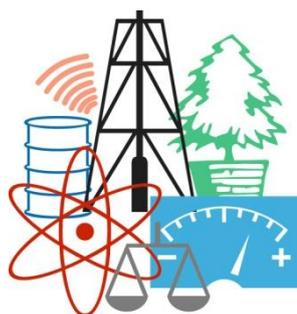


WASTE FORUM



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

RECENZOVANÝ ČASOPIS PRO VÝSLEDKY VÝZKUMU A VÝVOJE
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Úvodní slovo šéfredaktora

Vážení čtenáři,

tohoto čísla si važte, vzniklo levou rukou! Nechci tím říct, že vzniklo obzvláště lehce, nebo že jsem jeho přípravu odbyl. Naopak, vzniklo levou rukou doslova, protože den před začátkem sestavování čísla jsem nešťastně upadl a vykloubil a nalomil si pravý loket a mám jej od ramene po prsty v sádře. A jsem pochopitelně pravák!

Na rychlosti se psaní textu levou rukou v mém případě moc nepozná, jen u velkých písmen z pravé půlky klávesnice některých znaků musí při mačkání Shiftu pomoci prsty pravé ruky (nebo Caps lock). Taky

ovládání myši v levou rukou není nic moc, ale lepší se to!

Tolik na polidštění suchých textů, které na tomto místě jindy nacházíte. Říká se, že cizí neštěstí člověka potěší. Nicméně toto není žádné neštěstí, jen nepříjemná osobní i pracovní komplikace.

V říjnu úspěšně proběhl třikrát odložený Týden výzkumu a inovací pro praxi a životní prostředí, jehož podstatnou součástí bylo symposium ODPADOVÉ FÓRUM 2021/2022. Celkem bylo ve formě přednášek nebo vývěsek prezentováno 51 příspěvků, se kterými se můžete seznámit na stránkách www.tvip.cz, protože je tam vystaven jeho kompletní sborník. Jako jeho programový garant si říkám, že jsme termín konání zvolili šťastně. V době, kdy píšete tyto řádky (konec listopadu) bychom si to kvůli kovidové situaci pořádat netroufli. Zakázané to sice není, ale člověk cítí za účastníky jistou odpovědnost!

Příští ročník by se měl konat 20. – 22. 9. 2022 opět v Hustopečích. Když už jsme byli okolnostmi nuceni opustit náš tradiční jarní termín, tak jsme rozhodli pro září, abychom nekomplikovali život vysokoškolským pedagogům. Uvidíme, jak se osvědčí.

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Ondřej Procházka

Editorial

Dear readers,

This issue "sees the light of day" in the run-up to Christmas, I wish all publishing authors, collaborating reviewers and all regular and casual readers a nice and peaceful Christmas and good luck, health and success in personal and professional life.

Wondering why to publish in the WASTE FÓRUM magazine, which is in SCOPUS but does not have an impact factor? It's because:

1. The paper, if it is of good quality and passes the review, is published no later than 10 weeks after the editorial deadline;

2. The journal is Open access, which means that it can be accessed by your colleagues from all over the world and we have verified that this is indeed the case. Regularly, most downloads of all issues are from readers from the largest countries in the world, here the USA, Russia and China.

Finally, I would like to remind you that papers submitted for publication must be the author's own work and may not have been previously published elsewhere or sent to another publisher at the same time. For more, see [Publication Ethics](#) on www.WasteForum.cz.

Regards

Ondřej Procházka

Pro autory

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

Do redakce se příspěvky zasílají v kompletně zalomené podobě 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-strankach časopisu](http://www-strankach.casopisu.cz) 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 spoluautor. Je vždy dobré mít rezervu.

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Vydávání časopisu není nikým dotované. Proto, abychom příjmově pokryli náklady spojené s vydáváním časopisu, vybíráme publikační poplatek ve výši 500 Kč za každou stránku (bez DPH). V případě nepublikování příspěvku v důsledku negativního výsledku recenzního řízení je tato částka poloviční.

Uzávěrka nejbližšího čísla časopisu WASTE FORUM je 8. ledna 2022, další pak 8. dubna 2022. Příspěvky, které bez problému projdou nezávislým recenzním řízením, jsou publikovány do 10 týdnů po redakční uzávěrce!

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

Revenue to cover at least the costs associated with the issuance of the magazine, we select a publication fee **500 CZK per each new page of the paper**.

The deadline of the next issue is on January 8, 2022, more on April 8, 2022.

EU taxonomy and the principle of proportionality: Will increased costs of borrowing lead to more derogations from emission limits?

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Summary

The European Union has introduced a new taxonomy, which prohibits banking institutions from financing coal-related projects, even when they are aimed at emission abatement. This fact could significantly increase the costs of compliance with the latest emission limits for large combustion plants. Considering that plants may be granted a derogation from achieving the emission limits due to disproportionate costs, the new taxonomy could unintentionally contribute to a higher number of derogations in Europe. With the least expensive option of external funding being unavailable, facilities would have to rely on other options. This paper examines the sensitivity of costs of compliance to changes in several loan attributes such as the interest rate, the length of the payback period and the share of the funds that needs to be borrowed. Czech data were used to make a case study on a hypothetical power plant that needs to retrofit its current technology. The results show that in some cases even a slight change to the interest rate or other parameters may change the outcome of a proportionality assessment. With sources of external financing uncertain, the costs of borrowing could easily prove to be prohibitive, leading to disproportionate costs compared to environmental effects of the regulation.

Keywords: EU taxonomy; large combustion plants; best available techniques; principle of proportionality; emission limits

Introduction

The newly established EU taxonomy¹ shows that the EU is serious about the fight against climate change. Only “environmentally sustainable” activities that contribute to at least one of the set goals and do “no significant harm” should be allowed to receive external financing from European banking institutions. The taxonomy should be initially introduced to sectors such as energy, forestry, the productive sector and transport, with planned future extension to other sectors. Naturally, this represents yet another obstacle for companies that utilize fossil fuels. In recent years, a lot of effort has been put into emission reduction and many new regulations across various sectors have set stricter emission limits that both contribute to cleaner air in the EU member states and pressure on individual companies to comply with the stricter regulation. Gradual tightening has also been ever-present in the sector of large combustion plants (LCP). An important step in the regulation was the Industrial Emissions Directive², which consolidated previous regulation into a single directive and built on the goals of previous regulation such as the IPPC Directive³ later codified as Directive 2008/1/EC⁴.

The Industrial Emissions Directive (IED) focused on the emission limits for LCP and on Best Available Techniques (BAT) by strengthening the BAT Reference Documents (BREFs) concept. The regulation

covers approximately 50,000 installations with extensive permit requirements, but does not introduce criteria that would allow setting “emission levels associated with the best available techniques” for the individual sectors⁵. Whether a result of this omission or not, the latest emission limits set for LCP in the updated BREFs⁶ have been criticised by power plants as well as scholars^{7,8}, who point out that many installations will choose to finish their operation rather than undergo a modernization. This article shows that the newly established EU taxonomy may complicate things even further.

Installations point out that achieving the new emission limits with currently installed technologies is nearly impossible and conforming with the regulation proves to be quite difficult for many LCP⁸. However, the regulation offers a way out for installations for which the emission reduction would be too costly. Article 15 of the IED states that a derogation may be granted if “an assessment shows that the achievement of emission levels associated with the best available techniques as described in BAT conclusions would lead to disproportionately higher costs compared to the environmental benefits”. Specifically, the disproportionate costs must be caused by either geographical location, local environmental conditions or the technical characteristics of the installation. If a derogation is granted, the installation may continue its production under less stringent emission limits for a specified period of time.

A notable feature of the regulation is that there are no unified guidelines on how to make the proportionality assessment. Each member state sets up its own rules and therefore the procedure differs significantly across Europe⁹ with national states having been left with a great deal of discretion¹⁰. Indeed, the procedure is anything but homogenous. In 2018 only 14 out of 22 countries that responded to the questionnaire indicated that they had developed guidelines on implementation of Article 15 of the IED¹¹.

Another factor that contributes to such heterogeneous conclusions is the assessment of proportionality itself. Again, only five of the respondents had a clear definition of disproportionality in 2018¹¹. Poland and Wales use a specific benefit/cost ratio, meaning that if benefits are lower than 0.7 or 0.75 of costs, respectively, the assessment recommends granting a derogation^{12,13}. In France, the methodology requires a comparison of three scenarios: business as usual, technically feasible techniques, alternative solution¹⁴. Comparison of various scenarios together with assessment of additional emission reduction is the basis of the Czech methodology¹⁵, while in Slovakia a point system has been introduced, which takes into account selected key indicators¹⁶.

To comply with the new emission limits, most of the LCP need to invest in new abatement technologies. Considering that most of the installations invested not so long ago to comply with the emission limits introduced in the IED, the costs are significant. The plants will be forced to write off their existing technologies prematurely and invest in new ones. To obtain required funds, installations will most likely need to use external financing. However, the recently introduced EU taxonomy has created a guideline on financing projects based on their impact on the environment. As a result, it becomes highly unlikely to receive external funding from the banking sector to finance a coal-related project, even if the investment is aimed at emission reduction. Naturally, the costs of borrowing will increase for LCP, which raises an interesting question regarding the proportionality assessment. Such costs raise the total costs of conforming to the required emission limits, which should in theory make the derogation application more likely to succeed. With thresholds remaining constant (whether it is costs of conforming to older regulation or prevented external damage), an increase in the costs of compliance might just tip the scales.

The goal of this paper is to model several scenarios using mostly data from the Czech Republic's LCP and indicate the potential impacts that the new EU taxonomy may have on the results of future proportionality assessments. The paper compares the costs of compliance with the thresholds set by the most common methodologies described above and determines how much the costs of borrowing need to increase in order to alter the results of a proportionality analysis.

Data and methods

To estimate the potential effects of the EU taxonomy on proportionality analysis, it is important to understand how the process works in general. The proportionality assessment usually compares the costs of achieving the required emission limits and environmental benefits caused by lower air pollution

and subsequent effects. However, the Czech methodology¹⁵ makes two comparisons. One is a standard comparison of costs of compliance with the emission limits with environmental benefits and the latter is a comparison of two compliance costs – costs needed to comply with the previous regulation and with the most recent regulation. Such comparison allows one to discover whether achieving the new regulation is comparatively costly to previous rounds of emission limit tightening. If an installation applies for a derogation, it also proposes an alternative scenario, which decreases the overall emissions but is acceptable in terms of costs. Several additional criteria are used to determine proportionality and derogation application, each having a different weight in the assessment, which is based not only on the criteria themselves but also on whether other indicators are mostly positive/negative. Therefore, two categories of cost-related data and an estimate of the effect of the taxonomy are required for determining proportionality of meeting the new emission limits and the influence of the newly established EU taxonomy on the results.

First, data on costs of achieving the set emission limits are needed. Unfortunately, data on costs of emission abatement are quite inconsistent and estimates¹⁷⁻³² often differ by an order of magnitude. The main reasons for low validity of these results are³³:

- (i) The situation at individual plants is often modelled and not based on microeconomic data.
- (ii) Analyses use unrealistic assumptions such as no previously implemented abatement technologies.
- (iii) Analyses use data from macro models and estimate nation-wide effects as opposed to microeconomic effects on specific plants.

However, a recent study investigated the costs of complying with the new emission limits set in the latest BREFs for Czech LCP³³. The authors surveyed approximately half of the installed capacity of the Czech LCP and determined per unit costs of achieving both the new emission limits introduced in BREFs and the older limits set in the IED. These values were used by the Czech Ministry of the Environment in the update to the official methodology for assessing cost proportionality of emission abatement³⁴ and these data are used in this paper as one of the thresholds. A summary is shown in Table 1. If the costs of compliance are below the lower threshold, then there is no room for a derogation. If the costs exceed the higher threshold, then a derogation is recommended. If the costs fall in between those numbers, other criteria (such as length of derogation, significance for air pollution in absolute terms, additional cost indicators) will decide whether a derogation is recommended or not. The difference between the costs of achieving the new emission limits and costs of the alternative scenario is important in such cases.

Table 1: Overview of costs of achieving various levels of emission limits³⁴

Pollutant	Costs of achieving IED emission limits (EUR/t)	Costs of achieving BREFs emission limits (EUR/t)
SO ₂	2,150	11,800
NO _x	9,850	35,400
PM	7,900	59,000

Then, data on the costs caused by emitted pollutants on human health and property are needed. Data from the European Environment Agency present such damage for several pollutants calculated for individual member states. However, as Table 2 shows, the spread of the values (rounded for simplification) is quite large and strongly depends on the methodology used for the calculation (such as VOLY – value of a life year, and VSL – value of statistical life).

Table 2: Marginal damage costs on health, crops and forests and material damage by major air pollutants^{35,36}

Pollutant	EEA (2014)		EEA (2020)	
	Marginal cost EUR/t (VOLY)	Marginal cost EUR/t (VSL)	Marginal cost EUR/t (VOLY)	Marginal cost EUR/t (VSL)
SO ₂	12,500	36,500	22,500	71,300
NO _x	6,400	17,650	15,000	49,100
Dust (PM _{2.5})	39,900	115,150	88,100	282,450
Dust (PM ₁₀)	25,900	74,750	57,200	183,400

The table shows a significant increase in the most recent costs associated with air pollution compared to the report that was in place when the new emission limits were set.

And finally, we identify the effect of the newly established EU taxonomy on the costs of financing the steps that need to be taken in order to conform with the new regulation. European banks are expected not to finance any coal-related projects in the future, which will most likely include investments in more effective abatement technologies. As a result, the affected LCP will need to search for an alternative source of financing, meaning the costs of complying with the regulation will inevitably increase with the least expensive option becoming unavailable. Other options represented by non-bank loans, issuance of corporate bonds or savings may increase the total costs by a negligible amount as well as by a prohibitive amount. In this paper, different scenarios will be used to show how large a change would have a significant effect on the overall outcome.

To discover the severity of the effect caused by the EU taxonomy, it is necessary to perform a brief calculation for a hypothetical power plant that needs to retrofit its old technology with a more powerful selective catalytic reduction (SCR) unit. Let us assume that the power plant has an installed capacity of 360 MW_e and barely conforms with the NO_x emission limit set in the IED. Based on EPA³⁷ and the EPA's SCR cost calculation spreadsheet³⁸, it is possible to estimate costs of retrofitting a plant with an SCR unit, a technology necessary for the plant to comply with the current emission limits. Using the formulas suggested by the EPA³⁸ gives an estimation of roughly 86.3 million EUR. Assuming that we live in a pre-taxonomy world in which bank loans are available, let us say that the company will need to borrow 80% of this sum (69 million EUR) at an interest rate of 4% with a payback period of 10 years. The total costs for the company would be around 101.2 million EUR in such a case.

A hypothetical power plant of the chosen installed capacity going from, say, 200 mg/Nm³ of NO_x emissions to 175 mg/Nm³ (to be slightly below the limit set by BREFs) can realistically capture approximately an additional 200 tonnes of NO_x per year³³. A critical decision must be made about the lifetime of the installed SCR. Although the equipment itself can easily remain functional for over 30 years³⁸, there are several reasons against using such a value:

- (i) Companies usually write off a technology during a much shorter period of time.
- (ii) The EU lowers emission limits frequently and requires the use of best available techniques, which means it is unlikely that the SCR unit will still be considered best available in 30 years.
- (iii) With pressures to move towards non-fossil fuels and abandon coal no later than in 2038, it would be naïve to expect that the SCR unit will still be in use in the 2050s even if it is best available as coal will most likely be abolished by then.

For the reasons described above, a lifetime of 15 years was selected for the calculation. A simple division of the total costs by the number of abated tonnes and years in operation gives a final value of 33,721 EUR, which is significantly above both the old estimate of the damage caused by a tonne of emitted NO_x³⁶ and the estimated costs of conforming with the IED³³, slightly below the referenced costs of achieving the emission limits set in BREFs³³ and below the new estimate for externalities³⁵ as shown in Tables 1 and 2. The majority of countries use the estimate of caused external damage¹¹ but some have different conditions in place. The Czech methodology would lean towards granting a derogation although the estimated costs are slightly below the upper threshold. Other methodologies might be

weakly against based on such a result as the benefit/cost ratios used in Wales and Poland to determine proportionality are 0.75 and 0.7 respectively^{12,13}. This means that, at least in some cases, costs must significantly outweigh benefits for a case to be deemed disproportional.

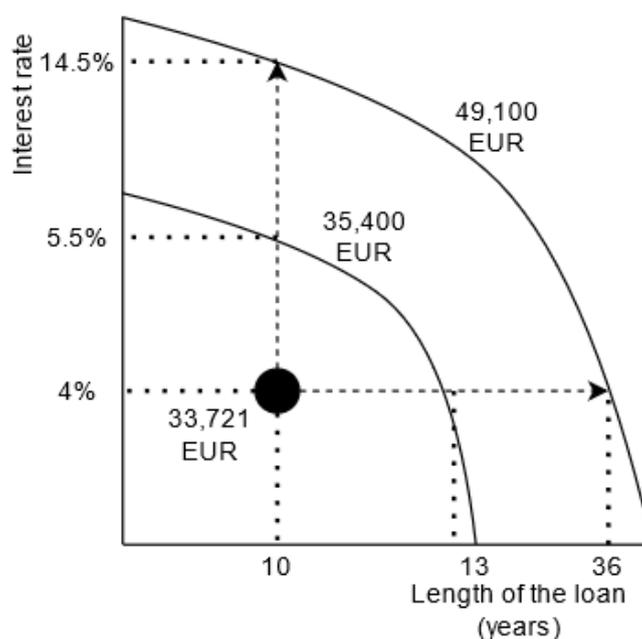
In the following section, several parameters of the hypothetical loan are altered to see how much they need to be changed for the costs of compliance to rise above the proportionality threshold. Specifically, values of the interest rate and the length of the loan that would increase the costs of compliance above the two study thresholds are computed.

Results

Let us focus on how much more expensive the external financing needs to become in order to increase the costs of compliance above the respective thresholds of 35,400 and 49,100 EUR. Specifically, it is interesting to know how much the interest rate needs to increase to get to these thresholds, holding other things constant. It turns out that raising the interest rate on the 69 million EUR loan from 4% to 5.5% will do the trick and will increase the annual cost per tonne to 35,730 EUR. As for the latter threshold, a much higher increase to the interest rate is required, specifically a rate of 14.5% leads to the cost of 49,480 EUR per abated tonne.

The final value will also strongly depend on the length of the loan. If the loan is to be repaid in 15 years instead of 10, the interest rate plays a larger role as the interest is accumulated over a longer period of time. It is clear from the calculations that the interest rate on the 69 million EUR loan would actually have to decrease from the original value of 4% below 3.5% in order to stay under the proportionality threshold used in the Czech Republic. If the original interest rate stays in place, then any length of the loan above 13 years breaks this threshold. In a similar fashion, a comparison to the external damage costs shows that an interest rate of 9.6% is enough to raise the costs per abated tonne to 49,271 EUR if the money is to be repaid in 15 years. Alternatively, holding the interest rate constant at 4%, the length of the loan would have to increase to unrealistic 36 years. Figure 1 indicates the results. The starting point represents the original conditions in the example – a payback time of 10 years and a 4% interest rate. Moving along the dashed arrows indicates the change needed in one parameter (holding the other constant) that needs to happen in order to reach one of the cost thresholds. Holding the interest rate at 4%, the lower threshold will be reached when the length of the loan increases from 10 to 13 years, while the upper threshold would be reached in the case of a 36-year loan.

Figure 1: Effect of interest rate and length of loan on costs of compliance



Source: Own construction

Another factor that plays a major role is the share of the funds that need to be collected externally. It is interesting to note that under the original scenario of a 10-year loan and 4% interest rate, the threshold would not be broken even if the whole sum needed to be borrowed. Alternatively, it is possible to change the original setting to 90% of the sum being loaned and interact with the interest rate just as in the case above. Under such circumstances, the lower threshold would be reached at a 4.7% interest rate if the borrowed amount increases to 90% of the total investment, while the higher threshold would be broken at 13%. Comparing these numbers to the scenario in which only 80% of the sum is loaned, lower interest rates are necessary to break the thresholds. An interest rate of 5.5% was needed in the original setting as opposed to 4.7% in this example and a similar story can be told about the upper threshold (14.5% compared to 13%).

Discussion and conclusion

First of all, it needs to be emphasized that the paper describes an example, although it is largely based on the real-world situation in the Czech Republic³³ and the cost estimates based on EPA³⁸ are close to scenarios considered by many installations in practice. The main purpose of the paper was to illustrate the effect the new EU taxonomy can have on the current scheme of derogations based on proportionality and the sensitivity of such analysis to the interest rate and other factors. To give an example, nobody can be sure how long European LCPs will remain active. While Germany will shut down its last coal-burning power plants in 2038, the Czech Republic, on whose plants this paper is based, is yet to give the final verdict with both 2033 and 2038 being discussed. This is something that needs to be considered in the calculation because it has a potentially huge impact on the result.

As indicated above, the effects of the EU taxonomy could be significant. In several cases even relatively small changes to the interest rate or the length of the loan are sufficient to make a significant impact on the result of the proportionality assessment. Some of the suggested interest rates seem to be unrealistic in today's world of nearly negative interest rates. However, with standard banking products becoming unavailable, it is not unreasonable to see the costs of borrowing for LCP skyrocket and reach values that were considered impossible not long ago. With only unconventional options remaining, the interest rates could go up and, in an extreme case where a source of financing cannot be found, the total

costs of achieving emission limits would essentially become infinite, making the investment costs prohibitive and the application for a derogation would therefore be easily justified.

The analysis was carried out for NO_x, which seems to be causing a lot of troubles to (at least Czech) facilities. However, similar issues may arise when it comes to SO₂ emission abatement. The new limit also seems to be quite challenging for the current setups. We do not expect this situation to occur in the case of PM as such a situation is usually not a question of a large one-time investment.

The main point of this article is that with the EU taxonomy in place, the new regulation could easily backfire if derogations based on cost proportionality remain available. Since LCPs nowadays use bank loans to finance their investments, it is without a doubt the least expensive money available on the market. With the costs of borrowing increased, the costs of compliance will increase as well, making it more likely that the conditions required for granting a derogation are met.

Considering how vigorously the EU fights against air pollution, such a state would certainly be undesirable. However, the EU taxonomy does increase costs of compliance and in the current situation may even be helping thermal power plants in their tough situation as it makes derogations achievable more easily. In the long term, though, the future of the principle of proportionality in the field is uncertain. If the EU is taking its fight against air pollution seriously, significant changes need to happen to make the principle of proportionality and the EU taxonomy compatible. Alternatively, the principle of proportionality needs to be abandoned completely, which could have some serious consequences on the energy markets in Europe.

Acknowledgment

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Evropská taxonomie a princip přiměřenosti: Povedou vyšší náklady na úvěr k většímu množství výjimek z plnění emisních limitů?

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Souhrn

Nově implementovaná taxonomie fakticky zakazuje bankovním institucím v Evropské Unii financovat projekty spojené s uhlím. A to i přesto, že mohou být zaměřené na snížení množství vypouštěných emisí. Tato skutečnost by mohla velkým spalovacím zařízením značně prodražit plnění nově stanovených emisních limitů. Právě nepřiměřená výše nákladů může být jedním z důvodů, pro které může zařízení obdržet výjimku z plnění emisních limitů. Nová taxonomie by tak mohla nezáměrně přispět k vyššímu množství takových výjimek v Evropě. Taxonomie znemožňuje využití nejdostupnějšího zdroje externího financování, zařízení by se tak musela spolehnout na alternativní možnosti.

Tento článek zkoumá citlivost nákladů na plnění emisních limitů na některé atributy případného úvěru – konkrétně na úrokovou míru, dobu trvání půjčky a podíl půjčených prostředků na celkové výši investice. Na základě českých dat byla provedena případová studie na hypotetické elektrárně, která ke splnění emisních limitů potřebuje instalovat novou účinnější technologii. Výsledky naznačují, že v některých případech stačí i mírná změna výše zmíněných parametrů, aby náklady plnění emisních limitů vzrostly nad hranici přiměřenosti. Vzhledem k nejistým zdrojům externího financování mohou náklady na náhradu současné technologie snadno vzrůst na prohibitivní hodnoty, které nebudou odpovídat environmentálnímu efektu dané regulace.

Klíčová slova: Evropská taxonomie; velká spalovací zařízení; nejlepší dostupné technologie; princip přiměřenosti; emisní limity

Possibilities of fly ash utilization in the cement matrix by superabsorbent polymers

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Summary

The paper deals with the possibilities of preparation, processing and basic properties of silicate mass - cement paste using superabsorbent polymer (SAP). SAP is a relatively new additive, which is used in silicate mixtures, where in the early stages of hydration it absorbs excess mixing water and then releases it in the later hydration stages and thus contributes to the elimination of shrinkage cracks. The article deals mainly with the influence of recipe modification with regard to the use of energy by-product of high-temperature fly ash from brown coal combustion and the effects of its use on basic physical and mechanical properties, such as compressive strength, flexural tensile strength and bulk density.

Keywords: superabsorbent polymer, hydrogel, cement, fly ash.

Introduction

Superabsorbent polymer (SAP) materials are cross-linked hydrogel networks consisting of water-soluble polymers^{1,2}. SAPs have been utilized in several industries like sanitary, agriculture, and medical³. As a type of concrete admixture is application of SAP relatively new⁴. It has been used as an internal curing mechanism to counteract autogenous shrinkage especially in ultra-high performance concrete^{5,6,7,8}. SAP can be designed in any shape or size, after its desorption it leaves a void in hardened matrix leading to reduced mechanical properties of cementitious composites³.

