ICCT
INTERNATIONAL CONFERENCE
ON CHEMICAL TECHNOLOGY

11th International Conference on Chemical Technology

15. – 27. 4. 2024
Mikulov, Czech Republic

www.icct.cz

proceedings

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CHEMAGAZÍN

Proceedings of the 11th International Conference on Chemical Technology

1st edition, November 2024

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PUBLISHED AND DISTRIBUTED BY

Czech Society of Industrial Chemistry
Novotného Lávka 5
116 68 Prague, Czech Republic

in cooperation with
Czech Chemical Society
Novotného Lávka 5
116 68 Prague, Czech Republic

ISBN 978-80-88307-21-1

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EXTRACTIVE RECYCLING OF TEXTILES

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Abstract

Textiles are a group of materials that are used in almost all areas of life, especially in the clothing industry. The textile industry thus faces significant environmental and resource challenges. Textiles are made up of fibres, which can be divided according to their origin into natural and synthetic fibres. However, many textile materials are composites or blends. A very common combination is a blended textile made up of natural cotton fibres and synthetic polyethylene terephthalate (PET) fibres. The recycling of textile waste is therefore a complex process that can be divided into three main technological approaches, which can also be combined. These approaches are divided into mechanical, chemical, and thermal. This work deals with the issue of textile chemical recycling, specifically the extractive separation of components from cotton/polyester textile blends. Extraction of cotton and catalytic decomposition of PET were employed.

Introduction

As the global population continues to expand and the associated demand for clothing grows, so too does the amount of waste generated. For instance, in 2018, textile production reached 110 million metric tonnes[1], while the garment industry accounted for approximately 2% of global GDP. The most common methods of treating textile waste are landfilling and incineration. However, both methods have significant disadvantages. Firstly, fabrics take up a large volume in landfill, and decompose very slowly, taking up to 20 years. Secondly, incineration produces environmentally hazardous and harmful substances such as dioxins.[2]

Cotton is one of the most widely used fibres in the world. It is employed in a diverse range of sectors, including clothing and fashion textiles, household goods, and industry. Cotton fibres are distinguished by their durability, absorbency, colour fastness when appropriate dyes are used, and heat resistance. Cotton fibres are vegetable fibres and are composed of cellulose. It is the purest form of cellulose in nature, with approximately 90% of cotton fibre composed of cellulose.[3]

Polyester fibres are distinguished by their inherent properties, which have made them a popular choice in numerous sectors of the textile industry. The fibres exhibit hydrophobic characteristics, which impart water repellency, rapid drying capabilities, and resilience to strength loss when subjected to moisture. Furthermore, polyester fibres exhibit excellent tensile strength and resistance to stretching and shrinkage, rendering them simple to maintain and highly abrasion-resistant products.[4] The most utilised polyester fibre is polyethylene terephthalate (PET), with other notable examples including polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT) and polyesters of ethylene glycol and naphthalene-2,6-dicarboxylic acid (PEN).

As illustrated by the examples provided, each fibre possesses distinctive advantages. Cotton, for instance, exhibits high absorbency and a soft, pleasant texture. In contrast, polyester fibres are considerably stronger than cotton, resulting in garments that last longer for the customer. There are several reasons why it may be desirable to blend textiles. These include the desire to improve or achieve a particular property of the resulting fabric or yarn, to compensate for a weaker property of one type of fibre, to improve processing properties, in particular spinning, weaving and knitting, and so on.

Textiles are almost 100% recyclable, although the waste generated from them is composed of a multitude of fibres, both natural and synthetic. When a textile has reached the point of no longer being fit for purpose, recycling techniques can be employed to recover the materials within it.

Textile waste recycling can be divided into three main technological approaches, which can also be combined. These approaches are divided into mechanical, chemical and thermal. Prior to the actual separation method, the material may undergo a pre-treatment process to clean it, remove dyes and additives and thus facilitate further processing of the fibres.

The process of chemical recycling can be viewed from two distinct perspectives. The first is the depolymerisation and repolymerisation route, whereby the waste material is depolymerised back into monomeric or oligomeric units, which are subsequently re-polymerised into new fibres or materials. The second method of recycling textiles is by dissolution, whereby the resulting solution is separated, filtered, and then the fibres are regenerated.[5]

Cellulose is not a readily soluble material and therefore specific solvents are employed, the most common of which is N-methylmorphine-N-oxide (NMMO). Ionic liquids can also be utilised. NMMO is a highly popular cellulose solvent due to its ability to dissolve cellulose without degrading the polymer chain, while also being environmentally friendly.[6]

Polyester fibres are suitable for recycling by depolymerisation. The advantage is that the smaller fragments can be more easily purified from impurities and dyes using common practices such as recrystallisation or distillation. The resulting purified solution of polyester monomers and oligomers is then polymerised back into a fibre with the same properties and quality.[7]

Experiments

Materials

Five samples of blended textiles were taken. Even though the composition of the textile blends was known from the information provided by the manufacturer, all samples were quantitatively analysed to determine their exact composition, based on the standards EN ISO 1833-1:2021, EN ISO 1833-11:2018 and EN ISO 1833 12:2021.

The quantitative analysis was based on the principle of mass loss of one of the components of the blended fabric in a specific solvent or by a specific reaction. The exact mass composition was calculated from equations (1) and (2).

$$w_{\mathrm{s}} = \frac{100 * m_1 * d}{m_0} \tag{1}$$

$$w_{\mathrm{l}} = 100 - w_{\mathrm{s}} \tag{2}$$

Where w_s is the percentage by mass of the dry, insoluble component; m_0 is the mass of the dry test sample fabric; m_1 is the mass of the dry residue fabric; and d is the correction factor for the loss of mass of the insoluble component in the reagent during the analysis.

The quantitative analysis of the cotton component is based on the dissolution of cotton fibres in the textile mixture with sulphuric acid. Following washing and drying, the residue is weighed, and the weight loss is used to express the weight of cotton in the textile according to equations (1) and (2).

The quantitative analysis of elastane in blended textiles is based on the dissolution of elastane fibres in dimethylformamide (DMF). After washing and drying, the mass fraction of elastane fibres in the textile is calculated from the weighed residue using equations (1) and (2).

Preparation of the NMMO

The cotton solvent N-methylmorpholine-N-oxide was made from an azeotropic mixture of N-methylmorpholine with water using column distillation, as this route yields a product with little impurities and discoloration. The azeotropic mixture of NMM (73.8% NMM) with water was prepared under atmospheric pressure.

The production of the azeotropic mixture was followed by the oxidation of NMM with hydrogen peroxide (molar ratio hydrogen peroxide:NMM = 0.7) with carbon dioxide catalyst to form NMMO under 30–40 °C.

Based on the NRTL model calculation, it was determined that to obtain a mass fraction of NMMO of 0.9 in a mixture with water, the boiling point of the liquid would be at 87.6 °C at 5 kPa. The distillation residue was the product of this distillation. The concentration of NMMO was determined by potentiometric titration.

Separation of cotton by extraction

The following procedure was selected for the initial extraction experiments. Textiles numbered 1 to 5, softened with scissors and tweezers, were transferred into a resealable pharmaceutical container in quantities that ensured each container contained 0.04 g of cotton. The total weight of the embedded fabric was calculated from the weight composition of the mixture as stated by the manufacturer. In the sixth drug container, 0.04 grams of cotton wool was placed. Subsequently, 4 grams of NMMO was weighed into each drug container, and the drug containers were placed in a steel thermocouple. The temperature of the system was maintained for one hour at 120 °C. In the next step, the solid undissolved residue was removed, and as much filtrate as possible was squeezed back into the container. Approximately 5 ml of demineralised water was added to the filtrate, thereby diluting the NMMO solvent and precipitating the cotton fibres. The resulting precipitates were transferred to petri dishes and dried in an oven at 95 °C overnight.

The following experiments were conducted with different textiles: the samples were first torn using tweezers and scissors, and the resulting fibres were then dried in an oven at 105 °C for a minimum of four hours. After drying, each sample was accurately weighed and placed in a 250 ml double-necked distillation flask with a magnetic stirrer containing 200 g of 84% NMMO, which had been preheated to 80 °C. The textile sample was weighed in order to ensure that the flask always contained 2 g of pure cotton per 200 g of solvent. Consequently, a greater quantity of the textile sample had to be weighed in accordance with the proportion of cotton by weight in the entire textile mixture (1 or 5). The flask was placed in an oil bath with a magnetic stirrer, which was heated by a magnetic stirring plate and a thermostat that maintained the temperature of the oil bath at 120 °C. The distillation flask containing the sample and solvent was kept in the oil bath for one hour.

Separation of polyethylene by methanolysis in dichloromethane/hydrolysis in NaOH solution
In order to facilitate the separation of the polyester component through methanolysis, a solvent system comprising dichloromethane and suitable basic catalysts was employed.
Textile sample 2 was divided into small pieces using scissors, which were shaped like 1 × 1 cm squares. The following materials were then transferred into a 50 ml single-neck distillation flask with a magnetic stirrer: 8.33 g of methanol, 22.11 g of dichloromethane, and 50 mmol of catalyst. The reaction flask was placed in a water bath with a stirrer heated by a magnetic stirring plate and a thermostat, which maintained the temperature of the oil bath at 70 °C. A reflux condenser, closed by a stopper, was attached to the reaction flask. The reaction mixture was then left for 22 hours.
Following the 22-hour period, the contents of the flask were filtered through an S4 pore size frit into an extraction flask connected to a vacuum pump. The filtrate obtained was analysed by a gas chromatograph with a mass spectrometer and by a gas chromatograph with a flame ionization detector in order to qualify and quantify the products of methanolysis/hydrolysis of polyester fibres.

Analyses
Qualitative analysis of liquid mixtures of unknown composition was conducted on a Shimadzu GC-2010 Plus gas chromatograph with a Shimadzu GCMS-QP2010 Ultra mass spectrometer. Helium was employed as the carrier gas, with a J&W Scientific DB-5ms column (length: 35 m, diameter: 0.25 mm, df: 0.32 µm). The temperature program commenced with an initial temperature of 100 °C, followed by a three-minute isothermal delay, before reaching a final temperature of 250 °C and final time 30 minutes. Quantitative analyses were conducted on the same chromatographic system, with the sole difference being the use of a flame ionization detector (FID) and a similar column with a length of 60 m.

Discussion and result analysis

From the results of the quantitative analysis of the textile mixtures, it was found that the actual composition of the textiles is close to the values stated by the manufacturer. However, the exception is textile number 2, where the difference in composition is significant.

Table I
Textile sample mass composition values given by the manufacturer and values obtained by quantitative analytical methods

	data from manufacturer			quantitative analysis		
Textile No.	w(BA) [w/w.%]	w(PE) [w/w.%]	w(EL) [w/w.%]	w(BA) [w/w.%]	w(PE) [w/w.%]	w(EL) [w/w.%]
1	65	35	0	61.4	38.6	0.0
2	35	65	0	57.3	42.7	0.0
3	35	65	0	35.3	64.7	0.0
4	95	0	5	95.3	0.0	4.7
5	50	45	5	49.8	43.7	6.5

Solvent extraction of cotton
Several solvents of cellulose and polymers have been trialled on a small scale in drug vials based on literature or experience. A cotton/polyester textile blend was dissolved in the vials at 120 °C for one hour. The solvents that were tested included N-methylmorpholine-N-oxide, dipropyl 2-methyl succinate, dimethyl 2-methyl succinate, diethyl 2-methyl succinate, methyl 3-hydroxybutyrate, tributyl glyceride, methyl acetoacetate, and ethyl acetoacetate. The textile was prepared in a weight ratio such way that the component, namely cotton or polyester, constituted 1% of the total weight. The results of these tests indicated that NMMO was the most

suitable solvent for the separation of components in blended textiles, outperforming all other solvents that were investigated.

