	450	450
Sand 0 - 4 mm Žabčice [g]	1350	1350	1350	1350	1350
Water [g]	250	250	250	250	250
Water-cement ratio w [-]	0,56	0,56	0,56	0,56	0,56
Mineral fibers [% from m_c]	0	2,2	3,3	4,4	8,9
Mineral fibers [g]	0	10	15	20	40

Table 2: Measured values of the samples at laboratory humidity, symbol ϕ the mean of value.

Sample	**n**	**ρ $[kg/m^3]$**	***ϕ* ρ $[kg/m^3]$**	**λ $[Wm^{-1}K^{-1}]$**	***ϕ* λ $[Wm^{-1}K^{-1}]$**	***w* [%]**	***ϕ w* [%]**
REF	1	2050	2060	1,372	1,335	5,08	4,91
	2	2090		1,290		4,59	
	3	2050		1,344		5,06	
1	1	2060	2040	1,142	1,230	4,32	4,54
	2	2060		1,217		4,43	
	3	1990		1,331		4,87	
2	1	2010	1990	1,303	1,107	4,87	4,96
	2	1960		0,907		5,18	
	3	1990		1,112		4,83	
3	1	1980	1990	1,031	1,144	5,41	4,85
	2	2020		1,112		4,91	
	3	1960		1,290		4,22	
4	1	1990	1990	1,194	1,177	4,58	4,62
	2	2010		1,252		4,58	
	3	1970		1,084		4,70	

Table 3: Measured values of the dried samples

Sample	**n**	**ρ $[kg/m^3]$**	***ϕ* ρ $[kg/m^3]$**	**λ $[Wm^{-1}K^{-1}]$**	***ϕ* λ $[Wm^{-1}K^{-1}]$**
REF	1	2000	1970	1,183	1,072
	2	1960		0,976	
	3	1960		1,057	
1	1	1980	1960	1,084	1,047
	2	1950		1,057	
	3	1960		0,999	
2	1	1880	1900	0,961	0,989
	2	1900		1,007	
	3	1920		0,999	
3	1	1920	1920	0,835	0,870
	2	1940		0,881	
	3	1910		0,894	
4	1	1890	1900	0,947	0,885
	2	1920		0,863	
	3	1880		0,846	

Table 4: Measured values of compressive R_c ***and tensile strength*** R_f

Sample	n	R_f [MPa]	ϕR_f [MPa]	R_c [MPa]		ϕR_c [MPa]
REF	1	10,70	10,9	32,8	36,9	33,6
	2	11,18		33,2	31,4	
	3	10,75		31,3	36,2	
1	1	9,49	10,5	34,7	23,3	30,0
	2	10,85		24,9	31,5	
	3	11,13		33,4	32,1	
2	1	10,89	10,0	23,4	35,1	27,6
	2	9,21		26,9	26,0	
	3	10,01		29,5	24,5	
3	1	11,31	11,6	28,5	26,2	27,5
	2	10,94		33,4	26,2	
	3	12,63		21,8	28,9	
4	1	12,26	12,6	35,6	24,9	29,4
	2	12,05		33,3	21,8	
	3	13,38		27,1	33,5	

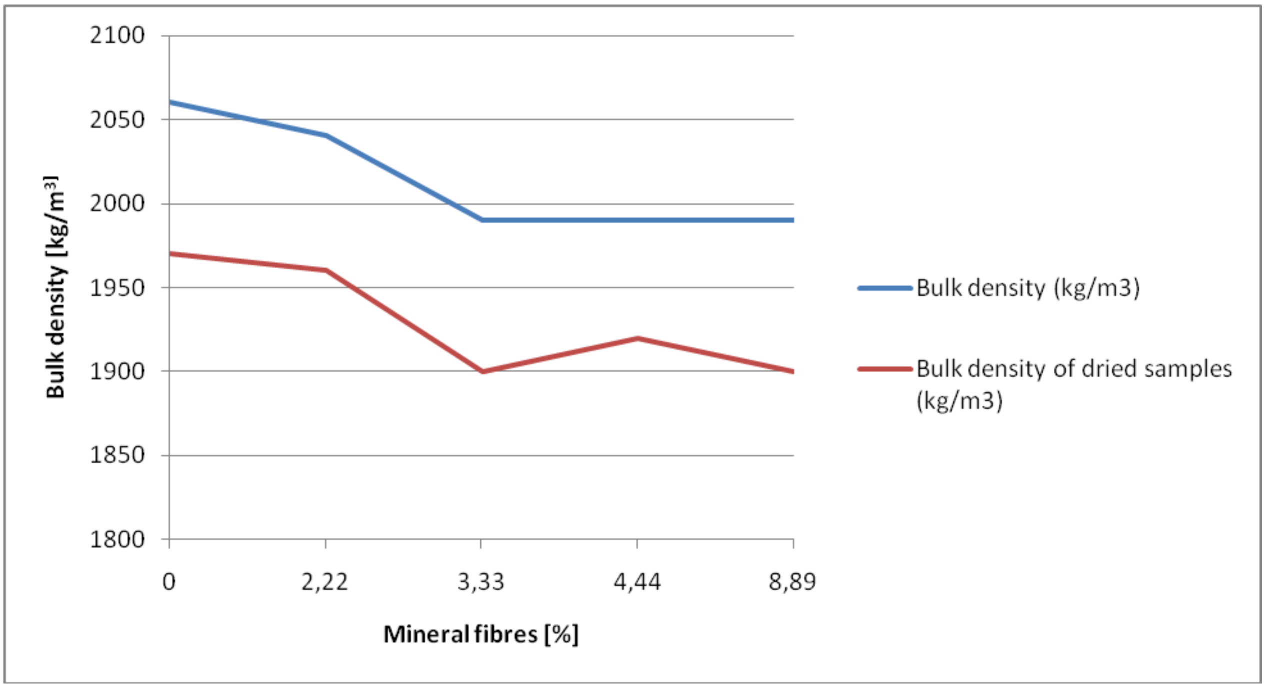

Figure 2: Influence of the quantity of fibers on bulk density

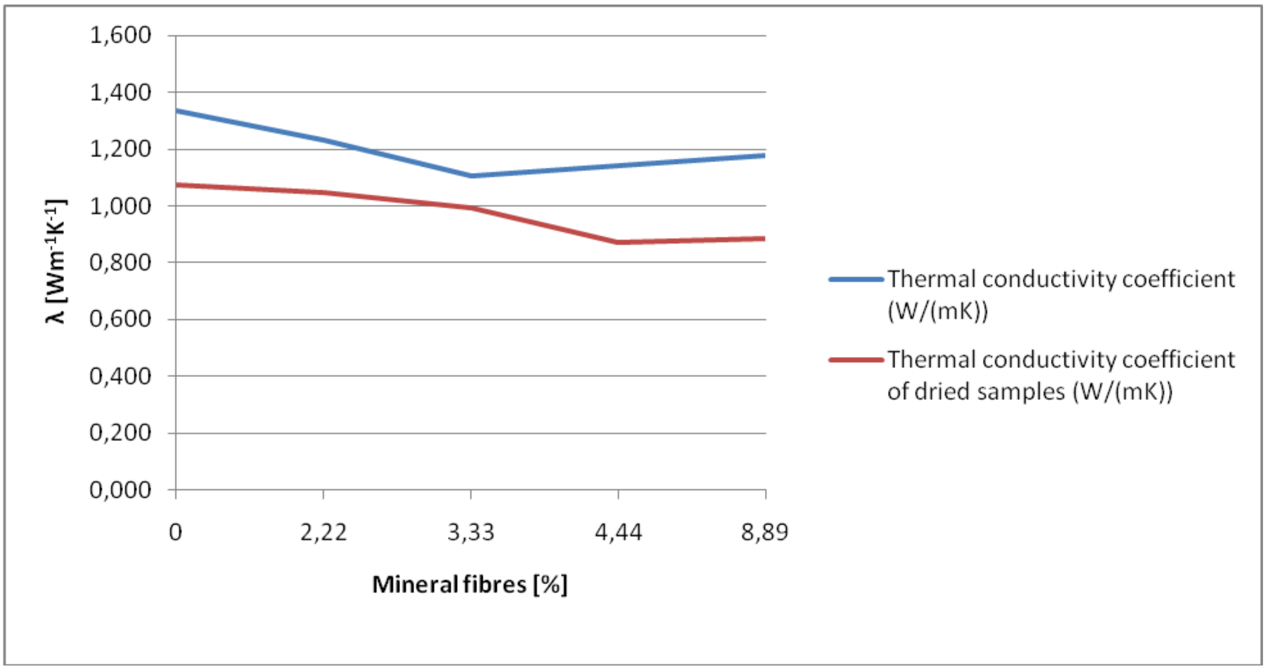

Figure 3: Influence of the quantity of fibers on thermal conductivity coefficient

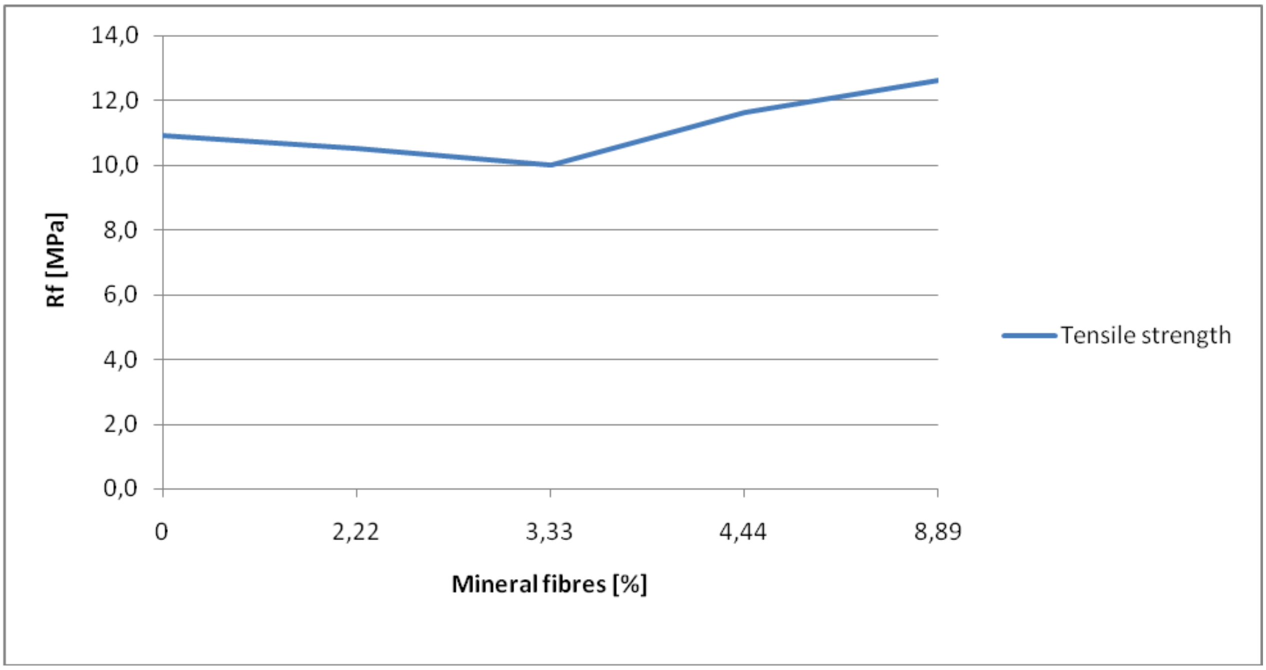

Figure 4: Influence of the quantity of fibers on tensile strength

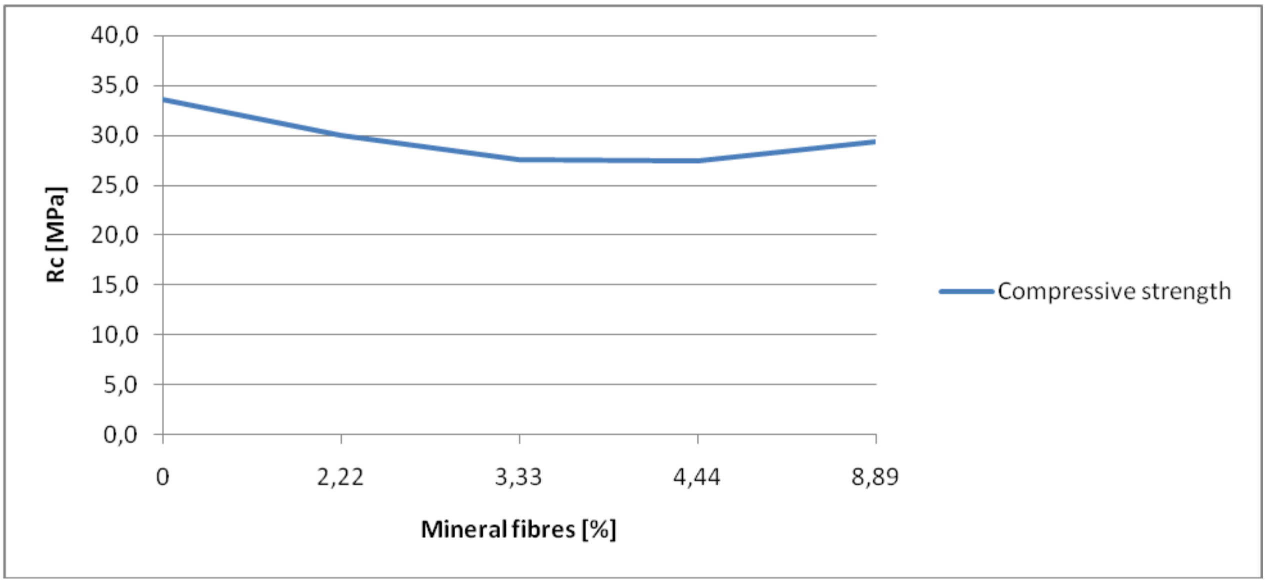

Figure 5: Influence of the quantity of fibers on compressive strength

According to the experiments we can prove that the addition of mineral fibres to cement mortar decreases bulk density ρ [kg/m^3] of mortar. This happens during higher doses (15 – 40 g on 2050 g of mortar) and about maximum value 70 kg/ m^3, it´s equivalent to decrease of the bulk density about 3,4 %. After drying of the testing samples was find out humidity *w*, which ranged from 4,54 to 4,96 % of the weight. The bulk density of the dried samples decreased and with every addition of higher amount of the mineral fibres, the bulk density was still decreasing. At the end the bulk density decreased about 70 kg/m^3, so 3,7 % (asi visible in Figure 2).