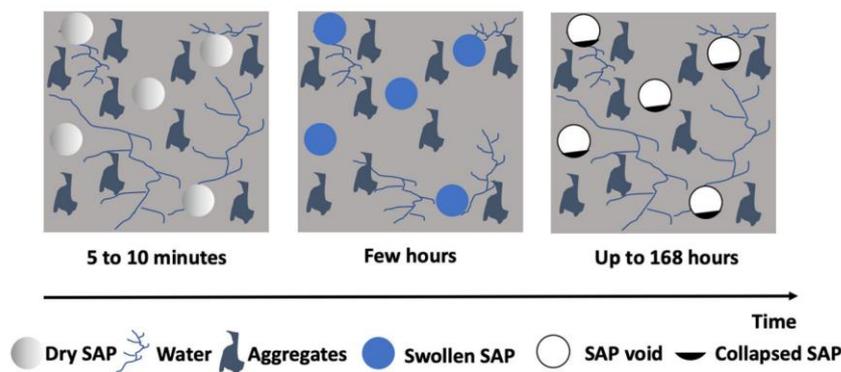


Figure 1: Behaviour of SAP in cementitious paste in different ages³

There are various types of SAP based on the source of the material (like natural polymers, synthetic, and semi-synthetic polymers) and production techniques (like radiation cross-linking, network formation, graft, and cross-linking polymerization)^{3,9}. Copolymer of acrylamide and acrylic acid, modified polyacrylamide¹⁰. These materials are used in ultrahigh performance concrete with cement binder^{2,11,12,13,14}, into fibre reinforced mortars^{10,15,16}, composites for cementitious material based on modified metakaolin¹⁷, pavement concrete⁵, self-healing and self-sealing cementitious materials^{18,19,20,21,22,23}, in cement materials in order to determine plastic shrinkage cracking^{24,25}

At an early age, the addition of SAP as weak points can reduce the compressive strength of UHPC; however, as age increased, the internal curing water from SAP can densify the microstructure of the vicinity of SAP and compensate the mechanical properties². For practical applications where frost resistance is important, it is necessary to choose a suitable SAP granulometry, which is larger, due to the larger pores, which can be accurately assumed.^{26,27}

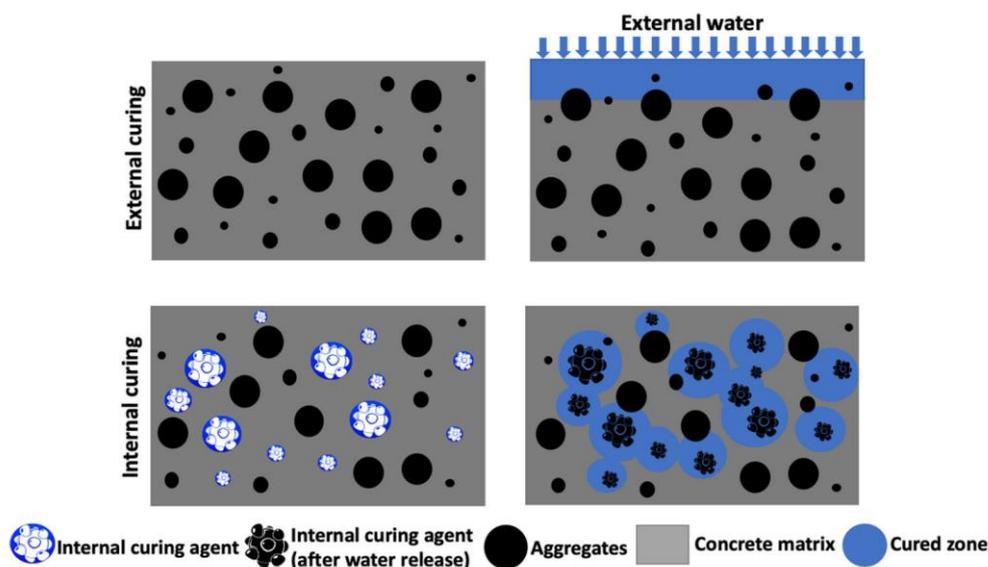


Figure 2: Internal and external curing mechanism^{3,27}

Based on the observations of Chindasiriphan and Yokota^{28,29}, mixtures should have a higher potential for self-healing due to a higher dose of replacement. These are cement mixtures with a high ash content of up to 45% and a high SAP dose of 4%, 6% and 8% by weight of cement. At such high SAP doses, the superabsorbent polymer may absorb most of the water in the mixture.³⁰ The first use of SAP in real construction, the construction of a pavilion for the FIFA World Cup in Kaiserslautern in 2006, used an amount of SAP of 0.4% by weight of cement with a water content (w/b) of 0.21 and was a sufficient dose to provide concrete up to 45 kg/m³ of internal curing water.⁴

SAPs are very effective in absorption and desorption, can also be incorporated in dry concrete as an admixture to absorb additional water during mixing^{3,31}, or it can be used presoaked³².

Materials

Cement, SAP and as secondary raw materials fly ash were used as input raw materials. Their properties are listed in the tables below.

Cement – CEM I 52.5 R

Powder binder produced in the Hranice cement plant by joint grinding of Portland clinker, calcium sulphate, additional components and additives.

Table 1: Properties of cement

CEM I 52.5 R	Average values	Units
Compressive strength after 28 days	≥ 52.5	MPa
Specific surface	4 400 – 4 900	cm ² /g
Bulk density	3100	kg/m ³
α	0.64	-

α - expected maximum degree of hydration

Superabsorbent polymer

It is a solid powder in various shapes, based on 2-Propenoicacid, potassium salt (1:1), polymer with 2-propenamide.

Table 2: Properties of superabsorbent polymer CREABLOC SIS

CREABLOC SIS	Average values	Units
Density	0.7	g/cm ³
Bulk density	720	kg/m ³

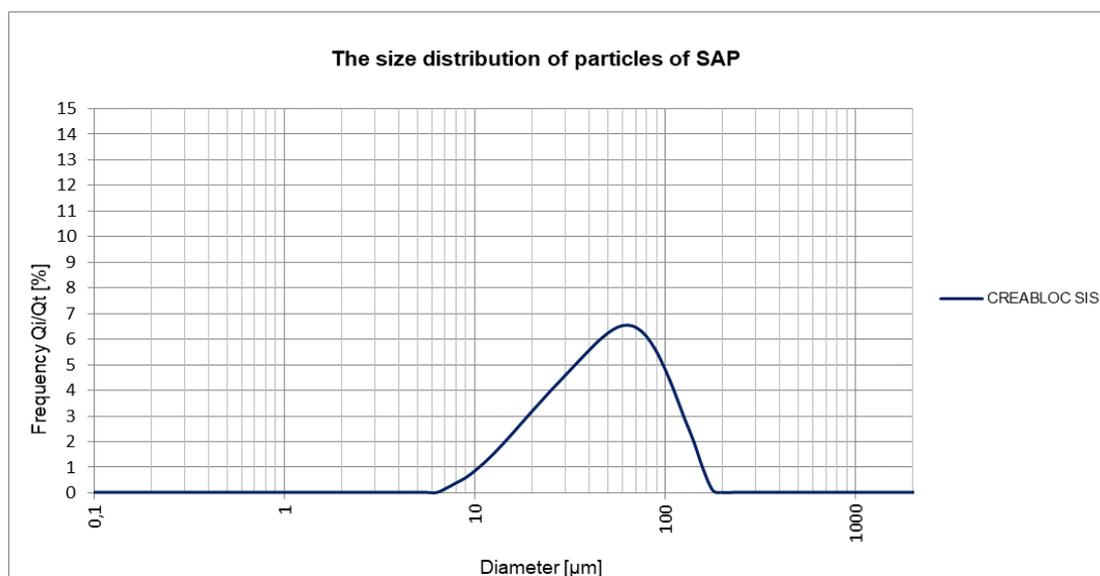


Figure 3: SAP particle size distribution

Fly ash

Used fly ash is a by-product of a brown coal burning thermal power plant in the north middle part of the Czech Republic.

Table 3: Properties of fly ash

Fly Ash - Chvaletice	Average values	Units
Specific surface	4870	cm ² /g
Bulk density	1150	kg/m ³

Formulations of the mixtures

Mixtures were proposed considering the properties of each input material in order to demonstrate the influence of presence of SAP.

Table 4: Proposed mixture

Mixture	CEM [%]	FA [%]	SAP [%]	w [%]
100 % CEM	100	0	0.00	0.39
90 % CEM + 10 % FA	90	10	0.00	0.40
80 % CEM + 20 % FA	80	20	0.00	0.37
65 % CEM + 35 % FA	65	35	0.00	0.36
100 % CEM + 0.25 % S	100	0	0.25	0.44
90 % CEM + 10 % FA + 0.25 % S	90	10	0.25	0.50
80 % CEM + 20 % FA + 0.25 % S	80	20	0.25	0.48
65 % CEM + 35 % FA + 0.25 % S	65	35	0.25	0.49
100 % CEM + 0.50 % S	100	0	0.50	0.51
90 % CEM + 10 % FA + 0.50 % S	90	10	0.50	0.53
80 % CEM + 20 % FA + 0.50 % S	80	20	0.50	0.55
65 % CEM + 35 % FA + 0.50 % S	65	35	0.50	0.56
100 % CEM + 0.75 % S	100	0	0.75	0.58
90 % CEM + 10 % FA + 0.75 % S	90	10	0.75	0.62
80 % CEM + 20 % FA + 0.75 % S	80	20	0.75	0.63
65 % CEM + 35 % FA + 0.75 % S	65	35	0.75	0.65

Methods

To determine the ideal amount of cement, fly ash and SAP in cement composite, 16 different recipes were proposed. The individual formulations are combinations of fly ash 10%, 20%, 35% and SAP 0.25%, 0.50%, 0.75% (dosing in % by weight of binder).

Mixing was performed in three stages. In the first phase, the loose raw materials were mixed by hand (cement, fly ash) for 2 minutes. In the second phase, a superabsorbent polymer was added to the mixture and mixed by hand for 2 minutes. The resulting bulk mixture had to be completely homogenized in a homogenizer type H2037 - MI800 Mixer Powder Tumbling for 10 minutes at a speed of 910 rpm. In the third (wet) phase, water was added to the completely homogenized mixture so as to achieve the same consistency. The amount of water needed to maintain the consistency of each mixture is recorded in Table 4. The resulting mixture was placed in a mold, the size of each test beam was 40 × 40 × 160 mm.

Consistency was determined in accordance with the standard ČSN EN 1015-3: Methods of test for mortar for masonry - Part 3: Determination of consistency of fresh mortar (by flow table). The ideal spill of the cement slurry was chosen to be 21 × 21 mm.

Bulk density - Determination of the bulk density of hardened mortar (EN 1015-10 - Methods of test for mortar for masonry - Part 10: Determination of dry bulk density of hardened mortar; ČSN EN 196-1: Methods of testing cement - Part 1: Determination of strength).

To determine the compressive strength, a test was performed according to the valid EN 12390-3: Testing of hardened concrete - Part 3: Compressive strength of test specimens and the flexural tensile strength was determined in accordance with EN 12390-5: Testing hardened concrete - Part 5: Flexural tensile strength of test specimens.

Evaluation of the microstructure of the tested materials was performed using scanning electron microscopy. In addition to the study of morphology, an energy-dispersive analysis of the characteristic X-rays was also performed, on the basis of which the chemical composition of selected microscopic subjects was determined.

Results and discussion

On Figure 4 it is possible to see how the strengths change according to the added ash replacement and SAP. With the addition of SAP in an amount of 0.25% of the weight of the cement, the flexural tensile strengths increased with an average amount of added fly ash by 8.8%. Another addition of SAP already had a rather destructive effect on the mixture, and with its further addition, the flexural tensile strength was reduced. The addition of FA in small amounts had a positive effect on flexural tensile strength. Due to the 10% replacement of the FA binder, there was a slight improvement in flexural tensile strength. A higher proportion of FA in the mixture (20% and more) meant a decrease in strength with an increasing proportion of FA.

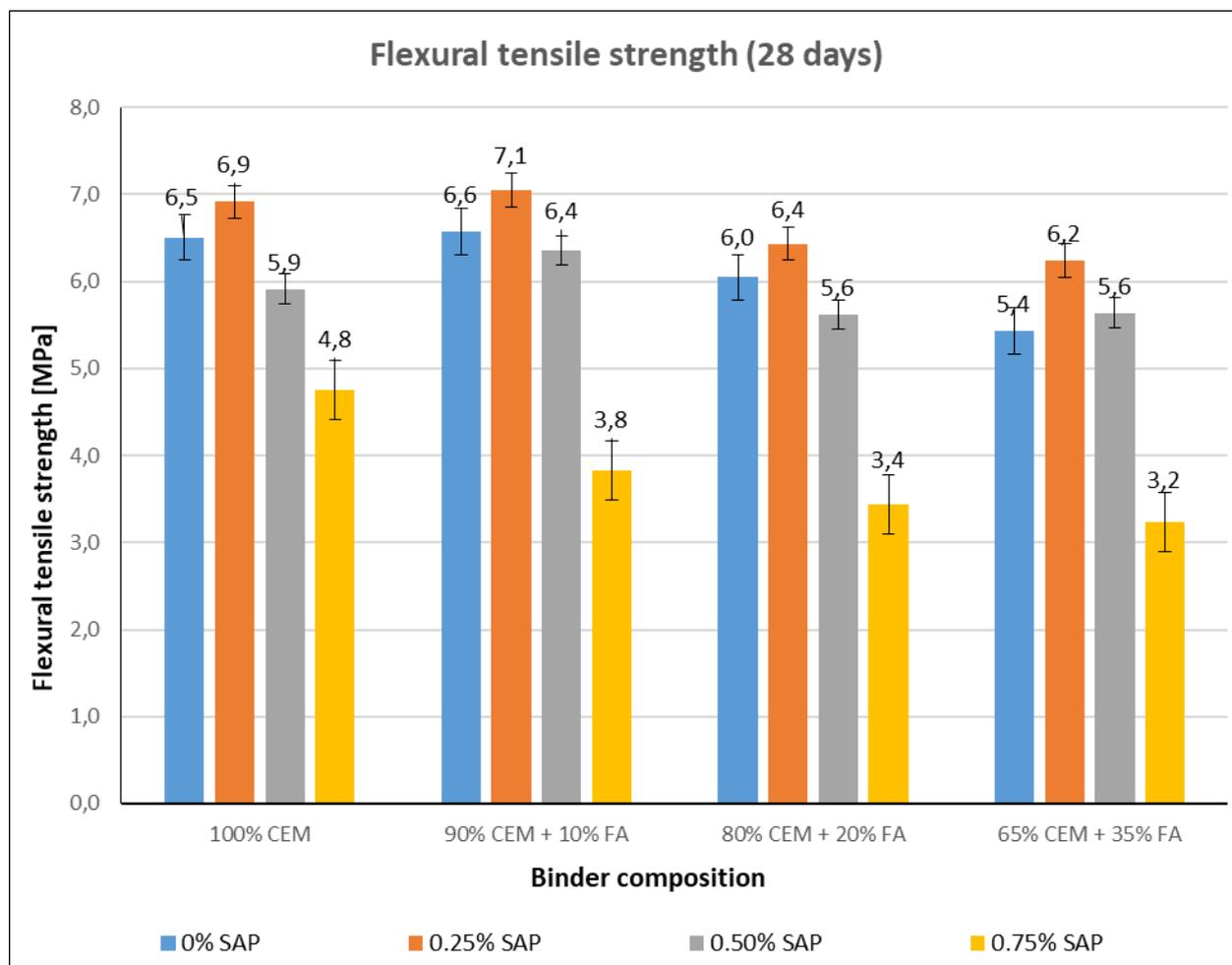


Figure 4: Flexural tensile strength (28 days)

Due to the addition of SAP, there was a slight decrease in compressive strength. Mixtures in which FA was used as a substitute for 10% of the binder component achieved strengths comparable to those in which FA was not contained. With a further increase in the share of FA and SAP, there was a decrease in compressive strength. The exception was the mixture with 20% FA binder replacement and 0.25% SAP, in which the decrease in compressive strength was not very significant compared to the reference mixture.

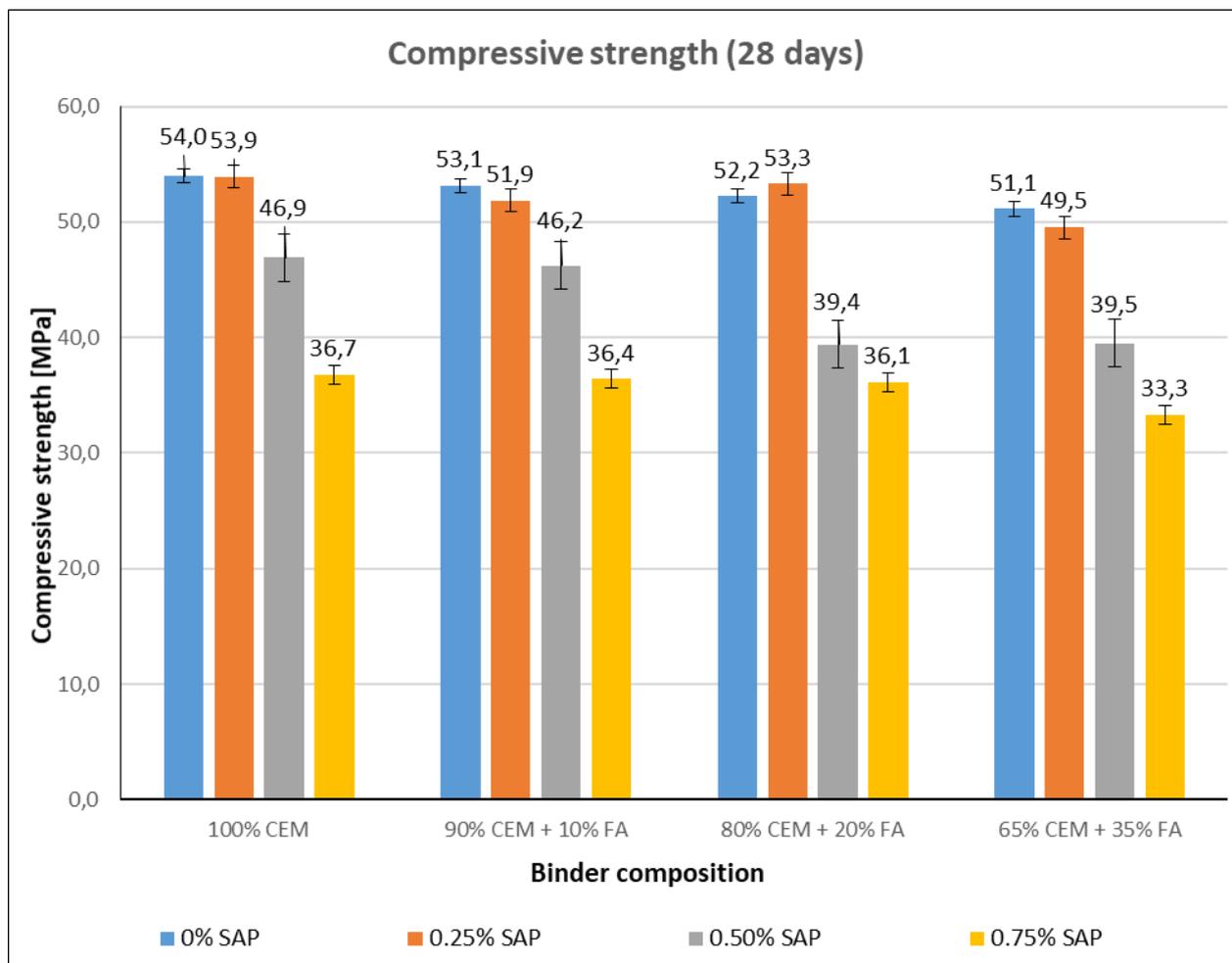


Figure 5: Compressive strength (28 days)

From the comparison of the bulk density of individual mixtures, it is evident that with the increasing share of the replaced binder component by FA, the bulk density decreases. It is also clear that as the amount of SAP used increases, the bulk density of the samples also decreases.

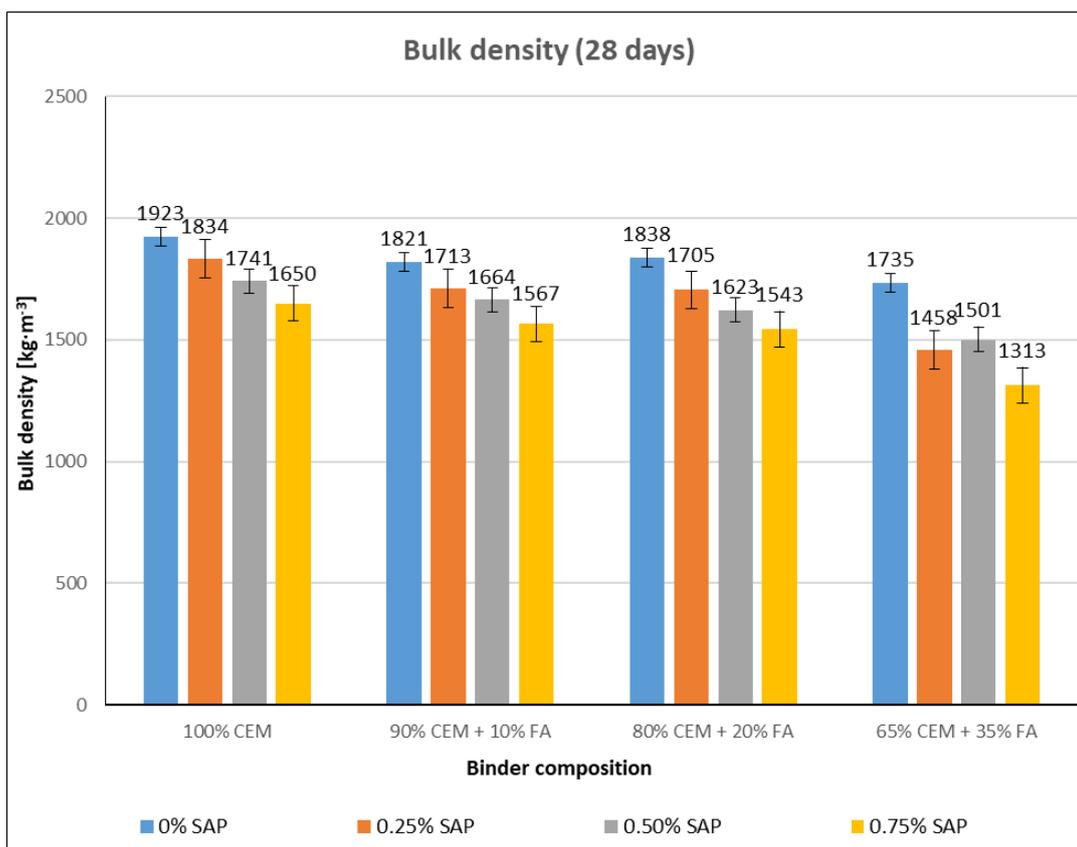


Figure 6: Bulk density (28 days)

Typical features detected by scanning electron microscopy are captured in the following images:

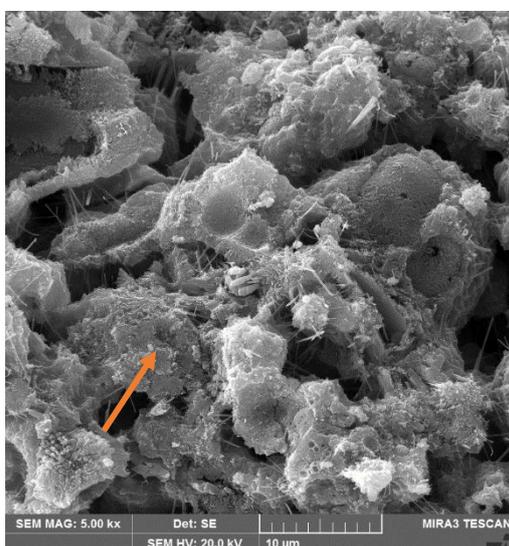


Figure 7: View of the mixture with 35% fly ash without SAP

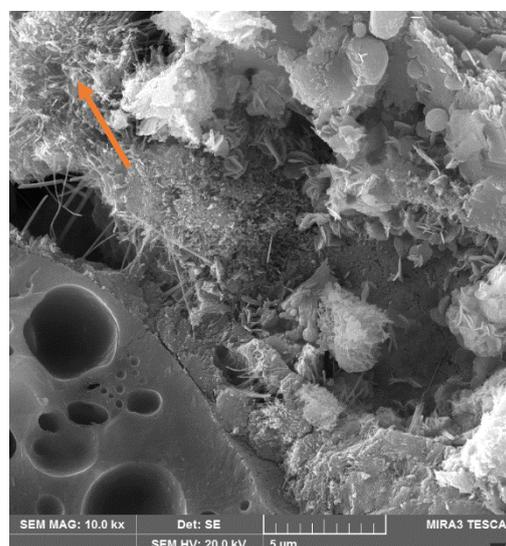


Figure 8: Detailed view of the contact zone of the cement matrix and fly ash grains in a composite with 35% cement substitution by fly ash, without SAP

On Figure 7 is a microstructure typical of cement fly ash composites. The presence of cement hydration products (especially calcium hydrosilicate gels), which surround the ash grains, is evident. (magnified 5,000 times). On Figure 8 presence of calcium hydrosilicate gels and prismatic crystals of primary ettringite is evident. (magnified 10,000 times).

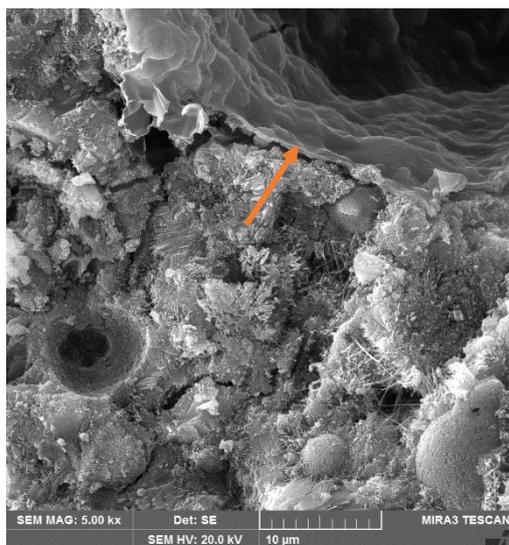


Figure 9: View of one of the pores in the microstructure of a composite with 35% fly ash and 0.75% SAP

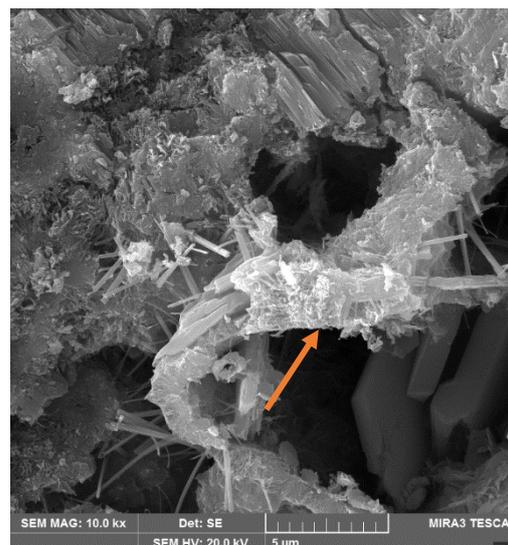


Figure 10: Detailed view of a polymer film in one of the pores of a composite with 35% fly ash and 0.75% SAP, indicated by an arrow

On Figure 9 a "coating" of organic polymer on the wall of one of the pores is indicated, indicated by an arrow (magnified 5,000 times). On Figure 10 the druses of portlandite are also noticeable. (magnified 10,000 times).

One of the essential findings of electron microscopy is a clear demonstration of the formation of a "coating" or. film of organic material (the SAP used is predominantly formed by organic substances) on the walls of some pores, at a dose of SAP 0.50%, and especially at a dose of 0.75%. The formation of this "coating" indicates a de facto redundant amount of SAP in the mixture at these doses. Furthermore, it has been shown that the mixtures with higher doses of SAP have a relatively lower portlandite content. This finding probably indicates the ability of SAP to bind calcium ions released by the gradual hydration of cement, which was confirmed by determining the chemical composition of the "coating" in the pores.

Conclusions

The article is focused on the optimization of the dose of superabsorbent polymer in connection with the possibility of substituting cement with power plant fly ash in such modified composites.

It was stated that while the substitution of cement with fly ash affects the rheology of the fresh mixture to a very limited extent, the SAP admixture significantly increases the requirements for the mixing water dose when the comparable workability of the fresh mixture is required. This is particularly striking at higher doses of SAP, for example at a dose of 0.75%, the dose of mixing water was increased by more than half to maintain the consistency of the fresh mixture. From the obtained results it is apparent that the utilization of fly ash in cement matrix by usage of superabsorbent polymers is possible. Concretely by improving final properties of mixtures containing these secondary raw materials. Especially flexural tensile strength was increased by the addition of SAP in various amounts compared to the reference samples at substitution rate of binder by FA 10%. At the substitution rate by FA 20% and higher meant decrease in flexular strength, but nevertheless the addition of 0.25% of SAP still increased the values compared to the reference samples. Compared to the reference samples the compressive strength was increased only by addition of 0.25% of SAP at the substitution rate of binder by FA at the rate of 20%. Considering the bulk density, it is apparent that the increasing share of FA as well as increasing content of SAP in samples both decrease the values of obtained bulk density of the mixtures. Only exception is

slight increase of bulk density of mixture 65% CEM + 35% FA with 0,50% SAP compared to mixture with 0,25% SAP. This fact might have been caused by the bigger deviation in measurements of mixture with 0,25% SAP, which can be observed in its error line.

The analysis of the microstructure revealed that SAP is very likely to enter into matrix formation reactions, being able to bind calcium ions released by cement hydration into its structure.