In initial dissolution experiments on all the above samples and pure cotton (reference material), the solvent (NMMO) was found to be strongly coloured in all cases. For further research in larger quantities, samples 1 and 5 were chosen. At a cellulose:NMMO ratio of 1:100, the yields were 91.5% and 89%, respectively. Upon injection of the filtrates obtained by dissolving cellulose in the ratio of cotton:NMMO 1:100 into demineralised water with a syringe, the fibres either did not form at all or the formed fibres disintegrated immediately after falling to the bottom of the beaker. This suggests that the concentration of cellulose in the NMMO was too low. The dissolution of sample 5 in NMM in the ratio cellulose: The dissolution of sample 5 in NMM in the ratio cellulose:NMMO = 5:100 was tested. The resulting cellulose yield in this case was only 45.4%.

The separation of cellulose from textile sample number 5 in a cotton:NMMO ratio of 5:100 was employed to produce fibres by syringe spraying. However, the properties of the resulting fibres, including tensile strength, elasticity, moisture absorption, and so forth, were not measured due to the absence of measuring instruments for these properties.

These results demonstrate that a low value of the cotton:NMMO mass ratio is necessary for the effective separation of the fibres from the blended fabric, but a higher value is required for the formation of fibres. However, these two conditions are in conflict, and therefore this methodology for the separation and recovery of cellulosic fibres is not deemed appropriate. A proposed manufacturing process involves the initial separation of cotton at a lower cotton:NMMO weight ratio, for instance 1:100, followed by dilution of the filter solution and centrifugation of the precipitated fibres. The centrifuged cellulose would then be dissolved in NMMO at a higher ratio, for example 5:100, and regenerated cellulose fibres would be produced. Nevertheless, this method requires further investigation from a chemical, technological, and economic point of view.

Separation of polyester by hydrolysis in NaOH solution

A separation method in which the polyester component was separated from the textile blend yielded unsatisfactory final yields of 3.7 wt.% when the blended fabric was ground into fibres and 5.0 wt.% when the fabric was in the form of 2 × 2 cm squares. In the case where the fabric was in the form of squares, an even better result was obtained compared to the case with the fabric in the form of fibres. These findings indicate that the mechanical pre-treatment of the input textile blend is not a significant factor in the separation process. Consequently, the method of polyester separation by hydrolysis with a 5% NaOH solution is deemed unsuitable, as minimal polyester loss was achieved.

Separation of polyethylene by methanolysis

In the initial phase of the research, a series of compounds were evaluated as methanolysis catalysts. These included N-methylimidazole (NMI), 1,4-diazabicyclo(2.2.2)octane (DABCO), sodium methanolate (MeONa), sodium hydroxide (NaOH), potassium hydroxide (KOH) and potassium carbonate (K2CO3). The outcomes of this investigation are presented in Figure 1.

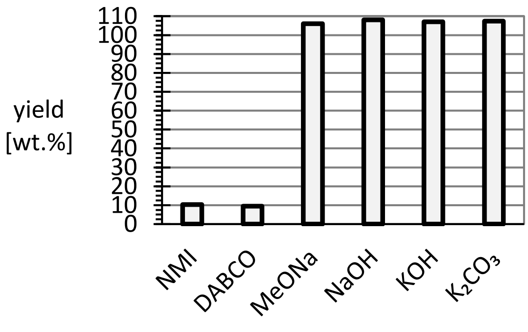

Figure 1. Yields of polyester by methanolysis in DCM at 70 °C after 22 h of textile 2 with different catalysts

N-methylimidazole and 1,4-diazabicyclo(2.2.2)octane were found to be unsuitable for the reaction, as the conversion of polyester was found to be significantly lower than that achieved with the other catalysts. In contrast, the catalysts sodium methanolate, sodium hydroxide, potassium hydroxide, and potassium carbonate were found to yield high polyester yields, even exceeding 100 wt.%. This indicates that either the mixture of methanol and DCM with the base catalyst also dissolved a certain amount of cotton, or that the cellulose fibres may have been released during various operations and subsequently passed through the frit into the filter solution.

The products of methanolysis of polyester fibres in blended textiles were analysed in the filtrate using gas chromatographs with mass spectrometers and flame ionisation detectors. The expected products, namely ethylene glycol and dimethyl terephthalate, were confirmed by mass spectrometry. In the case of methanolysis with NaOH, KOH, and MeONa catalysts, significantly less DMT was measured. This is likely due to the formation of sodium monomethyl terephthalate and disodium terephthalate salts, and potassium and dipotassium salts, respectively, by these basic homogeneous catalysts. A similar process could occur between these catalysts and ethylene glycol to form its alkaline salts. However, this issue did not arise in the experiments with sodium carbonate, as it did not dissolve in the reaction mixture. The results are presented in Figure 2.

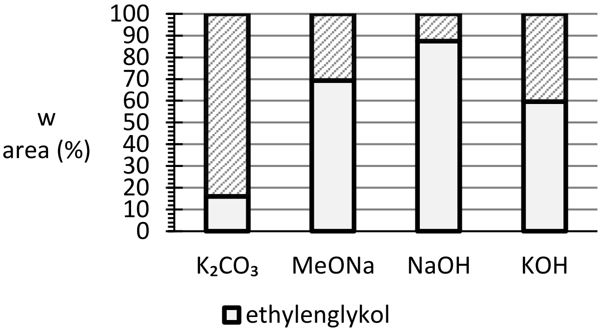

Figure 2. Percentages by weight of polyester fibre methanolysis products at 70 °C after 22 has a function of different catalysts

Furthermore, the impact of pre-treatment and the dimensions of fabric samples on the separation of polyester from a textile blend by methanolysis in DCM under potassium carbonate catalysis was examined. It can be concluded that the dimensions of fabric samples do not influence the efficacy of methanolysis in separating polyester after 22 hours under the aforementioned conditions. Consequently, conventional textile shredders could be employed in a potential textile waste recycling technology, negating the necessity for complex grinding methods.

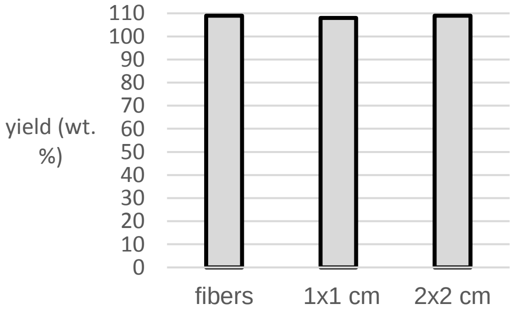

Figure 3. Yields of polyesters by separation of differently mechanically pretreated fabric 5 samples in DCM with K_2CO_3 catalyst at 70 °C for 22 h

Finally, the kinetics of the methanolysis of polyester fibres in DCM under potassium carbonate catalysis at an oil bath temperature of 70 °C were measured. The results of this are shown in Figure 4. It can be seen that the total conversion of polyester depolymerisation is achieved after 3 hours.

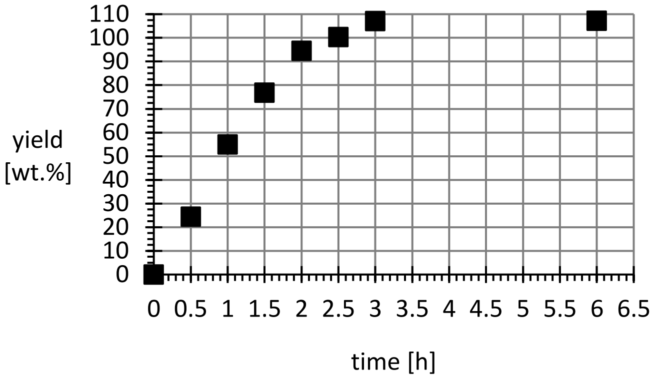

Figure 4.

Conclusions

The composition of the textile blend samples was quantified. Several fibre separation methods were experimentally investigated. Cotton separation with NMMO solvent separation was successful only when a large solvent excess was used. Hydrolysis of PE with sodium hydroxide gave only a low yield, and methanolysis of PE in DCM under K2CO3 catalysis was the most suitable procedure. A large solvent excess is likely to lead to poor economics of the process.

References

1. Palacios-Mateo, C., van der Meer, Y., Seide, G. Analysis of the polyester clothing value chain to identify key intervention points for sustainability. Environ Sci Eur 33, 2 (2021).
2. Sandin, G.; Peters, G. M., Environmental impact of textile reuse and recycling – A review. Journal of Cleaner Production, 184, 353 (2018).
3. Gordon, S.; Hsieh, Y.-l., Cotton: Science and technology. Woodhead Publishing, 2006.
4. Deopura, B. L.; Padaki, N. V., Chapter 5 - Synthetic Textile Fibres: Polyamide, Polyester and Aramid Fibres. In Textiles and Fashion, Sinclair, R., Ed. Woodhead Publishing, 97 (2015).
5. Dissanayake, D.; Weerasinghe, D., Fabric waste recycling: a systematic review of methods, applications, and challenges. Materials Circular Economy 3 (1), 1 (2021).
6. Kahoush, M.; Kadi, N., Towards sustainable textile sector: Fractionation and separation of cotton/ polyester fibers from blended textile waste. Sustainable Materials and Technologies 34, e00513 (2022).
7. Harmsen, P.; Bos, H. t., Textiles for circular fashion: Part 1: Fibre resources and recycling options. Wageningen Food & Biobased Research (2020).

BIOTECHNOLOGY AND BIOREFINERY

DETERMINATION OF THE PROPERTIES OF COTTON PULP WITH THE ADDITION OF NANOCELLULOSE

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Abstract

Nanocellulose application is an emerging field of study. This study aimed to apply nanocellulose to special paper products. For those purposes, beaten and unbeaten cotton pulp properties were determined with and without the addition of nanocellulose. Cotton is commonly used for special paper products because of its long fibers. Therefore it is interesting to investigate its properties for special purposes. In this research, tensile properties and burst index were evaluated for mechanical properties. For physical properties, Gurley air permeability was tested. Optical measurements were evaluated to assess the whiteness of paper samples. The tensile index for unbeaten cotton pulp without nanocellulose was on average 5.22 Nm/g and with 1% NC addition 9.05 Nm/g with a 73.37% increase. Same property, the tensile index for beaten cotton without nanocellulose was on average 18.23 Nm/g and with 1% NC addition 20.46 Nm/g with a 12.23% increase. Therefore, the determination of properties evaluated in this paper can be used for special paper products from cotton pulp.

Introduction

The main reason to research nanocellulose is the fact, that cellulose is one of the most abundant biopolymer in the world. That makes this material more sufficient to work with in terms of its appearance. Basically, nanocellulose can be obtained from any lignocellulosic material. With different technological approaches, nanocellulose can be manufactured. Generally, those approaches can be divided into mechanical, chemical, enzymatical, or combined.