A thermal conductivity coefficient λ of the tested samples of cement mortar decreased with addition of mineral fibres (as visible in Figure 3). The biggest decrease of the value λ of the cement mortar´s tested samples is 0,23 Wm^{-1}K^{-1} which corresponds with decrease of the value about 17 %. The biggest decrease of the value λ was in the tested sample, where was added 15 g of mineral fibres on 2050 g of mortar. The decreasing of the value λ is related to the samples which were placed in the laboratory environment. The biggest decrease of the thermal conductivity coefficient λ of the tested samples after drying is at the sample where added 20 g of mineral fibres on 2050 g of mortar was. Specifically it´s λ decrease about 0,20 Wm^{-1}K^{-1}, so 18,8 %.

Tensile strength R_f decreased with addition of small amount of fibres (10 and 15 g on 2050 g of mortar), the biggest decrease is at the sample 2 about 0,9 MPa, so 8,3 %. With bigger amounts of the mineral fibres tensile strength R_f increased, the biggest increase was at the sample 4 about 1,7 MPa, so 15,6 % (asi visible in Figure 4).

Compressive strength R_c was decreased at all tested samples with fibres, the biggest decrease was at the sample 2, so 18,2 %. At the sample 4 was compressive strength slowly increased, so the decrease was 4,2 MPa, at 12,5 % (as visible in Figure 5).

Conclusion

According to the measured values we can see that the mineral fibres in cement mortar decrease bulk density ρ. This decreasing is not significant so it´s negligible in practise. The value of the thermal conductivity coefficient λ was with the addition of fibres distinctly decreasing so we can prove that the mineral fibres in the cement mortar are decreasing the thermal conductivity coefficient λ and they are also improving an insulating capacity of the cement mortar. Tensile strength R_f increased at the samples with the bigger amount of fibres. It is caused by steady distraction of the fibres. Compressive strength R_c decreased after addition of mineral fibres, but the decrease is not significant. It can be summarized that the properties of the cement mortar are improved after addition of mineral fibres so it is appropriate to deal with this topic in detail.

Acknowledgement

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Vlastnosti cementové malty s přídavkem odpadu z minerální vlny

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Souhrn

Odpad na bázi minerálních vláken nenachází v dnešní době širšího využití. Cílem tohoto experimentu bylo zjistit, zda mohou odpadní minerální vlákna zlepšovat některé užitné vlastnosti cementové malty. Rohože minerální vlny byly nejprve rozdruženy na menší části a tyto shluky minerálních vláken byly přidávány do cementové malty. V první fázi byly shluky minerálních vláken zamíchány pouze s kamenivem frakce 0 - 4 mm, aby došlo k jejich rozvláknění. V dalších fázích byly vyrobeny trámce o velikosti 40 x 40 x 160 mm s různou dávkou minerálních vláken. Na těchto vzorcích byly provedeny zkoušky pevnosti v tlaku a v tahu za ohybu, byl zjištěn součinitel tepelné vodivosti vzorků a jejich objemová hmotnost.

Klíčová slova: *Cementová malta, odpad, minerální vlna*

Effect of autoclaving conditions on the final properties of aerated concrete

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Summary

Autoclaved aerated concrete is one of the few building materials whose production can use up to 70% of energy by-products. These by-products include fly ash from high-temperature as well as fluidized coal combustion and energogypsum. In addition to the raw material composition, one of the prerequisites for the production of aerated concrete with good physical and mechanical properties is the right choice of autoclaving mode. This mainly refers to the length of the isothermal heating phase and, obviously, to the appropriate choice of temperature and the related pressure in the autoclave. This article reviews the microstructure and physical-mechanical properties of aerated concrete autoclaved in three different modes. Particular attention is paid to tobermorite as the majority mineral of aerated concrete, especially to the shape and quality of its crystals.

***Keywords:** Tobermorite, fly ash, autoclaved aerated concrete, calcium hydro silicates, microstructure.*

Introduction

In order to obtain desired physical and mechanical properties, the aerated concrete product undergoes a process of autoclaving during which the aerated concrete mass is cured. Several theories apply to this process. One of them is the theory of Rabinděr according to which the creation of a solid spatial macrostructure is influenced by solubility and subsequent recrystallization of the basic components used.

The first period of recrystallization in aerated concrete mixtures and the related fundamental change in macrostructure takes place at an early stage of hydrothermal synthesis. The entire autoclaving process is accompanied by multiple conversions of crystalline phases without achieving the equilibrium state. The process produces various calcium hydro silicates and other compounds whose $CaO:SiO_2$ molar ratio ranges from about 0.5 up to 3.0. One of the most important calcium hydro silicates is tobermorite which is considered the main bearer of the strength of aerated concrete.[1] The structure of tobermorite ($5CaO·6SiO_2·5H_2O$) is orthosymetrical and consists of the centrally layer of Ca^{2+} octahedrons which is surrounded by continuous chains composed of silicate tetrahedrons. The layers are bonded to one another by an intermediate layer containing ions of Calcium and molecules of water. Small leaf-shaped crystals of this mineral are mutually well intergrown and for a compact skeletal structure of the autoclaved aerated concrete.[2]

The calcium hydro silicate components formed during autoclaving are very complex units frequently blended together and form a complete line of intermediate products from completely amorphous to well crystalline phases. Considering the fact the hydro silicates form in many cases and mainly in the beginning jellylike or imperfect crystalline products, their identification is very difficult namely with its lower content. Schematic representation of the main reaction occurring during autoclaving is shown in equation 1.[3]

$$Ca(OH)_2,\ SiO_2,\ H_2O \rightarrow CSH \rightarrow \text{tobermorite} \qquad (1)$$

Hydrothermal reaction first produces calcium hydro silicate CSH II and a certain amount of C_2SH that occur transiently, especially at the beginning of the autoclaving when there is a relative excess of CaO due to the limited reactive surface of siliceous material. In subsequent reactions with the remaining unreacted siliceous raw material, these initial products with a higher content of CaO relatively quickly turn into CSH I with a lower CaO content. During additional autoclaving, lasting at least 3 to 9 hours, mineral tobermorite begins to develop. Final product of the autoclaving process, formed at constant conditions usually after 20 to 72 hours and sufficient amount of CaO, is the mineral xonotlite C_2S_5H. In the production of aerated concrete, however, it is an undesirable product. [1]

Nevertheless, the gradual formation of tobermorite over the CSH gel is not the only process of its creation. Tobermorite partly arises also from the mineral katoite. Katoite ($Ca_3Al2(SiO_4)(OH)_8$) belongs to a group of hydrogranates that arise at the beginning of the hydrothermal reaction, even before the formation of tobermorite. Formation of tobermorite from CSH gel is a conversion in the solid phase; from katoite, however, tobermorite crystallizes in the system of solid phase-liquid phase. Both of these reactions are not dependent on each other but usually occur simultaneously. Scheme of the formation of tobermorite from the katoite phase is shown in equation 2.[3]

Quartz, katoite, hydroxylellestadite, CSH → Ca^{2+}, Si^{4+}, Al^{3+},OH^- → tobermorite (2)

Experimental part

For production of autoclaved aerated concrete specimens lime and cement were applied as a binder component. Siliceous component was represented by a mix of fly ash from high temperature combustion (HTC) together with fly ash from fluidized bed combustion (FBC); calcium sulphate is the auxiliary component. Aluminum powder was used as gas making component. Chemical composition of samples of fly ash from high temperature and fluidized bed combustion was determined; the results are given in Table 1.

Table 1: Chemical composition of the fly ash used

Fly ash	Chemical composition [%]					
	SO_3	CaO (available)	CaO (total)	SiO_2	Al_2O_3	Fe_2O_3
HTC	0.63	0.025	1.91	48.2	27.5	10.7
FBC	5.68	3.31	20.0	33.4	22.2	6.71

First, the dry ingredients were blended and then mixed with water at a temperature of about 50°C. Aluminium powder was dosed as a suspension just before casting the aerated concrete mixture into moulds 100x100x100 mm. Loosening and subsequent maturation of the mass took place in heat-insulated moulds. Demoulding of samples was possible only after about 18 hours when the samples had sufficient handling strength and their surface did not stick to the mould sides. The samples were then placed into a laboratory autoclave. The formula was maintained in all the samples, the only difference consists in autoclaving conditions. Table 2 below presents individual autoclaving modes.

Table 2: Autoclaving modes used

Autoclaving	Pressure [MPa]	Temperature [° C]	Isothermal holding time [hours]
1.	1.0	180	14
2.	1.0	180	6
3.	1.2	188	6

After drying, the autoclaved samples were subject to analyses of physico-mechanical properties, specifically the density and compressive strength.[4] Afterwards, the aerated concrete was analyzed regarding its microstructure. This related to determining its mineralogical composition using X-ray analyses and observing the samples under a SEM microscope.

Results and discussion

Physical and mechanical properties

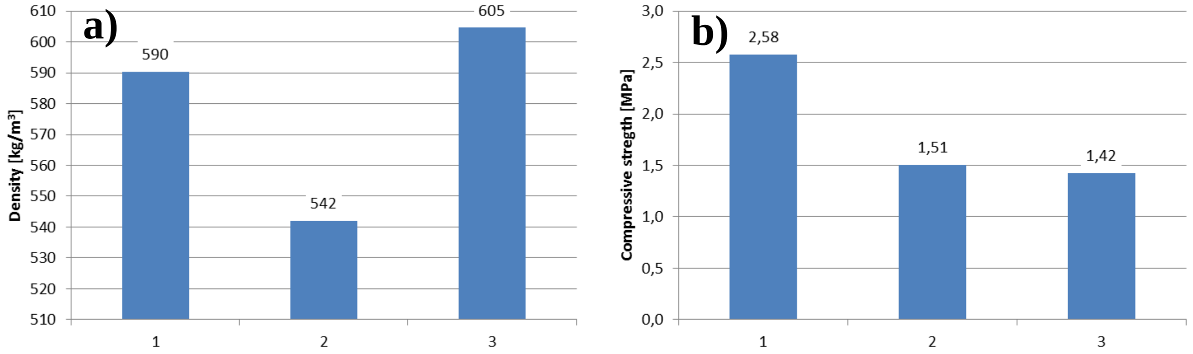

Figure 3: Density (a) and compressive strength (b) of aerated concrete samples autoclaved under different conditions

In aerated concrete, a very important factor is the ratio between density and compressive strength. It is considered that an ideal aerated concrete has the lowest possible density while maintaining the best possible mechanical properties. Under laboratory conditions, it is almost impossible to achieve such values as during a high-volume production in the plant. Density values measured by us are therefore higher than in industrially produced aerated concrete where it is possible to achieve the strength class of P2-420 (compressive strength of 2.0 MPa at a density of 420 kg.m^{-3}).

The highest strength showed aerated concrete autoclaved for the longest period of time in which we can also expect the best developed crystals of tobermorite. 14 hours of isothermal holding time during autoclaving, however, would be very uneconomical in practice. Conversely, a 6-hour isothermal holding time is realistic in practice and normally used. With this length of isothermal holding time, a better density-compressive strength ratio was achieved in aerated concrete autoclaved at a pressure of 1.0 MPa and the corresponding temperature of 180°C in a saturated water vapour.

Microstructure

The microstructure was characterized by X-ray analyses and images made under the SEM microscope. The results are shown in the following figures.

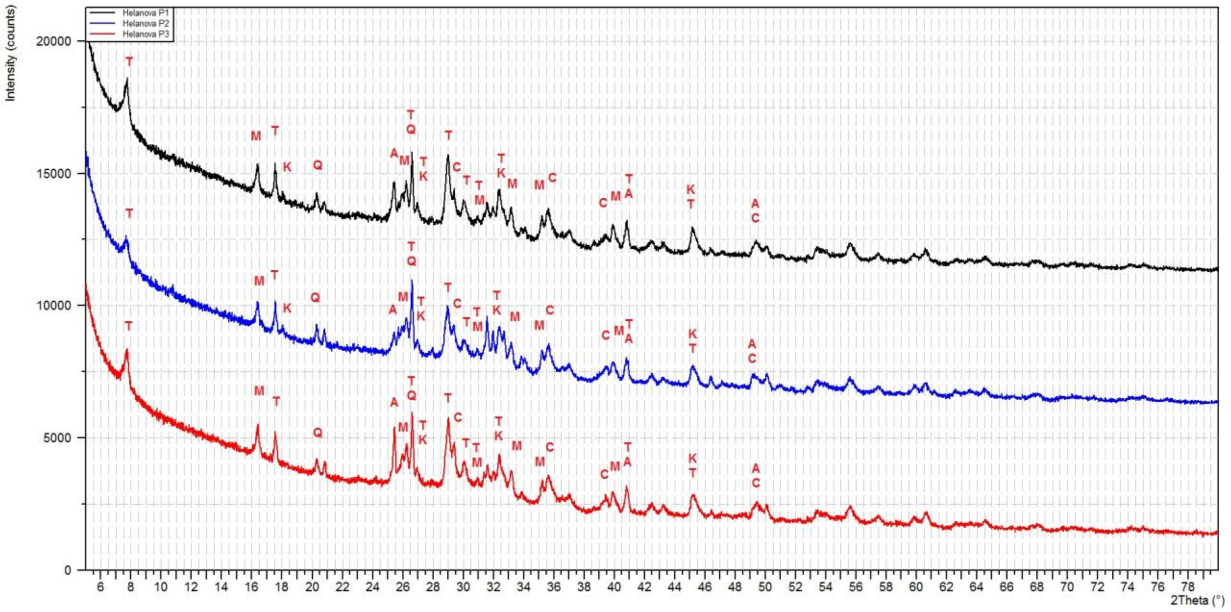

Figure 4: X-ray diffraction pattern of the tested aerated concrete samples. T – Tobermorite, M – Mullite, K – Katoite, A – Anhydrite, C – Calcite, Q – Quartz.

Mineralogical composition of all the aerated concrete samples is identical. In all autoclaving modes, the first main product of hydrothermal reaction was tobermorite while the presence of xonotlite was not observed.