List of symbols

SAP – superabsorbent polymer,
CEM – cement (CEM I 52,5 R),
FA – fly ash.

Acknowledgments

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Možnosti využití popílku v cementové matrici se superabsorpčními polymery

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Souhrn

Příspěvek se zabývá možnostmi přípravy, zpracování a základními vlastnostmi silikátové hmoty – cementové pasty s využitím superabsorpčního polymeru (SAPu). SAP je poměrně novou přísadou, která se používá v silikátových směsích, kde v raných fázích hydratace absorbuje přebytečnou záměsovou vodu a tu následně uvolňuje v pozdějších hydratačních stádiích a přispívá tak k eliminaci smršťovacích trhlin. Článek se zabývá zejména vlivem úpravy receptur s ohledem na využití vedlejšího energetické produktu vysokoteplotního popílku ze spalování hnědého uhlí a dopady jeho využití na základní fyzikálně mechanické vlastnosti, jako jsou především pevnost v tlaku, pevnost v tahu za ohybu a objemovou hmotnost.

Klíčová slova: superabsorpční polymer, hydrogel, cement, popílek.

Rheological properties of geopolymer binders and new method of measurements

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Abstract

The aim of this work is to study rheological changes of geopolymers in the initial phases of solidification of stabilization binders using two standard and one new method. Measurement of dynamic viscosity with a rotary viscometer and determination of the initial setting time of solidification with a Vicat instrument were used as standard. In order to better characterize the solidification process of geopolymer materials, a method for measuring the flow rate through the needle under defined conditions was designed and confronted. These methods were focused on the influence of the water content in initial stages of solidification. The results show that the rotary viscosimeter is not suitable for such measurements which is related to the thixotropy of the material. The Vicat's device gives relevant times of solidification, but it measures the already technologically unprocessable form of binders. The optimal method for practical use and for the estimation of the workability times of geopolymers is the designed measurement of the flow velocity through a needle under controlled and well defined conditions.

Keywords: geopolymer, binder, rheology, initial setting time, viscosity.

Introduction

A large amount of waste and its high variability are the problems of present waste processing and they exceed the recycling options and capacities now available. Therefore, some problematic waste has to be treated before disposal to prevent environmental contamination by dangerous compounds. In many cases, stabilization of the compounds can solve the problem and one of the most used stabilization processes is solidification.

For solidification and immobilization of dangerous or unsuitable wastes, that have either organic or anorganic origin, the solidifying binders on various bases are used. These can be cement binders, lime-based binders, ash, sulfur or asphalt based binders¹⁻⁵. Recently, alkali activated aluminosilicate based binders are used which are known as geopolymers. Such binders can be prepared from various precursors by many different ways. Resulting geopolymer then may have a broad range of properties (mechanical, structural or chemical etc.). The advantage over other materials is the possibility of preparing a stabilizing binder with properties optimized for a specific waste. Geopolymers are materials most often prepared by mixing aluminosilicate powder with an alkali metal hydroxide solution (usually NaOH and KOH) or with an aqueous alkali metal silicate solution (water glass)⁶. After mixing the raw materials and their homogenization, the alkaline hydrolysis process begins, where the aluminosilicate powder is partially dissolved. This is followed by a polycondensation process associated with the growth of a three-dimensional polymer network. The resulting geopolymer can have mechanical properties comparable (or even better) with concrete and it has very good ability to bind metal cations at the same time. Geopolymers can be used to stabilize e.g. waste sludge from alumina production, waste containing heavy metals, or radioactive waste⁷⁻¹¹.

Geopolymers can also be prepared from power plant fly ash¹²⁻¹⁴. The potential of such geopolymers is mainly in the construction industry. According to The Association for Utilization of Coal Combustion

Products, the Czech Republic produces 11 to 14 million tons of energy by-products as waste from coal power plants and heating plants annually. With price of tens of crowns (CZK) per ton, it is a very interesting raw material for the production of geopolymers in large volumes¹⁵. However, the disadvantage is that it is chemically very heterogeneous raw material, which often contains hazardous elements, because the fly ash chemical composition is strongly dependent on the input material and the combustion technology.

To ensure the stability of the geopolymer properties as binders for the solidification of waste, it is necessary to produce them from stable raw materials. A suitable raw material is aluminosilicate with high content of metakaolinite, which is produced on an industrial scale by calcination of kaolins or kaolinitic claystones^{16,17}.

For industrial applications of geopolymer binders, including solidification of waste, an important property is their viscosity and its changes over time, i.e. during the solidification of geopolymer binders. It is suitable to use aluminosilicate from kaolinitic claystone in case of low viscosity geopolymer binder, as reported in the literature^{16,17}.

However, a fundamental problem of geopolymers is the determination of rheological properties and their workability time. Standard methods, both the dynamic method using a rotary viscometer and the static method using a Vicat instrument, do not meet the real requirements for the workability time determination of geopolymers. Therefore, a new method better corresponding to the real needs was proposed and confronted in this work.

Materials

Industrially produced precursors were used for the preparation of the geopolymer binder. Aluminosilicate with a high content of metakaolinite with the trade name Mefisto L₀₅ produced by the calcination of kaolinitic claystone in a rotary kiln at a temperature of 750 °C (České lupkové závody, a.s., Czech Republic), potassium water glass KVS 3,2-3,4 (Vodní sklo, a.s., Czech Republic) and solid potassium hydroxide (G.R. grade, 88.2 wt% KOH, Lach-Ner, s.r.o., Czech Republic) were used. The chemical composition of the base materials is given in Table 1. The phase composition of Mefisto L₀₅ is shown in Figure 1. It is clear from the particle size analysis that 50 % of all Mefisto L₀₅ particles is smaller than 3.7 µm and 90 % of all particles is smaller than 10.6 µm. The particle distribution is shown in Figure 2.

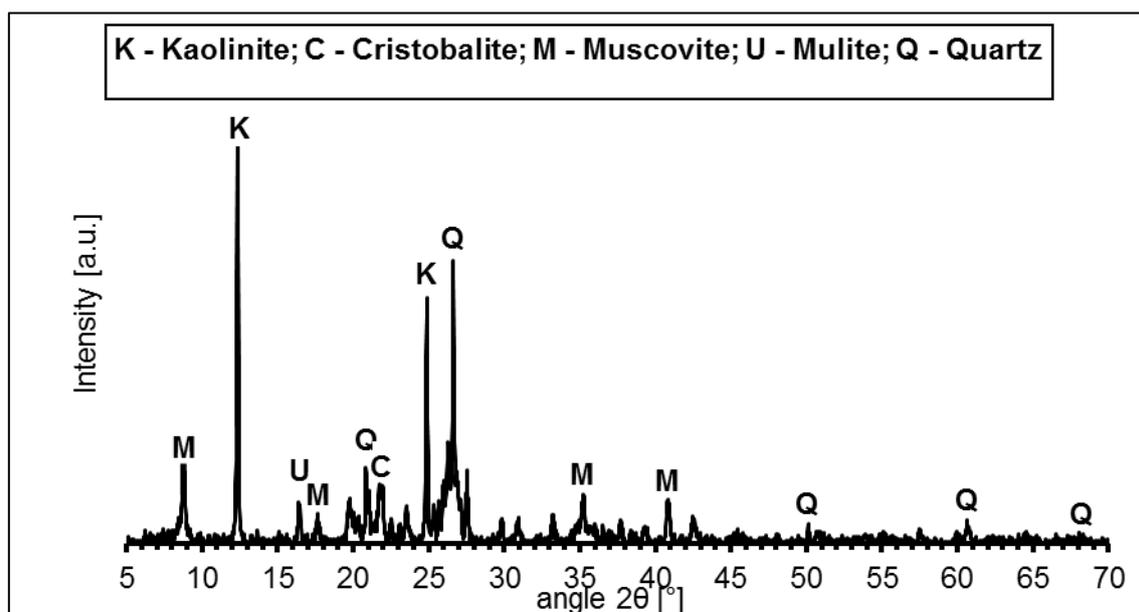


Figure 1: XRD patterns of aluminosilicate Mefisto L₀₅

Table 1: Chemical composition (wt%) of raw materials

	Mefisto L ₀₅	potassium silicate
LOI _a	1.53	-
H ₂ O	-	60.44
SiO ₂	51.9	27.00
Al ₂ O ₃	42.5	0.05
TiO ₂	1.66	-
Fe ₂ O ₃	0.88	-
K ₂ O	0.83	12.12
CaO	0.16	-
MgO	0.16	-
SO ₃	0.08	-
P ₂ O ₅	0.07	-
V ₂ O ₅	0.05	-
MoO ₃	0.04	-
Na ₂ O	0.04	0.38
Cr ₂ O ₃	0.03	-
ZrO ₂	0.02	-
ZnO	0.01	-
SrO	0.01	-
CuO	0.01	-
NiO	0.01	-
Ga ₂ O ₃	0.01	-
As ₂ O ₃	0.01	-

^a LOI = Loss on ignition.

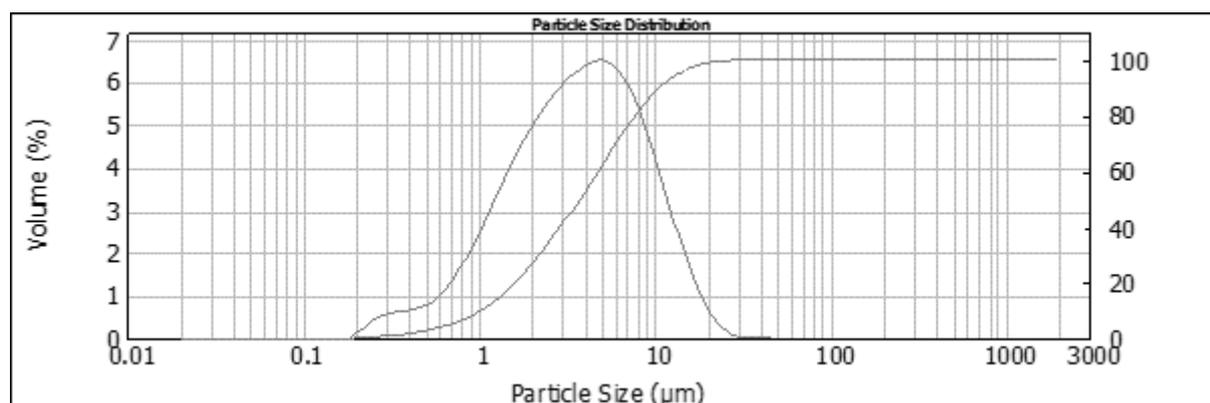


Figure 2: Particle size distribution of aluminosilicate Mefisto L₀₅

Experimental

Analytical and testing methods

The chemical composition of the aluminosilicate was determined by X-ray fluorescence (BRUKER S8 Tiger).

The phase composition of Mefisto L₀₅ was determined by X-ray diffraction (BRUKER D8 Advanced equipped with a BRUKER SSD 160 detector). The XRD was measured using Cu-K α radiation at 40 kV and 25 mA. A scan with steps of $2\theta = 0.02^\circ/\text{sec}$ for the angles ranging from 5° to 70° was used.

The chemical composition of the water glass was determined using an OPTIMA 8000 inductively coupled plasma optical emission spectrometer (Perkin Elmer). The total content of alkali metals and SiO₂ in the water glass was determined by conventional acid-base titration method.

The Mefisto L₀₅ metakaolinite particle size distribution was measured using a Mastersizer 2000 laser diffraction analyzer (MALVERN Instruments). Prior to the actual measurement, the agglomerates were disrupted by sonication.

The dynamic viscosity of the geopolymer binder was measured using a Rheotest RN 4.1 rotary viscosimeter (Rheotest Medingen) with an arrangement of concentric cylinders with a 1 mm gap. The outer diameter of the rotating cylinder was 36 mm and the inner diameter of the static cylinder was 38 mm. The static cylinder was tempered at 25°C by a thermostat. The binder was transferred to the measuring cylinder immediately after mixing and the dynamic viscosity measurement was started twenty minutes after the binder mixing began. The shear rate was 75 s^{-1} . The time curves of the dynamic viscosity had a characteristic shape consisting of three distinct parts. The initial part of each curve was almost linear until a significant convex part followed by another almost linear viscosity increase. Initial setting time was calculated from the intersection of the two linear parts of each curve. The first regression line based on the initial part of the measurement was considered to be a constant, i.e. a line parallel to the x-axis (the same values of viscosity were obtained for an extended period of time with sufficient accuracy). The second regression line corresponds to the linear part with a bigger slope. Furthermore, the slopes of the second part of the curves characterize the solidification rates of the binders. The larger the slope, the faster the binder is solidified. The initial setting time, measured with the rotary viscosimeter are discussed later.

Determination of the initial setting time of the geopolymer binders was performed using a Vicat's instrument VICATRONIC (MATEST). The measurement was performed according to the adapted standard ČSN EN 196-3:2017¹⁸. The Vicat apparatus was placed in an air-conditioned chamber at 25°C and 90 % relative humidity (r.h.) throughout the measurement, to ensure reproducibility of solidification conditions. The high humidity in the air conditioned chamber reduced the water evaporation from the geopolymer surface. The initial setting time was then determined by the time when the needle of the Vicat apparatus for the first time did not fall to the bottom of the test vessel, but remained above its bottom.

The determination of the geopolymer temperature during the initial setting time were recorded using the GMH 3250 electronic logger (GREISINGER electronic) with a standard K-type thermocouple. The temperature values were recorded every 5 minutes.

Determination of initial setting times of geopolymer binders with different water contents using a pressure needle apparatus was performed on an apparatus designed on the basis of previous experience with the test of geopolymer binders applicability using injection needles, described by Koutník et al.¹⁹. The test was based on measuring the flow of binder extruded through a needle with an outer diameter of 2.0 mm with constant air pressure of 13.3 kPa (100 Torr) generated by a pump. The air pressure in the apparatus was regulated by a needle valve and measured with an accurate digital pressure gauge. The binder flow rate was evaluated by measuring the weight of the binder passing through the needle in real time. Digital weighing scales with an accuracy of one mg connected to a PC with the weight being logged with interval of 1 s were used. The whole apparatus was placed in an air-conditioned chamber, which maintained constant conditions (25°C and 50 % r.h.). The measurement took place immediately after mixing the binder or with the start delayed by up to 240 minutes. For the

delayed start measurement, the binder sample was transferred to a syringe placed in the apparatus after mixing and the compressed air was not introduced into the syringe immediately, but with appropriate delay. The initial setting time of binder was defined as the delay time at which the binder flow in the first 10 s of the measurement reached 30 ± 5 % of the flow of freshly prepared binder. This limit was based on previous experience and a number of observations. Longer delay time of the binder before processing, which results in flow rates below 30 % of the initial value, usually does not allow its application with achieving comparable properties after hardening. A simplified diagram of the apparatus is shown in Figure 3.

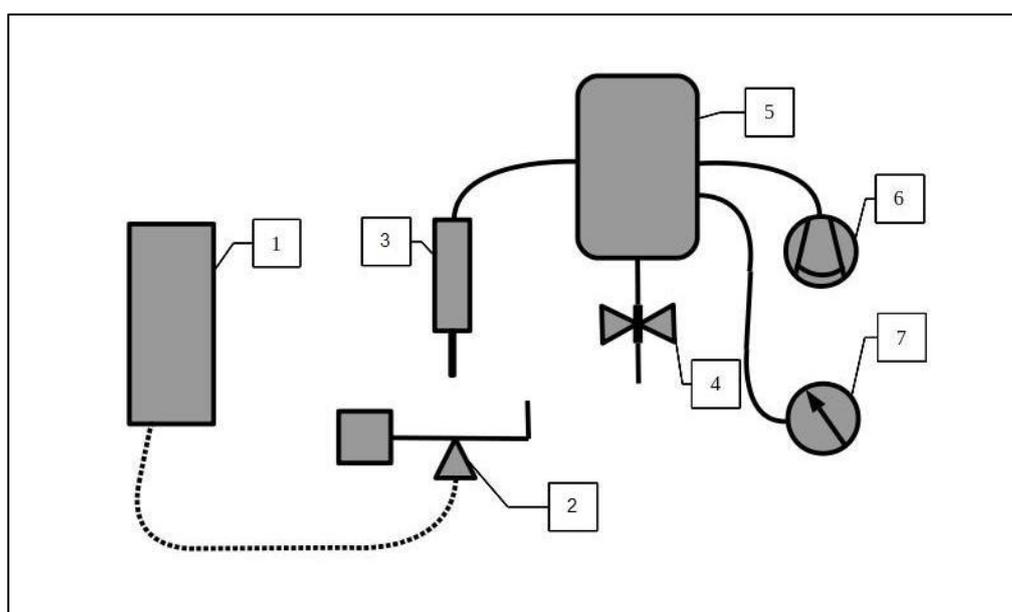


Figure 3: Schematical drawing of the needle pressure apparatus: 1 – control and data collection PC; 2 – digital weighing scales with digital output; 3 – 50 ml PP syringe with needle; 4 – air needle valve; 5 – expansion tank; 6 – diaphragm air pump; 7 – pressure gauge.

Preparation of geopolymer binders

The alkaline activator was prepared by dissolving potassium hydroxide in potassium water glass. To remove water absorbed during grinding and storage, Mefisto L₀₅ was dried in an oven at 110 °C. The preparation of the geopolymer binder itself consisted in mixing the alkaline activator with the dried aluminosilicate raw material in a planetary mixer at room temperature for 10 minutes. Then, distilled water was added to adjust the water content of the geopolymer binder, followed by further stirring for 5 minutes. Five binders with total water content of 30, 35, 40, 45 and 50 % were prepared. The total water content of the geopolymer binder is the sum of the water added during homogenization in the planetary mixer and the water contained in the raw materials. The Me/Al molar ratio was kept at 1.0 in all binders and the Si/Al molar ratio was always 1.5.

These values were chosen on the basis of the research of Koutník et al.¹⁶ due to the low viscosity of the binder after mixing and high strength of the binder after solidification at the same time.

The sample labeling is given in Table 2.

Table 2: Sample labeling and parameters. Ratios Me/Al, Si/Al and water content in weight %

Marking of geopolymer binders	GP 1.0-30	GP 1.0-35	GP 1.0-40	GP 1.0-45	GP 1.0-50
Molar ratio Me ^a /Al	1	1	1	1	1
Molar ratio Si/Al	1.5	1.5	1.5	1.5	1.5
Water content [%]	30	35	40	45	50

^aMe = Na + K

Results and discussion

Determination of dynamic viscosity with a rotary viscosimeter

The dynamic viscosity estimated by measurement with the rotary viscosimeter is shown in Figure 4 for binders with different water contents. Clear differences in time dependence of viscosities can be seen. All measured curves show an almost linear dependence of viscosity on time until a steep increase is detected as already mentioned (see Figure 4). Initial setting time was calculated from the two linear parts intersections as described in the Experimental section. Similarly, the results of viscosity measurements were evaluated e.g. in the works of Arnoult²⁰ and Archez²¹. For the curves corresponding to binders with 30, 35 and 40 % of water, the steep part of the curve shows a sharp increase in viscosity corresponding to the solidification process. The curves of 45 and 50 % binders obviously show the same change, however, the slope of the steeper part of their curves is significantly lower compared to 30-40 % binders. An example of the solidification time evaluation is shown in Figure 5 (binder with 30 % water in this case). Formally, the 45 and 50 % curves can be evaluated in the same manner, but the solidification does not take place in this range of the water content. Moreover, the initial setting time calculated by the method of two linear parts intersection for 45 % binder is shorter than in case of 35 % binder, which is rather unexpected and improbable. Figure 6 shows the initial setting times of geopolymer binders with different water contents. From above mentioned reasons, the use of the rotary viscosimeter for initial setting time calculation has some limitations and should be carefully checked. The most probable reason for such behaviour is the thixotropy of the geopolymer binders as described by Bong²².

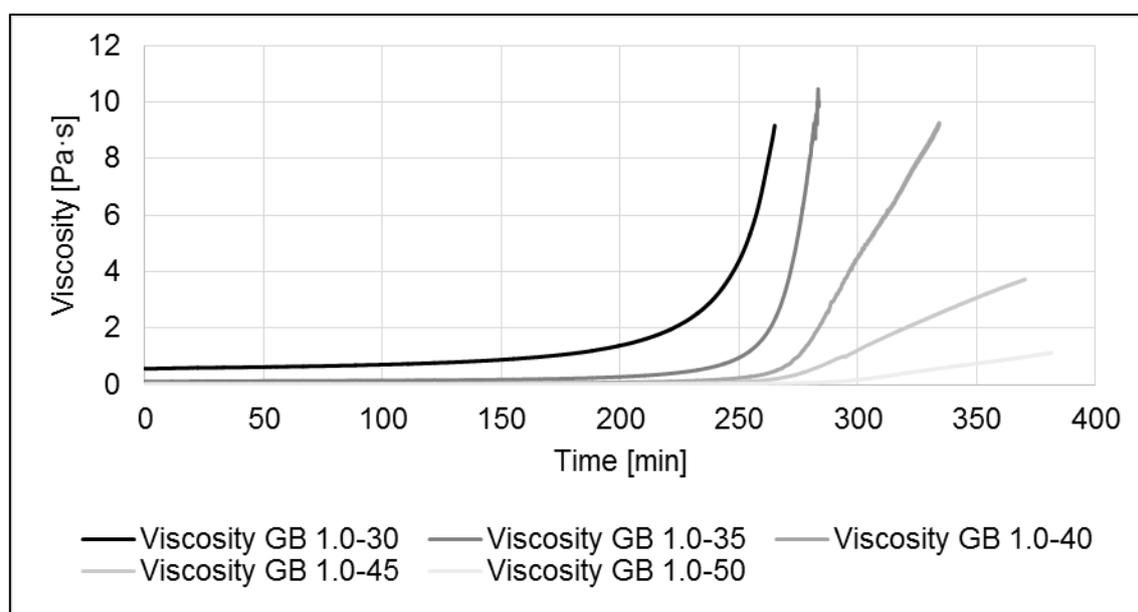


Figure 4: Time changes of dynamic viscosity measured by a rotary viscosimeter

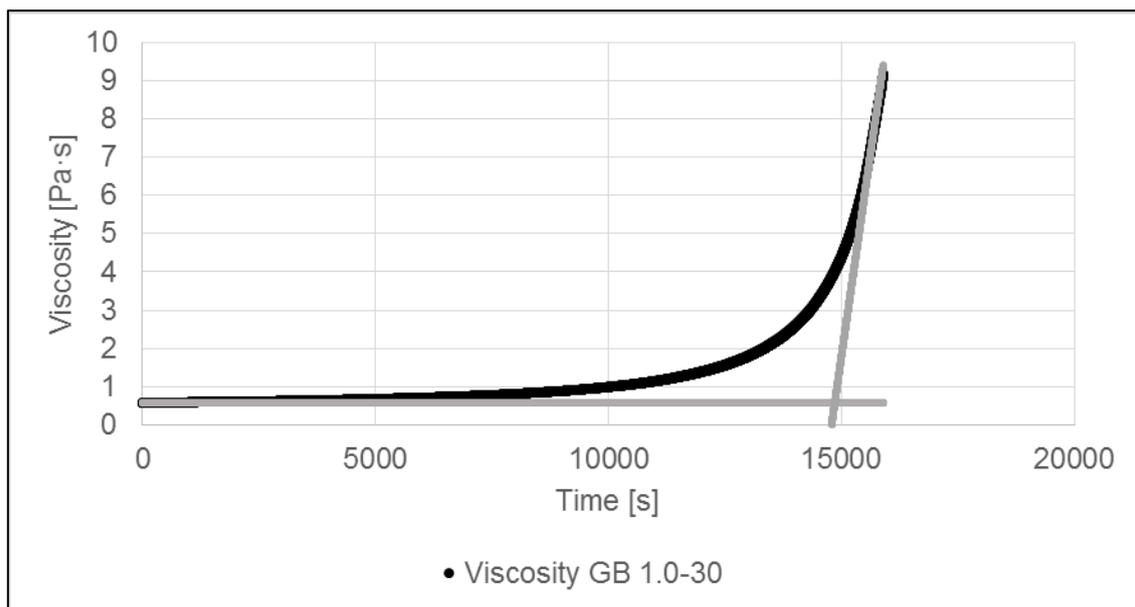


Figure 5: Example of initial setting time calculation from rotary viscosimeter measurements

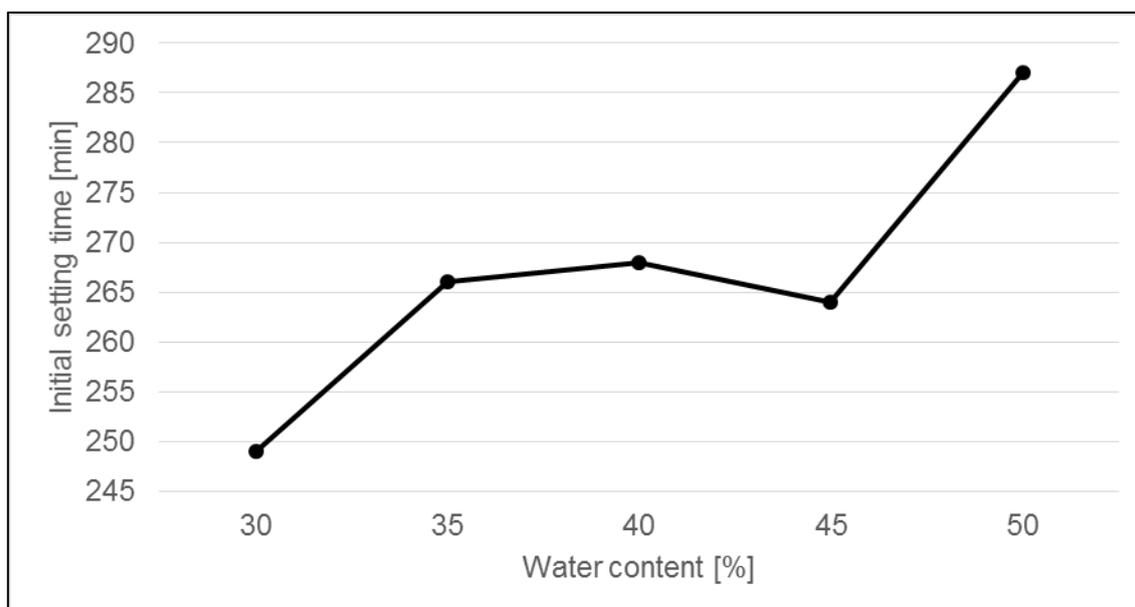


Figure 6: Initial setting times calculated from rotary viscosimeter measurements at 25 °C

Determination of initial setting time by a Vicat device

The results for geopolymer binders with different water contents GB 1.0 - 30 to GB 1.0 - 50 are shown in Figure 7. For all samples, control vessel (shape-identical to the vessel with the Vicat device) was used for the simultaneous temperature measurement. The temperature was always measured in the middle of the control vessel. The results of the temperature measurements are shown in Figure 8.

GB 1.0-30 binder started to solidify the fastest and the initial setting time of geopolymer binder increased with an increasing amount of water from 265 minutes (K2G80n GB 1.0 - 30) to 393 minutes for GB 1.0 – 50 binder. The Vicat test corresponded to the real behaviour of the geopolymer solidification time at rest, i.e. without any agitation, depending on the water content. However, the real workability time of the binder is shorter than the initial setting time, when the geopolymer is no longer in a liquid state. Gao²³ and Kaja²⁴ also used the Vicat apparatus and the standard EN 196-3¹⁸ to determine the initial setting time. However, their geopolymer mixtures were with the addition of limestone, so the initial setting times are incomparable.