For this research, cotton pulp was chosen to determine, whether it is possible to enhance its generally good properties mechanically or by adding nanocellulose. By nature, cotton pulp has properties ideal for special paper products. Mainly cotton pulp is used for special paper products, such as banknotes, currency and security papers. For this research, main objectives were, whether cotton properties can be further enhanced. For this reason, mechanical, physical and optical properties were evaluated. For mechanical measuring, tensile index, burst index, tensile work absorption index and breaking length were measured. For physical measuring, air permeability according to Gurley was measured and lastly for optical assessment, whiteness, brightness and fluorescence were measured.

Nanocellulose can also support the life cycle of the product that is apply on. Material, that has limited purposes and often ends as material that will be burned and release CO_2 can be further used as a biodegradable additive. So, the material with limited purposes can be transferred into the material with higher economic value with certain technological approaches. Manufactured nanocellulose can be then used for some materials and enhance its properties and also, for paper products, enhance its recyclability several times. With those aspects, nanocellulose can significantly support the life cycle assessment of some products, but also, further investigation on technological processes is needed to be done, as mentioned before[1]. It can be applied in many ways, generally, incorporating nanocellulose into the slurry or as a final surface treatment[2]. There were number of studies, that tried to apply nanocellulose into the slurry, as it is called at wet stage[3–5].

Nanocellulose has several great properties, such as sufficient mechanical strength, thermal stability, large specific surface area, good transmittance, low density, biodegradability, renewability and others[6–8]. An interesting fact could be also that nanocellulose could be modify in different ways to have higher grease barrier characteristics, more hydrophobic etc. with different reactions, such as phosphorylation, carboxymethylation, oxidation, sulfonation, acetylation, etherification, silytation, urethanization or amidation[9].

Materials and methods

Samples manufacture

For samples cotton pulp amount was calculated, so the final paper product has approximately 80 g/m^2. Then a mixture of cotton pulp with water was mixed into the pulper (Lorenzen & Wettre, Stockholm, Sweden) that homogenised this mixture for further manufacturing.

After that, the pulp-water mixture with or without the addition of nanocellulose particles CNF-Slurry-SMC was then introduced into a RAPID KÖTHEN RK-2A (Birkenau, Germany) laboratory device, where a wet hand sheet of paper was first formed. Subsequently, the laboratory hand sheet was also dried on this equipment and prepared for further processes and testing.

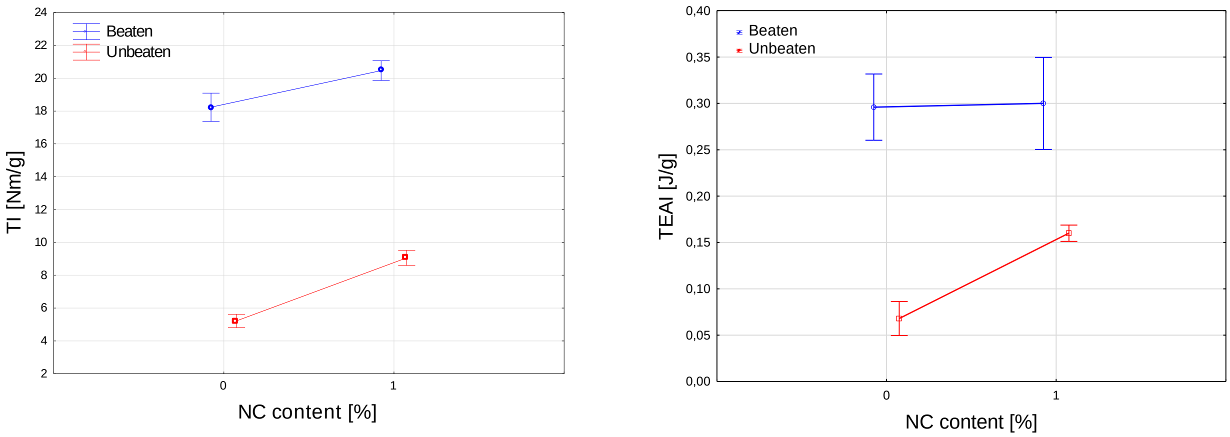
Materials

Kraft cotton pulp with Kappa number 15.0 from Miba Fibertec (Štětí, Czechia) was used for the experiments. As a nanocellulose particles, CNF-Slurry-SMC was used from CelluloseLab (Frederiction, Canada).

Methods

After samples manufacture, samples were first conditioned according to TAPPI T 402 sp-08[10]. After conditioning, tensile properties were measured according to ČSN EN ISO 1924-2[11] on equipment FRANK PTI (Birkenau, Germany). Measured properties were breaking length, relative elongation, tensile index, absorption tensile work, tensile work absorption index. Another measuring was on equipment FRANK PTI (Birkenau, Germany) for burst index determination according to ISO 2758:2014[12]. Air permeability was measured on equipment Lorenzen & Wettre (Stockholm, Sweden) according to ISO 5636-5:2013[13]. For optical properties, FRANK PTI CM-3830 (Birkenau, Germany) was used to assess Whiteness CIE and UV, Fluorescence and ISO Brightness and UV according to ISO 11475[14].

Results and discussion

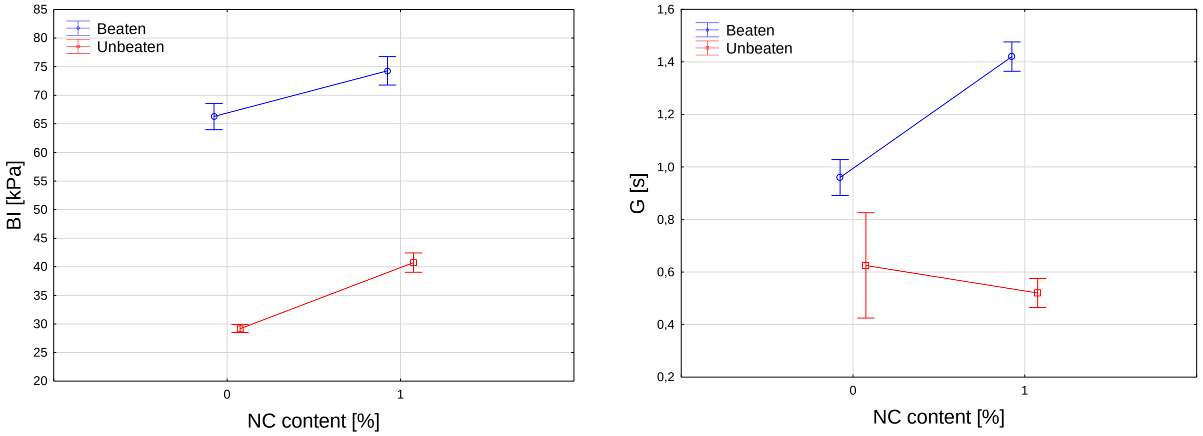


a) b)

Figure I. a) **Tensile index**, b) **Tensile work absorption index** of beaten and unbeaten cotton with the addition of nanocellulose

Tensile index increased for samples of unbeaten cotton pulp from 5.22 Nm/g to 9.05 Nm/g (73.4% increase) and for beaten cotton pulp samples from 18.23 Nm/g to 20.46 Nm/g (12.2% increase). It could have been seen, that nanocellulose particles improved tensile index more for unbeaten cotton pulp. This could be observed probably, because for beaten cotton samples, free –OH groups have already been attached together and with addition of nanocellulose particles, tensile index increased less. According to the study[15] tensile index was increased by 19% with 4% of nanofibrillated cellulose addition and up to 35% with 10% NFC utilization.

Tensile work absorption index (TEAI) has not changed significantly for beaten cotton pulp. For unbeaten cotton pulp, TEAI has increased from 0.07 J/g to 0.16 J/g (128.6% increase).

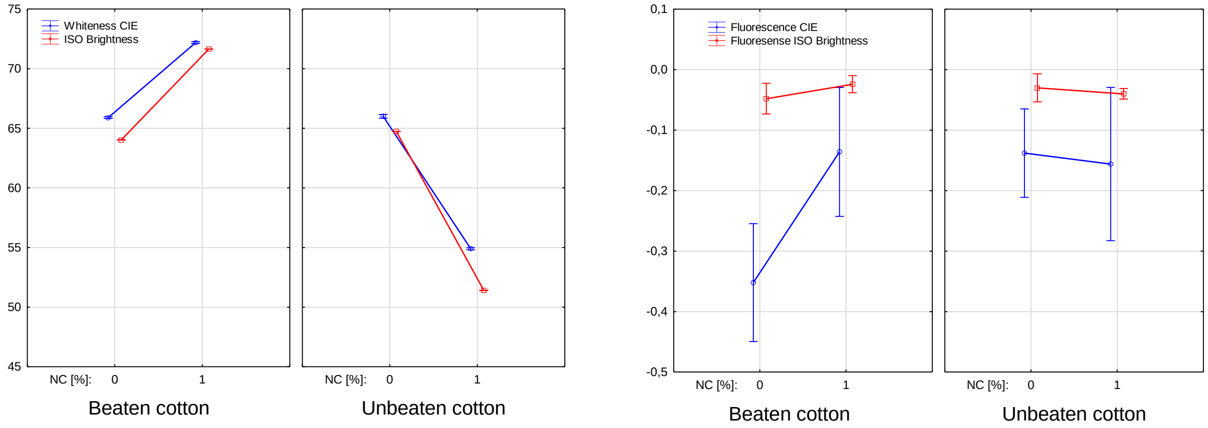


a) b)

Figure II. a) **Burst index**, b) **Air permeability** of beaten and unbeaten cotton with the addition of nanocellulose.

Burst index increased for beaten cotton pulp from 65.63 kPa to 75.28 kPa (14.7% increase) and for unbeaten cotton pulp from 29.33 kPa to 40.30 kPa (37.4% increase). According to study Deng *et al.*[6], burst index for cotton pulp was increased by 6.1% and 9.8% with addition of 2.5% nanofibrillated cellulose addition. A study[15] confirms, that burst index can be increased between 13 to 49% with NFC utilization between 2 to 10%.

Air permeability has decreased for unbeaten cotton pulp from 0.63 s to 0.52 s (17.5% decrease) and increased for beaten cotton pulp from 0.96 s to 1.42 s (47.9% increase). With the nanocellulose addition, theoretically, air permeability is supposed to decrease due to nanocellulose filling paper sample decreased its porosity. Study[15] confirms decreasing tendency of air permeability with the amount of nanocellulose addition from 2 to 10%.



a) b)

Figure III. a) **Whiteness CIE and ISO Brightness**, b) **Fluorescence CIE and Fluorescence ISO** of beaten and unbeaten cotton with addition of nanocellulose.

Parameters for Whiteness CIE and ISO Brightness have not changed significantly according to scale from 0 to 100. According to study[15]. Brightness did not change significantly with addition of 2 to 10% nanofibrillated cellulose particles to the paper sample.

Fluorescence parameters have not changed significantly with addition of nanocellulose.

Conclusions

- With just mechanical treatment with Hollander beater, most mechanical properties can be enhanced sufficiently.
- With nanocellulose particles addition, those mechanical properties can be enhanced further.
- Whiteness and brightness have not changed significantly with nanocellulose addition.

Acknowledgement

This research was supported by the Faculty of Forestry and Wood Sciences of the Czech University of Life Sciences Prague (Internal Grant Agency, Project No. A_03_24).
The research measurement was supported by SPM, a. s.
The attendance to this conference was supported by the European Liaison Committee for Pulp and Paper through a EUCEPA Student Grant.