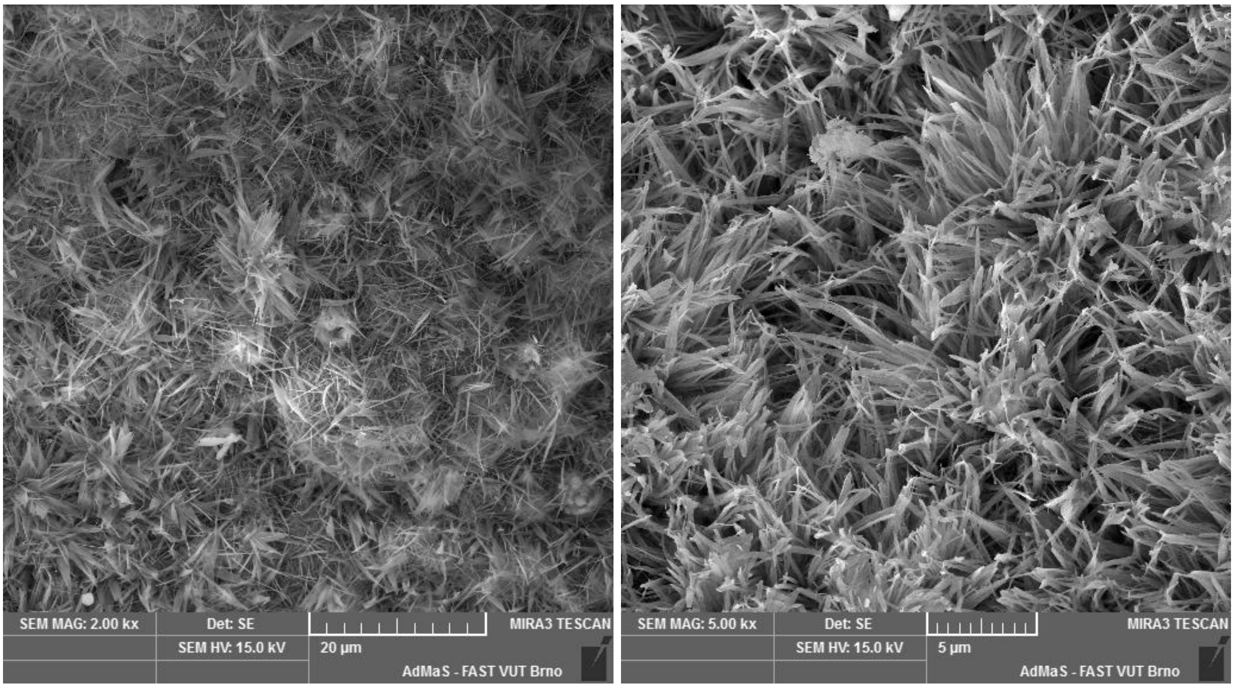

Figure 5: SEM images of aerated concrete from the 1st autoclaving mode

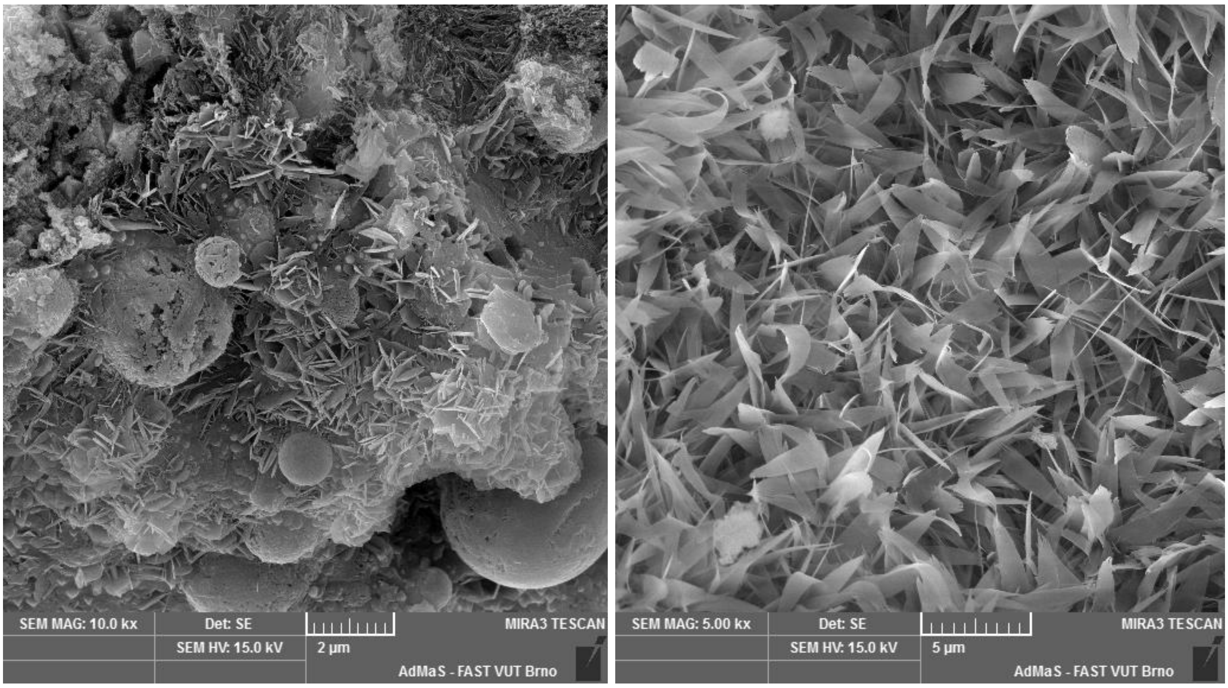

Figure 6: SEM images of aerated concrete from the 2nd autoclaving mode

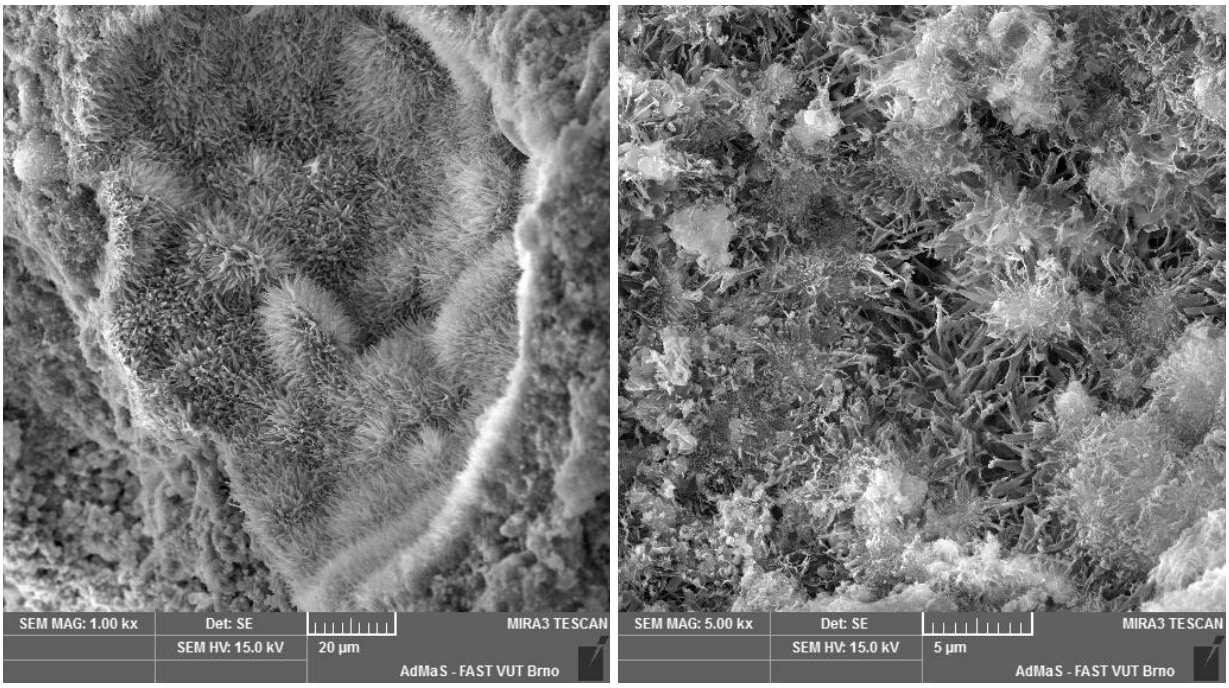

Figure 7: SEM images of aerated concrete from the 3rd autoclaving mode

SEM images of aerated concrete autoclaved under different conditions mainly show the presence of tobermorite as already proven by X-ray analyses. In a closer examination, however, it is possible to see a difference in the shape of its crystals. The first autoclaving mode produced tobermorite with narrow and long acicular crystals. Nevertheless, these crystals are slightly damaged. With reference to the compressive strength of this aerated concrete, however, it can be said that it is a very good microstructure of aerated concrete when the crystals are well intergrown.

The second autoclaving mode with the isothermal phase of 6 hours produced tobermorite crystals with wider lathy crystals. The sample also contained greater amount of unused residues of spherical grains of high-temperature fly ash. This may be one of the reasons for lower compressive strength and density of this aerated concrete. In such a case, the fly ash grains can function as lightweight filler which, on the other hand, weakens the tobermorite microstructure.

Autoclaved aerated concrete from the third autoclaving mode (6 hours, 1.2 MPa) is characterized by already considerably degraded tobermorite crystals. These crystals are long and acicular, and their shape is more similar to those from the first autoclaving mode. At a lower SEM magnification, it can be concluded that tobermorite crystals are still well intergrown and are certainly the majority mineral in the microstructure of this aerated concrete.

Conclusions

Choosing the right autoclaving in the production of autoclaved aerated concrete is undoubtedly one of the basic prerequisites of a high-quality product. Longer autoclaving times and higher temperature or pressure are not always the guarantee of better microstructure and improved mechanical properties. Based on the experiment presented in this article, it can be said that it is often the opposite. Longer autoclaving times as well as higher pressure (temperature) resulted in the formation of long needle-shaped tobermorite crystals which were often damaged. Larger crystal damage was observed in samples autoclaved at higher pressure (temperature). It can therefore be concluded that the autoclaving mode should be preferably modified by extending the time rather than increasing the pressure (temperature).

Density of the samples with prolonged autoclaving or higher temperature (pressure) was high. Regarding the compressive strength, the results were not so clear; the highest values of all samples tested (2.58 MPa) were achieved in autoclaving mode 1 (14 hours, 1.0 MPa) and, conversely, the lowest values (1.42 MPa) were found in autoclaving mode 2.

Tobermorite crystals autoclaved for a common time (6 hours, 1.0 MPa) had lathy shapes with no apparent damage. However, the larger quantities of fly ash grains visible in the sample point to the fact that not all SiO_2 was used in the hydrothermal reaction and that an extension of autoclaving by about 2 – 3 hours could have a positive effect on aerated concrete properties. This finding will be a starting point in our further research.

Acknowledgements

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Vliv podmínek při autoklávování na výsledné vlastnosti pórobetonu

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Souhrn

Pórobeton je jedním z mála stavebních materiálů, na jehož výrobu je možné využít až 70 % vedlejších energetických produktů. Mezi tyto VEP patří popílky z vysokoteplotního i fluidního spalování uhlí a energosádrovec. Kromě surovinového složení je však jedním ze základních předpokladů pro výrobu pórobetonu s dobrými fyzikálně mechanickými vlastnostmi i správná volba autoklávovacího režimu. Jedná se především o délku fáze izotermického ohřevu a samozřejmě vhodnou volbu teploty a s ní souvisejícího tlaku v autoklávu. Tento článek hodnotí mikrostrukturu a fyzikálně mechanické vlastnosti pórobetonu autoklávovaného při třech různých režimech. Zvláštní pozornost je věnována tobermoritu, jakožto majoritnímu minerálu pórobetonu, především pak tvaru a kvalitě jeho krystalů.

***Klíčová slova:** Tobermorit, popílek, pórobeton, kalciumhydrosilikáty, mikrostruktura.*

Lightweight polymer-cement based composite for extreme temperatures

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Abstract

The article presents research aimed at studying the effect of blended matrix on the properties and microstructure of composite materials containing sintered fly ash aggregate and designed for extreme temperature conditions. To improve the temperature resistance, the binder was partially replaced with blast-furnace slag and microsilica was added. Specimens were tested and analyzed after 28 days in combination with a thermal load up to 1000°C. Based on the results achieved, it has been found that the best variant seems to be a dose of microsilica up to 8% which also very favourably affects the resistance to extreme thermal loads.

Keywords: *Sintering, fly ash, filler, composite material, admixture, temperature resistance.*

Introduction

The fact that resistance of common cement composite materials is considerably limited is directly related to all used components – binders, aggregates, admixtures etc. With growing temperature water leaks as first – 100°C. The leak of free and physically bound water is terminated at 374°C, when water presence is not possible under common conditions. At temperatures around 400°C portlandite disintegrates which with complete disintegration to 800°C. Together with CSH gels portlandite belongs to dominant components of cement matrix. With respect to silica presence in the matrix and aggregates as well the temperature of 573°C can be assessed as one of the critical ones. At this temperature silica modification conversion occurs which is accompanied by considerable volume changes. For temperature 600°C is characteristic the second phase of CSH gel disintegration during which β-C_2S may originate. Also calcite contained either in matrix or in the aggregates starts to disintegrate at temperatures around 700°C. At 800°C ceramic bonds may originate which substitute hydraulic bonds. Over 1000°C it is possible to identify sulphate crystalline phases – silicocarnotite or yeelimite eventually. Further it is possible to record mayenite, larnite and brownmillerite. Wollastonite than may occur within 1100°C to 1200°C. On disintegration of the all mentioned components mainly the gases – H_2O, CO_2, and eventually SO_3 generally escape. Also residual products from disassociation reactions may mean a problem. For instance free lime which is able at contact with water (real situation of fire extinction) to react with formation of $Ca(OH)_2$. By this hydrating reaction volume grows and internal stress occurs in already degraded structure of the cement composite. Generally chemical bonds are broken, porosity grows and thus composite structure is degraded in the cement matrix, aggregates or their interface.

Considering physical and mechanical properties it is evident that at reaching of temperature 1000°C a considerable degradation of cement matrix occurs together with breaks of aggregate-matrix consistency. In terms of construction materials the strength is the decisive parameter. In case of mortars and concretes only compressive strength is considered. At temperatures 600°C to 1000°C straight reduction within 60% to 100% occurs with common composition composites (lime, feldspar or silica aggregates, Portland cement etc.). Therefore fire effects may be fatal - collapse of the construction. This is also intensified by presence of longitudinal steel reinforcement providing tensile strength at bend. With growing temperatures a deformation (prolongation) of the reinforcement occurs and then even results in loss of consistency with cement matrix.