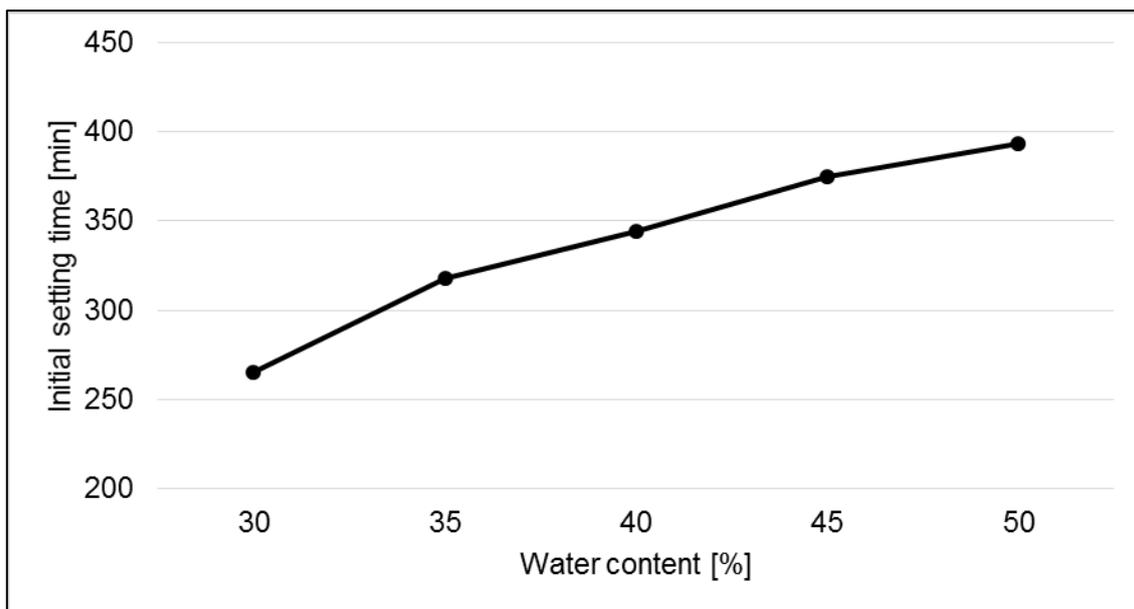


Figure 7: The initial setting times of geopolymer binders with 30 to 50 % of water at 25 °C determined by a Vicat apparatus

Figure 8 shows the temperature profiles inside the control specimen for samples GB 1.0 – 30 to GB 1.0 - 50 with different water contents, which were placed in an air-conditioned chamber with a constant temperature of 25 °C. Figure 8 shows the increase of temperature in the middle of the control vessel to 29 °C in the case of the GB 1.0 – 30 sample followed by gradual decrease to the tempering temperature. The highest maximal temperatures were recorded for samples with a lower amount of water, while the lowest maximal temperatures were recorded for the samples with higher water content. Similar measurements were performed e.g. by Novais²⁵, who measured the dependence of the temperature of the solidifying binder on the water content. His work describes the same trend, i.e. a rapid rise in temperature with gradual temperature decrease. It is clear that geopolymerization is an exothermic process. The heat generated by geopolymerization is used to increase the material temperature. Due to the high specific heat capacity of water and the inhibition of the geopolymer reaction, geopolymers with a higher water content do not reach such temperatures of geopolymers with lower water content.

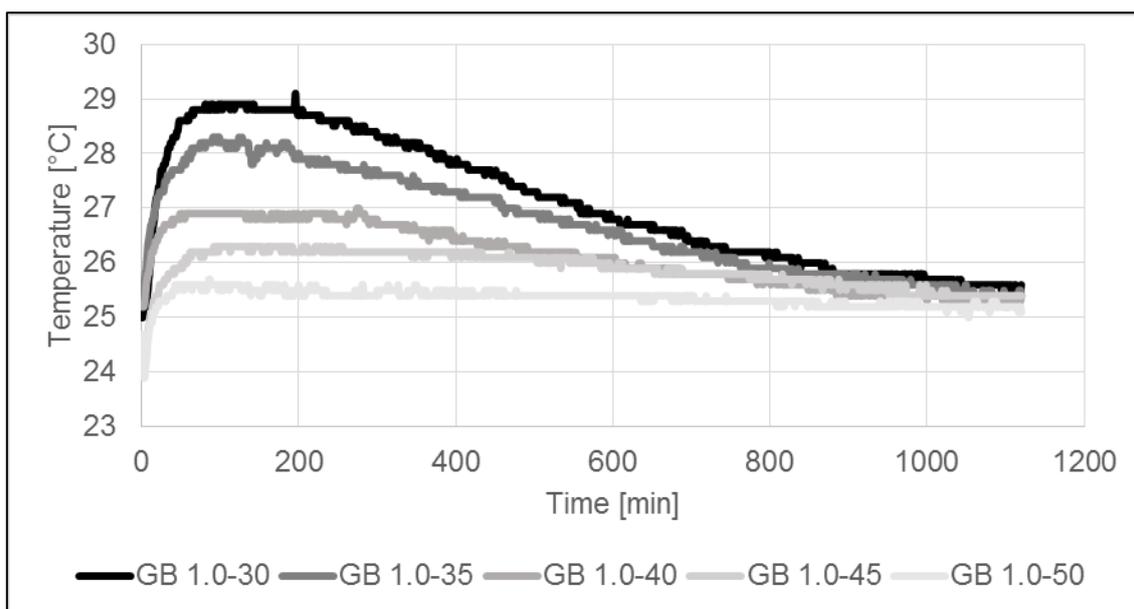


Figure 8: Dependence of sample temperature on time for samples GB 1.0 – 30 to GB 1.0 – 50.

Determination of the initial setting time using velocity of the flow through a needle

The results of the initial setting times measurements are shown in Figure 9. The initial setting times for binders with water content of 40 and 45 % are very similar. There are larger differences between binders with water content of 30, 35 and 40 %. It was not possible to determine the initial setting time for a binder with water content of 50 %. The binder was so thin that in case of a longer delay time before the measurement started, the undissolved aluminosilicate raw material sedimented to the needle, and thus the needle became blocked. The reason is that the lower viscosity results in lower resistance of the environment to the particle movement and in turn accelerates the sedimentation of the solid phase. However, geopolymer with 50 % water is very unsuitable for practical use, therefore this method is also suitable for most low-viscosity geopolymer binders applicable in practice. The results show that with increasing water content in the binder, the time corresponding to the initial setting time also increases and the binder is applicable for longer time.

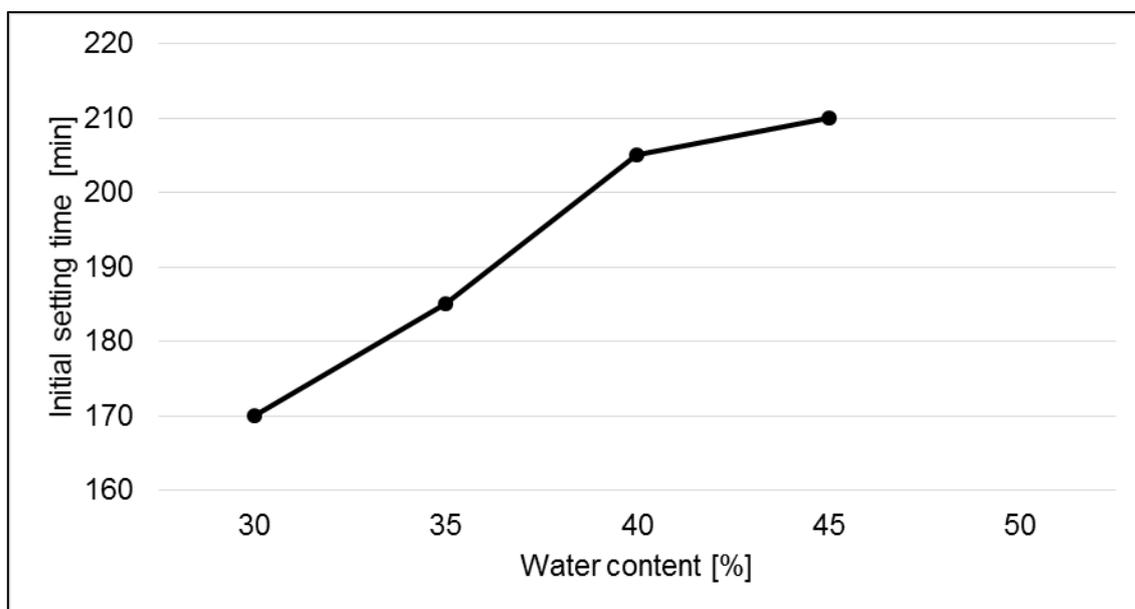


Figure 9: Dependence of the initial setting time of the binders on the water content given by the needle apparatus

Determining the initial setting time using a needle apparatus described the state of the binders with different amounts of water, when these were still processable. It was not a static process as in the case of measurement with the Vicat device, nor permanent mixing as in the case of the rotary viscosimeter. Therefore, the results of this method can be considered to be more corresponding to practical use.

Comparison of the initial setting times for various measurement methods

A comparison of the resulting initial setting times of geopolymer binders shows significant differences depending on the measurement method used. Figure 10 shows the initial setting times of the binders for all three methods mentioned in this work. The shortest initial setting times are obtained for the measurement of the flow through the needle (170 – 210 min for binders with 30 – 45 % water), followed by a rotary viscosimeter (248 – 287 min for 30 – 50 % water) and the highest values were measured with the Vicat apparatus (260 – 393 min for 30 – 50 % water). The Vicat device shows true solidification when the geopolymer is already beyond the workability time limit. The results from the rotary viscosimeter are affected by the thixotropy of the geopolymers with high water content (45 and 50 %) and do not correspond to the usual conditions of geopolymer aging at rest. On the other hand, the measurements confirm the expectation, that agitation of the mixture can prolong the workability time of the geopolymer. In comparison to the results from the static Vicat test, the curves for 45 and 50 % water (Figure 4) from

the rotary viscosimeter indicate that even after a long time there would be no complete solidification during mixing, which correlates with the verification in practice.

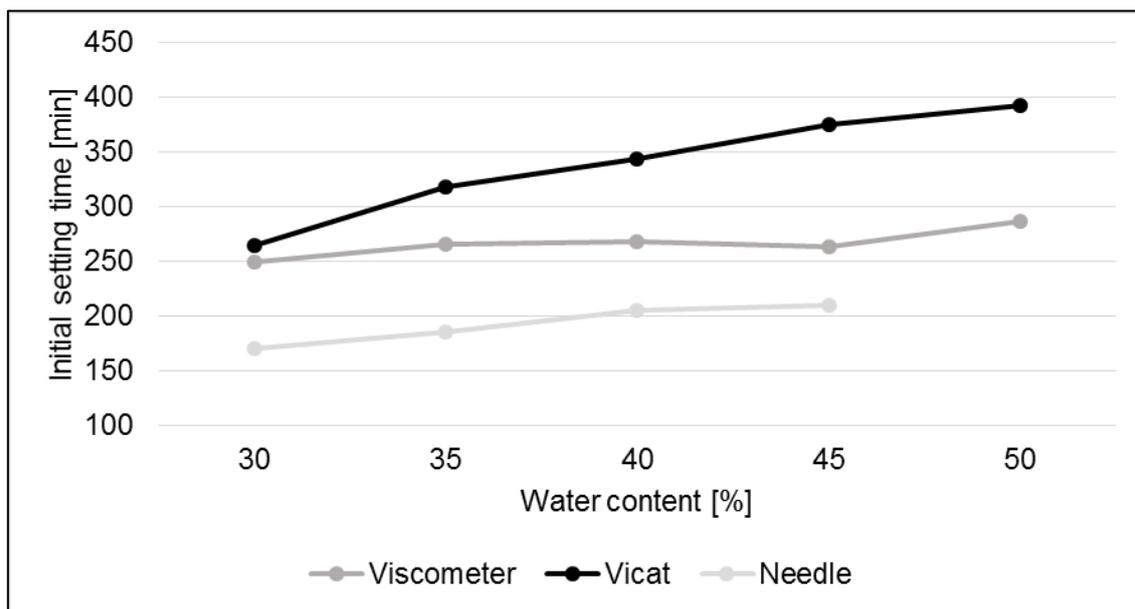


Figure 10: Initial setting times of the binders for three different measurement methods

Conclusions

In this work, the rheological properties of low-viscosity stabilizing geopolymer binders with different water content were investigated by three methods - monitoring the flow rate of the binder through the needle under defined conditions, determining the viscosity with a rotary viscosimeter and determining the solidification rate with a Vicat device. The tests were supported by monitoring the temperature of the geopolymer binder during solidification. The results of all the above tests are consistent and confirm the already known assumptions:

- with higher water content, the viscosity of the binders decreases and the initial setting time is prolonged, the workability time is prolonged as well.
- as the binder solidification is an exothermal process, heat is generated which results in increased temperature of the mixture. This temperature decreases with increasing water content which is probably related to high specific heat capacity of water.
- long-term mixing of the geopolymer binder prolongs the initial setting time.

The rheological tests used so far made it possible to monitor the rheological properties of geopolymeric binders in the fresh state (rotary rheometer) or in the almost solidified state (Vicat's apparatus). The newly developed method of measuring the flow rate of the binder through a needle of appropriate diameter at suitable overpressure together with modifications of the standard viscosity measurement procedure allow investigation of the change in rheological properties of geopolymer binders during the whole solidification process from mixing the precursors to the geopolymer solidification. The developed method of binders evaluation using the flow through the needle seems to be the most suitable for determining the real workability time of a geopolymer binder.

The tested binders were processable for a long time from the mixing of the basic raw materials. The solidification initial setting time of the GB 1.0-30 binder measured by means of the Vicat instrument corresponded to the time when the rheometer recorded the maximum viscosity of the binder.

According to these measurements, the workability of the most viscous binder was determined for at least 250 minutes from the mixing of the basic raw materials. However, this does not correspond to the

real situation that the workability time is significantly lower and corresponds to the time measured by the designed needle apparatus (approximately 160 minutes).

Acknowledgement

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Reologické vlastnosti geopolymerních pojiv a nová metoda měření

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Souhrn

Cílem této práce bylo charakterizování změn reologických vlastností na počátku tuhnutí stabilizačních geopolymerních pojiv s využitím dvou standardních a jedné nově navržené metody. Standardně bylo použito měření dynamické viskozity rotačním viskozimetrem a stanovení počátku tuhnutí Vicatovým přístrojem. Za účelem lepší charakterizace procesu tuhnutí geopolymerních materiálů byla navržena a konfrontována metoda měření rychlosti průtoku pojiva jehlou za definovaných podmínek. Výše uvedené metody byly také využity pro stanovení vlivu obsahu vody na počátek tuhnutí geopolymerního pojiva.

Bylo zjištěno, že rotační viskozimetr není vhodný pro měření počátku tuhnutí geopolymerních pojiv s ohledem na jejich tixotropii. Měření pomocí Vicatova přístroje dává dobré výsledky časů počátku tuhnutí, ale měří již technologicky nezpracovatelnou formu pojiv. Pro praktické využití, respektive určení doby zpracovatelnosti geopolymerních pojiv, nejlépe vyhovuje navržená metoda, při níž je měřena změna rychlosti průtoku pojiva jehlou.

Klíčová slova: geopolymer, pojivo, reologie, počátek tuhnutí, viskozita.

Long-term durability of cement-bonded particleboards with modified composition by waste dust

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Abstract

This paper presents research on long-term behaviour of cement-bonded particleboards exposed to adverse conditions. The boards were subjected to frosting / defrosting cycles, up to 300 cycles. Specifically, 100, 200, 300 cycles were performed at the age of 28 days, 6 months, 12 months, 18 months and 24 months. Composition of the particleboards was modified by by-product, which has its origin in production of cement-bonded particleboards. Dust from cutting and grinding of the particleboards was used in amount of 7% as a partial substituent of cement (6%) and spruce chips (1%). The goal of presented research is the assessing the effect of adverse conditions at different age of cement-bonded particleboards (with modified composition), when attention is paid to mechanical properties and microstructure, respectively. Bending strength, modulus of elasticity in bending, transverse tensile strength perpendicular to the plane of the board and microstructure (SEM) were studied with respect to the changes in time (up to 2 years).

Keywords: Cement-bonded particleboards, modification, composition, alternative raw material, properties, microstructure, long-term, durability, frost, development in time.

Introduction

Cement-bonded particleboards are a globally widespread building material, with the production of the domestic producer reaching approximately 55 thousand m³ of boards per year. These boards are characterized by very good durability. The creation of by-products is a typical part of the industrial production of building materials and components. These by-products very often have no further use and therefore have to be landfilled. One of the by-products created during production of cement-bonded particleboards is the dust from their formatting. This fine-grained particulate substance is produced in quantities of around 7 to 7.5 tonnes per year. With regard to the composition of the cement-bonded particleboards, there is a possibility of adding this unused by-product, suitably treated, back to the production of the boards. Each time the composition of the material is modified its properties change. Therefore, it is always necessary to assess and analyse the behaviour of the material in detail when carrying out any modification. Cement-bonded particleboards are no exception, as evidenced by many studies and research papers published to date. The authors discuss various aspects of the production of cement-bonded particleboards using various types of alternative raw materials, including the very important durability¹⁻⁸.

The aim of the research presented here was assessing long-term behaviour of cement-bonded particleboards with modified composition. The composition of the boards was modified by dust from the formatting of these boards. Basic characteristics including microstructure were monitored at six-month intervals. The analysis of the properties and behaviour of the particleboards were carried out over a period of 2 years. This time interval is sufficient for objective assessing the durability of the particleboards. The behaviour prediction and estimating the durability of cement-bonded particleboards in a real structure when exposed to adverse effects can be formulated by the mentioned procedure. A typical such influence is the cyclic freezing and thawing in the presence of water, which is characteristic of temperate climatic conditions.

Materials and Methods

Materials

Composition of the cement-bonded particleboards corresponds to standard boards produced commercially. These particleboards contain (in volume) Portland cement CEM I 42.5 R (25%) according to EN 197-1⁹, spruce chips (63%), aluminium sulphate ($Al_2 [SO_4]_3$), sodium water glass (total 2%), water (10%). Composition was modified by waste from formatting the particleboards in amount of 7%. Two following types of the cement-bonded particleboards were tested:

- Reference boards DR – standard composition of the cement-bonded particleboards, i.e. cement, spruce chips, water and hydration admixtures.
- Modified boards DP – standard composition of the cement-bonded particleboards was modified by dust, which is produced during trimming and grinding of these boards, in amount of 7% (partial substitution of 6% cement and 1% chips was carried out).

A detailed analysis of the dust generated during the machining of cement-bonded particleboards was presented by Melichar and Bydzovsky¹⁰. In the cited study, the authors present a comprehensive set of all relevant properties and behaviour of dust in terms of its use in cementitious composites. The results and findings of the authors¹⁰ clearly demonstrate the high potential, suitability and compatibility of cement-bonded particleboard processing dust for the manufacture of cement composites. Also significant is the fact that the wood chips contained in the dust are already mineralised and therefore show better properties than primary spruce chips.



Figure 1: Structure of the dust in detail, picture from optical microscope

Due to the environmental situation, the dust with a grain size of up to 2 mm was applied. Dust is an inert particulate substance with no active contribution to the forming structure of the new composite. The possibilities of replacing the primary raw materials of cement-bonded particleboards in quantities of 6, 8 and 10% were verified and evaluated in the laboratory. The production, testing of properties and microstructure was carried out in the laboratories of Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components. The tests were carried out in accordance with technical standards¹¹⁻¹⁵. Based on the results and findings amount of 7% was selected as an optimal possibility for the real production with minimal impact on the decrease of especially the utility properties of the particleboards.

Subsequently, cement-bonded particleboards were fabricated directly on the production line of the domestic manufacturer CIDEM Hranice, a.s. Boards with a thickness of 12 mm were manufactured. Test specimens with dimensions of 290 mm × 50 mm × 12 mm and 50 mm × 50 mm × 12 mm were made from fabricated boards for the determination of strength characteristics, modulus of elasticity and density with emphasis on long-term durability (resistance to frost influence, evolution over time) including subsequent microstructure assessment. In order to obtain the average value, including the deviation (absolute error) and the coefficient of variation (relative error) of each parameter, six test specimens were tested. Three test specimens were made in the longitudinal direction of the production line and three test specimens in the transverse direction, i.e. perpendicular to the direction of the cement-bonded particleboard production line.

Methods

The intention of the research was evaluating the long-term durability of cement-bonded particleboards of composition modified by waste dust. Therefore, the test specimens were stored in a climate chamber with a relative humidity of $(75 \pm 3) \%$ and a temperature of $(20 \pm 2) \%$. The reason for this was to ensure the hydration of the cement and at the same time the volumetric stability of the spruce chips throughout the storage of the test bodies. The chips would show greater volume changes in presence of higher humidity and thus, among other things, cause pressure on the adjacent cement matrix. This phenomenon could then result in possible deteriorating the structure of the particleboards. Conversely, lower humidity is not conducive to promoting hydration reactions of the cement matrix. Before each parameter determination, the test specimens were tempered in accordance with the requirements of the relevant technical standard, i.e. at a relative humidity of $(65 \pm 5) \%$ and a temperature of $(20 \pm 2) \%$.

The development of material characteristics over a period of 2 years was evaluated. Emphasis was placed on effect of modification on properties of the cement-bonded particleboards. Testing was carried out at the 28 days, and then at six-month intervals, i.e. after 6 months, 12 months, 18 months and 24 months. After reaching the required age, the test specimens were exposed to an alternating freezing/thawing environment in the presence of water in accordance with the requirements of EN 1328¹⁵. 100, 200 and 300 freeze/thaw cycles were carried out. This procedure made it possible to assess how the frost resistance develops with increasing particleboard age over a longer time.

The dried test specimens were weighed using KERN PCB 1000-2 scales with readability of 0.01 g and the dimensions were measured with a digital caliper KINEX 600/100 mm with a resolution of 0.01 mm. Density of the particleboards was determined and rounded to the nearest 10 kg/m^3 from the measured values. Strength and modulus of elasticity were tested on a Testometric M350-20CT device with a 20kN load cell and accuracy of $\pm 0.5\%$ of reading down to 1/1000 of the load cell capacity. Testing and determination of bending strength and modulus of elasticity in bending were performed in accordance with EN 310¹¹ (test specimens with dimensions 290 mm \times 50 mm \times 12 mm). Transverse tensile strength perpendicular to the plane of the board was tested and determined in accordance with EN 319¹² (test specimens with dimensions 50 mm \times 50 mm \times 12 mm). During all mechanical tests, the load was applied at a constant velocity so that the maximum, i.e. failure of the test specimen, was reached within $(60 \pm 30) \text{ s}$. Frost resistance was tested and determined in accordance with technical standard EN 1328¹⁵. This technical standard specifies the design of frost resistance on test specimens for the determination of bending strength. For the purpose of the research, the specimens were also subjected to freezing and thawing cycles to determine the tensile strength perpendicular to the plane of the board. The standard requires 50 freeze/thaw cycles to be performed. However, for the purposes of research and long-term durability assessment, the boards were subjected to up to 300 cycles in a freezing device. The microstructure of the particleboards was analysed by TESCAN MIRA3 XMU scanning electron microscope with resolution 1.2 nm at 30 kV (with EDX). Emphasis was put on board microstructure aged 24 months in climate chamber ($20 \text{ }^\circ\text{C}$ temperature and 75% relative humidity) – both tested types of the particleboards (reference and modified).

Results and discussion

Physical and mechanical parameters

The density (Figure 2) of all tested boards exceeds $1,000 \text{ kg/m}^3$, which is in accordance with the requirements of EN 634-2¹³. The average values of the both board types are very similar and in range from ca $1,230 \text{ kg/m}^3$ to $1,370 \text{ kg/m}^3$. In terms of the development of density over time, a slight increase in the values is noticeable, i.e. up to 5%. As the number of freeze/thaw cycles increases, a decrease in density is predominantly evident. Based on the results obtained, it cannot be clearly decided whether DR or DP plates are more resistant to the effect of freezing with respect to density changes. The effect of modification was not very pronounced in the case of density, even in terms of the long-term evolution of this parameter over a 2-year period.

Interesting information on the behaviour of the particleboards due to exposure to adverse frost conditions is also provided by the determined deviations (error bars - Figure 2). It is evident that the

deviation from the average density value increases with increasing number of cycles. This is related to the deterioration of the particleboard structure with regard to frost effect. The relative, i.e. percentage, deviations are expressed as a coefficient of variation in the following table (Table 1). The coefficient of variation values are in the order of a few percent. The lower coefficients of variation were mainly determined for the reference (DR) boards.

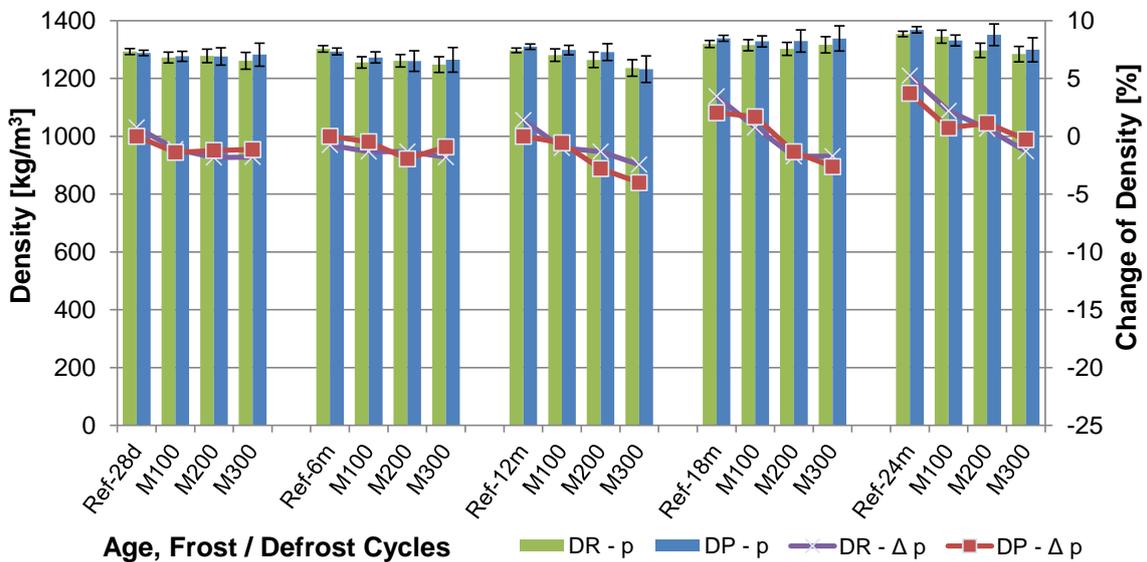


Figure 2: Comparison of cement-bonded particleboards density, red and violet curves represent decrease of density, black vertical bars represent deviations

Table 1: Coefficient of variation of density of the particleboards DR and DP

Age [days, months]	Density coefficient of variation – DR [%]				Density coefficient of variation – DP [%]			
	Cycles				Cycles			
	Ref	M100	M200	M300	Ref	M100	M200	M300
28 days	0.80	1.49	1.84	2.28	0.73	1.35	2.36	3.09
6 months	0.87	1.57	1.71	2.19	0.90	1.51	2.83	3.40
12 months	0.61	1.68	2.12	2.32	0.73	1.29	2.27	3.72
18 months	0.92	1.45	1.74	2.15	0.75	1.44	2.90	3.26
24 months	0.69	1.68	1.94	2.10	0.79	1.41	2.78	3.18

The bending strength (Figure 3) of the tested boards ranges from 12.9 N/mm² to 8.8 N/mm² (DR) and 12.7 N/mm² to 8.6 N/mm² (DP), respectively. The decrease in bending strength due to lower cement dosage in the boards corresponds to the results presented by Zhou et al.¹⁶. The minimum bending strength requirement of 9 N/mm² according to EN 634-2¹³ was met for boards without exposure to freezing cycles. Only some boards exposed to 300 freeze/thaw cycles showed strengths lower than 9 N/mm². Specifically, DR boards at 28 days and 6 months of age, and DP boards at 28 days of age. An adverse effect on the strength of the particleboards under cyclic exposure to moisture and temperature changes was also demonstrated by Miranda de Lima et al.⁵. A negative effect of water on the properties of the particleboards (when volume changes of chips occur) was also reported by Drdlova et al.¹⁹. During further maturation, all boards, even when subjected to 300 freeze/thaw cycles, reached a strength of at least 9 N/mm². With increasing age, a gradual increase in bending strength of about 1.1 N/mm² (DR) and 0.8 N/mm² (DP) was observed. Thus, by modifying the composition of the boards, the long-term strength increase was slightly slowed down. In terms of frost resistance, the two types of tested boards (DR and DP) can be evaluated very similarly. The resistance to the adverse conditions of

cyclic freezing and thawing improves slightly with increasing age. The error bars (Figure 3) are much more pronounced than in the case of density. This fact indicates a higher variability or bending strengths dispersion due to adverse climatic conditions.