References

1. Ryen E.G., Babbitt C.W., Williams E.: Environmental Science & Technology 49, 2549–2559 (2015).
2. Sharma, M., Roberto A., Dina M., Artur V., Antonio S., Paulo F.: International Journal of Biological Macromolecules 162, 578–598 (2020).
3. Samyn P., Ahmed B., Thomas Ö., Alain D.: Journal of Materials Science 53, 146–184 (2018).
4. Tayeb A.H., Ezatollah A., Shokoofeh G., Mehdi T.: Molecules 23(10), 2684 (2018).
5. Julkapli N.M., Samira B.: Journal of Wood Science 62(2), 117–130 (2016).
6. Deng X., Lingzhong W., Hui S., Changfeng L., Fangzhi L., Xiaoming Y., Kun L., Sihong Y.: BioResources 17(1), 714–724 (2021).
7. Feng Y., Li J., Wang B., Tian X., Chen K., Zeng J., Xu J., Gao W.: BioResources 13, 3030–3044 (2018).
8. Lu Z., An X., Zhang H., Guan M., Liu J., Sun Y., Nie S., Cao H., Lu B., Lie H.: Carbohydrate Polymers 210, 332–338 (2019).
9. Thakur V., Guleria A., Kumar S., Sharma S., Singh K.: Materials Advances 6(2), 1872–1895 (2021).
10. TAPPI T 402 sp-08: Standard Conditioning and Testing Atmospheres For Paper, Board, Pulp Handsheets And Related Products. Tappi Press, Atlanta 2013.
11. ČSN EN ISO 1924-2 (500340) Paper and Board – Determination of Tensile Properties. Czech Standard Institute, Prague 2009.
12. ISO 2758:2014 Paper — Determination of Bursting Strength. International Organization for Standardization, Geneve 2014.
13. ISO 5636-5:2013 Paper and board — Determination of air permeance (medium range) — Part 5: Gurley method. International Organization for Standardization, Geneve 2019.
14. ISO 11475:2017 Paper and Board – Determination of CIE whiteness, D65/10 degrees (outdoor daylight). International Organization for Standardization: Geneve 2017.
15. Latifah J., Nurrul-Atika M., Sharmiza A., Rushdan I.: Journal of Tropical Forest Science 32(2), 170–178 (2020).

OBTAINING EXTRACTS FROM PLANT MATERIALS AND EVALUATING THEIR BIOLOGICAL ACTIVITY

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Abstract

Plant materials represent a source of a wide spectrum of biologically active substances that may find further application in the field of research into new drugs. This article is focused on describing different extraction methods that can be applied to isolate active substances. The aim of our study was to perform several extractions of different types using changing extraction conditions on a series of selected plant species and to compare these methods. Another aim of this study was to test the biological activity of specific extracts, especially antioxidant and antimicrobial properties. Here we present the results obtained from the extraction and testing of the adaptogenic plant *Eleutherococcus senticosus.* The highest level of antioxidant activity corresponding to 4.40 mg of trolox/g plant was achieved in the sample extracted with ethanol, at 100 °C and 10 minutes. Sample **11** (100 °C, 10 minutes, ethanol) with 58.15% inhibition of *Staphylococcus aureus* demonstrated the greatest inhibitory properties of metabolism.

Introduction

Plant materials produce a spectrum of biologically active substances that may be part of their natural defense system. Important bioactive substances include polyphenolic substances such as flavonoids, tannins, quinones or coumarins, which exhibit strong antimicrobial activity and have been shown to have significant inhibitory properties on the growth of microorganisms. The group of terpenoids, saponins, glycosides or alkaloids form another group of active substances often found in plant extracts[1]. These groups of biologically active substances can be contained in different parts of plants such as leaves, stems, flowers or fruits. They belong to plant secondary metabolites that can cause pharmacological or toxicological effects in humans. Possible use in the pharmaceutical or food industry means the need to find the most suitable way to extract them.

Currently, there are many conventional and unconventional extraction methods. Extraction represents an important first step in the study of bioactive substances from plants and has a decisive influence on the final result. Among the most common parameters affecting the extraction process are: the properties of the matrix of the plant part, the type of solvent, temperature, pressure or time[2]. At the same time, the amount and quality of the extracted substances can also depend on the age of the plant, climate, soil composition, time and place of collection, as well as on selected extraction method[3,4]. Among the classic extraction methods belong Soxhlet extraction, maceration, hydrodistillation. Soxhlet extraction is often used for comparison with new extraction alternatives. One of the disadvantages, for example in hydrodistillation, can be high extraction temperatures, at which the loss of volatile components and the degradation of thermolabile compounds can occur. The main limitations leading to the development of newer extraction techniques guaranteeing a better extraction process are long extraction time, evaporation of a large amount of solvents, low extraction selectivity, thermal degradation of thermolabile compounds. Ultrasound-assisted extraction, enzymatic extraction, microwave extraction, pulsed electric field as controlled extraction, supercritical fluid extraction, and compressed fluid extraction appear to be the most promising[2].

These more modern extraction techniques appear to be more environmentally friendly, especially due to the lower consumption of organic solvents, shorter operating time, higher yield and better extract quality. Where, for example, the use of supercritical fluids can contribute to increasing the overall yield and selectivity[2]. To obtain bioactive substances, Supercritical Fluid Extraction – SFE (in which $scCO_2$ is used) is ranked among the most effective extraction methods that are recommended for extracting thermolabile compounds, as it is performed at low temperatures[5,6]. The method is fast, cheap, can be automated, selective and does not require the use of a large amount of solvent[5]. Supercritical fluid extraction uses the properties of a supercritical fluid, which under the conditions of reaching its critical point has both the properties of a liquid and a gas.

A supercritical fluid is also defined as a fluid above its critical temperature and pressure. It behaves more like a gas but has the solvating properties of a liquid. The main advantages are good solvability of non-polar analytes, low toxicity of CO_2, obtaining concentrated dry matter due to easy evaporation of CO_2. At the same time, the solubility of more polar substances can be increased by adding a small proportion of ethanol or methanol[7].

Another suitable extraction method is the Pressurized Liquid Extraction – PLE, or accelerated solvent extraction, in which high pressure is applied, while the solvent remains in a liquid state above the boiling point. The advantage is a short extraction time, minimal consumption of solvent, high solubility, high rate of diffusion of hydrophobic compounds in the solvent and high penetration of the solvent into the matrix. In addition, this method can be automated. From available literature data, this method appears to be successful in extracting of flavonoids from various plant matrices. A subtype of PLE can be a variant of or Pressurized hot water extraction – PHWE, which is known as pressurized low-polarity water extraction or supercritical water extraction. Using the special properties of water and replacing it with ethanol or methanol significantly reduces costs and represents a more environmentally friendly technique[7].

Eleutherococcus senticosus, known as *Acanthopanax senticosus* or also as Siberian or Russian ginseng, belongs to the plant family *Araliaceae*[8]. In Chinese is called as *Ciwujia*. It occurs mainly in the southeast of Russia, northeast of China, in Korea and Japan. It is a woody medicinal plant. It has been known for its healing properties since ancient times[9]. In traditional medicine, it was used mainly for its valuable effects on the cardiovascular, immune, nervous or endocrine systems. It is classified as an adaptogenic plant. Other data describe it as a suitable medicinal product for the treatment of infections or suitable against fatigue. Among the substances responsible for various physiological reactions are eleutherosides contained in the roots and ciwujianosides contained in the leaves. Its protective properties against oxidative stress, thus antioxidant properties, have been linked to improvements in the treatment of diabetes, cancer and inflammation. Antimicrobial and antiviral activities have also been reported[8]. Root extracts have been found to effectively inhibit the replication of human *Rhinovirus*, *Respiratory syncytial virus* and *Influenza A virus*[9].

Simulation and experiment

Preparation of plant material

For the subsequent extraction, the root of one batch was used (herbslife.cz – root harvested in Russia and imported to the Czech Republic). Before extraction, the root was ground and homogenized (particle size 0.5 mm).

Pressurized Liquid Extraction (PLE)

Solvents were used: ethanol, methanol, acetone, isopropyl alcohol and acetonitrile. SPEED SFE-Applied Separations (USA) equipment was used.

UV-VIS spectrophotometer Evolution 200 (Thermo Fisher Scientific, USA) with INSIGHT software (range 200-1000 nm).

First, 10 g of homogenized ground root was weighed into a beaker, which was then inserted into an extractor, i.e. into a high-pressure column (V = 75 ml and d = 3 cm). This was placed vertically in a heated oven and connected to capillaries. After the temperature stabilized, a high-pressure pump was turned on, with the help of which the solvent was pumped through the column (7 ml/min), and the inlet valve, which let the solvent into the capillaries. The solvent was pumped until a pressure of 10 MPa (100 bar) was reached in the column. After the delay time, the expansion valve is opened, which drives the extract with the solvent into the vial. Finally, the rest of the solvent extract is removed from the column using CO_2. In this way, individual fractions were taken. The solvent is subsequently evaporated from the extracts using a rotary vacuum evaporator. Over 40 samples were extracted in this way, but a total of 13 PLE extracts were selected for further measurements. During each extraction, three fractions were always taken successively, each time after the given length of the cycle. The individual samples were different in extraction conditions – temperature, type of solvent and long extraction time.

Preparation of samples used for antimicrobial activity testing

Amount of 0.005 g of the extracted samples were weighed and then this amount was dissolved in 1 ml of DMSO (dimethyl sulfoxide). Stock samples were diluted with MHB up to a concentration of 200 µg/ml. Antibiotic solutions (kanamycin and vancomycin) were used as a positive control.

List of microorganisms used: *Staphylococcus aureus* CCM 4516, *Enterococcus faecalis* CCM 4224, *Escherichia coli* CCM 4517, *Pseudomonas aeruginosa* CCM 1961 (CCM = Czech Collection of Microorganisms).

Content of phenolic substances and flavonoids

Determination of the total phenolic substances content (TPC – Total Phenolic Content)

The determination was made by the Folin-Ciocalteu spectrophotometric method. First, approximately 10 mg of the extract, which was diluted in 2 ml of methanol, was weighed into the vials on an analytical balance. Samples were made in four replicates. 0.05 ml of the extract dissolved in methanol was measured into a 5 ml flask with a Hamilton syringe. To this, 0.25 ml of Folin-Ciocalteu reagent and a few drops of distilled water were immediately added. The thus mixed reactants were allowed to react for 8 minutes and then 0.75 ml of 20% sodium carbonate (Na_2CO_3) was added. The rest of the volume of the flask was made up to the mark with distilled water and the flasks were carefully shaken and allowed to settle for one hour. After an hour's incubation, the solutions were prepared for spectrophotometric analysis at a wavelength of 750 nm. First, it was necessary to measure the blank (blind sample) using a cuvette with distilled water. The amount of phenolics was calculated from the calibration curve using a regression equation and the result was expressed as gallic acid equivalent, i.e. GAE (gallic acid equivalent)/g plant.