The possibility of mortar and cement resistance growth towards actuation of extreme temperatures has been studied by many scientists. It was found that attention shall be paid to binders, aggregates and scattered reinforcement as well. Polymeric scattered reinforcement play an important role at escaping of gaseous phases from cement composites and possibly also at expansion of some components. At equal distribution and optimal batch (approx. to 5%) of polymeric fibres the thermal resistance of cement composites is considerably increased. According to polymer type the fibres completely disintegrate within approx. 350°C. According to [7] the best results were obtained at modification of cement matrix with blast-furnace slag. Ash can be used in amounts of 20% to 30% of the cement weight. However significant improvement of cement matrix is noticeable only to 600°C. Positive findings in connection to cement composite parameter degradation due to high temperatures were found at cement substitution by volcanic ash within 20% [8]. In the publication [5] the authors present their research dealing with mixing binder. As cement substitution with 25% the ash, microslica and their combinations were tested.

Maximum exposition temperature was 800°C. Upon obtained results micro silica in 10% amount was selected as optimal substitution component. The research presented in [4] is focused on study of cement ash substitution influence in combination with silica nanoparticles. In case of formulas with content of both tested components strengths comparable with specimens not stressed with high temperatures were obtained with test samples at temperature of 700°C. XRD analysis results refer to formation of new bonds in the matrix at 700°C. Research of mortars with aluminium oxide nanoparticle content is stated in [3]. More significant improvement in compressive strength can be seen only within temperatures 400°C to 600°C. At 1000°C the influence of aluminium oxide nanoparticles is insignificant. Positive influence of titan nanoparticles at temperatures even to 600°C was shown in [10].

Compressive strength improvement by 14% was verified in comparison with reference specimens. Influence of aggregate types on cement composite parameters exposed to high temperature actuation was analyzed for instance in [6]. Here the scientists studied the possibility of lightweight aggregates application - perlite, vermiculite and pyrofilite. The best stability considering stress by high temperatures showed mortars with content of expanded perlite. Development and research of fire resistant mortars to 900°C is presented in [9]. Possibility of application of the blast-furnace slag as binder substitution even to 80% was also tested. Pumice-stone was used as aggregate. Mortars with 40% content of blast-furnace slag were evaluated as the best ones considering the findings. Compressive strength of these mortars after having been exposed to 900°C reached residual compressive strength 44 % at gradual cooling. At quick cooling (with water) the mortar showed residual compressive strength 40 %.

Experimental part

On proposing of developed material compositions all findings and knowledge gained from study of foreign special literature were considered. Blended cement – 65 % of CEM I 42,5 and 35 % blast-furnace slag was used as a binder. Aggregates to cement volume ratio was 3.7:1. In order to obtain the required workability, consistency with base and adhesion of the mixture in fresh condition a polymeric admixture in amount of 3% (related to cement weight) was applied. The water-cement ratio was always modified to provide a 160 mm diffusion of the mixture. This value characterizes a mortar with good workability for manual application on repaired construction. At selection of the aggregates the attention was paid to lightweight aggregates – ash agloporite.

These aggregates formed the only one aggregate component with fraction 0 to 4 mm. For improvement of parameters at high temperatures polymeric fibres were used. Because it is a material intended for thicker repairs fibres of larger sizes than usual for this type of material were tested. Polyolefin fibrillated fibres were added in the mortars in amounts of 5 $kg.m^{-3}$. To provide sufficient parameters according to [9] a very fine-grained active admixture based on amorphous SiO_2 was used. It was dosed in 5 to 10 % (related to cement weight). It was not a binder substitution.

Test specimens with dimensions 40 × 40 × 160 mm were stored 28 days and treated in accordance with [12]. Subsequently they were loaded with temperatures 200°C, 400°C, 600°C, 800°C and 1000°C.

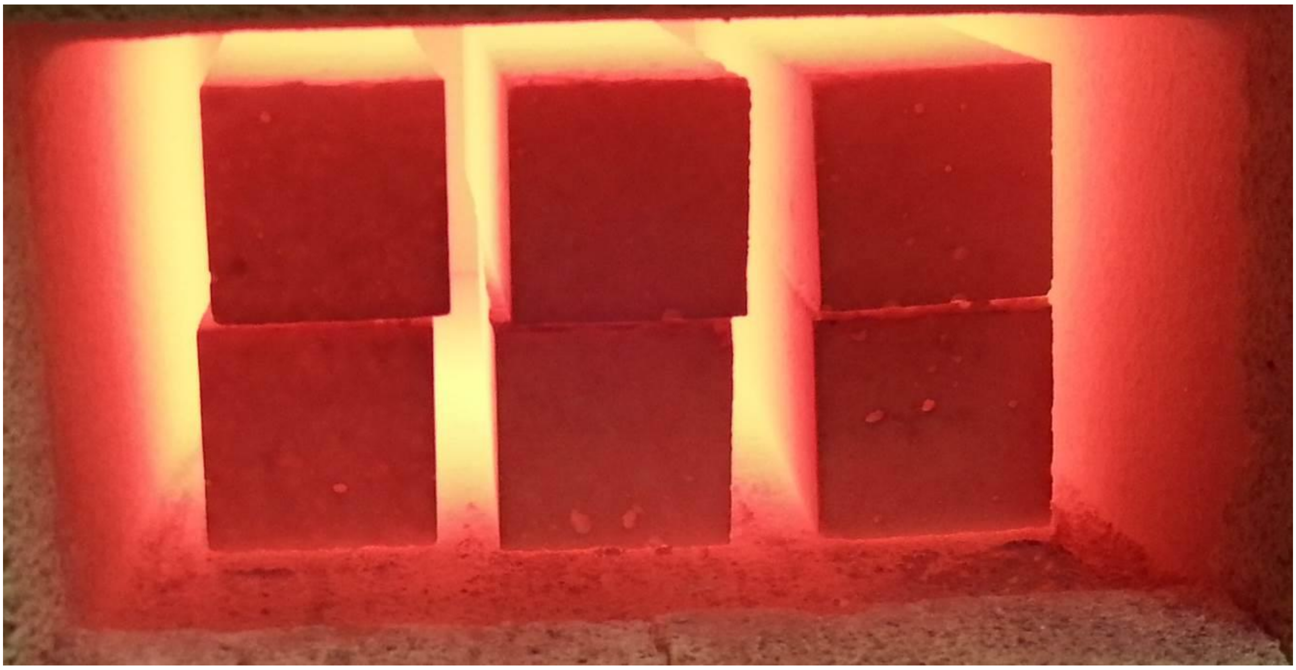

Figure 1: Test specimen during the heating in furnace – temperature 1000 °C

Reference specimens were not thermally exposed. Temperature curve course is defined in [13]. Cooling was carried out gradually in the furnace, i.e. speed approx. 1°C.min^{-1}. In accordance with relevant standards – [11], [12] and [14] the basic physical and mechanical parameters were tested and their changes (density, compressive strength and tensile strength at bend). From the selected specimens samples were taken for evaluation of microstructure.

Results and disscussion

The following charts (see Figs. 2 to 4) show comparison of results for setting of monitored material characteristics and their percentage changes at samples exposures to high temperature ambient. All the formulas contain agloporite and different micro silica doses (for instance CAS7 means formula with 7.5% micro silica content).

Bulk density courses are with growing temperatures relatively stabile for particular formulas. At 1000°C a density decrease occurs within 19% to 21%. The steepest decrease of values is evident within 22°C to 400°C. Microsilica influence on density is insignificant. Instead bulk density changes the weight changes were determined (left axe of graph – see Fig. 1). Weight decreases to approx. 20 % after 1000 °C exposure. The sharp decrease in weight within the range up to 400°C is most likely related to the leakage of moisture contained in the porous structure of the aggregate used. Prior to thermal loads in furnaces, the samples were not dried up. Furthermore, the drop is negligible in the temperature range of 400°C to 1000°C.

With respect of compressive strength the formula CAS7 of micro silica can be evaluated as the best. Very interesting strength value course is seen with samples exposed to 400°C and 600°C. Residual strengths of samples exposed to 1000°C reach approx. 17% in case of reference formula and also formulas with 5% micro silica admixture. Materials containing 7.5% to 10% of admixture retain approximately 24% compressive strength. It is therefore obvious that the most significant difference is between samples containing 5% and 7.5% micro silica. Compressive strength of CAS7 formula after loading with temperature 1000°C was set to approx. 7.9 N.mm^{-2}. When comparing a trend of the decrease in weights and a compressive strengths (see Fig. 2 and 3), it is clear that the courses of curves are different. It is therefore evident that only a minimal weight loss occurs from the exposure time while strength characteristics continue to decline. This may result, for example, from a predominant effect of different expansions of the filler and matrix.

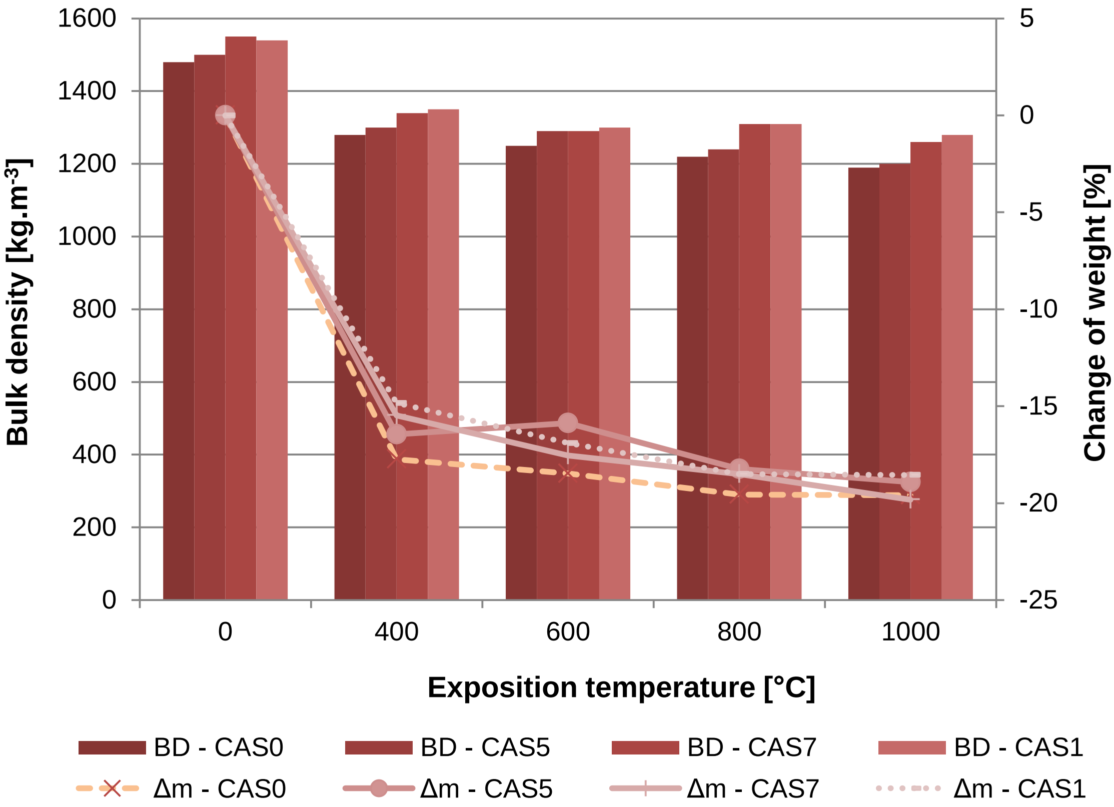

Figure 2: Comparison of bulk density (BD – bulk density, Δm – change of weight)

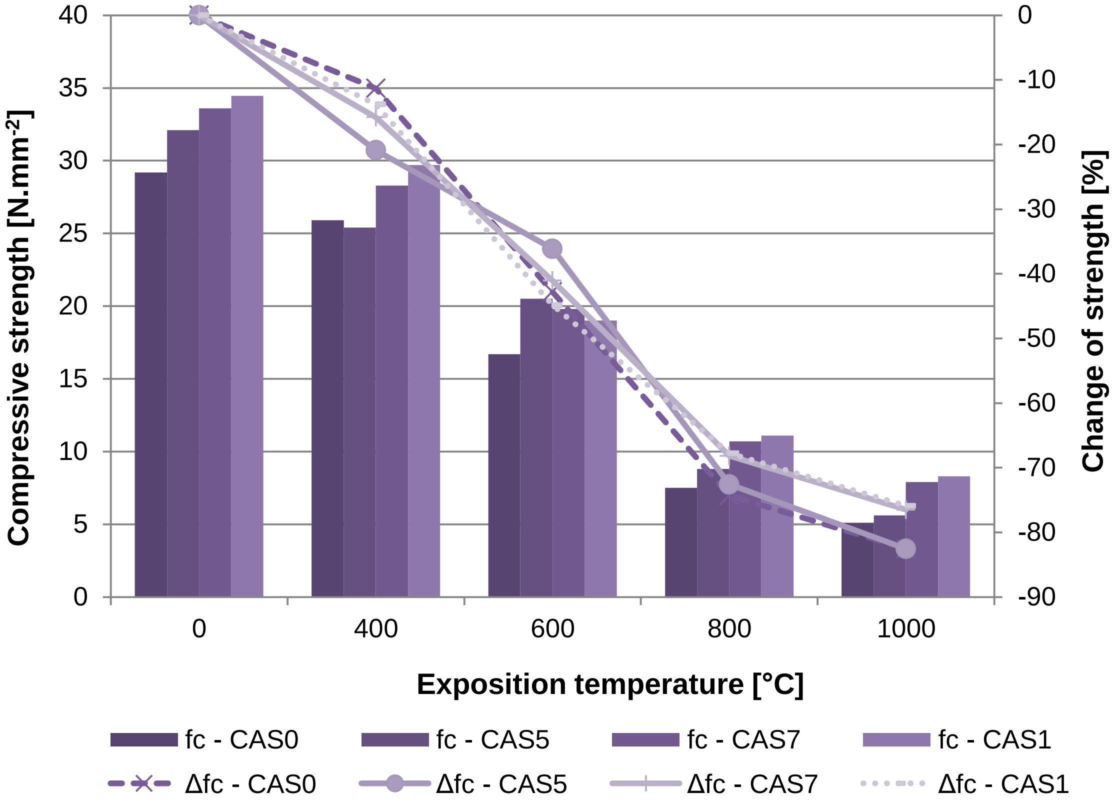

Figure 3: Comparison of compressive strength (fc – compressive strength, Δfc – change of compressive strength)