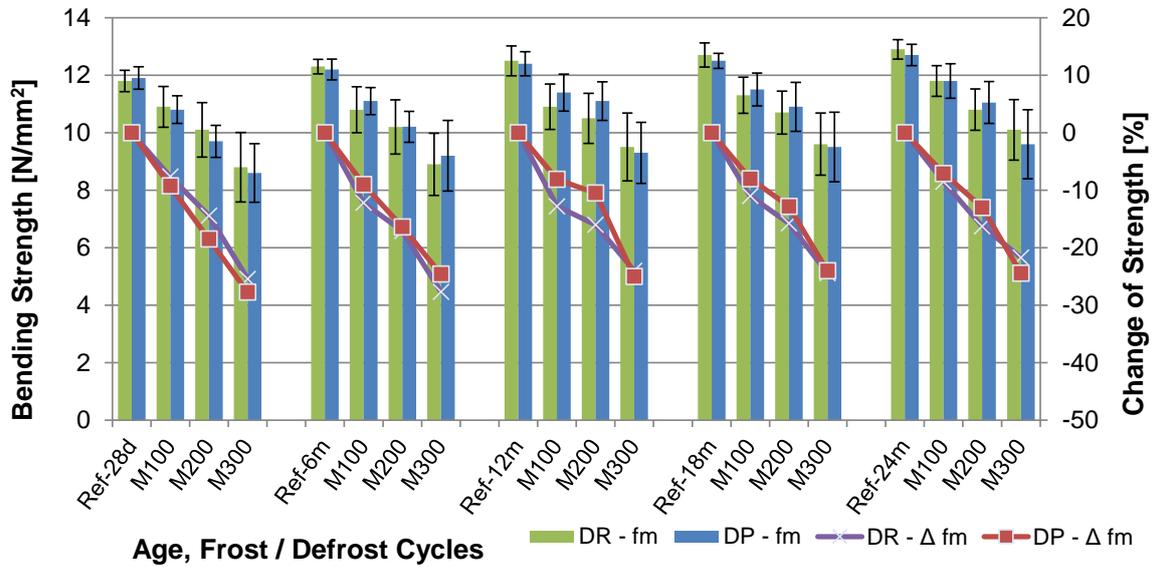


Figure 3: Comparison of cement-bonded particleboards bending strength, red and violet curves represent decrease of strength, black vertical bars represent deviations

Table 2: Coefficient of variation of bending strength of the particleboards DR and DP

Age [days, months]	Bending strength coefficient of variation – DR [%]				Bending strength coefficient of variation – DP [%]			
	Cycles				Cycles			
	Ref	M100	M200	M300	Ref	M100	M200	M300
28 days	3.14	6.51	9.41	13.75	3.28	4.44	5.77	11.86
6 months	2.03	7.41	9.22	12.13	2.95	4.23	5.29	13.37
12 months	4.16	7.25	8.29	12.42	3.39	5.62	6.04	11.40
18 months	3.31	5.58	7.01	11.25	2.08	4.96	7.80	12.74
24 months	2.64	4.50	6.67	10.39	2.93	5.07	6.60	12.46

The coefficients of variation (Table 2) of the boards before exposure to freeze/thaw cycles range from ca 2% to 4%, whereas after 300 cycles these coefficients reach values from ca 10% to 14%. Thus, it is evident that the degradation of the board structure due to exposure to adverse conditions will have a more pronounced effect on the bending strengths (rather than the densities). DR boards are slightly better in this respect. Comparing the results and findings of Fuwape et al.¹⁷, it is evident that DR and DP boards are characterized by very low variability. In fact, Fuwape et al. report values for cement-bonded particleboards of modified composition corresponding to a coefficient of variation ca 25%.

The modulus of elasticity in bending (Figure 4) of the tested boards ranges from 8,021 N/mm² to 5,213 N/mm² (DR) and 7,965 N/mm² to 4,872 N/mm² (DP), respectively. The requirement for a minimum modulus of 4,500 N/mm² according to EN 634-213 was met in all cases even plates subjected to 300 freeze/thaw cycles. A gradual increase in modulus of approx. 767 N/mm² (DR) and 817 N/mm² (DP) was observed with increasing age. The increase in stiffness and bending strength with increasing age is supported by the results of Vu et al.¹⁸. The slowing of the modulus increase was not confirmed as in the case of bending strength due to modification of the board composition. The DR boards performed slightly better in terms of frost resistance, which is particularly obvious after 300 freezing cycles. It is also evident that the resistance to the adverse freeze conditions improves slightly with increasing age.

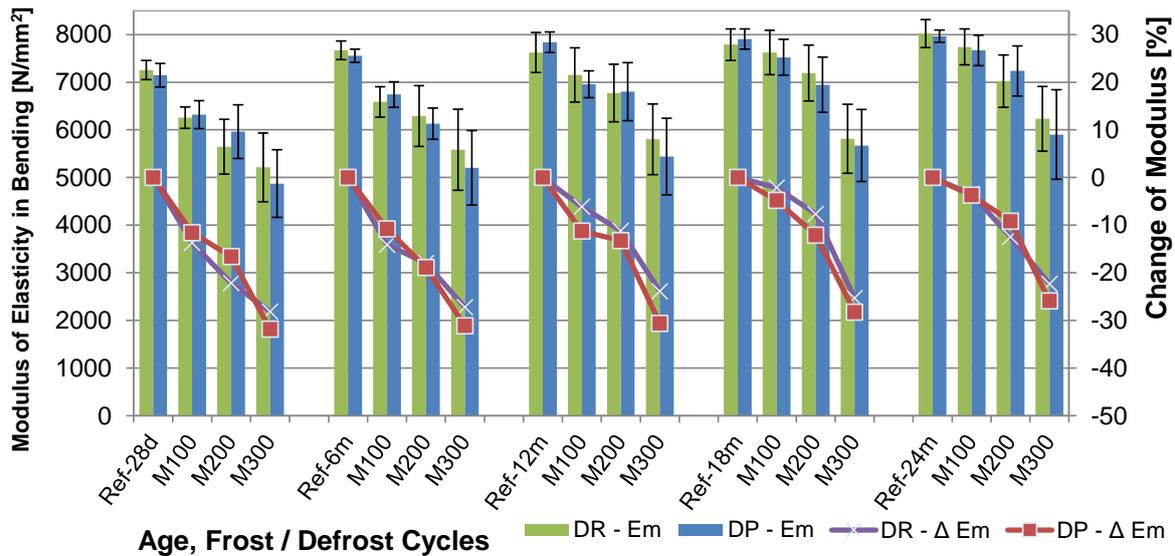


Figure 4: Comparison of cement-bonded particleboards modulus of elasticity in bending, red and violet curves represent decrease of modulus, black vertical bars represent deviations

Table 3: Coefficient of variation of modulus of elasticity of the particleboards DR and DP

Age [days, months]	Modulus of elasticity coefficient of variation – DR [%]				Modulus of elasticity coefficient of variation – DP [%]			
	Cycles				Cycles			
	Ref	M100	M200	M300	Ref	M100	M200	M300
28 days	2.77	3.60	10.15	13.83	3.47	4.64	9.46	14.54
6 months	2.54	4.87	10.14	15.26	1.82	3.95	5.32	15.07
12 months	5.52	7.94	8.90	12.77	2.77	4.03	8.96	14.81
18 months	4.22	6.13	8.16	12.47	2.69	5.03	8.33	13.34
24 months	3.64	4.84	7.82	10.88	1.64	4.16	7.27	15.96

The coefficients of variation (Table 3) of the boards before exposure to freeze/thaw cycles range from ca 2.5% to 5.5%, whereas after 300 cycles the coefficients of variation reach values from approx. 11% to 16%. It is therefore evident that the degradation of the board structure due to frost exposure will have a more pronounced effect on the elastic modulus, than in the case of bending strength and density. DR particleboards reach better resistance in this respect.

The tensile strength perpendicular to the plane of the board (Figure 5) ranges from 1.16 N/mm² to 0.55 N/mm² (DR) and 1.13 N/mm² to 0.50 N/mm² (DP), respectively. The requirement for a minimum tensile strength of 0.5 N/mm² according to EN 634-2¹³ was met in all cases even boards subjected to 300 freeze/thaw cycles. A gradual increase in tensile strength of approximately 0.26 N/mm² (DR) and 0.27 N/mm² (DP) was observed with increasing age. The slowing down of the increase in tensile strength was not confirmed as in the case of bending strength due to the different composition of the boards. The DR plates performed slightly better in terms of frost resistance, which is particularly evident after 300 freezing cycles. The resistance (tensile strength) to the adverse conditions of cyclic freezing and thawing improves slightly with increasing age.

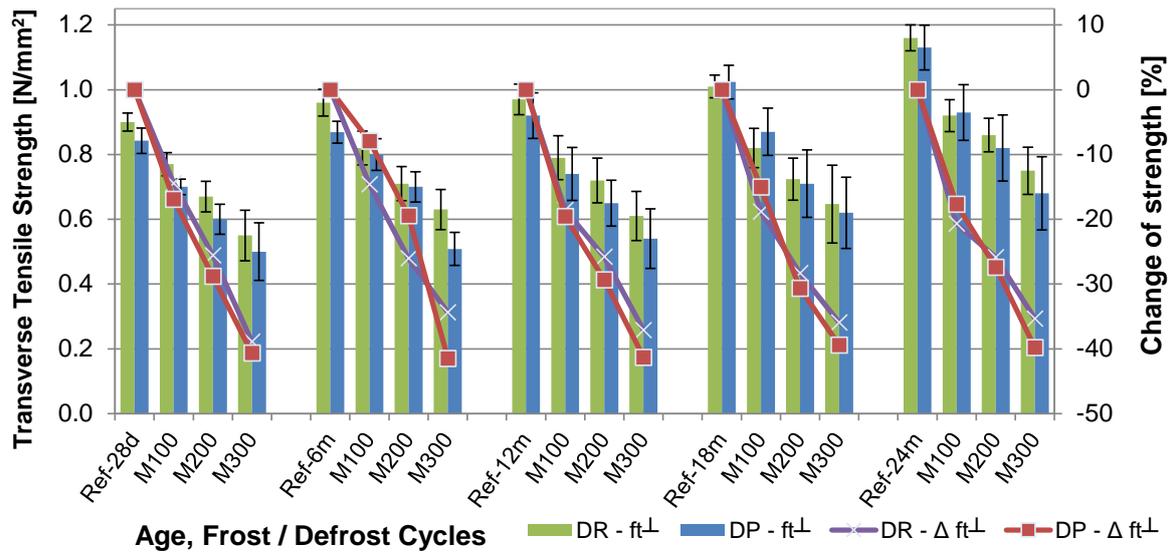


Figure 5: Comparison of cement-bonded particleboards transverse tensile strength perpendicular to the plane of the board, red and violet curves represent decrease of strength, black vertical bars represent deviations

Table 4: Coefficient of variation of transverse tensile strength perpendicular to the plane of the board – particleboards DR and DP

Age [days, months]	Transverse Tensile strength coefficient of variation – DR [%]				Transverse Tensile strength coefficient of variation – DP [%]			
	Cycles				Cycles			
	Ref	M100	M200	M300	Ref	M100	M200	M300
28 days	3.47	4.64	9.46	14.54	4.63	3.47	7.74	17.80
6 months	1.82	3.95	5.32	15.07	3.91	6.08	6.71	10.03
12 months	2.77	4.03	8.96	14.81	7.61	11.08	10.92	17.04
18 months	2.69	5.03	8.33	13.34	5.08	8.39	14.65	17.74
24 months	1.64	4.16	7.27	15.96	6.12	9.25	12.44	16.62

The coefficients of variation (Table 4) of the boards before exposure to freeze/thaw cycles range from ca 1.6% to 6.1%, whereas after 300 cycles the coefficients of variation reach values from about 10% to 17.7%. Thus, it is evident that the board structure deterioration due to adverse conditions exposure has a more pronounced effect on the modulus of elasticity (than in the case of bending strength and density). DR boards can be better evaluated in this respect. By comparing all the parameters determined, it can be concluded that the tensile strength perpendicular to the plane of the board is the most subject to degradation due to the action of adverse effects. This is indicated by the highest decreases in this strength with increasing number of freeze/thaw cycles and by the highest coefficients of variation. This is due to the anisotropy of the cement-bonded particleboards. The swelling and shrinkage in the thickness direction is the greatest when contact with water and temperature changes occur. Orientation of the spruce chips and manufacturing process are major cause. The particleboards are pressed and subjected to heat treatment during their production. In this way, tension is brought into the boards in the thickness direction. During contact with water, the volumetric changes in the chips cause the stresses are released in the thickness direction. When the release of this stress occur, the wood chips then exert pressure on the surrounding cement matrix. This fact is confirmed, for example, by the findings of Rowell et al. ²⁰. When the cohesive value of the matrix is exceeded due to this pressure, the structure of the boards gradually fails, which is most evident when the tensile strength is tested perpendicular to the plane of the board.

Microstructure

Microstructure analysis revealed that the cement matrix of the particleboards is compact and the crystalline phases are extensively developed with no structural defects. The microstructure images of the particleboards at 24 months of age before and after 300 freeze cycles are shown below (Figure 6 to 9). The interface between the cement matrix and spruce chips is compact in the case of the boards not subjected to freeze/thaw cycles. In the case of all analysed boards, it is evident that both crystalline and amorphous phases of the cement matrix grow into the surface layers of the cellular structure of the chips. The differences between the reference and the adversely stressed boards are mainly evident by the identified cracks.

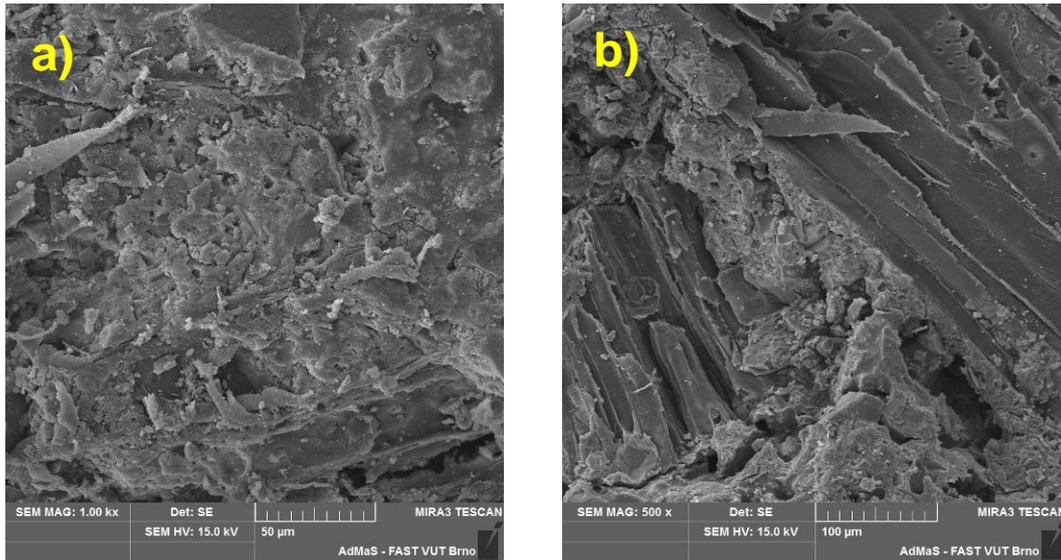


Figure 6: SEM pictures of DR Ref-24m board; a) microstructure of cement matrix, b) detail of interfacial transition zone

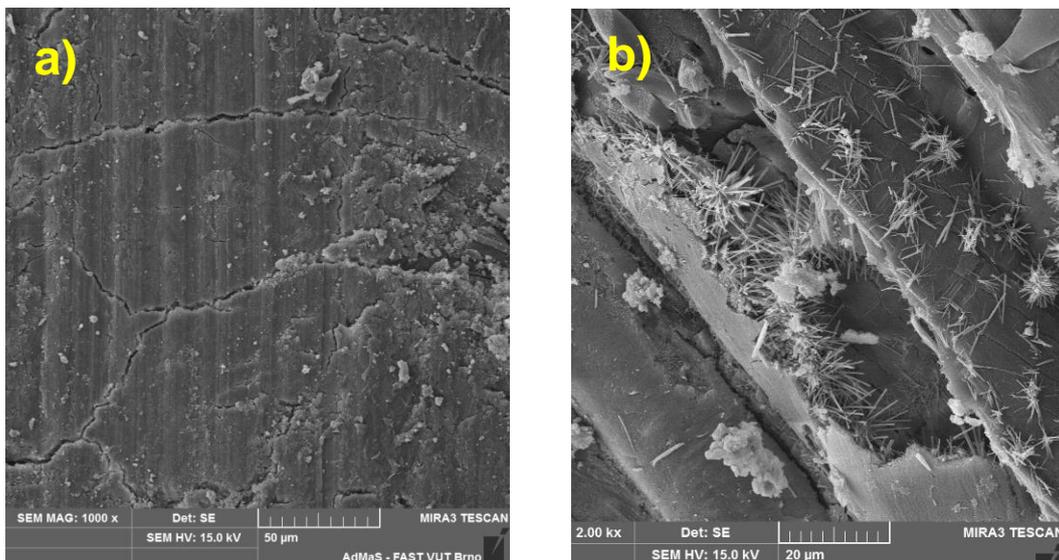


Figure 7: SEM pictures of DR 24m M300 board; a) microstructure of cement matrix under spruce chip, b) detail of interfacial transition zone

Microscopic cracks are in the area where spruce chips were present in the cement matrix (DR boards) (Figure 7a). This indicates matrix degradation, which relates, among other things, to volumetric changes in the adjacent spruce chip. The volumetric changes in the chips are due to the alternating effects of positive and negative temperatures combined with the presence of water. The crystalline phases of the cement matrix in the cellular structure of the spruce chips can be seen in Figure 7b. Microscopic cracks in the chip with widths of a few μm were also identified at this location. Considering the microstructure of the dust-modified particleboards, i.e. DP, it is clear that the matrix of the reference test specimens is compact with a well-developed and compact crystalline structure (Figure 8, 9). This is supported by the results of the determined mechanical parameters, where negligible differences were observed between DR and DP particleboards. Synergic interaction of wood chips in the cement matrix is obvious. Such as in the case of DR, exposure to freezing cycles resulted in degradation of the structure on a microscopic scale. However, the identified failures (cracks) are rather local character without affecting the evolution of the matrix structure. Minor defects were also identified in the ITZ between the spruce chips and the cement matrix (Figure 9b).

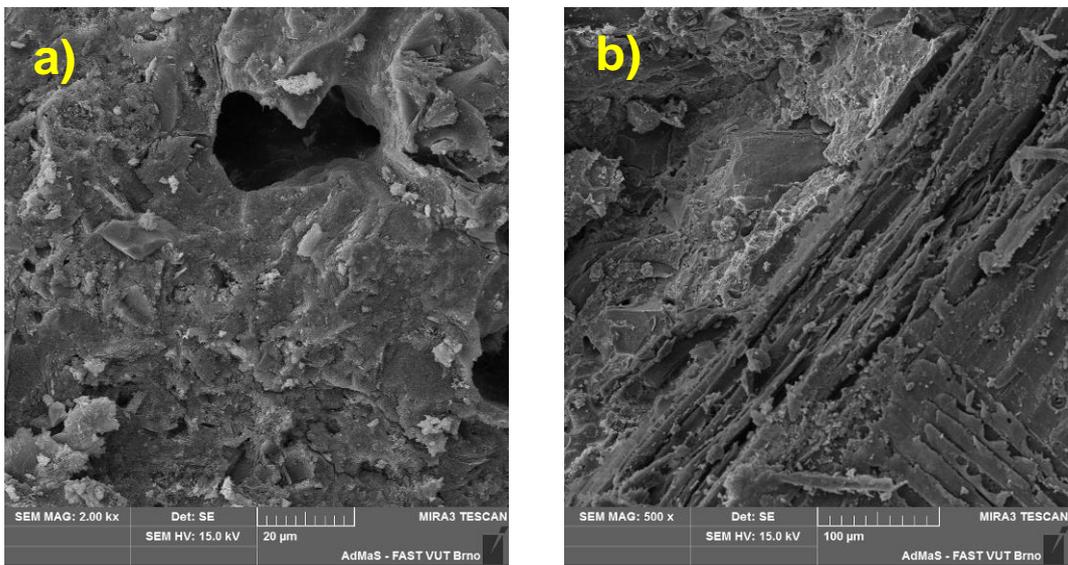


Figure 8: SEM pictures of DP Ref-24m board; a) microstructure of cement matrix, b) detail of interfacial transition zone

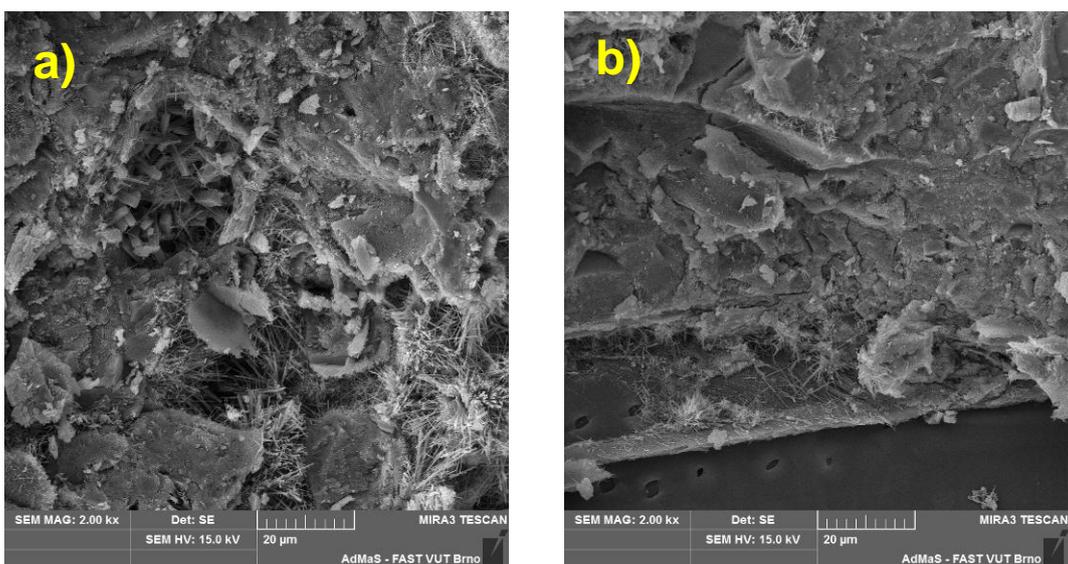


Figure 9: SEM pictures of DP 24m M300 board; a) microstructure of cement matrix under spruce chip, b) detail of interfacial transition zone

Conclusions

Based on the results obtained and the findings concluded in the scope of long-term durability of cement-bonded particleboards of modified composition, the following can be stated:

- Waste dust from formatting the cement-bonded particleboards can be used for their re-production in amount of 7% as substituent of cement (6%) and spruce chips (1%). This way could save circa 2,600 tons of cement and 140 tons of spruce chips per year in production of cement-bonded particleboards.
- Effect of the composition modification on mechanical properties and microstructure including their development in time is negligible.
- Particleboards modified by waste dust meet requirements of technical standard EN 634-2 (density, strength characteristics, modulus of elasticity and frost resistance).
- In terms of long-term development, there is a slight improvement in frost resistance. Boards subjected to 300 freeze/thaw cycles reach a bending strength of at least 9 N/mm² after 2 years maturing.
- Microstructure analysis showed very good interactions between the spruce chips and the cement matrix, even after exposure to 300 freeze/thaw cycles. Identified microscopic failures were rather local.
- The crystalline phases of the cement matrix penetrated into the surface parts of the cellular structure of the spruce chips over a period of 2 years. This has the effect of forming a more compact ITZ structure between the chips and the adjacent matrix. It is therefore evident that in the long term the interaction between the spruce chips and the cement matrix in the cement-bonded particleboards improves. The ITZ has a relatively significant effect on, among other things, the durability of cement-bonded particleboards and therefore an improvement in this respect can be predicted with time.
- For further research, it would be interesting to study the durability under other adverse conditions such as temperature shocks, CO₂, SO₂ etc.

Acknowledgment

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Dlouhodobá trvanlivost cementotřískových desek modifikovaného složení odpadním prachem

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Souhrn

Článek prezentuje výzkum zaměřený na dlouhodobé chování cementotřískových desek vystavených nepříznivým vlivům. Desky byly podrobeny zmrazovacím / rozmrazovacím cyklům, do 300 cyklů. Konkrétně bylo realizováno 100, 200 a 300 cyklů, a to ve stáří desek 28 dní, 6 měsíců, 12 měsíců, 18 měsíců a 24 měsíců. Složení desek bylo modifikováno vedlejším produktem vznikajícím při opracování právě cementotřískových desek. Prach z formátování a broušení cementotřískových desek byl použit v množství 7 % jako parciální náhrada cementu (6 %) a smrkových třísek (1 %).

Cílem prezentovaného výzkumu je posouzení vlivu nepříznivých podmínek v rozdílném stáří cementotřískových desek (modifikovaného složení), kdy je pozornost věnována mechanickým vlastnostem, resp. mikrostruktuře. Byla analyzována pevnost v ohybu, modul pružnosti v ohybu, pevnost v tahu kolmo na rovinu desky a mikrostruktura (rastrovací elektronová mikroskopie) s ohledem na změny v čase (do 2 let).

Klíčová slova: Cementotřísková deska, modifikace, složení, alternativní surovina, vlastnosti, mikrostruktura, dlouhodobý, trvanlivost, mráz, vývoj v čase.

Cementotřískové desky s vyšším obsahem netradičních alternativních surovin substituujících pojivo a třísky

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Souhrn

Článek prezentuje laboratorní výzkum zaměřený na posouzení vlastností a mikrostruktury cementotřískových desek modifikovaných alternativními surovinami. Konkrétně bylo modifikováno složení pojiva jemně mletým vápencem a škvárou. Současně byla provedena úprava složení plniva, tj. substituce smrkových třísek. Jako substituent byly využity druhotné třísky získané úpravou odřezků, které vznikají jako vedlejší produkt výroby cementotřískových desek. Pojivo bylo nahrazováno v množství do 10 % a smrkové třísky substituovány v množství 10 % až 20 %. Vlastnosti cementotřískových desek byly analyzovány po 28 dnech zrání v laboratorních podmínkách, vč. ověření mrazuvzdornosti (100 cyklů).