Determination of total flavonoid content (TFC – Total Flavonoid Content)

The determination was made by the spectrophotometric method using aluminum chloride and potassium acetate. The samples were made in three replicates, when 100 µl was measured into a small vial with a Hamilton syringe. A 10% solution of aluminum chloride ($AlCl_3$) and a 1M solution of potassium acetate (CH_3COOK) were used as reagents. 20 µl of each reagent was measured with a Hamilton syringe and mixed with the measured sample. Finally, another 860 µl of methanol was added and the fractions were allowed to incubate (react) for 30 minutes. After 30 minutes, the absorbance was measured in a spectrophotometer at a wavelength of 515 nm. First, a blank (blind sample) was again measured in the spectrophotometer using a cuvette with methanol. The amount of flavonoids was calculated from the calibration curve using a regression equation and the result was expressed as quercetin equivalent, i.e. QE (quercetin equivalent)/g plant.

Antioxidant activity

Determining the total antioxidant effect (TAC – Total Antioxidant Capacity)

The experiment was performed using the DPPH (2,2-diphenyl-1-picrylhydrazyl) method. In this measurement, a diluted solution was used as in the TPC measurement (10 mg of extract + 2 ml of methanol). The samples were again made in three replicates – each repetition of 20 µl of the sample together with 1 ml of suitably diluted radical. The DPPH radical needed to be diluted with methanol so that its absorbance was as close as possible to 1 at a wavelength of 515 nm in the spectrophotometer. The samples were then incubated in the dark for 30 minutes. Again, after 30 minutes, the samples were measured in cuvettes in a UV/VIS spectrophotometer at a wavelength of 515 nm and the data were evaluated. First, a blank sample was measured using a cuvette with methanol. Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was used as a standard. Antioxidant activity was expressed as trolox equivalent from the calibration curve in mg (or mmol after conversion) TE (trolox equivalent)/g sample. This is the concentration of the standard – trolox with the same activity as 1 g of the sample.

Antimicrobial activity

Dilution method

The dilution method is considered to be an accurate quantitative method established for determining the bacteriostatic effects of antimicrobial agents. In the dilution plate method, 96-well microtitre plates are used, in which it is possible to measure multiple samples at different concentrations at once. 100 µl of individual tested samples with a concentration of 200 µg/ml was pipetted into the plate, to which 100 µl of a 2x diluted 0.5 McF bacterial culture solution with a corresponding concentration of $5 \cdot 10^5$ KTJ/ml was subsequently added. The total volume of one well was chosen to be 200 µl, and the final concentration of the tested samples was thus 100 µg/ml corresponding to a 2% DMSO solution. The determination of each sample of the test substance was carried out in three parallels. Subsequently, absorbance values of bacterial growth in individual wells were measured for 24 hours in a Synergy spectrophotometer at a wavelength of 625 nm and 28/35 °C. From these values, growth curves can be made.

Resazurin test

Cell viability will be measured using the resazurin test. This test uses a reaction accompanied by a colour change from the low-fluorescence reducing blue dye resazurin to the high-fluorescence pink resorufin. After 24 hours of cultivation of the 96-well microtiter plate used for the dilution test, 100 µl was transferred by pipette to a new 96-well microtiter plate. 100 µl of resazurin blue solution was added to each well immediately afterwards. After approximately 30 min, a colour change was observed, which was quantified by measuring fluorescence in a Synergy spectrophotometer by setting two wavelengths $\lambda_{excitation} = 560$ nm, $\lambda_{emission} = 590$ nm, from which the % inhibition and the number of metabolically active cells was determined, thus a bactericidal effect was detected.

Discussion and result analysis

In this experiment, it was confirmed that the yields of individual extracts are dependent on the chosen extraction conditions. The aim was to find optimal extraction conditions leading to maximum yield of desired substances, but also their antioxidant and antimicrobial activity. In our case, the dependence of the concentration of desired substances on the influence of temperature, cycle length and type of solvent was monitored. The constant parameter was the pressure of 10 MPa (100 bar). All samples were extracted with a PLE method with a static flow. The results of the yield of phenolic substances and the total yield and level of antioxidant activity are shown in Graphs A–F.

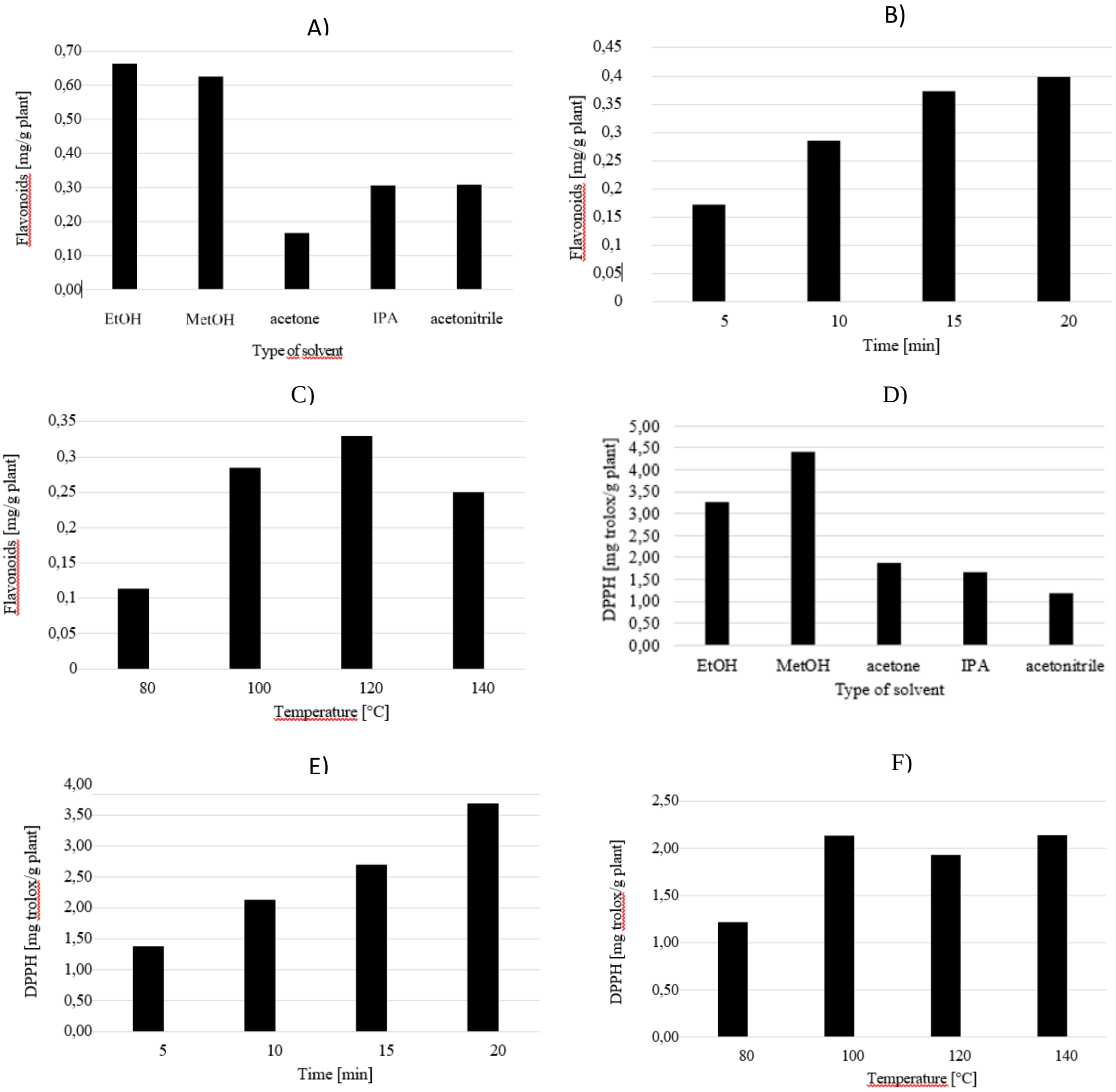

Figure 1. The results of the total yield of flavonoids and level of antioxidant activity. Flavonoid content in mg/g of plant depending on the type of solvent (Graph A), the length of the cycle (Graph B) and the temperature (Graph C). Graph A: From left-extracts number 14 (ethanol), 2 (methanol), 5 (acetone), 6 (IPA) and 7 (acetonitrile). Graph B: Ascending-sample number 18 (5 min), 11 (10 min), 12 (15 min) and 15 (20 min). Graph C: samples number 19 (80 °C), 11 (100 °C), 17 (120 °C) and 1 (140 °C). Antioxidant activity depending on the type of solvent (Graph F), the length of the cycle (Graph E) and the temperature (Graph F).

The result of the detected flavonoid content in mg/g of plant depending on the type of solvent can be arranged in the following order: ethanol > methanol > acetonitrile > IPA > acetone. This result corresponds to an extraction performed under conditions of 100 °C and a cycle time of 10 minutes. The most suitable solvents included methanol and ethanol, which showed the greatest dissolving power. In this experiment, 99% ethanol was used, with a yield of 0.66 mg of flavonoids per g of raw material, and in the case of methanol, a 6.06% lower amount of flavonoids and phenolic substances was obtained. In the case cycle length at a temperature of 100 °C, a trend of a gradual increase in the yield of the extract was observed, where the yield of flavonoids at a residence time of 20 minutes corresponded to 0.39 mg/g of raw material. The last observed parameter was the content of flavonoids in mg/g of the plant depending on the growing temperature. The temperature of 80 °C was chosen as the initial temperature, as this is the approximate boiling point of the ethanol that was used as the solvent. The constant parameter in these extractions was the cycle length, which was set to 10 minutes. The temperature was gradually increased with an interval of 20 °C. It was found that the yield of flavonoids increases in direct proportion to increasing temperature. The highest yield was evaluated at a temperature of 120 °C, when increasing the extraction temperature from 100 °C to 120 °C, the flavonoid content increased from 0.28 to 0.33 mg/g of raw material. At a temperature of 140 °C, the content of flavonoids in the extract was already decreasing, probably due to the thermal degradation of phenolic substances and the flavonoids themselves. Diego Santos et al. (2012) stated in their research that a temperature of 120 °C, a pressure of 50 bar and a cycle length of 8–11 min corresponded to the optimal conditions for obtaining the highest total yield of phenolic substances and flavonoids during PLE extraction from jabuticaba (*Plinia cauliflora*), which agrees with our result[10].

Table I
Inhibition of metabolic activity [%] measured using the resazurin assay.

Inhibition of metabolic activity [%]

Tested extracts	*Staphylococcus aureus*	*Pseudomonas aeruginosa*	*Escherichia coli*	*Enterococcus faecalis*
2% DMSO	0.00	0.00	0.00	0.00
Vancomycin	100.00	–	–	100.00
Kanamycin	–	100.00	100.00	–
1 (EtOH, 140 °C, 10 min)	38.05	41.48	–	15.83
2 (MeOH, 100 °C, 10 min)	13.40	–	–	–
6 (IPA, 100 °C, 10 min)	9.59	–	–	–
11 (EtOH, 100 °C, 10 min)	58.15	–	–	21.66
12 (EtOH, 100 °C, 15 min)	–	52.92	–	23.17
15 (EtOH, 100 °C, 20 min)	–	–	–	38.82
17 (EtOH, 120 °C, 10 min)	18.19	–	–	8.78
18 (EtOH, 100 °C, 5 min)	12.63	–	–	–
19 (EtOH, 80 °C, 10 min)	–	–	–	–

(– metabolic activity without inhibition)
deviation of results ± 15 %.