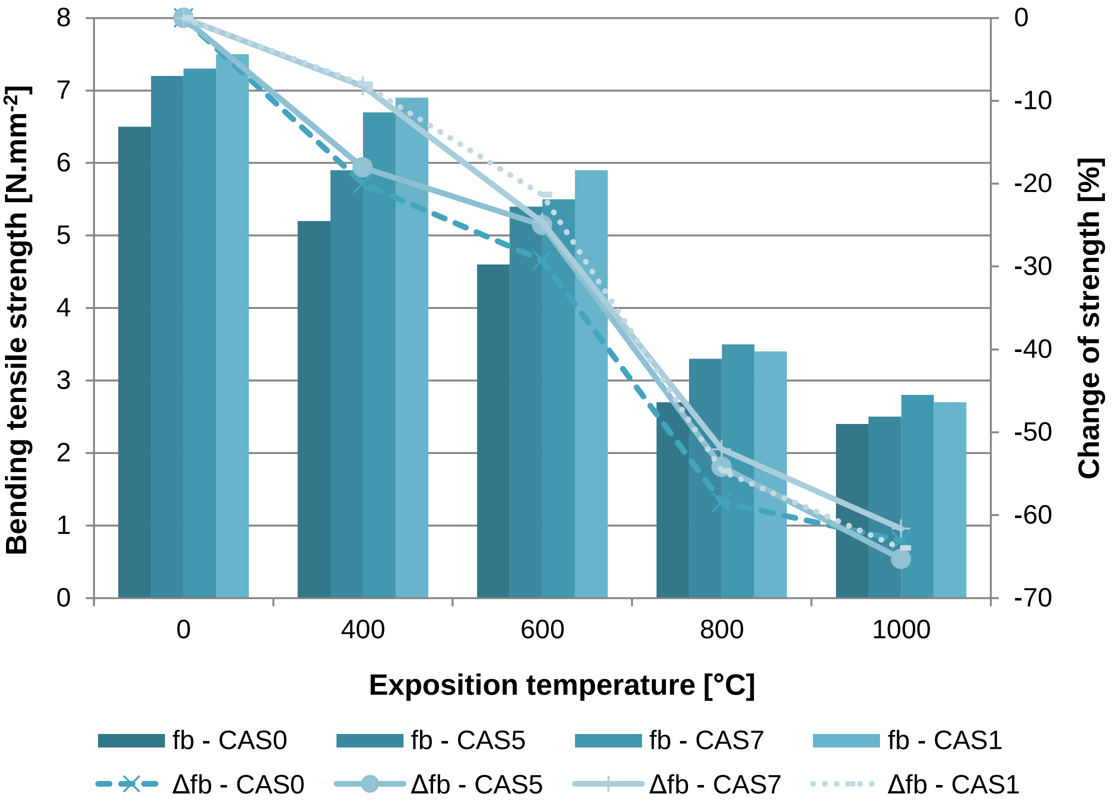

Figure 4: Comparison of bending tensile strength (fb – bending tensile strength, Δfb – change of bending tensile strength)

Various courses of the curves of changes in compressive strength and bending tensile strength indicate a significant effect of microsilica on the temperature resistance exactly in terms of bending strength. After exposure at 1000°C, residual strengths achieve about 34% up to 38 %. Again the 7.5% micro silica addition can be assessed as the most effective. For both the obtained strengths and thermal resistance of mortars as well. The following figures (see Fig 5) show structure of selected formulas with 10 % micro silica content and exposed to 1000°C.

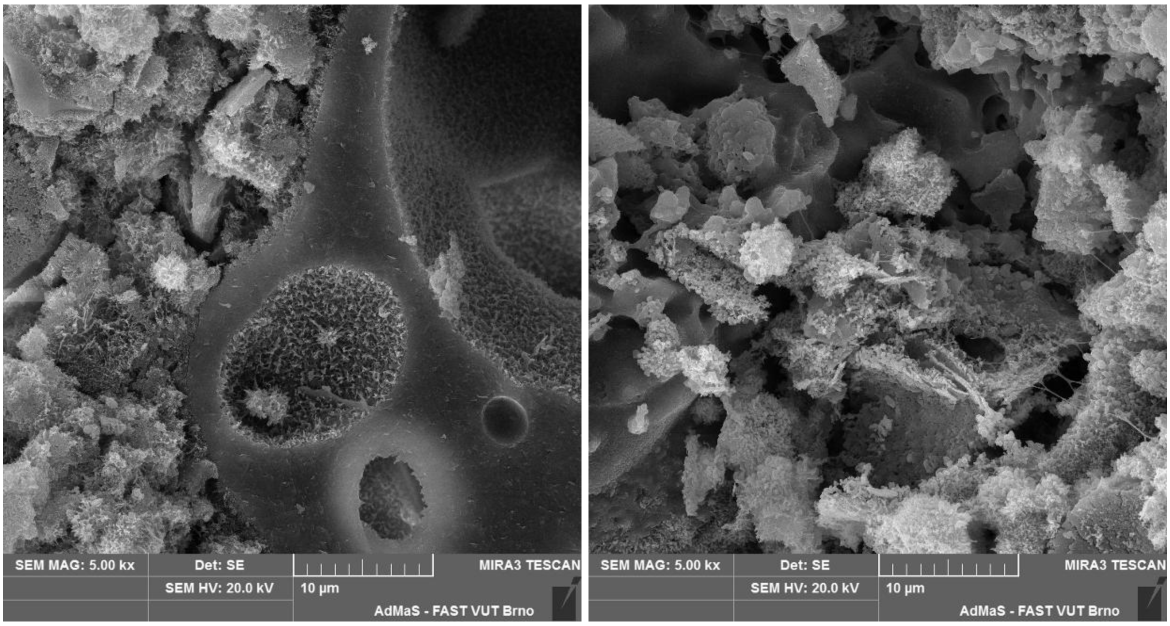

Figure 5: Microstructure CAS1, exposure temperature 600°C (left) and 1000 °C (right), magnification 5000×

Analyses of microstructure confirmed a substantial degradation of the polymer-cement structure when the bodies were exposed to environments with a temperature of 1000°C. We mainly observed an increased porosity which is related to the decomposition of hydration products. Using XRD, the microstructure was assessed in terms of quantity and partly also in terms of quality (according to the intensity of peaks). The influence of increased temperature caused the reduction of diffraction lines of portlandite.

Differences in morphology between formulas containing different doses of microsilica were recorded only to a slight extent and, therefore, they seem to be irrelevant. It was possible to observe only differences in the background that represents the amorphous phase which can be CSH gels or unreacted grains of microsilica. Increasing doses of microsilica were associated with increasing background of diffraction curves. However, these differences between individual formulas decreased with increasing temperatures. In studying the microstructure, the attention was further paid to the matrix - filler interface. Here, we observed only sporadic imperfections that were manifested by cracks.

Conclusions

Within the research presented in this article, it was found that the blended silicate matrix (containing cement, blast furnace slag and microsillica) in combination with aggregate based on sintered fly ash are suitable components for composite materials intended for extreme thermal loads. The optimal dose of microsillica is up to 8 %, higher amount is not too effective. In the future follow-up research, it would be especially appropriate to verify also unfavourable climatic conditions and chemically aggressive environments, i.e. the resistance to frost, chlorides, sulfates, etc. Examining the impact of higher temperatures, namely 1200°C to 1400°C, also seems to be interesting. Tested composite materials based on the polymer-cement matrix could then find applications such as repair materials for structures affected by shock exposures to extreme temperatures where their reoccurrence can be assumed (a fire with temperatures up to 1400°C). If the developed materials were considered as repair mortars, it would be necessary to verify also their adhesive properties in both fresh and hardened state, including the effect of high temperatures on this parameter.

List of symbols

BD – bulk density [$kg.m^{-3}$]
m – weight [kg]
fc – compressive strength [$N.mm^{-2}$]
fb – tensile bending strength [$N.mm^{-2}$]
Δ – change of parameters
CAS0 – formula without microsilica
CAS5 – formula containing 5 % of microsilica (related to the content of binder, i.e. cement and slag)
CAS7 – formula containing 7.5 % of microsilica (related to the content of binder, i.e. cement and slag)
CAS1 – formula containing 10 % of microsilica (related to the content of binder, i.e. cement and slag)
XRD – x-ray diffraction analysis

Acknowledgement

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Lehký kompozit na bázi polymer-cementové matrice pro extrémní teplotní podmínky

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Souhrn

Článek prezentuje výzkum zaměřený na studium vlivu směsné matrice na vlastnosti a mikrostrukturu kompozitních materiálů obsahujících kamenivo na bázi spékaného popílku a určených do náročných teplotních podmínek. Pro zlepšení teplotní odolnosti byla část pojiva nahrazena vysokopecní struskou a dále byla přidávána mikrosilika. Zkušební tělesa byla testována a analyzována ve stáří 28 dní v kombinaci s teplotním zatížením do 1000 °C. Bylo zjištěno, že jako nejvýhodnější varianta se na základě dosažených výsledků jeví dávka mikrosiliky do 8 %, která také velmi příznivě ovlivní odolnost při extrémním teplotním zatížení.

***Klíčová slova:** Spékání, popílek, plnivo, kompozitní materiál, příměs, teplotní odolnost.*

MIP-IN: New device for combined detection of pollutants and injection of reagents

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Summary

The innovative MIP-IN device combines (1) detection of pollutants by membrane interface probe (MIP) and (2) a simultaneous correlated injection (IN) during direct push of the device using a drilling machine. The MIP-IN device is the basis for a new detection-injection technology with the main advantage of the nearly simultaneous coupling of detection of pollutants at a certain depth and injection of a suitable amount of reactive agent at that precise spot. In this way, the injected reagent is more targeted towards the real location of the pollution with reduced remediation time and cost.

Key words: *remediation, contaminated site, ISCO, direct push, injection, investigation*

Introduction

In-situ remediation technologies are considered more sustainable and cost-efficient compared to many ex-situ technologies like pump and treat (US EPA, 2001). A crucial aspect for the success of in-situ remediation technologies is the contact between reagents and pollutants. One of the difficulties is often the lack of knowledge about the exact location of the contaminants in the subsurface. This implies that reagents may be injected in areas where no pollution is present, while other parts with significant contaminant concentrations are not treated (Bastiaens et. al., 2013).

The MIP-IN concept was developed within the FP7 UPSOIL project (EU GA 226956). The innovative MIP-IN device combines (1) detection of pollutants by membrane interface probe (MIP) and (2) a simultaneous correlated injection (IN) during direct push of the device using a drilling machine (Figure 1). Thus, the injected reagent is more targeted towards the real location of the pollution. The first tests of MIP-IN concept were performed within the FP7 UPSOIL project. Results proved that the patented MIP-IN device (Bastiaens & Stubdrup, 2012) has potential for simultaneous detection of contaminants and injection of reagents for contaminants removal (Uyttebroek et al., 2012).

Since the end 2013, the MIP-IN device is being further developed and tested within the MIP-IN EUROSTARS-project (E!8246 MIP-IN) where VITO (Belgium), Ejlskov (Denmark), Dekonta (Czech Republic) and Ecorem/ABO (Belgium) cooperated. The main goals of the MIP-IN EUROSTARS project are to (1) improve the MIP-IN device, (2) validate the MIP-IN device in relevant environments and define boundary conditions, and (3) develop an innovative MIP-IN based remediation strategy closely linked with site investigation, based on MIP data interpretation.

Materials and methods

The MIP-IN device consists of several basic parts, schematically represented in Figure 1. It consists of a MIP probe (2) that is driven into the contaminated geological environment using a drilling machine (1), a control unit (6), a gas chromatograph with PID, FID, and XSD detectors (7), and a PC (5) for displaying the measured data in real time (8) (Figure 1). The MIP probe is heated for the whole penetration time, and the mobilised contaminants enter the system, on the principle of diffusion through a special semi-permeable membrane located at the lower end of the probe (12). Thanks to this arrangement, the probe may be used both in saturated and unsaturated zones of the geological environment. After entering the system, the mobilised contaminants are transported by carrier gas into the control unit (6) by means of a tube (capillary) system found inside the penetration set of tubes (3).

Outputs of the MIP probe are graphs depicting signal intensities of the individual detectors (PID, FID, and XSD), in the context of the vertical profile of the geological environment. The following relation is valid: the higher the signal value, the higher amount of mobilised contaminants entered the carrier system. The signal intensity is given, usually, in mV or V units. Further, a hose is installed inside the penetration set of tubes of the drilling machine, into which reagent solution is pumped from a storage tank (10) by means of a high-pressure pump (9). At the end of the drilling set of tubes, the hose enters injection jets (11), through which the reagent solution is injected into the geological environment. The operator of the device monitors the measured signal of the MIP probe (8), and in the case that pollution is detected, predetermined amount of reagent is injected into the geological environment by means of the pump (9).

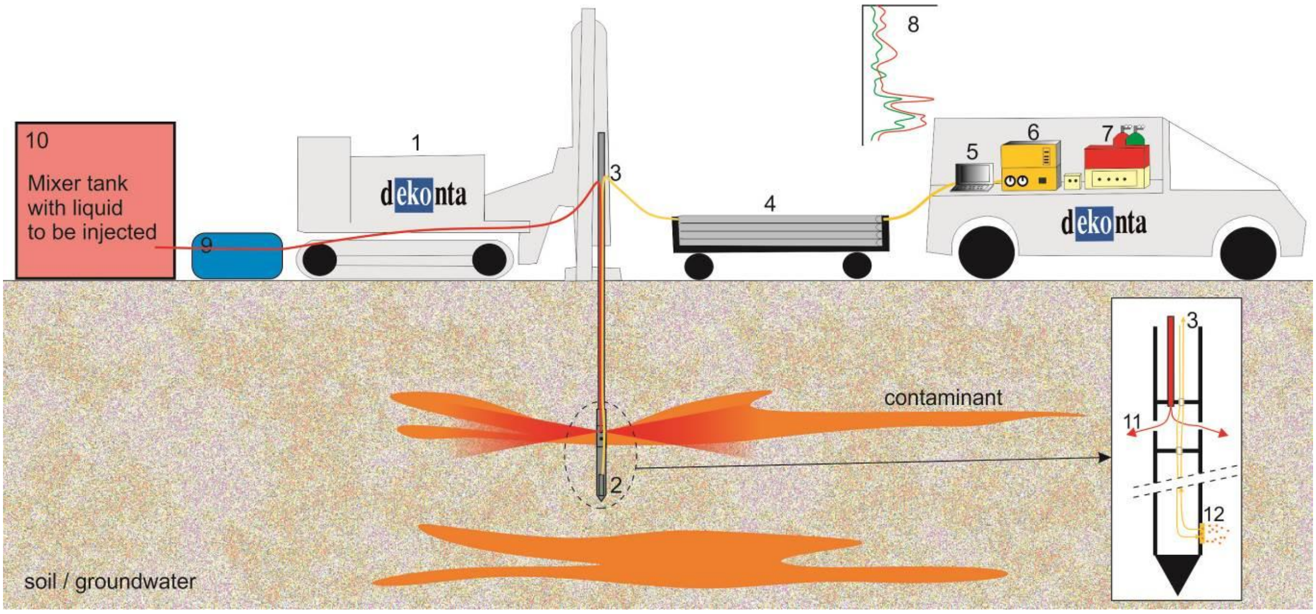

Figure 1: Schematic representation of the MIP-In detection-injection device, 1) drilling machine, 2) MIP-IN probe, 3) tubes with the carrier gas and MIP cables (so-called trunkline), 4) drilling rods holder, 5) PC for MIP data processing, 6) MIP control unit, 7) gas chromatograph with 3 detectors and gas cylinders (N_2, H_2), 8) measured signals of MIP probe, 9) high pressure injecting pump, 10) mixer tank with the liquid remediation reagent, 11) reagent injected via jets, 12) contamination entering through the semipermeable membrane

Within the framework of the MIP-IN project (E!8246), pilot tests of the new remediation technology were carried out in real conditions of contaminated sites. In three sites (Table 1), with different geological conditions and different pollution types, the following parameters and qualities were verified:

- Pollution type, namely contamination detectability by means of the MIP probe;
- Technical execution of the injection (injection pressure; diameter, number, and geometry of the injection jets;
- Properties of the reagents that may be injected;
- Maximum depth that may be reached;
- Injection reach in different geological environments;
- Possibility of automation of the reagent injection process on the basis of the MIP probe signal;
- On-site 3D visualisation of the measured data as a tool for remediation works control.