Výsledky prezentovaného výzkumu lze shledat jako přínosné. Využitím alternativních surovin, které jinak nejsou využity (vyjma vápence) a představují tak odpad, dojde k snížení zátěže životního prostředí a současně zachování užitných vlastností cementotřískových desek bez negativního vlivu na jejich mikrostrukturu.

Klíčová slova: *Cementotřísková deska, odřezky, škvára, vápenec, drcení, mletí, smrkové třísky, vedlejší produkt, odpad, mechanické parametry, mineralogické složení, mikrostruktura.*

Úvod

Výroba cementových kompozitů vyztužených dřevní hmotou s využitím alternativních surovin je poměrně podrobně zkoumána¹⁻¹⁰. Přes značný počet publikovaných výzkumných prací stále existuje poměrně široký prostor pro nové alternativy v této oblasti. Tyto alternativy vyplývají mimo jiné z aktuální environmentální situace. Záměrem prezentovaného výzkumu je podrobné posouzení vlastností a mikrostruktury cementotřískových desek modifikovaných dosud nevyužívanými alternativními surovinami, z nichž některé takto představují odpad. Konkrétně byl využit jemně mletý vápenec, škvára a upravené odřezky, které vznikají při opracování cementotřískových desek. Mletý vápenec je primárně vyráběná surovina, která má uplatnění nejen ve stavebním průmyslu, ovšem při výrobě cementotřískových desek se tato surovina dosud nepoužívá. Co se týká škváry a odřezků, tak se jedná o vedlejší produkty, které prozatím nemají dalšího využití. Teplárenská škvára je dostupná v množství cca 850 tis. tun (halda v Oslavanech). Odřezky vznikající při formátování cementotřískových desek jsou ročně produkovány v množství cca 5,5 tis. tun (data tuzemského výrobce desek CIDEM Hranice, a.s.). Z hlediska materiálové báze a zamýšleného účelu lze vybrané alternativní složky charakterizovat jako vysoce kompatibilní. Průzkumem odborných publikací (např.¹⁻¹⁰) nebylo zjištěno, že by se někdo podrobně zabýval problematikou vhodně upravených odřezků s ohledem na jejich zpětné využití během produkce cementotřískových desek.

Použité suroviny, receptury

Pro modifikaci složení cementotřískových desek byly vybrány odřezky vznikající při výrobě těchto desek tuzemského výrobce – výrobní závod CIDEM Hranice, a.s. Odřezky bylo nutné nejprve vhodně upravit. Záměrem totiž bylo využít především smrkového dřeva obsaženého v odřezcích. Proto byly odřezky nejprve podrobeny drcení v čelistovém drtiči. A dále pak vyseparovány třísky, resp. částice

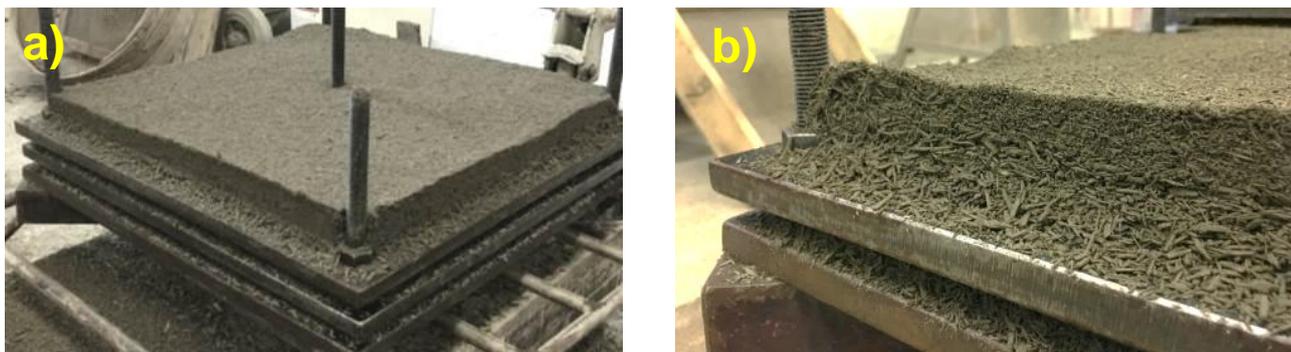
o velikosti 0,5 až 1 mm, a pak také částice o velikosti 1 až 2 mm. Tento postup byl zvolen s ohledem na předchozí podrobné analýzy odřezků a možností jejich úpravy^{11, 12}. Částice velikosti 0,5 až 1 mm a 1 až 2 mm obsahují největší podíl dřevní hmoty, což bylo prokázáno fyzikálně-chemickými i termickými analýzami (popis metod – viz^{11, 12}). Pojivo desek bylo modifikováno škvárou a vápencem. Byl použit vápenec VMV-15/F (Kotouč Štramberk) s obsahem 96,5 % CaCO₃ (stanoveno rentgenovou fluorescenční analýzou). Vápenec je primární surovina, která ovšem není pro výrobu desek běžně využívána. Dále byla jako substituent pojiva využita teplárenská škvára (Oslavany). Škvára je alternativní surovina bez dalšího využití, tj. deponována na skládce. Vzhledem ke složení, zejména granulometrického, bylo nutné škváru upravit. Cílem bylo získání suroviny o měrném povrchu převyšujícím hodnoty cementu. Proto bylo realizováno mletí v kulovém mlýnu a tak získána partikulární látka o měrném povrchu 510 až 540 m²/kg (stanoveno permeabilní metodou na Blainově přístroji dle ČSN EN 196-6¹³). Suroviny byly analyzovány s ohledem na všechny jejich podstatné charakteristiky¹¹⁻¹⁴. Škvára obsahuje vysoký podíl amorfní fáze, SiO₂ (51 %) a Al₂O₃ (22,4 %). Amorfní fáze byla stanovena kvantitativní rentgenovou difrakční analýzou (se standardem CaF₂; použitý přístroj – viz následující kapitola). Indexy účinnosti (stanovené principiálně dle ČSN EN 450-1¹⁵) rovněž vykazují velmi dobré hodnoty z hlediska aktivity této alternativní složky jako substituentu primárního pojiva. Pro výrobu desek byl použit portlandský cement CEM I 42,5 R (závod Mokrý), jehož parametry odpovídají požadavkům EN 197-1¹⁶. Dále byly použity smrkové třísky dodané přímo od výrobce desek CIDEM Hranice, a.s., včetně hydratačních a mineralizačních přísad (sodné vodní sklo, síran hlinitý). S ohledem na výsledky analýz alternativních surovin^{11, 12} a jejich vliv na cementové kompozity¹⁴ byly navrženy konkrétní receptury cementotřískových desek (Tabulka 1).

Tabulka 1: Složení cementotřískových desek

Složka	Receptura – složení [%]								
	REF	V1/DT11	V1/DT12	V1/DT21	V1/DT22	S1/DT11	S1/DT12	S1/DT21	S1/DT22
Cement CEM I 42,5 R	25	22,5	22,5	22,5	22,5	22,5	22,5	22,5	22,5
Vápenec VMV-15/F	0	2,5	2,5	2,5	2,5	0	0	0	0
Teplárenská škvára	0	0	0	0	0	2,5	2,5	2,5	2,5
Smrkové třísky – primární	63	56,7	50,4	56,7	50,4	56,7	50,4	56,7	50,4
Druhotné třísky 0,5-1 mm	0	6,3	12,6	0	0	6,3	12,6	0	0
Druhotné třísky 1-2 mm	0	0	0	6,3	12,6	0	0	6,3	12,6
Hydratační přísady	2	2	2	2	2	2	2	2	2
Voda	10	10	10	10	10	10	10	10	10

Metodika experimentů

Cementotřískové desky byly vyrobeny v laboratořích Ústavu stavebních hmot a dílců, Fakulty stavební, VUT v Brně. Výroba probíhala tak, aby byly co nejvěrněji simulovány reálné podmínky výroby tuzemského producenta desek (CIDEM Hranice, a.s.). V prvním kroku výroby byla připravena směs pro zhotovení desek. Nejprve byl do navlhčených třísek s příměsí síranu hlinitého a sodného vodního skla přidán cement, příp. substituční alternativní složky. Následně byla směs důkladně promíchána po dobu 3 minut pomocí stavebního míchadla. Dále byla na desky ocelové formy 450×450 mm přes síto s velikostí ok 2 mm nakladena vrstva směsi v tloušťce přibližně 1 – 2 mm. Pokračovalo vrstvení jádrové vrstvy směsi přes síto o velikosti oka 6 mm v tloušťce přibližně 30 mm. Finální vrstva byla opět kladena přes síto s oky o velikosti 2 mm v tloušťce 1 – 2 mm. Na takto připravenou směs byla umístěna ocelová deska. Dotažením matic byla směs ocelovou deskou slisována na požadovanou vrstvu do tloušťky cca 14 mm. Vrstvená směs je zachycena na obrázku 1.



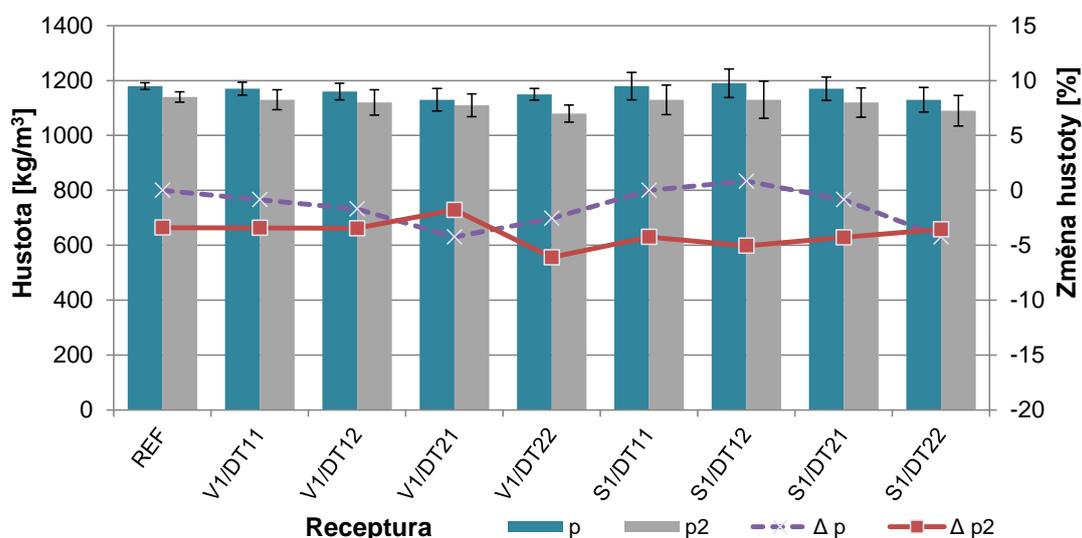
Obrázek 1: Laboratorní výroba cementotřískových desek; a) forma s navrstvenou směsí a slisovanými deskami; b) detail navrstvené směsi před slisováním

Slisovaná směs mezi ocelovými deskami byla vložena do propařovací komory. Zde byla po dobu 6 hodin udržována teplota 40 až 45 °C, což jsou podmínky zajišťující potřebnou manipulační pevnost vzniklých desek. Následně byly desky vyjmuty z forem a umístěny do laboratorního prostředí o teplotě 20 °C a relativní vlhkosti vzduchu 50 %, kde desky zrály po dobu 6 dní. Po zrání 6 dní byly desky sušeny při teplotě 70 až 75 °C po dobu 11 hodin. Následně byla z cementotřískových desek řezáním zhotovena zkušební tělesa (6 ks pro každý testovaný parametr) o rozměrech v souladu s příslušnými technickými normami¹⁷⁻²¹. Probíhalo zrání těles do dosažení celkové doby 28 dní. Dále byla zkušební tělesa temperována při teplotě 20 °C a relativní vlhkosti vzduchu 65 %. Polovina zkušebních těles byla podrobena cyklickému zmrazování a rozmrazování dle ustanovení technické normy ČSN EN 1328²¹.

Vážení těles probíhalo na vahách KERN PCB 1000-2 s přesností 0,01 g. Rozměry byly stanoveny digitálním posuvným měřítkem KINEX 600/100 mm s rozlišením 0,01 mm. Z naměřených hodnot byla stanovena hustota cementotřískových desek dle ČSN EN 323²⁰ a zaokrouhlena na nejbližších 10 kg/m³. Mechanické vlastnosti byly testovány na elektro-hydraulickém zařízení Testometric M350-20CT s přesností záznamu ±0,5 % o citlivosti čtení zatěžovací síly 1/1000 th. Stanovení modulu pružnosti a pevnosti v ohybu bylo provedeno v souladu s požadavky ČSN EN 310¹⁷. Pevnost v tahu kolmo na rovinu desky byla stanovena dle ustanovení technické normy ČSN EN 319¹⁸. Mineralogické složení bylo analyzováno s využitím přístroje X-ray diffractometer Empyrean Panalytical (CuK α radiation) s úhlovým rozlišením 0,026 ° na práškových vzorcích o maximální velikosti zrna 63 μ m. Mikrostruktura byla pozorována a hodnocena na rastrovacím elektronovém mikroskopu TESCAN MIRA3 XMU s rozlišením 1,2 nm při 30 kV. Fyzikálně-chemické a mikrostrukturální analýzy byly provedeny na vzorcích odebraných ze zkušebních těles po 28 dnech zrání.

Výsledky a diskuze

Dosažené výsledky hustoty (p_1 – před zmrazováním, p_2 – po zmrazování) prokazují, že vliv provedené modifikace složení cementotřískových desek teplárenskou škvárou a druhotnými třískami nemá na stanovené hodnoty výrazný vliv. Průběh hodnot (Obrázek 2) poukazuje na spíše minoritní rozdíly mezi jednotlivými typy desek (Δp). Změna hustoty desek se výrazně neprojevuje ani vlivem působení nepříznivého prostředí (Δp_2), tj. střídavého zmrazování a rozmrazování. Změny hustoty se pohybují v řádu jednotek procent. Zajímavější jsou z hlediska modifikace složení desek chyby, tj. odchylky jednotlivých hodnot od průměru. Výraznější odchylky od průměru sledovaného parametru byly zaznamenány v případě receptur obsahujících jako substituent teplárenskou škváru. S přihlédnutím k hodnotám stanovených variačních koeficientů (Tabulka 2) je evidentní, že desky modifikované teplárenskou škvárou vykazují vyšší míru variability. Vzhledem k dosaženým hodnotám se ovšem nejedná o příliš výrazné diference. Lze usuzovat, že vápenec přispívá ke tvorbě struktury matrice desek lépe, což může mít pozitivní vliv na proměnlivost dosažených výsledků hustoty. Z hlediska variability hustoty se jednoznačně projevuje negativní vliv mrazu, kdy byly stanoveny vyšší variační koeficienty desek podrobených cyklickému zmrazování a rozmrazování.

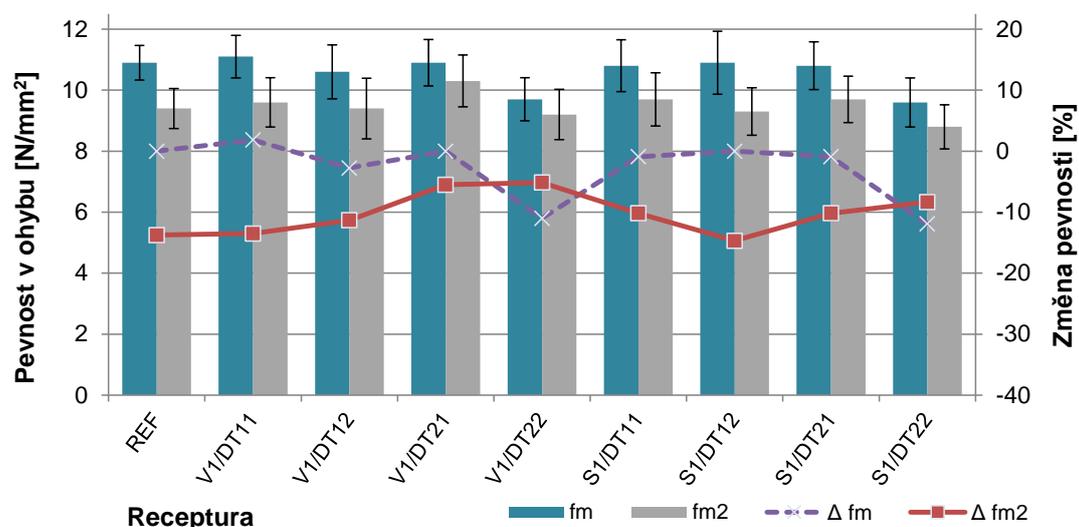


Obrázek 2: Hustota cementotřískových desek – referenčních (standardní receptura) a modifikované vápencem, škvárou a druhotnými třískami; včetně zobrazení chybových úsečků

Tabulka 2: Variační koeficienty hustoty desek referenčních a modifikovaného složení, včetně komparace různého prostředí uložení desek

Zkušební tělesa	Hustota – variační koeficient [%]								
	Receptura								
	REF	V1/DT11	V1/DT12	V1/DT21	V1/DT22	S1/DT11	S1/DT12	S1/DT21	S1/DT22
Srovnávací	1,03	2,03	2,61	3,65	1,84	4,25	4,38	3,64	3,96
Zmrazovaná	1,64	3,22	4,12	3,71	2,90	4,76	5,99	4,77	5,10

Podstatnou užitou vlastností cementotřískových desek je pevnost v ohybu (f_m – před zmrazováním, f_{m2} – po zmrazování). Stanovené výsledky pevnosti v ohybu (Obrázek 3) vykazují již mezi jednotlivými typy desek patrnější diference, než v případě hustoty. V případě téměř všech hodnocených typů desek se projevila vliv dávky druhotných třísek, kdy při 20% náhradě primárních smrkových třísek druhotnými lze zaznamenat výraznější poklesy ohybové pevnosti (fialová křivka, hodnoty Δf_m – Obrázek 3).



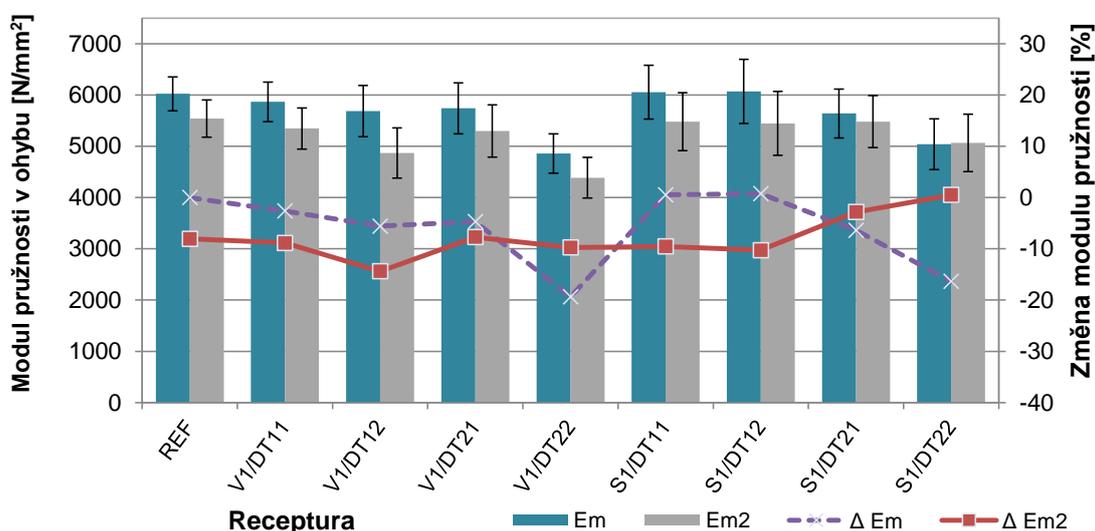
Obrázek 3: Pevnost v ohybu cementotřískových desek – referenčních (standardní receptura) a modifikované vápencem, škvárou a druhotnými třískami; včetně zobrazení chybových úsečků

Výsledky pevnosti indikují příznivý vliv druhotných třísek na mrazuvzdornost (f_{m2} , Δf_{m2}), a to konkrétně varianta třísek o velikosti v rozmezí 1 až 2 mm. Tento pozitivní vliv byl zaznamenán jak v případě modifikace matrice vápencem, tak škvárou. Pozitivní vliv druhotných třísek lze připisovat jejich větší stabilitě z hlediska expozice v prostředí o zvýšené vlhkosti. Druhotné třísky byly totiž získány z drcených odřezků cementotřískových desek. Proto jsou již tyto třísky poměrně dobře mineralizovány (vodním sklem, sírany a vápennými ionty z cementové matrice). Druhotné třísky jsou tedy mnohem více odolné vůči objemovým změnám při kontaktu s vodou a při výkyvech teploty. V důsledku pak působí při bobtnání menším tlakem na obklopující matici. Stejně jako v případě hustoty se projevil vliv mrazu na variabilitě ohybové pevnosti, kdy desky vystavené střídavému zmrazování a rozmrazování dosahují mírně vyšších hodnot variačního koeficientu (Tabulka 3).

Tabulka 3: Variační koeficienty pevnosti v ohybu desek referenčních a modifikovaného složení, včetně komparace různého prostředí uložení desek

Zkušební tělesa	Pevnost v ohybu – variační koeficient [%]								
	Receptura								
	REF	V1/DT11	V1/DT12	V1/DT21	V1/DT22	S1/DT11	S1/DT12	S1/DT21	S1/DT22
Srovnávací	5,21	6,32	8,32	6,98	7,29	7,87	9,50	7,25	8,38
Zmrazovaná	6,97	8,45	10,57	8,26	8,97	8,97	8,41	7,85	8,23

Průběh hodnot modulu pružnosti v ohybu (Obrázek 4, E_m – před zmrazováním, E_{m2} – po zmrazování, ΔE_m – změna modulu vlivem modifikace složení) do značné míry kopíruje trend pevnosti v ohybu (Obrázek 3). Zajímavá je mírná odlišnost průběhu křivek charakterizujících pokles sledovaného parametru vlivem cyklického zmrazování a rozmrazování (ΔE_{m2}), kdy desky S1/DT21, tedy na bázi škváry a druhotných třísek 1 až 2 mm vykazují velmi nízký až nulový pokles ohybového modulu pružnosti. Nicméně je patrné, že v případě modifikace matrice desek škvárou i vápencem s využitím třísek o velikosti 1 až 2 mm dochází ke zlepšení mrazuvzdornosti, tj. obdobně jako v případě pevnosti v ohybu.



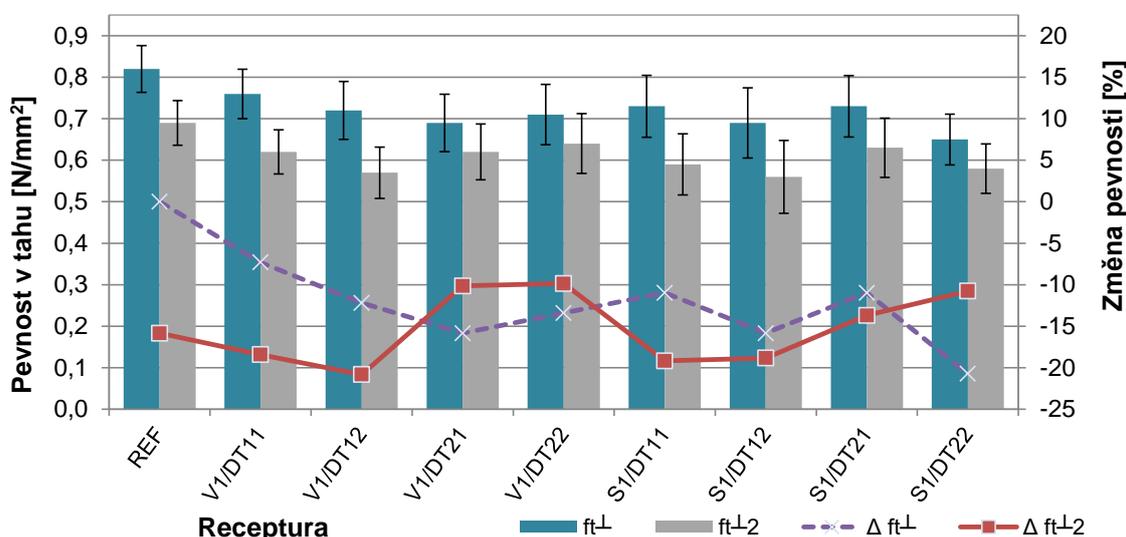
Obrázek 4: Modul pružnosti v ohybu cementotřískových desek – referenčních (standardní receptura) a modifikované vápencem, škvárou a druhotnými třískami; včetně zobrazení ohybových úseček

S ohledem na variabilitu hodnot modulu pružnosti v ohybu (Tabulka 4) je evidentní, že rozptyly těchto hodnot jsou mírně vyšší v porovnání s variabilitou hodnot ohybových pevností (Tabulka 3). Modifikace složení cementotřískových desek se tedy z hlediska variability i poklesu dosažených hodnot projeví ve větším měřítku na modulu pružnosti nežli na ohybové pevnosti.

Tabulka 4: Variační koeficienty modulu pružnosti v ohybu desek referenčních a modifikovaného složení, včetně komparace různého prostředí uložení desek

Zkušební tělesa	Modul pružnosti v ohybu – variační koeficient [%]								
	Receptura								
	REF	V1/DT11	V1/DT12	V1/DT21	V1/DT22	S1/DT11	S1/DT12	S1/DT21	S1/DT22
Srovnávací	5,49	6,58	8,78	8,67	7,89	8,65	10,29	8,47	9,83
Zmrazovaná	6,57	7,51	10,06	9,64	9,02	10,32	11,47	9,25	11,08

Podstatnou užitečnou vlastností cementotřískových desek je rovněž pevnost v tahu kolmo na rovinu desky, tj. rozlupčivost (Obrázek 5, $f_{t\perp}$ – před zmrazováním, $f_{t\perp 2}$ – po zmrazování). Vzhledem k poklesu tohoto hodnoceného parametru vlivem modifikace složení desek ($\Delta f_{t\perp}$) lze konstatovat, že se zde úprava složení desek projevila v největším měřítku. Pokles rozlupčivosti dosahuje až přes 20 % vlivem úpravy složení desek. Dále je patrné, že modifikace vápencem se projevila pozitivněji na odolnosti desek vůči vlivu mrazu ($\Delta f_{t\perp 2}$), což potvrzují i výsledky pevnosti v ohybu (Obrázek 3).



Obrázek 5: Pevnost v tahu kolmo na rovinu desky cementotřískových desek – referenčních (standardní receptura) a modifikované vápencem, škvárou a druhotnými třískami; včetně zobrazení chybových úsečků

Míra variability pevnosti v tahu kolmo na rovinu desky (Tabulka 5) je nejvyšší z posuzovaných parametrů. Tuto skutečnost bylo do značné míry možné predikovat, neboť největší objemové změny probíhají s ohledem na orientaci smrkových třísek v deskách právě ve směru tloušťky. V tomto směru totiž také probíhá hutnění (lisování) desek při jejich výrobě. Tímto jsou do třísek, resp. desek vnášena napětí, která se pak následně při kontaktu desek s vodou mohou uvolňovat a působí právě ve směru tloušťky. Tuto hypotézu také podporují výsledky jiných autorů^{24, 25}. Negativní vliv působení napětí v deskách vyvolané objemovými změnami smrkových třísek pak ještě umocní případné poruchy soudržnosti matrice (např. zhoršení vlivem modifikace složení matrice).