When determining the antioxidant activity, this activity was expressed as mg trolox/g plant depending on the type of solvent, the length of the cycle and the temperature. The highest antioxidant activity of the sample was obtained using ethanol solvent, which corresponded to 4.40 mg trolox/g plant. The order of solvents according to the antioxidant activity results is different compared to the result evaluated for the flavonoid content: ethanol > methanol > acetone > IPA > acetonitrile. The antioxidant activity increases in direct proportion with increasing cycle length, i.e. at a cycle length of 20 minutes, the highest activity corresponding to a value of 3.69 mg trolox/g plant was found. The level of antioxidant activity of the extraction performed at 80 °C corresponded to a value of 1.21 mg trolox/g plant. At a temperature of 100 °C, the activity was significantly higher by 76.9%. However, when determining the antioxidant activity depending on the increasing temperature, these values fluctuate, unlike the yield of flavonoids. For a total of 9 tested extracts from the root of *Eleutherococcus senticosus*, it was found that almost all of the tested samples did not show significant antimicrobial activity. But the most often the obtained extracts showed inhibition of metabolic activity against Gram-positive bacteria compared to Gram-negative bacteria. Our examined samples showed moderate sensitivity in the case of the resazurin test for the *Staphylococcus aureus* strain. Sample **11** (ethanol, 100 °C, 10 minutes) demonstrated the greatest inhibitory properties of metabolism with 58.15% inhibition of *Staph. aureus*.

Conclusion

It has been confirmed that the yield of flavonoids in *Eleutherococcus senticosus* root extracts depends on the type of solvent, temperature and length of extraction time. During extraction from the root of *Eleutherococcus senticosus*, the content of the investigated substances increased with temperature, but when exceeding 120 °C, the substances also began to degrade and the content of flavonoids began to decrease. The resulting optimal extraction conditions were found to be the extraction solvent ethanol, a temperature of 120 °C and an ideal cycle length of 20 minutes. However, the highest flavonoid yield of 0.66 mg flavonoids/g plant was achieved in the sample extracted with ethanol, at 100 °C and 10 minutes, which also showed the highest level of measured antioxidant activity corresponding to 4.40 mg trolox/g plant. However, these extracts did not show significant antimicrobial properties, only in the case of sample **11**, which inhibited by 58.15% the metabolic activity of *Staph. aureus*. From these results, it is clear that there is still a need in the future to find optimal conditions for extracting biologically active substances such as flavonoids extracted from *Eleutherococcus senticosus*, which can provide significant protection against oxidative stress of the cell.

Acknowledgement

This work was financially supported by the Technological Agency of the Czech Republic with the project no. TN02000044.

References

1. Hossain T. J.: Eur. J. of Microbiol. and Immuno. 14, 97 (2024).
2. Azmir J., Zaidul I.S.M., Rahman M.M., Sharif K.M., Mohamed A., Sahena F., Jahurul M.H.A., Ghafoor K., Norulaini N.A.N., Omar A.K.M.: J. of Food Engineer. 117, 426 (2013).
3. Fayed S. A.: Not. Bot. Horti Agrobo. 43, 320 (2015).
4. Jafari-Sales A., Pashazadeh M.: Int. J. Life Sci. and Biotechnol. 3, 62 (2020).
5. Peng, C. H., Su J. D., Chyau C. C., Sung T. Y., Ho S. S., Peng C. C., Peng R. Y.: Biosci. Biotechnol. Biochem. 71, 2223 (2007).
6. Allegra A., Tonacci A., Pioggia G., Musolino C., Gangemi S.: Nutrients 12, 1 (2020).
7. Tzanova M., Atanasov V., Yaneva Z., Ivanova D., Dinev T.: Processes 8, 1222 (2020).
8. Arouca A., Grassi-Kassisse D. M.: Health 5, 1509 (2013).
9. Yan-Lin S., Lin-De L., Soon-Kwan H.: J. of Med. Plants Res. 5, 5946, (2011).
10. Santos D. T., Veggi P. C., Meireles M. A. A.: J. of Food Engineer. 108, 444 (2012).

THE PROPERTIES OF LAVENDER PAPER AS A POTENTIAL WASTE MATERIAL FOR PAPER PRODUCTION

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Abstract

Nowadays, the emphasis is on the use of waste crops in the context of the circular economy and waste management. For this reason, waste lavender has been used for paper production. The main reason for using lavender as a raw material is that a large amount of waste stem remains after harvesting. This paper deals with the mechanical and physical properties. Tensile strength and burst strength were evaluated as the fundamental mechanical properties. At the same time, the physical property, namely Gurley air permeability, was also tested. Surprisingly, the highest strength values were achieved by the 80 $g \cdot m^{-2}$ paper with a breaking length of 1.71 km and a tensile strength of 16.76 $N \cdot m \cdot g^{-1}$ compared to the higher basis weights of 100 and 120 $g\ m^{-2}$. The results of this research show lavender waste as another potential raw material for paper production.

Introduction

In the context of circular economy and waste management, non-wood raw materials, including agricultural residues, are some crops that could be an efficient source for pulp and paper production with added properties or economically viable in countries with scarce forest resources[1]. In Asia, specifically in China and India, non-wood raw materials already account for 70% of raw materials for production[2].

Lavender has not yet been used as a raw material for paper production, but there are publications on the use of lavender essential oil as an antibacterial treatment for paper or coating or as a fungicidal post-treatment[3,4,5]. Todorova *et al.*[6] reported that paper treated with lavender essential oil is a promising prospect against microbial deterioration and extends the paper's durability compared to the untreated sample.

This work aimed to cook a nitrate-alkali pulp from lavender (*Lavandula Officinalis*) and to investigate the mechanical properties of the paper made from it. This study focuses on lavender because of the possible use of waste biomass, e.g., in Provence (France).

Experiment

Waste lavender (*Lavandula Officinalis*), stripped of its flowers and grown in the Central Bohemian Uplands, was used in the brewing process to obtain pulp.

The raw material was first subjected to chemical analyses according to Tappi standards[7]. Specifically, this involved the analysis of the individual chemical components of the biomaterial, such as cellulose, which was determined by the Seifert method[8], lignin according to Klason (Tappi T 222 cm-02)[7], and holocellulose according to Wise[9]. The representation of hemicelluloses was then calculated from the holocellulose. In addition to macromolecular matter, inorganic ash (Tappi T 211 cm-02)[7] and organic extractives to acetone and ethanol-toluene (Tappi T 204 cm-97)[7] were determined.

The chemical pulp was produced by the nitrate-alkali method, in that the lavender was disintegrated into approximately 1 cm long pieces before boiling. This boiling was carried out under laboratory conditions. When approximately 100 g of material was contained in the cooking vessel, the ratio of cooking chemicals to raw material was 10:1. The cooking was carried out in nitric acid solution for 30 minutes, followed by extraction in sodium hydroxide for 10 minutes. This was followed by washing, neutralization with 1% acetic acid and separation of the uncooked pulp, and determination of the total yield and Kappa number of the cooked lavender pulp similar to that of black mustard[10].

After cooking the pulp, sheets of 80, 100, and 120 $g.m^{-2}$ were produced on a laboratory sheeting machine. Thus, the paper was tested for tensile strength according to ČSN ISO 1924-2[11] and ISO 2758:2014[12] to determine the compressive strength. In addition to the strength properties, the air permeability was tested according to Gurley's air permeability according to ISO 5636-5:2013[13].

Discussion and result analysis

Chemical composition

The plant's chemical composition gives an idea of how suitable the plant is as a raw material for papermaking. The main component of paper fibres is cellulose. The non-cellulosic components of the cell walls include hemicelluloses, lignin, extractives, and some minerals.

Table I

Chemical composition (in mass % of oven dried samples)

Sample	Ash	Extractives		Lignin	Cellulose	Holo-cellulose	Hemi-celluloses
		Acetone	Ethanol-Toluene				
Lavender stalks	5.25	7.25	9.28	24.10	29.43	77.90	48.47
Lavender blossom	5.50	13.79	12.03	20.52	26.73	60.19	33.46

*Standard deviation values are in parenthesis.

Since the representation of the individual chemical components is defined as a weight to absolute dry sample, moisture content was first determined for all samples. For lavender, a similar amount was obtained as for corn stalks 5.1%[14], wheat straw 4.7%[15], and rapeseed straw 4.8%[16]. For woody plants, the amount of ash is significantly lower, 0.5% in birch and 0.2% in pine[17], due to the greater amount of pulp in annual plants.

The extracts were analysed using a binary mixture of ethanol-toluene and acetone. The amount of extractives transferred at the stalks to the ethanol-toluene binary mixture was similar to that for corn stalks at 9.9%[18]. Compared to wood, it was similar to pine 10.4%, but significantly higher than that of beech 2.6% and spruce 2.7%[19]. In the case of the flower, of course, the amount of extractives is high, and this is mainly due to the content of tannins, flavonoids, coumarin, and essential oil.

Klason lignin was more abundant than other raw materials, with wheat straw at 15.3%, rapeseed straw at 20.0%, corn at 17.4%, and sunflower stems at 18.2%[15]. Our value is, however, similar to beech 24.5%[19] and at the same time lower than that of conifers, spruce 30.4%, and pine 29.5%[19]. However, the representation of Seifert cellulose was lower than that of sunflower stems 37.5%[15], wheat straw 38.2%[20], birch 41.0% or pine 47.0%[17]. The contents of hemicelluloses and holocellulose were similar to those of Potůček *et al.*[21].

Pulp properties

The nitrate-alkaline pulp from lavender stalks was cooked to a Kappa number of 15.9, the total yield was only 24.2%, and the rejects contained in the pulp were only 0.28%.

Mechanical and physical properties

Mechanical properties such as breaking length, relative elongation, tensile index, burst index, as well as the physical air permeability according to Gurley are given in Table II for 80, 100, and 120 g·m^{-2}.

Table II

Measured mechanical properties of investigated pulp compared to other pulps

Nitrate-alkaline pulp	AP, s	BL, km	ε, %	TI, N·m·g^{-1}	TEAI, J·g^{-1}	BI, kPa
Lavender 80 g·m^{-2}	1.80	1.71	0.68	16.76	0.08	26.93
Lavender 100 g·m^{-2}	2.33	0.57	0.35	5.58	0.01	30.53
Lavender 120 g·m^{-2}	3.87	0.98	0.59	9.58	0.04	36.17
Corn(18)	78.74	0.52	1.54	5.06	0.04	112.66
Black Mustard(10)	–	7.16	2.31	40.16	1.15	–
Camelina(10)	–	3.66	1.12	35.83	0.27	–

AP – air permeability (Gurley), BL – breaking length, ε – relative elongation, TI – tensile index, TEAI – tensile absorption index, BI- burst index

Mechanical properties were evaluated mainly in terms of tensile strength, where lavender pulp showed better properties than corn pulp[18] and slightly worse than black mustard or camelina[10].

In the case of breaking length, where the paper is damaged by its weight, the same value at a specific gravity of 120 g·m^{-2} is even greater than when recycled fibres are processed by the kraft method[16].

From the relative elongation point of view, the nitrate-alkaline pulp from lavender does not appear to be a suitable material for pulp and, subsequently, paper production.

The tensile strength index of lavender has values significantly higher than those of corn nitrate-alkaline pulp[18] or corn soda pulp[14] 3.23 N·m·g^{-1}. Yet, it is low compared to other crops by the nitrate-alkaline method[10]. Bhardwaj *et al.* produced pulp from bagasse using the soda method. Their tensile strength index was about 35 N·m·g^{-1}, similarly, compared to sulphite semi-pulp produced from rapeseed straw, about 40 N·m·g^{-1} and about 30 N·m·g^{-1} [22,23].