Table 1: Characteristic of locations for MIP-IN pilot tests

Country, site	Geological conditions	Type of contamination	Injected liquid reagent
Czech Republic, Velká Hleďsebe	Compact clays	Chlorinated hydrocarbons	nZVI
Denmark, Copenhagen	Sandy and clay sediments	Oil products	Bio activated active carbon suspension (BOS)
Belgium, Antwerp	Sandy soil containing high amount of shells	Trichloroethylene (TCE)	EHC-L®, mZVI+guar gum

In order to evaluate the radius of reagent injection by means of the MIP-IN technology, drill cores were taken at various distances from the place of injection, and, subsequently, the presence of the injected reagent therein was analysed.

Further, another pilot site was selected in Ghent in Belgium, where a new dynamic approach was tested for carrying out investigation and remediation of the contaminated sites. It consists in contamination detection by means of the MIP-IN device, its exact localisation directly on-site (both concerning area and depth), and control of further procedure of remediation and investigation works, through computer visualisation of the measured data. Whereas the standard approach to remediation of a contaminated site includes a number of steps that must follow each other often with certain time delay (for example, waiting for results of laboratory analyses), the new dynamic approach using the MIP-IN device leads to more exact localisation of the pollutants in the geological environment, enabling targeting of remediation works on places that are actually contaminated, and to time optimisation of the remediation procedure. This results also in economic optimisation of the remediation works.

Results and discussion

In the end of 2014, one of the four pilot tests of the MIP-IN technology was carried out in a contaminated site in Velká Hleďsebe in the Czech Republic. 4 reagent injections were carried out in connection with detection of volatile organic compounds by means of the MIP probe.

Figure 2 depicts situation of the area of interest in the pilot site in Velká Hleďsebe. It shows hydrogeological wells that are present in the site and used for pilot test monitoring (CV3, HJ25, SV18). Further, it shows MIP probes carried out in March 2014 within the framework of pilot site selection and its pre-investigation (MIP1, MIP3, MIP4, and MIP5). Within the framework of the pilot test in November 2014, in total four nZVI injections by means of the MIP-IN device were carried out (MIP-IN1, MIP-IN2, MIP-IN3, and MIP-IN4).

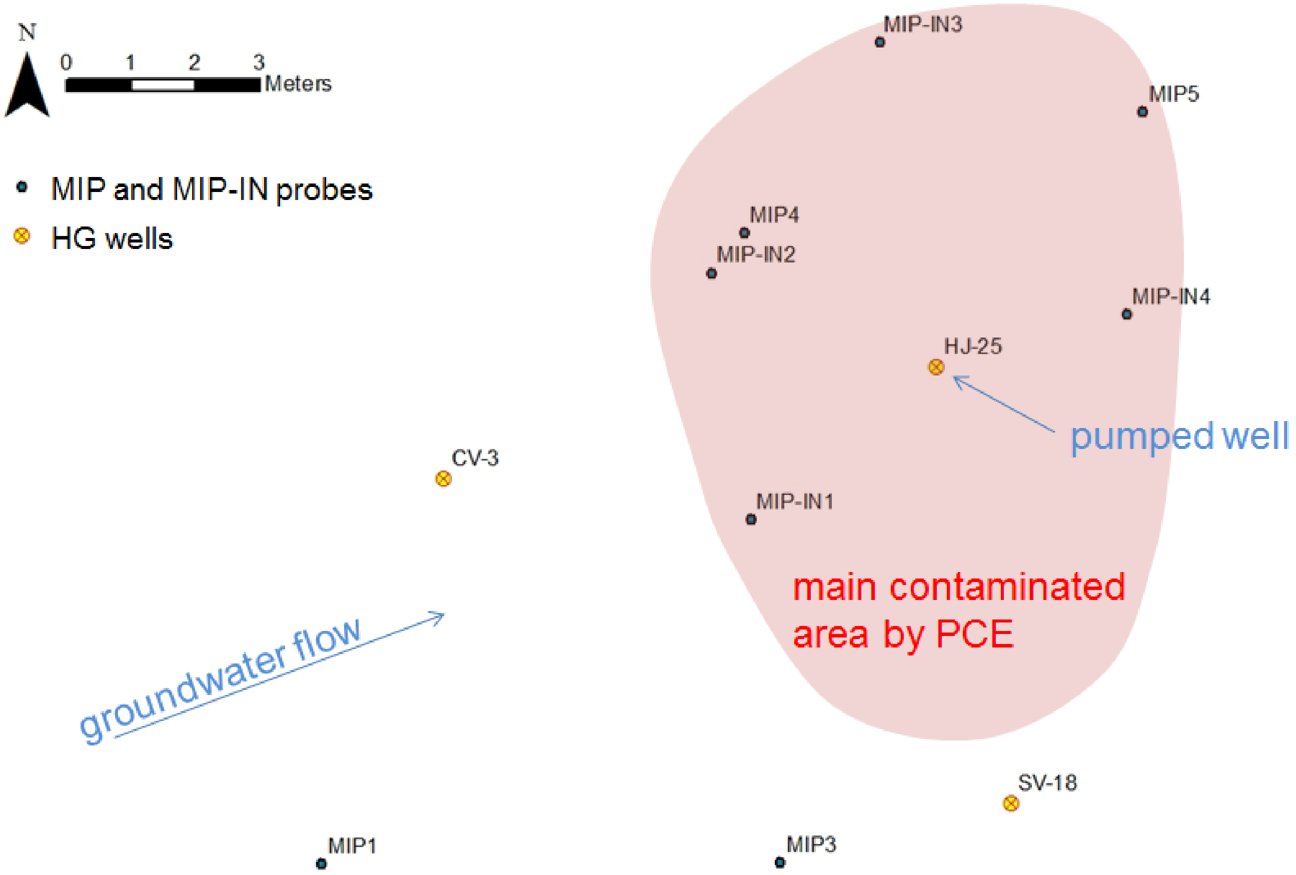

Figure 2: Pilot site for MIP-IN testing in the Czech Republic
MIP1, MIP3, MIP4 and MIP5 – pre-investigation via MIP probe
MIP-IN1, MIP-IN2, MIP-IN3 and MIP-IN4 injections within the pilot tests
CV3, HJ-25 and SV18 – monitoring hydrogeological wells

According to the results of the previous laboratory tests, nano zero valent iron (nZVI) NANOFER 25S, manufactured by NANO IRON, s.r.o., was used as the reagent. nZVI in concentration of 10 g/L, or, optionally, 20 g/L, was prepared directly on site in mixed storage tanks, using suspension supplied by the manufacturer, and water.

The reaction zone with chlorinated hydrocarbon contamination presence was found between 3 and 10 m below ground level. In the case of pollution detection, nZVI injection was carried out in the amount of ca 50 L each 0.5 m in the vertical depth profile. In the places where MIP probe signal indicated higher concentrations of chlorinated hydrocarbons (response higher than 1 V), double, or, optionally, higher nZVI amount was injected.

Within the framework of the MIP-IN pilot tests, there were injected in total 650 L of nZVI having the concentration of 10 g/L, and 1200 L of nZVI having the concentration of 20 g/L. Figure 3 represents record of the MIP signal of MIP-IN1, showing curves of the individual MIP probe detectors (PID, FID, and XSD), and places where nZVI was injected and in what amounts.

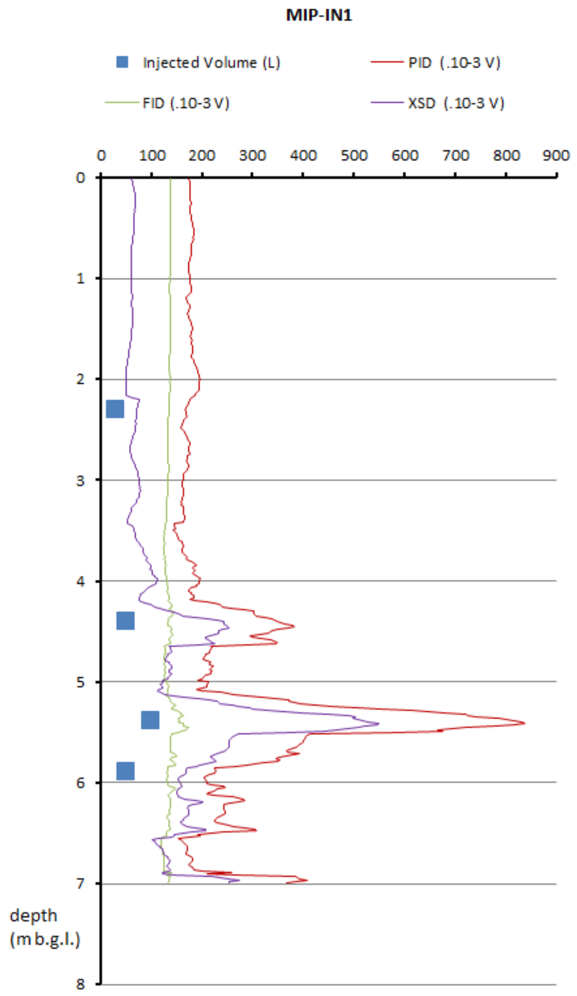

Figure 3: MIP-IN1 probe record including records of injected reagent volume

Within the framework of monitoring of pilot operation tests, regular monitoring of underground water had been planned in wells HJ-25 and SV-18, before pilot test start and after pilot test termination, that was finished in June 2015. The monitoring focused, in particular, on concentrations of chlorinated ethenes, and chemical-physical parameters (ORP, pH, temperature, and conductivity). Figure 4 shows curve of concentrations of chlorinated ethenes, as their sum. The following processes may be seen:

- Decrease of amounts of chlorinated ethenes in the period of one month after nZVI injection by means of the MIP-IN device, connected, on the one hand, with direct contact of nZVI particles with the contaminated places, and start of the processes of degradation of chlorinated ethenes, and, on the other hand, also with the fact that certain amount of nZVI entered directly the monitoring wells.
- In the following period, repeated inflow of contamination into places of nZVI injection took place, due to mobilisation of contamination in low-permeable places where contamination had been fixed in the long term. This caused repeated increase of chlorinated ethenes.
- 5 months after the injection, processes of degradation of chlorinated ethenes by the present nZVI particles were started again, and gradual decrease of concentrations of chlorinated ethenes took place.

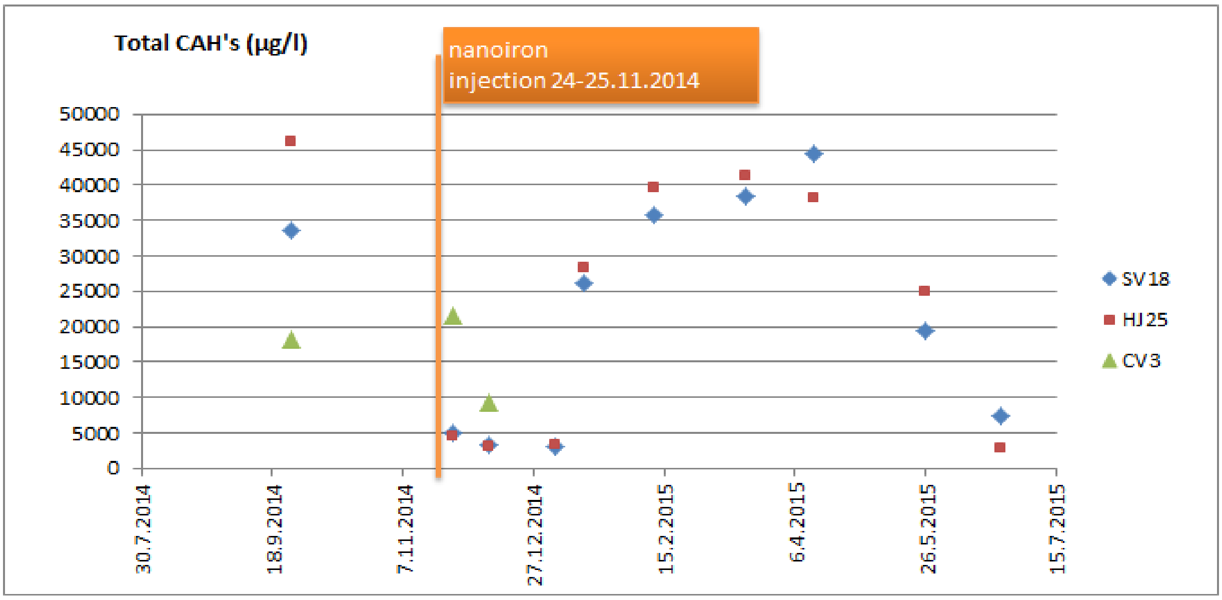

Figure 4: Development of chlorinated hydrocarbons in the period before the MIP-IN pilot test and in the following monitoring period in monitored wells.

Thanks to the pilot tests of the MIP-IN technology, it was possible to define the scope of usability of this technology in the real conditions of the contaminated sites.