Tabulka 5: Variační koeficienty pevnosti v tahu kolmo na rovinu desky zkušebních těles referenčních a modifikovaného složení, včetně komparace různého prostředí uložení desek

Zkušební tělesa	Pevnost v tahu kolmo na rovinu desky – variační koeficient [%]								
	Receptura								
	REF	V1/DT11	V1/DT12	V1/DT21	V1/DT22	S1/DT11	S1/DT12	S1/DT21	S1/DT22
Srovnávací	6,87	7,84	9,68	10,02	10,23	10,24	12,26	10,16	9,41
Zmrazovaná	7,81	8,57	10,84	10,84	11,26	12,47	15,69	11,32	10,27

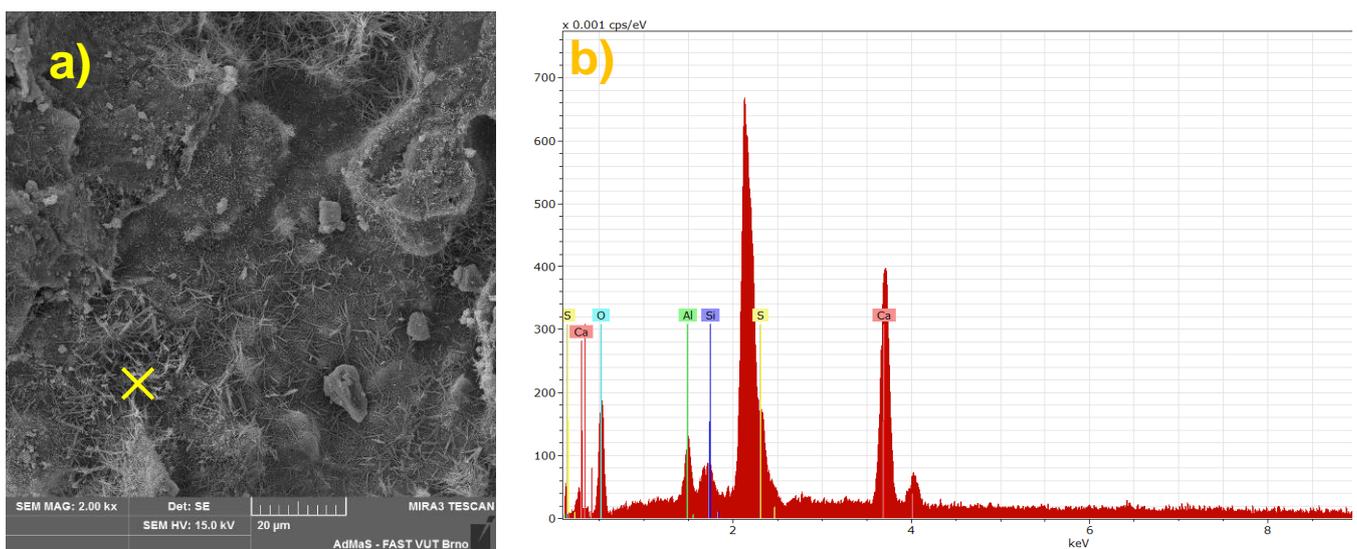
Původ použitých třísek má na finální vlastnosti dřevo-cementového kompozitu, tj. i cementotřískových desek velmi významný vliv, což se v rámci zde prezentovaného výzkumu potvrdilo nejvýrazněji na odolnosti desek vůči vlivu mrazu. Velmi výraznou závislostí na použitém druhu odpadního dřeva do dřevěnými třískami vyztužených cementových kompozitů podporují i výsledky prezentované Nasserem a kol.¹⁰

Provedeným mineralogickým rozbořem bylo prokázáno, že fázové složení všech analyzovaných typů desek je obdobné. Ve všech deskách byly nalezeny obdobné minerály a gelové struktury, tj. dominantně portlandit, kalcit, CSH struktury a amorfní fáze, stopově pak ettringit a slinkové minerály. Diference lze zaznamenat spíše v intenzitě difrakčních linií, kdy receptury s obsahem vápence vykazují výraznější píky kalcitu a naproti tomu desky s obsahem škváry jsou charakterizovány navíc přítomností mulitu, hematitu a výrazněji zvýšeným pozadím (skelná fáze). Přítomnost skelné fáze v deskách s obsahem teplárenské škváry indikuje, že ne všechna zrna této škváry se aktivně zapojila do utváření struktury cementové matrice desek. Tvorba ettringitu byla v mírně větší míře zaznamenána v případě referenční receptury, což ovšem souvisí s vyšším obsahem C₃A. Desky obsahující druhotné třísky o velikosti 0,5 až 1 mm se vyznačují vyšším množstvím portlanditu a CSH fází, což koresponduje se skutečností, že použité druhotné třísky obsahují i zbytky cementové matrice. Cementová matrice ulpívající na povrchu druhotných třísek má původ v přípravě této alternativní suroviny, kdy zdobňovací a třídící proces nevykazuje 100% úspěšnost separace cementové matrice a dřevní hmoty. V případě druhotných třísek o velikosti 1 až 2 mm se již tento faktor neprojevil v tak výrazné míře.

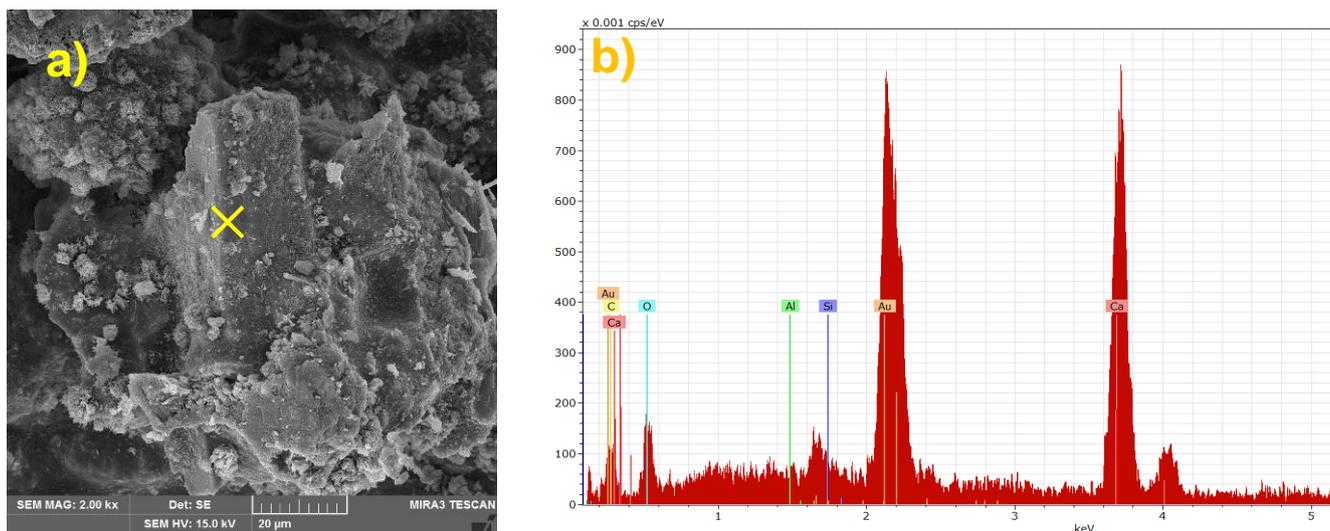
Mikrostruktura a prvková analýza analyzovaných desek (Obrázek 6 až 9) je kompaktní bez zjevných poruch mezi jednotlivými fázemi matrice. Obě modifikační složky matrice synergicky spolupůsobí s hydratačními produkty a parciálně se zapojují při utváření struktury matrice. Vápenec je v tomto ohledu výhodnější variantou substituentu cementového pojiva.

Interfaciální zóna matrice a smrkových třísek nevykazuje poruchy či defekty a hydratační produkty pronikají do buněčné struktury třísek (Obrázek 9). K obdobnému zjištění dospěl i Capari a kol.⁸, kdy bylo mikrostrukturální analýzou prokázáno, že dochází k migraci iontů cementové matrice do struktury dřeva. Dle Frybort a kol.²⁶ dochází mezi dřevní hmotou a cementovou maticí k výměně iontů, což přispívá k zlepšení zakotvení matrice k povrchu dřevěných třísek.

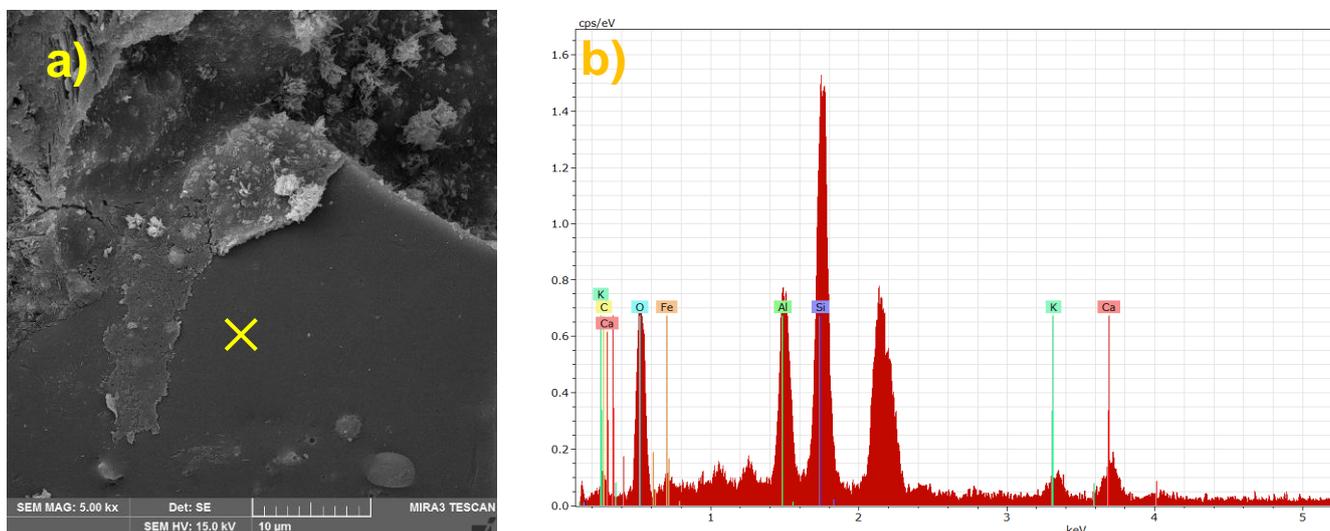
Na základě prvkové analýzy se potvrdil předpoklad, že ne všechna zrna škváry a v menší míře i vápence se aktivně nepodílela na utváření struktury cementové matrice, kdy působila spíše jako inertní mikroplnivo (Obrázek 7 a 8). Elektronovým mikroskopem bylo prakticky nemožné rozlišit třísky druhotné a primární.



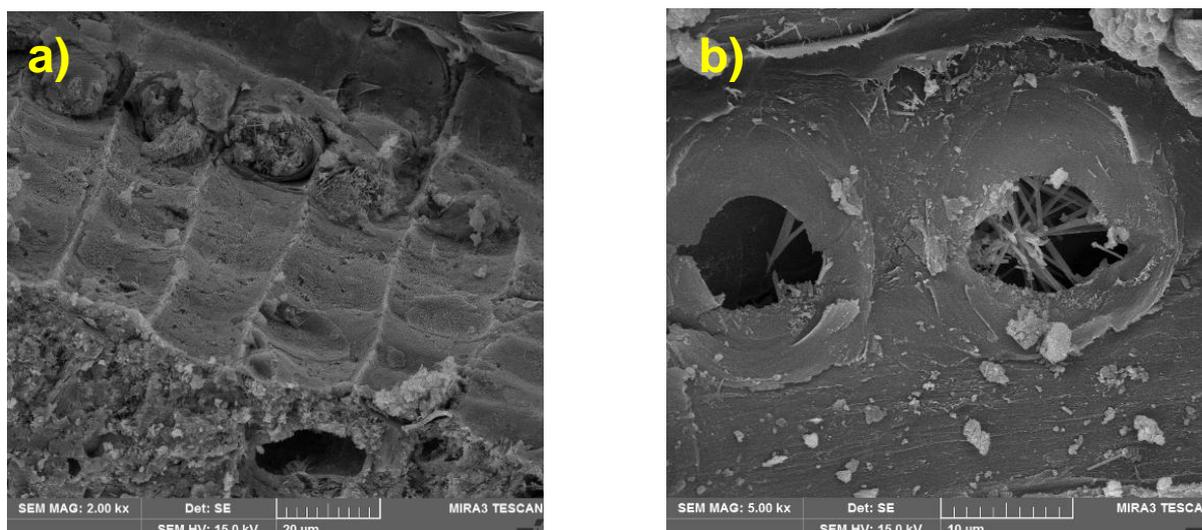
Obrázek 6: Mikrostruktura desek REF; a) vyznačení lokality výskytu ettringitu; b) identifikace prvků



Obrázek 7: Mikrostruktura desek V1/DT22; a) vyznačení lokality výskytu vápence; b) identifikace prvků



Obrázek 8: Mikrostruktura desek S1/DT22; a) vyznačení lokality výskytu škváry; b) identifikace prvků



Obrázek 9: Mikrostruktura desek a) V1/DT22; b) S1/DT22 – produkty matrice v buněčné struktuře smrkových třísek

Závěr

Dosažené výsledky a zjištění prokázaly, že modifikace složení cementotřískových desek jemně mletým vápencem, teplárenskou škvárou a druhotnými třískami (z drcených odřezků cementotřískových desek) vykazuje značně vysoký potenciál. Vyjma vápence, všechny zmíněné suroviny prozatím nenalézají dalšího uplatnění a tak představují zátěž pro životní prostředí a v případě odřezků i finanční zátěž pro jejich původce, kdy je nutné tento vedlejší produkt výroby cementotřískových desek skládkovat. Žádná z analyzovaných surovin není v současnosti využívána jako složka receptury pro výrobu cementotřískových desek.

S ohledem na nižší náročnost přípravy alternativních složek lze shledat jako výhodnější variantu V1/DT21, kde 10 % vápence nahrazuje primární pojivo (portlandský cement) a 10 % druhotných třisek substituují primární třísky (oba typy – smrkové dřevo).

Jako environmentálně šetrnější lze pro další komerční využití shledat recepturu S1/DT21, kde 10 % teplárenské škváry nahrazuje primární pojivo (portlandský cement) a 10 % druhotných třisek substituují primární třísky (oba typy – smrkové dřevo). Nevýhodou této varianty je nutnost mletí škváry na měrný povrch přesahující 500 m²/kg.

S uvážením stanovených materiálových vlastností a chování desek během cyklického zmrazování a rozmrazování lze konstatovat, že všechny testované desky vyhovují požadavkům dle příslušných technických norem.

Jednoznačně se projevil pozitivní vliv druhotných třisek na mrazuvzdornost, a to poměrně výrazně v případě náhrady primárních třisek druhotnými třískami o velikosti 1 až 2 mm. Důvodem je lepší objemová stabilita druhotných třisek, což souvisí s jejich předchozí mineralizací (v rámci výroby cementotřískových desek). Tyto druhotné třísky tedy vstupují do výrobního procesu s již poměrně stabilizovanými vlastnostmi.

Mineralogické složení analyzovaných variant cementotřískových desek souvisí s původem jejich surovin, což bylo prokázáno kvalitativním XRD rozbohem fázového složení. Podstatná je skutečnost, že škvára se do 28 dní zrání uplatní spíše jako inertní plnivo. Tuto skutečnost potvrzují i předchozí zjištění¹⁴.

Rastrovacím elektronovým mikroskopem byla potvrzena zjištění XRD analýzy. Rovněž je patrné, že mikrostruktura modifikovaných desek je kompaktní s minimální odlišností od referenčních desek. Rozhraní cementové matrice a smrkových třisek nevykazuje poruchy a hydratační produkty matrice pronikají do buněčné struktury dřeva. Bohužel nebylo možné jednoznačně rozlišit primární a druhotné třísky.

V rámci navazujícího výzkumu nyní probíhá dlouhodobá expozice desek v laboratorním a dále i jiných agresivních prostředích (CO₂, SO₂, atp.), čímž bude následně možné zpřesnit a rozšířit stávající výsledky a zjištění. Dále budou realizovány i doplňkové zkoušky, pro ucelení souboru materiálových charakteristik desek (tloušťkové bobtnání, rozměrové změny atd.), čímž bude umožněno komplexní posouzení chování navržených variant materiálového složení.

Poděkování

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Cement-bonded particleboards with higher content of non-traditional alternative raw materials substituting binder and chips

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Summary

This paper presents a laboratory research focused on assessing the properties and microstructure of cement-bonded particleboards modified by alternative raw materials. Specifically, composition of the binding agent was modified by finely ground limestone and heating plant slag. Simultaneously a composition of wood content was modified, i.e. spruce chips. Secondary spruce chips obtained from the treatment of offcuts, which are a by-product of the production of cement-bonded particleboards, were used as a substituent. The binder was substituted in quantities of up to 10 % and the spruce chips were substituted in amount of 10% to 20%. The properties of the cement-bonded particleboards were analysed after 28 days of ageing in laboratory conditions, including evaluating frost resistance (100 cycles). The results of the presented research are beneficial (in terms of environmental aspect and science). Utilization of alternative raw materials, which are otherwise not used (except for limestone) and thus represent waste, will reduce the environmental burden and at the same time preserve the utility properties of cement-bonded particleboards without negatively affecting their microstructure.

Keywords: *Cement-bonded particleboard, offcuts, slag, limestone, crushing, grinding, spruce chips, by-product, waste, mechanical parameters, mineralogical composition, microstructure.*

Vplyv granulometrického zloženia prachu cumaru na riziko iniciácie

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Súhrn

Príspevok sa zaoberá analýzou granulometrickej skladby frakcií dreveného brúsneho prachu cumaru (*Dipteryx odorata*) pripraveného pomocou ručnej vibračnej brúsky Makita 9556CR 1400W, sandpaper. Za účelom selektovania percentuálnych podielov jednotlivých frakcií (<63; 63; 71; 200; 315; 500 μm) vzoriek dreveného prachu sa vzorky sitovali na automatickom vibračnom sitovacom stroji Retsch AS 200 control. Tento typ exotického dreva bol vybraný s ohľadom na jeho využitie pri výrobe podlahových krytín, nábytku a interiérových dekoratívnych predmetov.

Cieľom článku je prezentácia granulometrického zloženia prachu cumary a sledovanie vplyvu frakcií na správanie sa prachu pri jeho tepelnom zaťažení.

Výsledky ukazujú rozdielne správanie pri termickej degradácii jednotlivých frakcií počas ich tepelného zaťaženia. Teplota vznietenia rozvíreného prachu bola stanovená na 410 °C pre frakciu 500 μm a so zmenou veľkosti častíc sa znížila na 370 °C (frakcia 71 μm). Výsledky ukazujú rozdielne správanie pri termickej degradácii jednotlivých frakcií počas ich tepelného zaťaženia. Dôsledkom zníženia teploty iniciácie je v zmene rozmerov a plochy prachových častíc. So znižujúcim sa rozmerom drevených prachových častíc narastá riziko tvorby výbušnej prachovzdušnej zmesi v pracovnom prostredí a klesá hodnota minimálnej teploty vznietenia.

Riziko iniciácie bolo sledované aj metódou termickej analýzy (TGA – termogravimetrická analýza), kde sa potvrdil dvojstupňový termický rozklad dreva. Prvé zmeny (sušenie) nastávajú pri 67 °C, maximálnu rýchlosť rozkladu sledujeme pri 329 °C a v druhom stupni pri 447 °C.

Kľúčové slová: cumaru, drevený prach, teplota iniciácie

Úvod

Prach je definovaný ako malé pevné častice v atmosfére, ktoré sa usadzujú vlastnou váhou, ale ktoré môžu zostať rozprášené/rozvírené vo vzduchu nejaký čas^{1,2}. Pod pojem prach je vo všeobecnosti možné zahrnúť rozomleté pevné látky označované ako púder, múčka, prášok, úlomky vlákien apod.³. Drevený prach, ako vedľajší produkt pri spracovaní dreva^{4,5,6,7,8,9}, zohráva negatívnu úlohu pri posudzovaní nebezpečenstva vzniku požiaru^{10,11} alebo výbuchu^{12,13,14,15,16}. Ďalším významným, ale nežiadúcim efektom je vplyv dreveného prachu na ľudský organizmus^{3,17}.

Negatívny účinok dreveného prachu je ovplyvnený veľkosťou častíc. Frakcie s väčšou veľkosťou majú tendenciu sa usádzať^{16,18,19}. Početnosť mikrofrakcií (<100 μm) evokuje vznik rozvírenej formy prachu. Vo výrobnom procese vznikajú takmer výlučne prachy polydisperzné, obsahujúce častice rôznych veľkostí^{4,20}. Granulometrickou analýzou sa zisťuje stupeň rozdrvenia základného materiálu, ktorý je jednou z charakteristických schopností prachu vytvárať disperznú sústavu²¹. Sitovaním je vytváraný súbor častíc do jednotlivých veľkostných intervalov, odkiaľ sa potom príslušným postupom odvodí kumulatívna krivka zrnitosti²².

Prach sa vyskytuje v pracovnom prostredí vo forme ako usadený (aerogel) a rozvírený (aerosól). Uvedené formy môžu ľahko meniť stav z usadeného na rozvírený (napr. vibráciami, otrasmi alebo prúdom vzduchu)^{3, 23}. Požiarne nebezpečenstvo dreveného prachu závisí od jeho formy. Usadený drevený prach má sklon k samovznieteniu a bezplameňovému horeniu (tleniu). Bezplameňové horenie (tlenie) je nebezpečné kvôli produkcii veľkého množstva splodín horenia, predovšetkým oxidu uhoľnatého.

Nebezpečnejšou formou z hľadiska protipožiarnej bezpečnosti je rozvírený prach, ktorý je zdrojom rizika explózie^{23, 24}. Horľavý prach v rozvírenom stave je schopný prudko oxidačne reagovať a táto reakcia má charakter výbuchu a za určitých podmienok môže tento dej prejsť až do detonácie^{3, 20}. Kľúčový parameter hodnotiaci nebezpečenstvo vzniku iniciácie rozvíreného prachu je teplota vznietenia. Sleduje sa v predpísanom skúšobnom zariadení (v peci) podľa EN 50281-2-1: 2002², kde je rozvírená vzorka dreveného prachu vystavená pôsobeniu sálavého tepla. Teplota vznietenia rozvíreného prachu je najnižšia teplota horúcej vnútornej strany pece, pri ktorej dôjde k vznieteniu rozvíreného prachu vo vzduchu vnútri tejto pece³.

Cumaru (*Dipteryx odorata*) patrí do skupiny amazonských drevín^{25, 26} a používa sa pri výrobe podlahových krytín, nábytku a interiérových dekoratívnych predmetov^{27, 28}. Drevo tohoto stromu má netradičnú červenooranžovú farbu a zaujímavú kresbu^{29, 30, 31}. V porovnaní s európskym drevom sú tropické dreveniny tvarovo stálejšie z dôvodu rastu vo vyššej relatívnej vlhkosti vzduchu a v stálejších klimatických podmienkach. Tropické dreveniny sú viac homogénne (nie je taký výrazný rozdiel medzi letným a jarným drevom) než európske dreveniny^{32, 33}. Tropické drevo má vyššiu hustotu a vyššiu tvrdosť, a preto sú menej náchylné na opotrebovanie^{34, 35}. Tropické dreveniny majú vyššiu životnosť a sú vhodné aj pre umiestnenie do vlhkého prostredia. Preto sa tropické drevo často využíva do exteriérov napr. ako drevená podlaha na terasy, stoly, stoličky, obklady bazénov a podobne³⁵. Zvýšená odolnosť proti poveternosti ho predurčuje na použitie ako fasádneho obkladu drevených stavieb^{36, 37}. V súčasnosti sa exotické dreveniny čoraz častejšie spracovávajú v našich podmienkach a to prináša tvorbu ich dreveného prachu. O parametroch posudzujúcich riziko vznietenia cumaru dreva a jeho prachu je málo poznatky.

Tropická drevenina cumaru je v centre pozornosti^{38, 39, 40, 41}. Soriano a kol.⁴² stanovil hustotu cumaru v rozpätí 1060 – 1070 kg.m⁻³. Cumaru (*Dipteryx odorata*) patrí do skupiny tvrdých drevín.

Cieľom príspevku je analýza dreveného prachu Cumaru (*Dipteryx odorata*) prostredníctvom granulometrickej sitovej analýzy, identifikácia morfolologickej štruktúry a stanovenie vybraných fyzikálnych vlastností. Jednou z experimentálne skúmaných charakteristík hodnotiacich požiarne riziko drevených prachov bola aj teplota vznietenia, ktorá bola stanovená pre rôzne frakcie dreveného prachu cumaru. Zároveň je cieľom príspevku sledovať vplyv veľkosti častíc rozvíreného prachu na zmenu minimálnych teplôt vznietenia.

Metodika a materiály

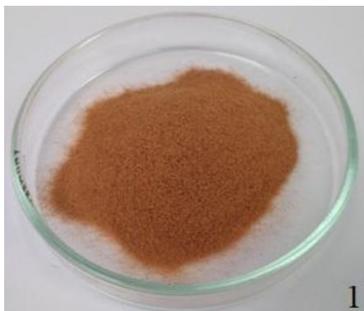
Výskum zvolených parametrov cumaru vyplýva z požiadaviek slovenských spracovateľov, ktorí zaradili uvedenú drevinu do ponuky predávaného tovaru a dochádza k spracovaniu a úprave uvedenej dreveniny v našich prevádzkach.

Východiskový tvar vzoriek Cumaru (*Dipteryx odorata*) (Obrázok 1) boli hranoly o rozmeroch 152 mm (dĺžka) x 38 mm (šírka) x 38 mm (výška). Vzorky boli vysušené na vlhkosť cca 8 ÷ 10 % a pripravené v drevárskej dielni súkromnej firmy, ktorá vyrába interiérové prvky.



Obrázok 1: Vzorka Cumaru (*Dipteryx odorata*)

Brúsené boli vzorky cumaru (*Dipteryx odorata*) (Obrázok 2) pomocou ručnej kotúčovej brúsky Makita 9556CR 1400W, brúsny papier K36, pričom vznikol drewný prach. Vzorky pripravoval skúsený odborník na brúsenie, aby sa proces brúsenia, čo sa týka prítlaku brúsiaceho prostriedku na povrch dielca, rýchlosti brúsenia ako aj smeru brúsenia (krížové), čo najviac priblížil realite. Nabrúsený prach bol zbieraný do zásobníka na kotúčovej brúske, odkiaľ bol následne presypaný do sklenenej hermeticky uzavretej nádoby, aby sa nezvyšovala vlhkosť získaného prachu. Po každom brúsení bol zásobník vyčistený a brúsenie sa opakovalo 3x. Z každej drewny bol získaný prach o hmotnosti 300 g ako základ pre granulometrickú analýzu.



Obrázok 2: Pripravený experimentálny materiál - drewný prach cumaru

Fyzikálne vlastnosti drewných prachov a sitová analýza

Vlhkosť vzoriek drewného prachu bola stanovená gravimetricky a sytná hustota drewných prachov bola stanovená podľa ISO 23145-1⁴³ (Tabuľka 1). Vzorky boli vystavené prostrediu približnému stolárskej dielni, aby sa dosiahli čo najreálnejšie výsledky. Toto prostredie predstavovalo uzatvorený priestor s teplotou 22 °C, tlakom prostredia 91 870 Pa a relatívnou vlhkosťou miestnosti 39 %. Následne boli vzorky prachov umiestnené do sklenených hermeticky uzavretých nádob a boli prenesené na testovanie vlhkosti váhovou metódou. Testovanie vlhkosti bolo vykonané podľa EN 13183-1⁴⁴.