The tensile absorption index is mainly related to the performance of sack paper, indicating the strength of the paper withstanding rough handling. Sack paper from the collection paper reaches values of 1.78 J·g^{-1}, which are significantly higher than those we obtained[24]. Therefore, lavender pulp is not suitable for sack paper production.

However, the burst index was lower compared to corn[18]. However, in comparison with Barbash *et al.*[17], who studied pulp made with peroxyacetic acid, the lavender pulp is almost ten times stronger than wheat straw pulp at 4.26 kPa, rapeseed straw at 5.43 kPa, amaranth at 4.05 kPa, lavatera at 3.63 kPa, sverbiga at 3.06 kPa, and schavnat at 6.26 kPa.

Air permeability in papermaking is also essential for specialty papers. In this case, values significantly lower than for corn pulp were achieved, meaning that our paper is better filled with fibres and has lower air permeability by Gurley.

Conclusion

Using agricultural waste materials is essential, especially in countries with a shortage of primary wood resources. As paper consumption increases, wood resources in other countries decrease. Therefore, the demand for raw materials made of non-wood pulp is rising. The advantage of non-wood raw materials is their annual renewal and low cost compared to wood.

It should be noted that the chemical composition of non-wood raw materials varies widely, as indicated in this document. In the case of low lignin content in non-wood raw materials, the energy and chemical consumption is also lower than in producing pulp from wood. Many different delignification processes are used to make paper from annual plants.

- Based on its chemical composition, lavender is a suitable potential material for paper production due to its cellulose content and relatively low lignin content.
    - Stalks: lignin 24,10%, cellulose 29,43%
    - Blossom: lignin 20,52%, cellulose 26,73%
- Lavender pulp cooked using the nitrate-alkali method yields less than pulp cooked from black mustard or camelina. However, it is higher than that of pulp cooked from maize. For future lavender processing, it would be advisable to use a different delignification method.
- In the case of mechanical properties, the tensile index is comparable to torn straw pulp but, unfortunately, does not reach the values of kraft wood pulp. The burst index was similar to other pulps cooked by nitrite-alkaline and significantly higher than wheat pulp cooked by peracetic acid.

Lavender is a potential source of fibre, but this issue needs to be further investigated through other delignification methods and cooking parameters.

Acknowledgement

Thanks to the support of the Department of Wood Processing and Biomaterials at the Faculty of Forestry and Wood Technology.

References

1. Mohieldin, S:D. Journal of Forest Products and Industries *3(2)*, 84–88 (2014).
2. Saijonkari-Pakhala, K. *Non-Wood Plants as Raw Materials for Pulp and Paper*. The University of Helsinki, Helsinki 2001.
3. Kandirmaz, E.A., Birtane, H., Cigil, A.B., Ozcan, A. Flavor and Fragnance Journal *35(2)*, 127–242 (2020).
4. Rungwasantisuk, A., Raibhu, S. Progress in Organic Coatings *149*, 105924 (2020).
5. Bidar, L., Noohi, N., Dehkordi, M.H. Journal of Research on Archaeometry *8(2)*, 101–114 (2022).
6. Todorova, D., Yavorov, N., Lashea, V., Damyanova, S., Kostova, I. Coating *13(1)*, 32 (2023).
7. Tappi Test Methods.Standard and Test Method. Tappi Press, Peechtree Corners 2004.
8. Seifert, K. Das Papier *10*, 301–306 (1956).
9. Wise, L.E.; Murphy, M.; D'Addieco, A.A. Paper Trade Journal *122*, 35–43 (1946).

10. Hájková, K., Bouček, J., Procházka, P., Kalous, P., Budský, D. Materials *14(13)*, 3673 (2021).
11. *ČSN EN ISO 1924-2 (500340) Paper and Board – Determination of Tensile Properties*. Czech Standard Institute, Prague 2009.
12. *ISO 2758:2014 Paper — Determination of Bursting Strength.* International Organization for Standardization, Geneve 2014.
13. *ISO 5636-5:2013 Paper and board — determination of air permeance (medium range) — Part 5: Gurley method*. International Organization for Standardization, Geneve 2019.
14. Fagbemigun, T.K., Fagbemi, O.D., Otitoju, O., Mgbachiuzor, E., Igwe, C.C. International Journal of AgriScience *4(4)*, 209–213 (2014).
15. Housseinpour, R., Latibari, A.J., Farnood, R., Fatehi, P., Sepiddehdam, S.J. IAWA Journal *31*, 457–464 (2010).
16. González, I., Alcalá, M., Arbat, G., Vilaseca, F., Mutje, P. Bioresources *8*, 1967 (2013).
17. Barbash, V., Poyda, V., Deykun, I. Cellulose Chemistry and Technology *45*, 613–618 (2011).
18. Hájková, K., Jurczyková, T., Filipi, M., Bouček, J. Biotechnology Reports 37, e00786 (2023).
19. Potůček, F., Miklík, J. Acta Facultatis Xylologiae Zvolen *53*, 49–58 (2011).
20. Enayati, A.A, Hazem, Y., Mirshokraie, S.A., Molaii, M. Bioresources *4*, 245–256 (2009).
21. Potůček, F., Gurung, B., Hájková, K. Cellulose Chemistry and Technology *48(7–8)*, 683–691 (2014).
22. Ahmadi, M., Latibari, A.J., Faezipour, M., Hejdazi, S. Turkish Journal of Agriculture and Forestry *34(1)*, 11–16 (2010).
23. Kasmani, J.E., Samariha, A., Kiaei, M. World Applied Science Journal *12*, 1996–2001 (2011).
24. Boček, S. *Use of Secondary Fibre to Produce Sack Paper* (in Czech). University of Pardubice: Pardubice 2003.

DECARBONISATION

OPERATING PARAMETERS OPTIMIZATION BASED ON PILOT TESTING OF CO₂ MEMBRANE SEPARATION FROM FLUE GAS

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Abstract

Gas membrane separation of carbon dioxide (CO_2) from flue gas is a compact technology aiming to make small sources of flue gas more carbon neutral. Our pilot unit fits inside of a 20 ft. shipping container and can process up to 100 $Nm^3\,h^{-1}$ of flue gas with CO_2 content of 6 % while producing up to 9 kg of CO_2 per hour. The technology utilizes ambient and subambient cooling of flue gas, a blower, one membrane module and a vacuum pump used to minimize the energy requirements as opposed to a setup with a compressor. The highly permeable membrane with high CO_2/N_2 selectivity is also a key factor in optimizing the cost of the process. This setup allows to produce concentrated stream with more than 50 % CO_2 by volume. We suspect that the higher concentration CO_2 in flue gas, the better separation performance and lower cost of separation. Exact numbers are simulated via DWSIM software using pilot testing data.

Introduction

The politics of "Green Deal" require the development of technologies capable of turning our fossil fuel dependent industries into ones able to function within the circular economy model. With our vast understanding of combustion and petrochemical processes, one of the goals of this transformation is not to just abandon our old ways, but to transform them into carbon neutral ones via innovative techniques. We have identified an opportunity, which utilizes the strengths of membrane separation technology, to try to circularize small carbon sources using an existing infrastructure expanded with a compact membrane unit. Pilot testing was carried out to verify the simulations of the processes, identify potential pitfalls and study the possibilities of expanding the technological scale of the membrane separator into other fields.

Theory

Gas membrane separation technology is based on different rates of solubility and diffusion rate of various gases through membrane. The separation behavior can be described using a physical quantity "permeance". Permeance is defined as pressure-normalized molar flux through membrane defined as (1)

$$\frac{P}{l} = \frac{Q_\mathrm{p}}{A\,\Delta p}\,10^6 = \frac{F}{\Delta p}\,10^6, \tag{1}$$

where P/l is permeance (GPU = 10^{-6} $cm^3(STP)\,cm^{-2}\,s^{-1}\,cmHg^{-1}$), Q_p is permeation rate ($cm^3(STP)\,s^{-1}$), A is membrane area (cm^2), Δp is transmembrane pressure difference (cmHg) and F is permeation flux ($cm^3(STP)\,cm^{-2}\,s^{-1}$). P is permeability (barrer), which is a material constant for given membrane material, and l is thickness of membrane separation layer (µm). Selectivity between compound A and B $\alpha°_{A/B}$ is defined as (2)

$$\alpha^{\circ}{}_{\mathrm{A/B}} = \frac{\left(\frac{P}{l}\right)_\mathrm{A}}{\left(\frac{P}{l}\right)_\mathrm{B}}, \tag{2}$$

where $(P/l)_A$ and $(P/l)_B$ are permeance values of compound A and B respectively. For a gas mixture, stage cut Θ is calculated as (3)

$$\theta = \frac{Q_\mathrm{P}}{Q_\mathrm{F}}, \tag{3}$$

where Q_P is molar flow rate of permeate and Q_F is molar flow rate of feed[1].

Experimental

Our testing was realized via an in-house constructed pilot unit capable of processing up to 100 Nm h^{-1} of wet flue gas from point sources such as natural gas plant, CHP engine, incinerator plant etc. The technology was housed within a 20 ft. shipping container with plenty of room to spare, suggesting a higher flue gas capacity unit would also fit within such a container. The technology contained an air cooler designed to pre-cool the flue gas to temperatures of 45 °C or lower, a compressor-based subambient cooler (chiller) combined with a gas-liquid separator for flue gas drying, a one-stage blower with discharge pressure of up to 1.2 bar(a), a spiral wound membrane module and vacuum pumps with pumping capacity from 10 up to 180 m^3 h^{-1} able to reach vacuum pressure of 0.05 bar(a) or lower. The technology was operated using a unified control computer with measurement and control devices. Our setup allowed us to test a wide range of flue gas flow from 20 up to 100 Nm^3 h^{-1}, condensation temperature 5 °C, separation temperatures from 10 to 50 °C and various vacuum levels to find the optimal operating parameters for maximizing either the CO_2 recovery or concentration and minimizing the specific energy consumption for separating a fixed amount of CO_2.

Natural gas heating plant was chosen as the first pilot testing location mainly for its convenient site location near MemBrain company for on-the-go repairs and modifications of the pilot unit during the first phase of testing. There, the flue gas contained approximately 6 % CO_2, 6 % O_2 and 88% of N_2 in dry gas. The temperature of the flue gas was only 60 °C due to efficient flue gas heat exchangers within the plant. The content of NO, NO_2 and SO_2 gas was also extremely low in the order of tens of ppm.

Flue gas flow rates from 25 to 90 Nm^3 h^{-1} of dry gas, feed gas pressures from 1.05 to 1.18 bar(a), permeate vacuum of 0.05 to 0.50 bar(a) and separation temperatures from 10 to 50 °C were tested. Quickly, a realization was made that deeper vacuum was crucial for the efficiency of the process. Four vacuum pump arrangements were tested – displacement of 10, 20, 40 and 180 m^3 h^{-1}. While the 10 m^3 h^{-1} vacuum pump was sufficient for vacuum of 0.5 to 0.2 bar(a), the 180 m^3 h^{-1} one was able to reach vacuum of 0.04 bar(a). Vacuum pressure was affected by separation temperature – higher temperatures led to higher permeate flow through the membrane and thus not as deep of a vacuum pressure due to the pumps following their performance curves.