Usability for various pollution types depends, on the one hand, on the possibility to detect the pollution by means of the MIP probe, with subsequent processing in the gas chromatograph, and, on the other hand, on properties of the reagent. The reagent must be able to react efficiently with the pollution in such a way to cause decrease of its concentration, and, simultaneously, its physical properties (for example, viscosity, contents and size of solid particles) must enable its pumping, and injection into the geological environment. The following Tables 3 and 4 summarise findings of all the pilot tests carried out within the framework of the MIP-IN project. It was verified that the MIP-IN device is very suitable in the case of chlorinated hydrocarbon contaminations, this being verified in sites in Belgium and in the Czech Republic. Similarly, the MIP-IN device may be used for detection and remediation in the case of BTEX and petroleum substances. However, from the point of view of detection, it is difficult to distinguish BTEX, petroleum substances, and mineral oils. They may be detected within the framework of one sum parameter by means of the PID and FID detector, forming part of the MIP probe.

From the point of view of geological conditions, it was found that depth that could be actually reached in compact, low-permeable sediments, that were present in the pilot site in the Czech Republic, was at most up to 10 m below ground level. In the sites in Belgium and Denmark, depths up to 12.5 m below ground level were successfully reached. Depth and environment type are factors that depend, in particular, on the used drilling machine, however, it must respect the fact that the drill point is formed by the MIP detector. Because of that, use in rocks is impossible.

From the point of view of physical properties of the reagents it could be stated that any pumpable substance may be injected into the geological environment. At present, high-pressure hydraulic pumps are used for the injection that are able to inject fluids under the pressure of several dozen bars. In the case of suspensions there should be ensured that sedimentation of solid particles does not take place in the storage tanks. Within the framework of the MIP-IN project, addition of guar gum into mZVI suspension was tested. Guar gum is a high-viscosity polysaccharide, enabling mZVI to stay suspended.

From the point of view of the radius of the reagent injection using the MIP-IN device, it was proved that the injection reach was 1 - 2 m from the injection place in the real conditions of the geological environment formed by sedimentary rocks, in the case of use of high-pressure hydraulic pumps (achieved pressures approximately 10 - 30 bars), in all the pilot sites. This was verified, in particular, by means of taking samples in the vicinity of the injection place, and detection of the injected reagents and/or their products in the samples.

Table 3: Contaminants detectable by MIP probe

Detectable contaminants	**Undetectable contaminants**
chlorinated hydrocarbons BTEX petroleum hydrocarbons mineral oils	free phase (LNAPL, DNAPL) metals pesticide MTBE (Methyl tert-butyl ether) poly-aromatic hydrocarbons (PAH)

Table 4: Geological condition suitable for MIP-IN application

Depth / type of sediment	**Sandy sediment**	**Loamy sediment**	**Compact clay**	**Rock**	**Gravel**
0 - 5 m	yes	yes	yes	no	no
5 – 10 m	yes	yes	yes	no	no
10 - 15 m	yes	yes	no	no	no
15 – 20 m	no	no	no	no	no

Thanks to its advantages described above, the MIP-IN device may be utilised for a new dynamic approach to investigation and remediation works in contaminated sites. Within the framework of carrying out the MIP-IN project (E!8246), a new dynamic approach to contaminated site investigation and remediation was proved. This approach is schematically depicted in Figure 5, and may be divided into several basic steps:

- The first MIP-IN application is carried out in the contamination source zone, or in its close vicinity.
- Further MIP-IN applications are carried out in the distance 4-times higher than the injection reach, in the direction opposite to underground water flow, and also in the direction of underground water flow, in order to determine boundaries of the contaminated area subject to remediation.
- In the case of each MIP-IN application, the injected amount and concentration of the reagent is determined on the basis of the height of the MIP signal in the particular depth and in the particular place of the contaminated site, but also on the basis of results of the neighbouring MIP signal in the direction opposite to underground water flow. In places where pollution is not detected, there is proceeded to further MIP-IN application without injection.
- In the next stage, the network where injections have been carried out already is made denser by further MIP-IN applications, in the distance of 2-times the radius of injection in the environment in question.

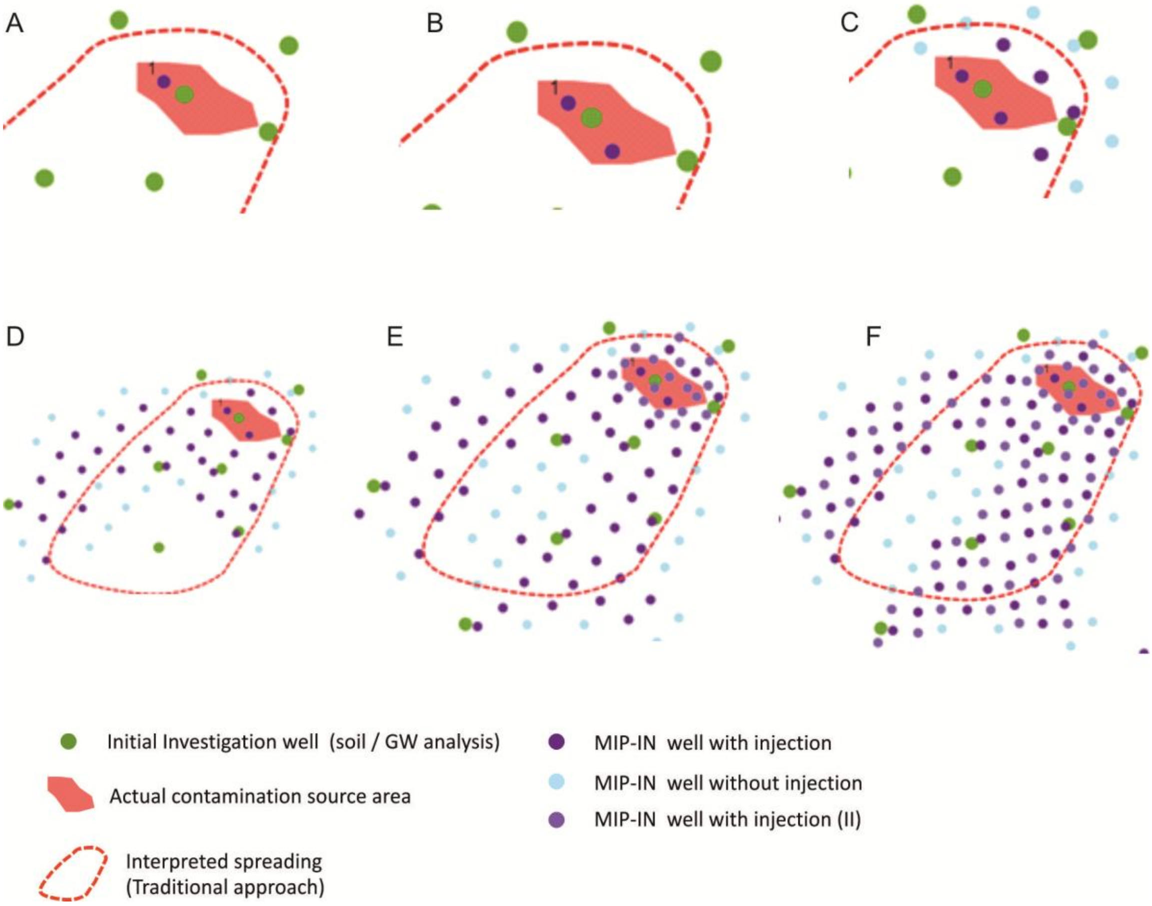

Figure 5: Dynamic site remediation and investigation approach using the MIP-IN device, from the start (A) to the end (F)

The dynamic approach to contaminated site investigation and remediation leads, in comparison with the conventional remediation approach, to lower reagent consumption, thanks to injections in the places of actual pollution presence only, this resulting, on the one hand, in savings of time and financial costs, and, on the other hand, also in more efficient reaction of the injected reagent with the contamination (Figure 6).

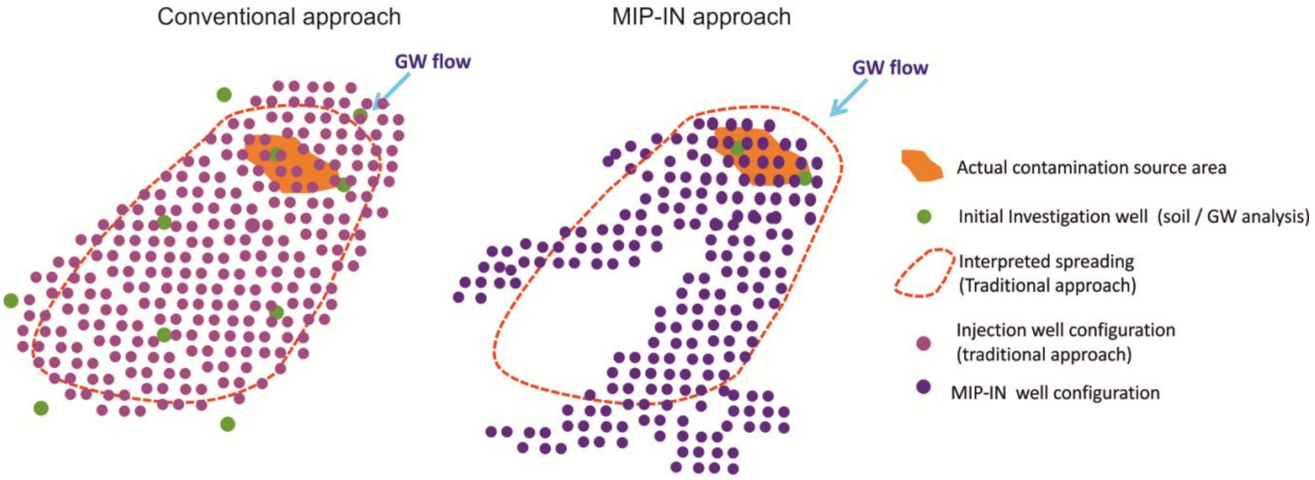

Figure 6: Conceptual model of the conventional remediation approach and MIP-IN dynamic approach

Conclusions

Thanks to the pilot tests within the framework of the Eurostars project (E!8246), there was verified that the MIP-IN device is suitable for in-situ remediation of contaminated sites showing such conditions of geological environment that enable use of penetration drilling machine. Injections of nZVI and mZVI suspensions, and of active carbon suspension, by means of the MIP-IN device were successfully tested in the places where contamination presence was detected. The depth reach of the MIP-IN device is up to 10 m in low-permeable compact sediments, and up to 15 m below ground level in other sediments.

Finally new dynamic approach to contaminated site remediation using the MIP-IN device was verified. This approach allows time and economic optimisation of the overall process of remediation works.

List of symbols

MIP	Membrane Interface Probe
nZVI	nano zero valent iron
mZVI	micro zero valent iron
TCE	trichloroethylene
FID	flame ionization detector
PID	photoionization detector
XSD	halogen specific detector
EHC-L®	emulsion of a controlled-release food-grade carbon, nutrients, and iron - liquid variant

Acknowledgement

This publication is a result of the project no. E!8246 supported by the Ministry of Education, Youth and Sports of the Czech Republic within the programme EUREKA - EUROSTARS. The Eurostars programme is a joint initiative of EUREKA and the European Community.

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MIP-IN: Zařízení pro kombinovanou detekci znečištění a injektáž reakčních činidel na kontaminovaných lokalitách

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Souhrn

Cílem projektu MIP-IN je vývoj inovativního zařízení (MIP-IN) a metodiky jeho aplikace v rámci sanací podzemní vody a zemin. Zařízení MIP-IN je in-situ sanační technologie, která kombinuje detekci znečištění v podzemní vodě a zeminách a zároveň umožňuje injektáž účinných látek pro odstranění znečištění. Hlavními cíli jsou (1) vývoj prototypu zařízení MIP-IN, (2) testování technologie MIP-IN v různých geologických, hydrogeologických a kontaminačních prostředích a (3) vyvinout nový postup průzkumných a sanačních prací s použitím technologie MIP-IN.

***Klíčová slova:** sanace, kontaminované území, ISCO, direct push, injektáž, průzkum kontaminace*

Program TRIO podpoří ověřené technologie v oblasti životního prostředí

Ministerstvo průmyslu a obchodu vyhlásilo dne 25. listopadu 2015 jednostupňovou veřejnou soutěž ve VaVaI podle zákona o podpoře výzkumu, experimentálního vývoje a inovací z veřejných prostředků v programu TRIO. Mezi podporované oblasti také patří environmentální technologie a ekoinovace. Návrhy projektů lze podávat do 15. 1. 2016.

Program TRIO je určen na podporu aplikovaného výzkumu a experimentálního vývoje se zaměřením na rozvoj potenciálu České republiky v oblasti klíčových technologií, jako jsou fotonika, mikroelektronika a nanoelektronika, nanotechnologie, průmyslové biotechnologie, pokročilé materiály a pokročilé výrobní technologie.

Uchazeči o podporu mohou být **podniky** (právnické i fyzické osoby), které řeší projekt v účinné spolupráci **s alespoň jednou výzkumnou organizací**. Dalšími účastníky projektu mohou být podniky a výzkumné organizace.

Uchazečem řešícím projekt samostatně může být pouze subjekt se statutem výzkumné organizace, musí ovšem v navrhovaném projektu vystupovat z hlediska veřejné podpory jako podnik, musí prokázat schopnost spolufinancovat řešení projektu z neveřejných zdrojů a doložit zajištění implementace výsledků do praxe. V takovém případě projekt nemusí být řešen v účinné spolupráci více subjektů.

V prioritní oblasti 3 – Prostředí pro kvalitní život je podporována také oblast Environmnetální technologie a ekoinovace. Tato část se skládá z dalších pěti podoblastí, které mají své specifické cíle VaVaI:

- Technologie, techniky a materiály přátelské k životnímu prostředí
    - Cíl: Technologie a výrobky zvyšující celkovou účinnost využití primárních zdrojů
- Biotechnologie, materiálově, energeticky a emisně efektivní technologie, výrobky a služby
    - Cíl: Získat kvalitativně nové primární produkty využitím biotechnologických metod
    - Cíl: Připravit biotechnologické postupy pro komplexní bezodpadové využití biomasy
- Minimalizace tvorby odpadů a jejich znovuvyužití
    - Cíl: Nové recyklační technologie, jejichž výstupem jsou látky srovnatelné kvalitou s výchozími surovinami
    - Cíl: Nové efektivní postupy energetického využití odpadů s minimalizací negativních dopadů na ŽP
- Odstraňování nebezpečných látek – starých škod z životního prostředí
    - Cíl: Zvýšení efektivnosti sanačních technologií a zavedení nových metod sanace
- Minimalizace rizik z chemických látek
    - Cíl: Technologie pro minimalizaci rizik POPs, toxických kovů, hormonálních disruptorů, residuí léčiv a pesticidů a dalších polutantů na zdraví člověka a živých organismů
    - Cíl: Technologie pro náhradu rizikových látek, které podléhají legislativě REACH a náhrada nebezpečných látek méně škodlivými

Každý projekt musí předpokládat dosažení alespoň jednoho z následujících výsledků, uvedených v Metodice hodnocení výsledků výzkumných organizací a hodnocení výsledků ukončených programů. Mezi výsledky tedy patří patent, poloprovoz a **ověřená technologie**.