Sitová analýza bola vykonaná na sitovacom stroji Retsch AS 200 podľa ISO 3310-1:2007-03⁴⁵. Vrecko sa po každej drewnine vyčistilo použitím priemyselného vysávača. Na základe sitovej analýzy boli jednotlivé druhy drewných prachov rozdelené do šiestich frakcií (500 µm, 315 µm, 200 µm, 100 µm, 71 µm, 63 µm a < 63 µm). Sitá boli odvážené spolu s navážkou drewného prachu na laboratórnych váhach s presnosťou váženia 0,001 g. Postup merania bol vykonaný s hmotnosťou navážky 30 g v 5 meraniach, po dobu 10 minút.

Určenie tvaru a veľkosti častíc drewných prachov

Stavba dreva môže byť pozorovaná na makroskopickej a mikroskopickej úrovni⁴⁶. Určenie tvaru a veľkosti častíc drewných prachov bolo realizované mikroskopickou analýzou mikroskopom Nikon Eclipse Ni s kamerou Nikon DS-Fi2. Štruktúra drewných prachov bola sledovaná pod stereomikroskopom Nikon SMZ 1270. Stereomikroskop Nikon SMZ sa používa na pozorovanie trojrozmerných mikroskopických predmetov. Mikroskopické analýzy drewných prachov boli scenované pre frakciu 100 µm.

Stanovenie teploty vznietenia rozvírených prachov

Experimenty boli realizované v skúšobnom zariadení na meranie minimálnych teplôt vznietenia rozvírených prachov, ktoré bolo doplnené automatickými váhami HL 100, ZU, kompresorom na stlačený vzduch EINHELL a zariadením ALMEMO na meranie teploty vo vnútri experimentálneho zariadenia. Postup merania sa realizoval podľa STN EN 50281-2-1². Podrobný popis experimentu a fotodokumentácia je v príspevku Vandličkovej a kol.⁴⁷.

Brúsenie, sitová a gravimetrická analýza a stanovenie teplôt vznietenia sa realizovali v Požiarnochemickom laboratóriu na Katedre požiarneho inžinierstva Fakulty bezpečnostného inžinierstva v Žiline.

Realizácia termogravimetrickej analýzy (TGA)

Termogravimetrická analýza (TGA) je rýchly spôsob odhadu zmeny lignocelulóзовého materiálu pri tepelnej degradácii v laboratórnych podmienkach⁴⁸. Dosiagnuté TG krivky ukazujú vzťah medzi rastom alebo poklesom hmotnosti na teplote. Tepelnou analýzou sa sleduje rýchlosť degradácie, úbytok hmotnosti, zmena teploty rozkladu, zmeny v exotermických a endotermických efektoch atď. Vodorovné časti TG, DTG krivky, sa vyznačujú konštantnou hmotnosťou a strmosť charakterizuje rýchlosť zmeny hmotnosti a prechod maximálneho bodu ($dm/dt \max$)⁴⁹. TG analýza bola uskutočnená na prístroji METTLER STARe SW 9.01, vyhodnocovaná príslušným softwarom na Fakulte bezpečnostného inžinýrství TU-VŠB v Ostrave. Z experimentálnych meraní boli získané TG, DTG krivky, ktoré sú prezentované v nasledovných častiach. Úbytok na hmotnosti bol udávaný v percentách z pôvodnej hmotnosti vzorky.

Výsledky a diskusia

Výsledky stanovenia fyzikálnych parametrov prachov cumaru

Príprava vzoriek bola spojená so základným testovaním, a to stanovením hustoty vzoriek dreva (Tabuľka 1) a sypnej hustoty dreveného prachu cumaru. Dezintegrácia drevenej hmoty na prach nemení elementárne chemické zloženie⁵⁰, ale mení pomer veľkosti povrchu k objemu dezintegrovanej častice (príklad Obrázok 1 a Obrázok 2) ako aj hustotu (Tabuľka 1).

Tabuľka 1: Gravimetrické stanovenie hustoty vzoriek a sypnej hustoty drevených prachov

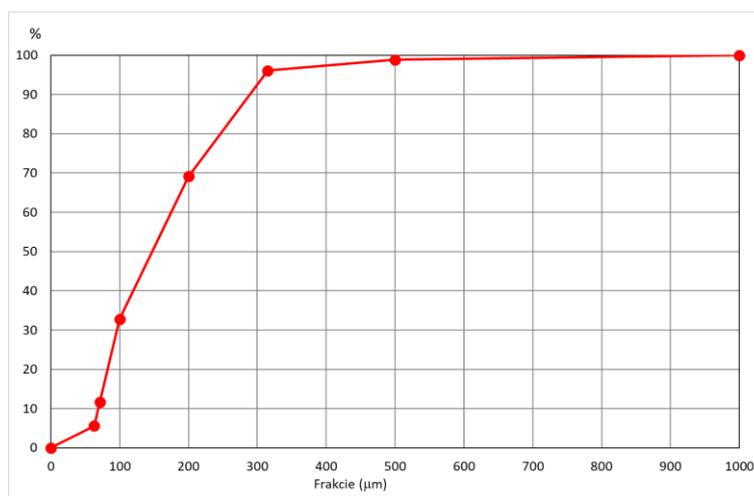
Prach	Hustota vzoriek [kg.m ⁻³]	Priemerná sypná hustota [kg.m ⁻³]	Vlhkosť [%]
Cumaru	1075,69±12,25	190,30±2,46	5.93±0.05

Výsledky sitovej analýzy

Percentuálne podiely frakcií prachu cumaru (Tabuľka 2) sú prezentované od frakcie 500 µm, keďže vyššie podiely sa pohybovali okolo 1 % u všetkých vzoriek (Obrázok 2), čo je v zhode s výsledkami domácich drevín^{22,51}.

Tabuľka 2: Vyhodnotenie % podielov frakcií prachu cumaru

Vzorka	% podiel frakcií vzoriek drevených prachov						
	500 µm	315 µm	200 µm	100 µm	71 µm	63 µm	< 63 µm
Cumaru prach	1,15 ±0,07	2,78 ±0,75	26,92 ±0,78	36,37 ±1,20	21,14 ±0,87	6,07 ±0,59	5,18 ±0,49



Obrázok 2: Kumulatívna krivka prachu Cumaru

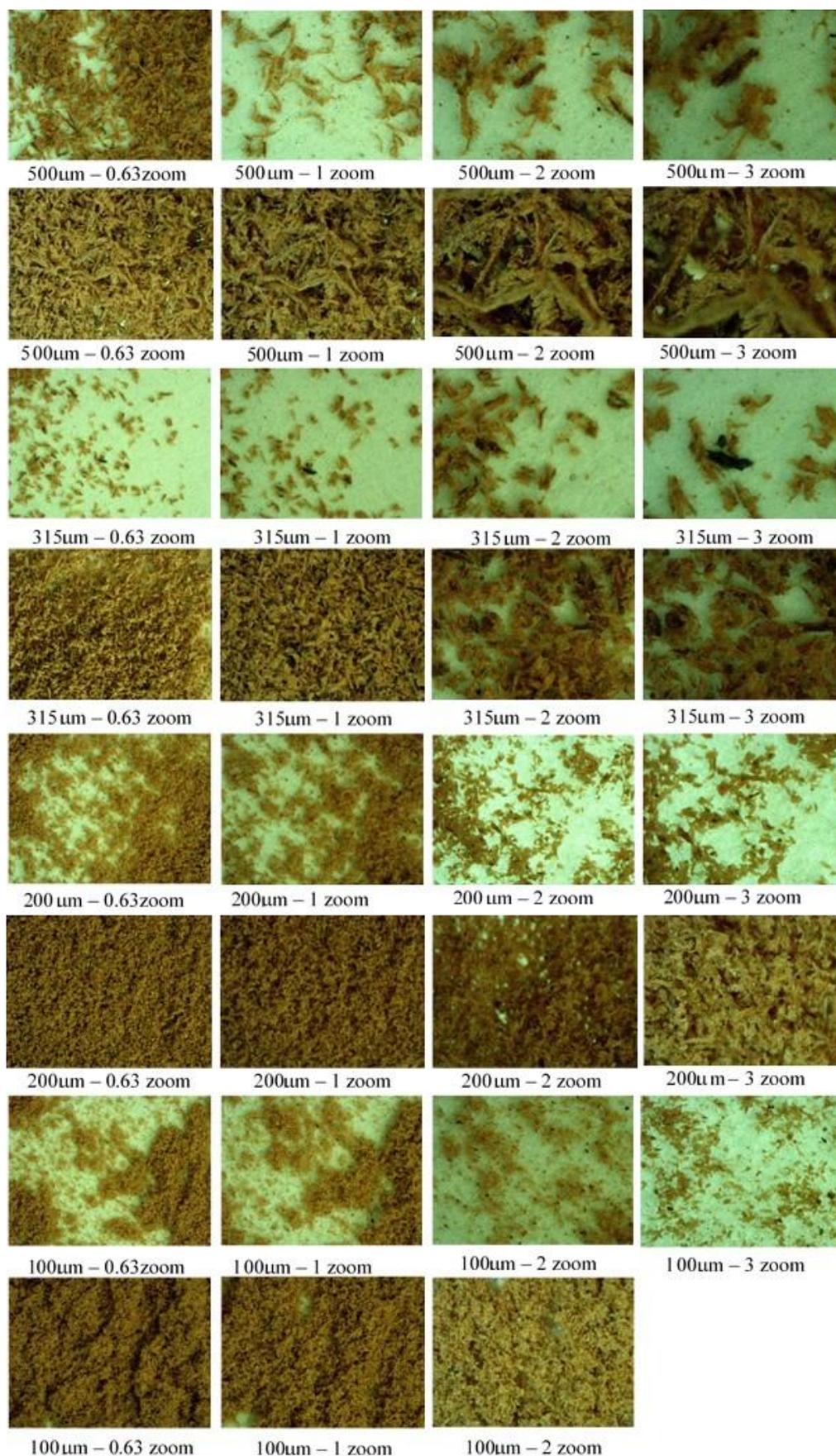
Výsledky stanovenia tvaru, veľkosti častíc a mikroskopická analýza prachových častíc Cumaru

Prach je rozdrvená (disperzná) pevná látka a so vzduchom tvorí disperzný systém. Disperzia prachu, t.j. veľkosť jeho častíc, sa stanoví sitovou analýzou (granulometricky), ktorá stanoví percentá častíc určitého rozmeru^{8,9,22}. Cieľom všetkých techník pre určenie veľkosti častíc je poskytnúť jednoduché číslo, ktoré udáva veľkosť častíc. Avšak častice sú trojrozmerné objekty, pre ktoré sa vyžadujú najmenej 3 parametre (dĺžka, šírka a výška) za účelom poskytnutia kompletného opisu. Rozmer častice je daný najdlhšou hranou d pravouhlého rovnobežníka opísaného okolo častice, dĺžka d je najväčší rozmer, hrúbka je najmenší rozmer, šírka je medziľahlý rozmer⁵²

Pozorovaný 3D tvar vybraných drevných prachov cumaru (Obrázok 3) pod stereomikroskopom Nikon SMZ 127 bol realizovaný priblížením 0,63 zoom (čo predstavuje 27,72x násobné zväčšenie) 1, 2 a 3 zoom (čo predstavuje 44x, 88x a 132x zväčšenie sledovaného objektu) na uvedenom stereomikroskope. Tvar a štruktúra drevných prachov bola pozorovaná pri všetkých určených veľkostných frakciách.

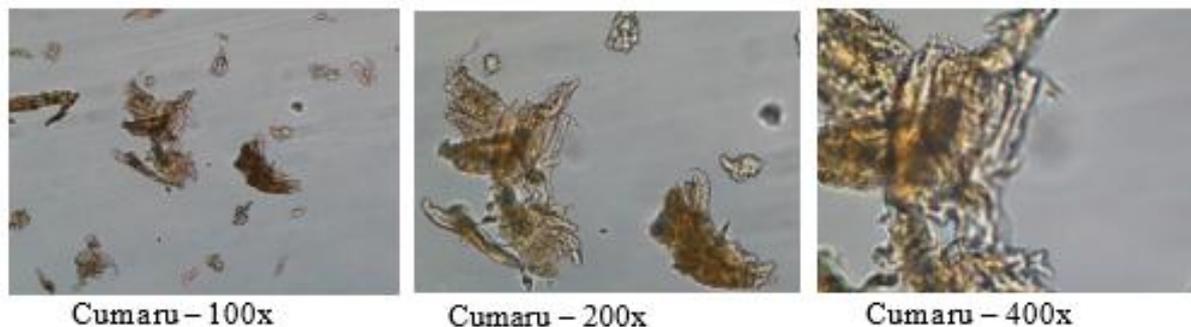
Účelom analýz je ukázať rozmanitosť tvaru u jednotlivých frakcií. Pre každú frakciu je vybraná séria scenov. Prvá štvorica je monovrstva prachu, zväčšená 0,63; 1; 2 a 3 zoom. Druhá štvorica je 1mm súvislá vrstva prachu pod mikroskopom, opäť zväčšená 0,63; 1; 2 a 3 zoom. Samozrejme, čím menšia frakcia, tým bola príprava monovrstvy väčší problém. Monovrstva frakcie pod 100 μm už nie je čistá (Obrázok 3). Forma častíc sa s veľkosťou mení. Frakcie 500, 315 a 200 μm sú vláknité, skučeravené, článkovité. Frakcia pod 100 μm vytvára zhluky a tvar je ťažko identifikovateľný.

Vizualizácia ukazuje rozdielnosť tvaru a plochy frakcií. Uvedená skutočnosť sa potvrdila aj na zmene hodnoty minimálnej iniciačnej teploty vznietenia rozvíreného cumaru prachu (Tabuľka 3).



Obrázok 3: Scany Cumaru prachu pre frakcie 500, 315, 200 a 100 μm so zväčšením 0.63, 1, 2 a 3 zoom

Skúmané vzorky drewného prachu Cumaru si zachovávajú svoju anatomickú štruktúru. Identifikované častice drewných prachov vzorky Cumaru (Obrázok 4) sú vo veľkostnej frakcii <math><100 \mu\text{m}</math>. Tvar veľkosti častíc drewných prachov je možné sledovať prostredníctvom mikroskopickej analýzy. Scany ukazujú tvar prachových častíc so zachovaním anatomickej štruktúry^{46,53}.



Obrázok 4: Mikroskopické častice drewného prachu Cumaru
Legenda: modrá línia prezentuje veľkosť 100 μm v 2D rozložení

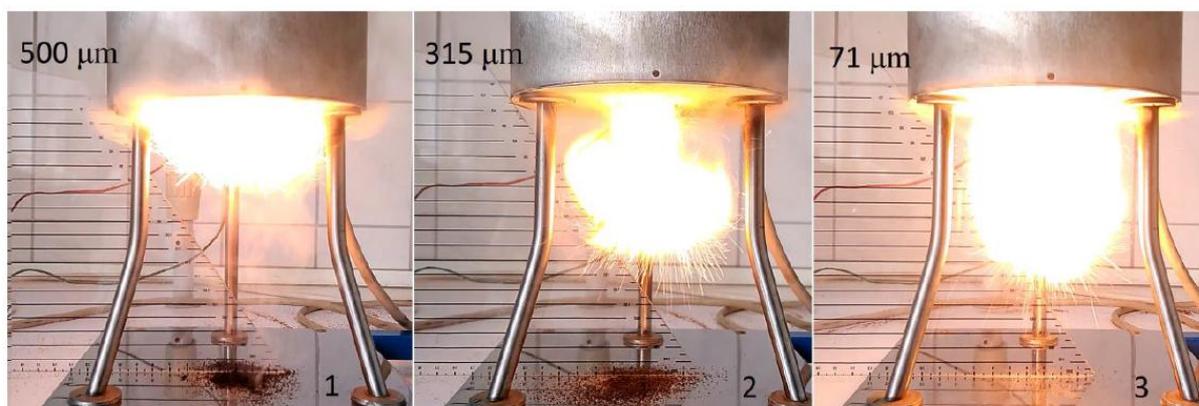
Wang a kol.⁴¹ sledoval mikroskopické zloženie cumaru s hustotou $941 \text{ kg}\cdot\text{m}^{-3}$. Vlákňové bunky cumaru mali husté bunkové steny, takmer žiadne bunkové lúmeny a hrúbka bunkovej steny vlákien cumaru a taun bola 6,80 a 2,82 μm .

Výsledky stanovenia teploty vznietenia rozvíreného prachu

Je možné konštatovať, že vznietenie drewných prachov v rozvírenom stave má špecifický priebeh⁵⁴, ktorý môžeme charakterizovať v nasledujúcich fázach:

1. Iniciácia výbuchu vo výhrevnej peci po rozprášení prachu,
2. čiastočný prepad nespáleného drewného prachu a vznik splodín horenia,
3. vznietenie drewného prachu s najintenzívnejším plameňom,
4. dohorovanie prachovej zmesi s miernym iskrením a pomalým ústupom vznietenia,
5. vyhorenie prachovej zmesi nachádzajúcej sa vo výhrevnej trubici.

Prezentácia maximálneho plameňa bola urobená pre frakcie 500 μm , 315 μm a 71 μm . Intenzita plameňa sa menila - rástla so zmeňujúcimi sa veľkosťami častíc. Explózia väčších častíc drewného prachu bola s menšou intenzitou plameňa (Obrázok 5). Podmienky vo výhrevnej peci boli nasledovné: navážka 0,2 g prachu, privádzaný tlak vzduchu 30 kPa, teplota pece 500 $^{\circ}\text{C}$.



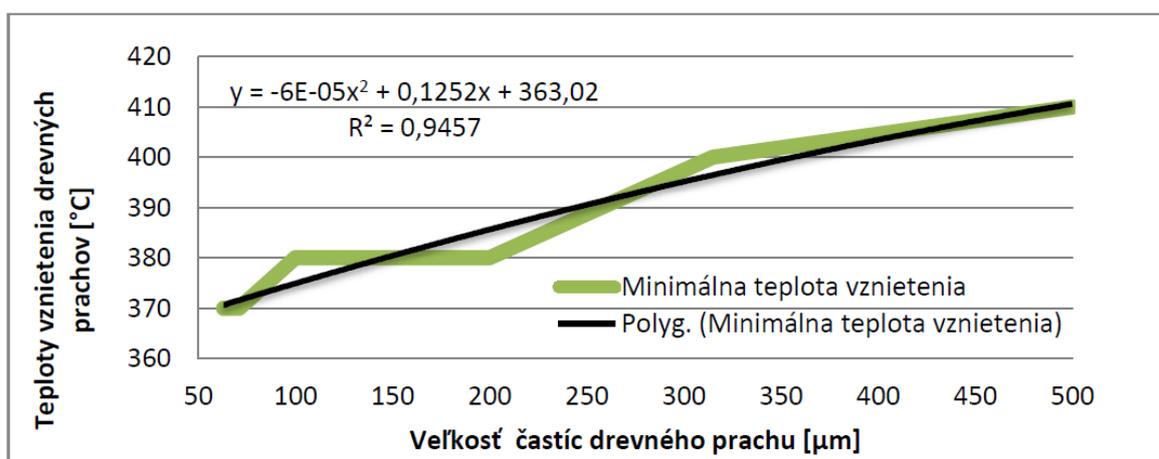
Obrázok 5: Vyšlahnutie plameňa pri vznietení

Výsledky jednotlivých minimálnych teplôt vznietenia vzoriek drewného prachu Cumaru je možné vidieť v tabuľke 3, kde so zmenou veľkosti častice prachu dochádzalo k zmene minimálnej teploty vznietenia.

Tabuľka 3: Stanovenie teploty vznietenia jednotlivých frakcií drewného prachu Cumaru

Frakcie (µm)	500	315	200	100	71	63	< 63
Teplota vznietenia (°C)	410	400	380	380	370	370	370

Pri najväčšej veľkostnej frakcii 500 µm začala minimálna teplota vznietenia na hodnote 410 °C, ktorá sa následne so zmenou veľkosti častíc priamoúmerne znižovala (Obrázok 6). Najvýraznejšia zmena minimálnej teploty v závislosti od veľkosti častíc sa pohybuje od veľkosti pod 200 µm. Najvýraznejší vplyv na zmenu minimálnej teploty majú najjemnejšie častice, konkrétne 71 µm a menej.



Obrázok 6: Vplyv veľkosti častíc vzorky Cumaru na minimálnu teplotu vznietenia

Posudzovanie rizika výbuchu rozvíreného drewného prachu na základe teploty vznietenia je všeobecne uplatňované a akceptované. Ale je potrebné brať do úvahy aj ostatné faktory, ktoré môžu mať významný vplyv na teplotu vznietenia^{9,12,15,16}.

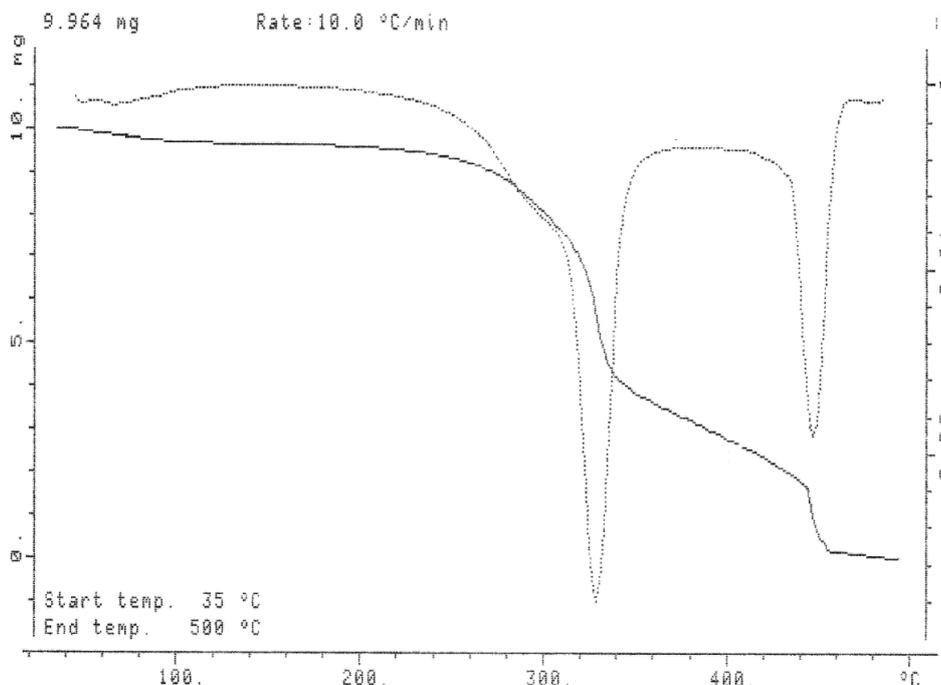
Výsledky termickej analýzy

Termogravimetria meria hmotnosti vzorky ako funkciu jej teploty pri plynulom ohreve vzorky. Ohrev je z 20 °C na 1000 °C s rýchlosťou ohrevu 10 °C.min⁻¹. Získané údaje (Tabuľka 4) sa zaznamenávajú ako tepelná závislosť straty hmotnosti v dôsledku termickej degradácie vzoriek a štúdiom tohto grafu (Obrázok 7) sa získavajú hlavné parametre, čiže teplota, pri ktorej začínajú degradačné reakcie T_p ; maximálna teplota úbytku hmotnosti T_{pmax} , čo predstavuje výťažok prchavých látok z procesu pyrolýzy, a úbytok hmotnosti Δm , zodpovedajúci vzorke tepelne degradovanej³. C_{rezist} predstavuje percentuálny zostatok vzorky počas daného termického procesu (Tabuľka 4). Analyzovala sa vzorka celej zmesi. Analýza bola robená pred sitovaním na jednotlivé frakcie.

Jones a kol.⁵⁵ realizoval súbor experimentov za účelom hodnotenia rizika vzniku explózie u vybraných druhov biomasy (vzorky olív, slnečnicových semiačkov, miskantusu, drewného prachu ako borovica a jalovec). Spôsob hodnotenia rizika vzniku explózie skúmal na základe aktivačnej energie pre pyrolýzu a stanovenia charakteristických teplôt pomocou TGA analýzy. Konštatuje, že nízke aktivačné energie pyrolýzy zvažujú riziko vznietenia biomasy. Makovická a kol.⁵⁶, pre vybrané tropické drevniny (Cumaru, Garapa, Ipe, Kempas, Merbau) zisťovali vzťah medzi neizotermickými termogravimetrickými chodmi a stratou hmotnosti dreva pri plameni počas skúšky horľavosti kónickým kalorimetrom. Tiež konštatujú termickú degradáciu v 3 stupňoch, ako je rozklad dreva na samotné prchavé látky, oxidácia uhlíkových zvyškov a tvorba popola.

Tabuľka 4: TGA analýza prachu cumaru

Drevný prach	Procesy sušenia		Procesy termickej degradácie				
			I. stupeň		II. stupeň		
	T_p (°C)	Δm (%)	T_{pmax} (°C)	Δm (%)	T_{pmax} (°C)	Δm (%)	$C_{rezist.}$ (%)
Cumaru	67	3,68	329	64,37	447	32,08	0,01



Obrázok 7: Termogravimetrická krivka drevného prachu cumaru

Záver

Na základe získaných experimentálnych výsledkov je možné konštatovať nasledujúce:

- Cumaru (*Dipteryx odorata*) ako tropická drevina má porovnateľné fyzikálne vlastnosti s domácimi drevinami. Jeho spracovanie je sprevádzané tvorbou prachových častíc podobného zloženia ako (smrek, dub a buk – najpočetnejšie drevin v našom prostredí).
- Sitová analýza ukázala percentuálne podiely pre určené frakcie. Najpočetnejšia frakcia bola 100 μm (37 %). Celkový percentuálny podiel častíc < 100 μm bol 69 %.
- Tvar častí zachováva morfológiu dreva a mikroskopia potvrdzuje zachovanie anatomickej štruktúry vlákien drevnej hmoty.
- Teplota vznietenia rozvíreného prachu stanovená v experimentálnych podmienkach pre rozvírený stav začala na 410 °C (frakcia 500 μm) a so zmenou veľkosti častíc sa znížila na 370 °C (frakcia 71 μm).
- V dôsledku plynulého ohrevu 10 °C.min⁻¹ drevného prachu sa sleduje proces vysušenia vzorky už od 67 °C a k termickej degradácii dochádza v dvoch stupňoch. Prvý stupeň nastáva pri teplote 329 °C a druhý pri teplote 447 °C.

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Effect of particle size distribution of cumar dust on risk of initiation

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Summary

The paper deals with granulometric analysis of selected samples of oriental wood dust Cumaru (*Dipteryx odorata*) of grinders Makita 9556CR 1400W, sandpaper K36 for the purpose of selecting the percentages of the various fractions (< 63; 63; 71; 200; 315; 500 μm) of samples of wood dust. Samples of wood were selected with regard to their used in the production of floor coverings, furniture and interior decorative items. Wood dust samples were made using a hand orbital sander Makita 9556CR 1400W and sizing on the automatic mesh vibratory sieve machine Retsch AS 200 control.

The aim of the article is to present the particle size distribution of cumara dust and to monitor the influence of fractions on the behavior of dust under its thermal load.

The results show different behavior in thermal degradation of individual fractions during their thermal loading. The ignition temperature of the airborne dust was determined to be 410 °C for the 500 μm fraction and decreased to 370 °C with a particle size change (71 μm fraction). The results show different behavior in thermal degradation of individual fractions during their thermal loading. The consequence of lowering the initiation temperature is a change in the dimensions and area of the dust particles. As the size decreases of wood dust particles, the risks of creating an explosive airborne dust in the working environment increase and the value of the minimal ignition temperature decreases.

The risk of initiation was also monitored by thermal analysis method (TGA), where the two-stage thermal decomposition of wood is confirmed. The first changes (drying) occur at 67 °C, the maximum rate of decomposition is monitored at 329 °C and in the second stage at 447 °C.

Keywords: cumaru, wood dust, ignition temperature



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