Z pohledu „Ověřené technologie“ se jedná o obdobu poloprovozu s tím rozdílem, že novost je aplikována u výrobního postupu (technologie). Podmínkou je testování (ověření) technologie podložené protokolem o ověření a bezprostředně navazujícím uplatněním ve výrobě, které je doloženo uzavřením smluvního vztahu. Ověřenou technologií lze např. označit výsledek, který je předmětem smlouvy o uplatnění výsledku uzavřené mezi autorem výsledku (příjemcem nebo dalším účastníkem) a uživatelem výsledku. Podmínkou je i technická dokumentace výsledku.

V této souvislosti uvádíme, že České ekologické manažerské centrum, z. s. (CEMC) nabízí, jako jediné v Česku, nezávislé ověřování environmentálních technologií metodou EU ETV. K této činnosti je CEMC akreditován Českým institutem pro akreditaci. Podrobnosti je možné dohledat na *http://www.tretiruka.cz*.

Intenzita podpory celkově na projekt může dosáhnout nanejvýše 80 % celkových uznaných nákladů, a to v závislosti na velikosti podniku a kategorie činnosti. Maximální výše účelové podpory jednoho projektu v Programu je stanovena na 20 mil. Kč.

U projektů, které budou podpořeny, se předpokládá zahájení řešení v období od 1. 1. 2016 do 31. 12. 2016 a ukončení řešení nejpozději do 31. 12. 2020. Doba trvání řešení projektu je maximálně 48 měsíců.

Návrhy projektů budou hodnoceny z hlediska splnění podmínek veřejné soutěže a dále na základě následujících kritérií:

- naplnění cílů Programu,
- technicko-ekonomická úroveň a komplexnost navrhovaného řešení,
- přiměřenost časového plánu a finančních požadavků,
- uplatnění výsledků,
- aktuálnost a potřebnost projektu a vhodnost jeho podpory z veřejných prostředků,
- prokázání odborné a ekonomické způsobilosti uchazeče,
- naplnění účinné spolupráce mezi podnikem a výzkumnou organizací.

Žádost o podporu programového projektu musí být do veřejné soutěže podána na předepsaných formulářích, vytištěných jako závěrečná fáze (poslední krok) vyplňování interaktivní elektronické přihlášky, a to v jednom vyhotovení. Žádost musí být doručena do podatelny MPO, do 12 hodin 15. 1. 2016 nebo podána na poště nejpozději 15. 1. 2016 (rozhodující z hlediska dodržení stanovené soutěžní lhůty je razítko podatelny MPO nebo razítko pošty).

Hodnoticí lhůta bude trvat od 16. 1. 2016 do 31. 7. 2016. Výsledky veřejné soutěže budou zveřejněny dne 31. 7. 2016 na webu Ministerstva průmyslu a obchodu (MPO).

Veškeré podklady k vyhlášené výzvě je možné si stáhnout ZDE.

TRIO program will support environmental technology verification

The Ministry of Industry and Trade has prepared a new program to support research and development, called **TRIO**. The program will be implemented through public tenders in research, experimental development and innovation by Law no. 130 / 2002 Coll., on support for research, experimental development and innovation.

TRIO program will run from **2016 — 2021** and the total amount of support in this period amount to 3,700 miles. CZK. The first public tender will be announced in the second half of 2015 and for 2016 is to support the approved projects allocated a total of 300 mil. CZK.

The program focuses on the development potential of the Czech Republic in the field of key enabling technologies (Kets) such as photonics, micro- and nanoelectronics, nanotechnology, industrial biotechnology, advanced materials and advanced manufacturing technologies. The output of each project might be patent, pilot project or technology verification. Conditions and complete documentation of the first call for projects in TRIO program, in which applications can be submitted till **15th January 2016.■**

České ekologické manažerské centrum zve na

TÝDEN VÝZKUMU A INOVACÍ PRO PRAXI A ŽIVOTNÍ PROSTŘEDÍ 2016

(TVIP 2016)

15. – 18. 3. 2016, Hustopeče, hotel Centro a hotel Rustical

TVIP zastřešuje tři tematicky specializovaná setkání: konferenci **APROCHEM**, symposium **ODPADOVÉ FÓRUM 2016** a **nově** i konferenci **PRŮMYSLOVÁ EKOLOGIE.** Oproti minulým ročníkům **rozšiřuje svůj oborový záběr** a komplexně pokrývá **celou oblast životního prostředí.**

Naším cílem je poskytnutí prostoru k prezentaci výsledků aplikovaného výzkumu souvisejícího s ochranou životního prostředí a šetřením přírodních zdrojů směrem k podnikatelské sféře a pomoc při navazování kontaktů mezi výzkumnou sférou a praxí.

TVIP je určen:

- **k prezentaci výsledků** (především) aplikovaného **výzkumu** z celé oblasti průmyslové a komunální ekologie,
- **pro zástupce podnikatelské sféry a veřejné správy**, aby se seznámili s výzkumnými tématy a projekty s cílem eventuálního převzetí nebo rozvinutí dosažených výsledků v praxi,
- **k seznámení** představitelů **výzkumné obce s potřebami reálného „podnikového života“** a případnému **navázání spolupráce.**

Tematické oblasti:

<table>
<tr><td>APROCHEM
<i>"Připravme se na budoucnost"</i></td><td colspan="2">Nově do programu zařazujeme tematickou oblast Využití alternativní energie ve vztahu k průmyslu a oblast Plastikářský průmysl a jeho význam pro oběhové hospodářství. Na konferenci nebudou chybět tradiční tematické oblasti: řízení rizik, aplikace inovací v průmyslové praxi a při správě regiónů, měst a obcí ku prospěchu životního prostředí.</td></tr>
<tr><th>Rizika</th><th>Energie</th><th>Materiály</th></tr>
<tr><td>1) Prevence závažných havárií</td><td>1) Efektivní nakládání s energiemi</td><td>1) Inovativní postupy a technologie</td></tr>
<tr><td>2) Posuzování a řízení rizik</td><td>2) Obnovitelné zdroje energie</td><td>2) Nanomateriály</td></tr>
<tr><td>3) Odstraňování následků havárií</td><td>3) Smart Cities a chytré sítě</td><td>3) Zdravotní aspekty nanomateriálů a nanotechnologií</td></tr>
<tr><td>4) Rizika při nakládání s chemickými látkami a přípravky</td><td>4) Skladování energie, elektromobilita, CNG, LNG, vodík, palivové články</td><td>4) Plastikářský průmysl a oběhové hospodářství</td></tr>
<tr><td>5) BOZP</td><td></td><td></td></tr>
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<table>
<tr><td>ODPADOVÉ FÓRUM
<i>"Výsledky výzkumu a vývoje pro průmyslovou a komunální ekologii"</i></td><td colspan="2">11. ročník symposia rozšiřuje svůj oborový zájem z odpadového hospodářství a sanací ekologických zátěží na celou oblast průmyslové a komunální ekologie zařazením témat souvisejících s vodním hospodářstvím a emisemi škodlivých látek do ovzduší.</td></tr>
<tr><th>Odpady</th><th>Voda</th><th>Ovzduší</th></tr>
<tr><td>1. Systémové otázky odpadového hospodářství</td><td>1. Čištění průmyslových odpadních vod</td><td>1. Čištění odpadních plynů a spalin</td></tr>
<tr><td>2. Materiálové, biologické a energetické využití</td><td>2. Získávání cenných látek z odpadních vod</td><td>2. Snižování a měření emisí</td></tr>
<tr><td>3. Nebezpečné odpady, odstraňování odpadů</td><td>3. Recyklace vody</td><td>3. Doprava a lokální zdroje</td></tr>
<tr><td>4. Sanace ekologických zátěží a následků havárií</td><td>4. Nakládání s kaly, kapalné odpady</td><td>4. Kvalita ovzduší a zdravotní dopady znečištění ovzduší</td></tr>
</table>

PRŮMYSLOVÁ EKOLOGIE 2016

„Oběhové hospodářství v teorii a praxi“

1) Oběhové hospodářství
2) Posuzování životního cyklu (LCA)
3) Zelené veřejné zakázky
4) Udržitelné hospodaření s fosforem

Konference Průmyslová ekologie již popáté otevírá prostor pro výměnu zkušeností a názorů v oblasti problematiky interakcí lidské společnosti a životního prostředí. Průmyslová ekologie není zaměřena na úzký segment problematiky, ale snaží se chápat jednotlivá opatření v širších souvislostech a návaznostech. Jedním ze základních principů průmyslové ekologie je **posuzování životních cyklů** produktů, technologií či služeb.

Na každém ročníku konference bylo zvoleno několik aktuálních ústředních témat. V tomto ročníku se jedná o **zelené veřejné zakázky**, které mají potenciál stát se hnací silou zavádění ekoinovací a environmentálních postupů do praxe, a o problematiku **udržitelného hospodaření s fosforem**. Obě témata jsou nanejvýš aktuální a bude jim v rámci konference dán dostatečný prostor.

*Mediálním partnerem TVIP je **WASTE FORUM**, elektronický recenzovaný časopis pro průmyslovou a komunální ekologii (www.wasteforum.cz), který usiluje o zařazení do vědecké databáze SCOPUS a přidělení impakt-faktoru. Příspěvky, které budou prezentovány na TVIP a které doporučí redakční rada WASTE FORUM, budou v případě souhlasu autora v tomto časopisu uveřejněny.*

Klíčové termíny:

Přihlášky příspěvků	4. 1. 2016
Zaslání plných textů do sborníku	15. 2. 2016
Přihlášky účasti	15. 2. 2016
Termín konání	15. – 18. 3. 2016

Pozn.: Příspěvek je automaticky přijat, pokud do 2 týdnů není autorovi sdělen opak. Přihlašují se a vložné platí i autoři příspěvků

Přihlášky příspěvků a prezentace přednášek. Příspěvky na TVIP mohou mít povahu: plenární přednášky (obvykle zvaný přednášející, délka přednášky dohodou, optimum 30 min.), přednášky v odborné sekci (15 min. přednáška a 5 min. diskuse) a vývěsky. Vývěsky mohou být až do formátu A0 na výšku, větší rozměry je třeba konzultovat s pořadateli.

Přihlášky výhradně cestou přihlašovacího formuláře na www.tvip.cz. Ten obsahuje vedle názvu příspěvku, informací o autorech, anotace příspěvku také prostor pro vzkaz pořadatelům. Tam může přihlašující připsat např. zájem o komerční prezentaci nebo uvést sekci, kam doporučuje zařadit svůj příspěvek. Nicméně pořadatelé si vyhrazují právo konečného rozhodnutí o přijetí příspěvku, formě jeho prezentace a zařazení do konkrétní sekce.

Termín přihlášek příspěvků je 4. 1. 2016. Pokud do 2 týdnů není autorovi sdělen opak, znamená to, že příspěvek byl přijat. Po tomto uvedeném datu je možno přihlásit příspěvek buď po výzvě přípravného výboru, nebo do naplnění kapacity (sestavení konečného programu). Jednací jazyk je čeština a slovenština. Zahraniční přednášející (i posluchači) jsou vítáni, ale tlumočení nezajišťujeme. Komerční prezentace na konferenci je možná, více na www.tvip.cz.

Druhý cirkulář s upozorněním na předběžný program a připomínkou přihlášky účasti bude rozesílán v první polovině února.

Plné texty přednášek: Autory všech příspěvků, přednášek i vývěsek, žádáme o včasné předání konečného, graficky upraveného plného textu příspěvku v elektronické podobě v MS Word nejpozději do 15. 2. 2016. Požadavky na grafickou úpravu textů do sborníku jsou uvedeny na internetových stránkách TVIP, kde je rovněž i vzorová šablona pro psaní textů. Sborník TVIP je vydáván v elektronické formě na CD-ROM s označením ISBN.

Příspěvky, které budou odprezentovány a které doporučí redakční rada WASTE FORUM, budou v případě souhlasu autora v tomto elektronickém recenzovaném časopisu bezplatně uveřejněny.

Termín pro přihlášky účasti (formulář rovněž na www.tvip.cz) **je 15. 2. 2016**. Autoři příspěvků se rovněž přihlašují k účasti (a platí vložné), přednášky nejsou honorované. Za neodpřednášenou přednášku či za nevystavený poster fakturujeme poplatek 1000 Kč za zařazení příspěvku do programu a uveřejnění textu ve sborníku.

Další informace k TVIP, jako ceny vložného, ubytování, stravy, dopravní informace, možnosti firemní prezentace atd., které průběžně aktualizujeme, a později i předběžný program najdete na portálu www.tretiruka.cz v sekci TVIP (přímý přístup přes www.tvip.cz). Konkrétní dotazy a připomínky adresujte buď na níže uvedené garanty nebo na společnou adresu tvip@cemc.cz.

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The Czech Environment Management Center invites you to attend the
Week of research and innovation for practice and environment 2016 (TVIP 2016)
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TVIP contains 3 thematic rvents: **APROCHEM** conference, **WASTE FORUM 2016** symposium and the newly held conference **Industrial Ecology**. In comparison with the previous years it expands its thematic range on the whole subject of environmental issues.

Topics for APROCHEM department: Usage of alternative energy in relation to industry, Plastic industry and it role for circular economy, Risks and applications of innovations in industrial production and municipal administration.

Topics for Waste Forum: Industrial and municipal ecology, wastes/air/water.

Topics for Industrial Ecology: Circular economy, LCA, Government procurements, Sustainable use of phosphorus.

The aims of TVIP are to present the results of the applied research relevant to industrial ecology and to interconnect researchers and industrial practitioners.

WASTE FORUM is a media partner of TVIP 2016 and therefore all presented papers recommended by the Editorial Board will be published there for free.

Key deadlines:

Paper submission: 4.1.2016
Providing of the full paper: 15.2.2016
Registration conference: 15.2.2016

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