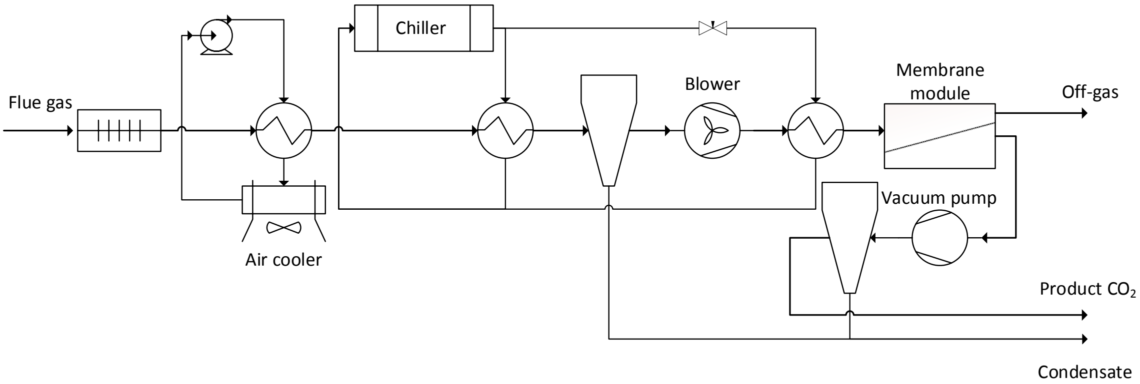

Figure 1. Simplified PFD of the pilot unit

Simulation

DWSIM modelling software was used to create a so-called "digital twin" of the pilot unit to understand the behavior of the system and to determine if the influence of various operating parameters could be correlated with the experiments. The following simulation settings were used: compounds list: carbon dioxide, water, oxygen, nitrogen; thermodynamics: Peng-Robinson (PR); blower and vacuum pump adiabatic efficiency: 35%; air cooler efficiency: 3,500%; chiller cooling efficiency: 200%; condensation temperature: 5 °C; efficiency of vapor-liquid separator: 95%. Membrane separation was modeled using internal custom-made membrane separator inserted as python module into DWSIM. For simulations at separation temperature of 25 °C, following parameters were used: CO_2 permeance: 1,450 GPU, N_2 permeance: 55 GPU, O_2 permeance: 140 GPU, H_2O permeance: 6,000 GPU. At 45 °C, following parameters were used: CO_2 permeance: 2,900 GPU, N_2 permeance: 110 GPU, O_2 permeance: 300 GPU, H_2O permeance: 6,000 GPU. Membrane surface: 14 m^2 for both temperatures.

Result analysis and discussion

The results showed a dependence of CO_2 flow through the membrane mainly on vacuum pressure and temperature, where deeper vacuum led to higher CO_2 flow, so did higher temperatures. It was shown that higher flow rate of flue gas does not necessarily lead to much higher CO_2 flow. It was shown that it is possible to get to up to 80% recovery of CO_2 (higher stage cut) without a significant deviation from expected temperature dependence of the rate of CO_2 flow through membrane as opposed to test with low recovery (lower stage cut). On the other hand, increasing the flue gas flow rate through the module by the factor of 2 only led to an increase in flow of CO_2 through membrane by 20 to 30%.

Due to the inaccuracies during the testing, it was not possible to analytically calculate the exact permeance. Its values were determined by fitting the simulation results to pilot test results.

Figure 2 shows the pilot data plotted with regards to pilot unit power draw and CO_2 production. As with any other technology, the goal is to maximize the production rate while minimizing the power requirement. While these two goals are in opposition to each other and a compromise must be made between the two, there are criteria based on which one can decide which arrangement fits their case the best. Isoenergy lines can be drawn, indicating a region where the specific separation energy is the same. Evident from the graph, most of the pilot results land between the 1 and 2 kWh $kgCO_2^{-1}$ bounds. While in the bottom left corner, tests with vacuum pumps with displacement of 10, 20 and 40 $m^3\ h^{-1}$ are located, the top right corner houses tests with pump with displacement of 180 $m^3\ h^{-1}$. As can be seen, 40 $m^3\ h^{-1}$ pump performs strictly better than the 10 and 20 $m^3\ h^{-1}$ ones, showing the possibility of 1 to 2 kWh $kgCO_2^{-1}$ separation. The 180 $m^3\ h^{-1}$ pump is also firmly placed between the region bounds. Each vacuum pump covers wider power draw interval. This is caused by variations in power draw of other components – blower and chiller specifically. Blower variation is caused by different speed settings, where higher speeds increase the feed flue gas flow and power consumption. With higher feed flow, the requirements for cooling also increase, causing the chiller to draw more power as well. Additionally, increasing the separation temperature increases the permeate flow, thus also increasing the vacuum pump power draw.

While it would seem that operating with smaller vacuum pumps can also be favorable, it is important to state that, while the specific separation energy is the same for 40 $m^3\ h^{-1}$ pump as with the 180 $m^3\ h^{-1}$ pump, the total CO_2 production is much lower. This means that the capital costs associated with purchasing the equipment is much higher in relation to CO_2 production rate, increasing the time until profitability. The graph then suggests that it is more worth it to install a large vacuum pump, increasing the separation performance from just one membrane module.

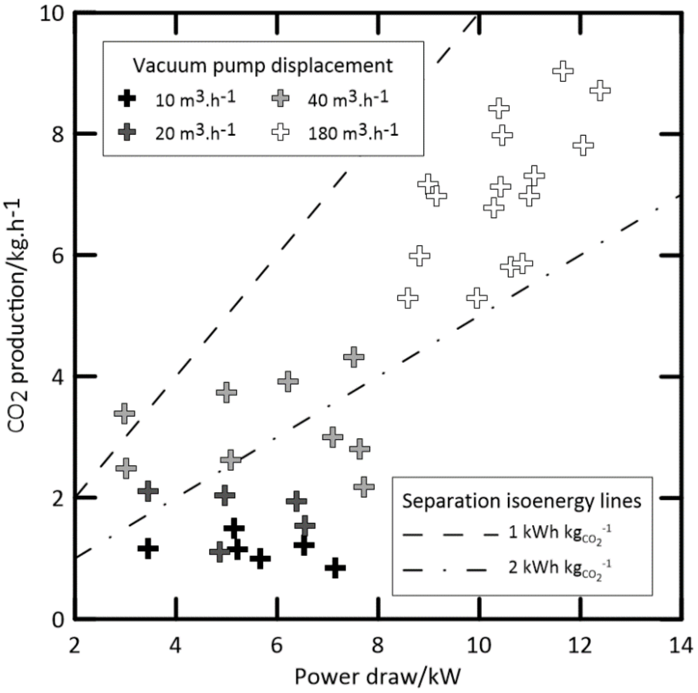

Figure 2. Dependence of CO2 production on power draw of the pilot unit

Figure 3 shows a plot of specific separation energy dependence on stage cut. While not visible in the graph, higher stage cut with a given vacuum setup was achieved by increasing the separation temperature. Temperature is yet another way to increase the yield from a single membrane module. Because there is plenty of waste heat available at possible technology deployment sites, the separation temperature increase would not lead to a power draw increase. If anything, the need for cooling is decreased, thus decreasing the power draw a little. A clear preference for higher stage cuts with regards to minimizing specific separation energy is visible. This is caused by that fact that with more energy used by the main machinery (blower, pump), the relatively smaller is the auxiliary power draw caused by measurement and control devices, circulation pumps, etc. Most of the auxiliary power draw is fixed and does not vary with the increased flow through the membrane.

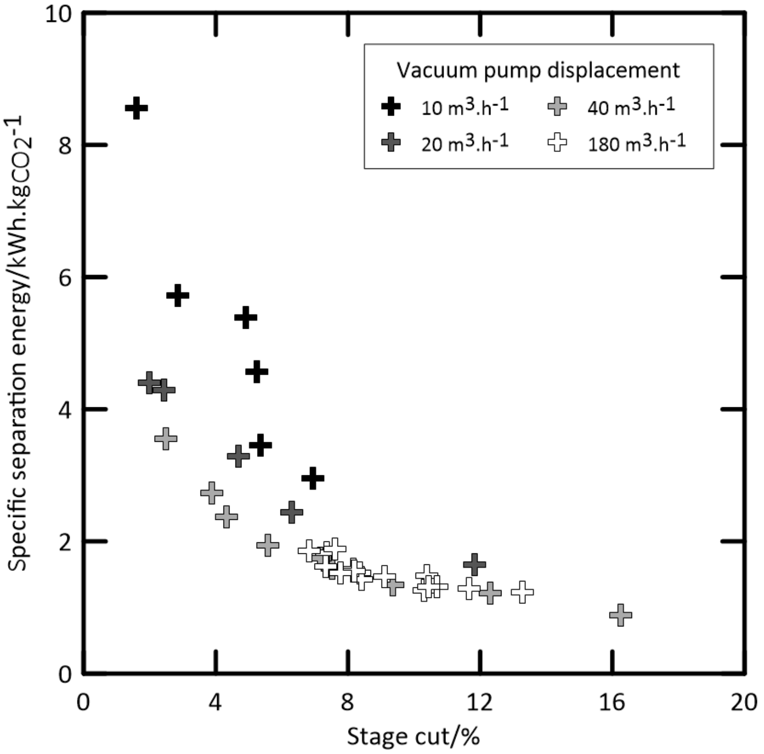

Figure 3. Stage cut vs specific separation energy

Increasing the separation temperature, however, causes a decrease in selectivity of CO_2 relative to the other components of the flue gas. While the overall increase in permeance is reflected positively in the specific energy consumption, the quality of the product (CO_2 content) decreases. From temperature of 15 to 50 °C, we observed a drop in CO_2 content from 58 to 45 vol. %. This, however, is an expected membrane behavior. This is shown in figure 4. Many processes utilizing CO_2 as a source material (e.g. dry ice manufacturing, e-fuels and chemicals synthesis or CO_2 injection underground) require much higher CO_2 concentrations than even the 58 vol. % produced by our pilot. This could be solved by deploying an additional membrane separation step where the product from first stage serves as the feed for second stage. On the other hand, there are some use-cases for this diluted CO_2 product – namely cases when CO_2 needs to be further diluted with air. While the concentration of CO_2 in air is approximately 0.04%, some plants provide better yield with concentrations of 0.1% or higher. Thus, many modern agricultural greenhouses employ a CO_2-enrichment technology used to inject pure CO_2 into the indoor air. Many farms also produce biogas, which is burned in a CHP engine that releases high CO_2 concentration flue gas.

Lastly, figure 5 shows dependence of CO_2 recovery dependence on flue gas flow rate through the membrane. Evaluation of the experimental data has shown that with deep enough vacuum and high enough temperature, it is possible to reach an extremely high total CO_2 recovery rate of up to 90%. However, occasional analysis of retentate off-gas has shown that the calculated recovery can be overvalued by up to 20%. A maximum recovery rate of 75%, then, seems more realistic. It is to be said that, while high recovery was achieved for flue gas containing just 6% CO_2, it is unclear whether the same performance can be expected when treating flue gas containing 10% CO_2 or more. Certainly, a limit exists for the maximum CO_2 flow rate through the membrane module given an economically viable flue gas flow, pressure and composition, separation temperature and vacuum pressure. The limit however, indicated by the extremely high CO_2 recovery, was not reached for our experimental arrangement.

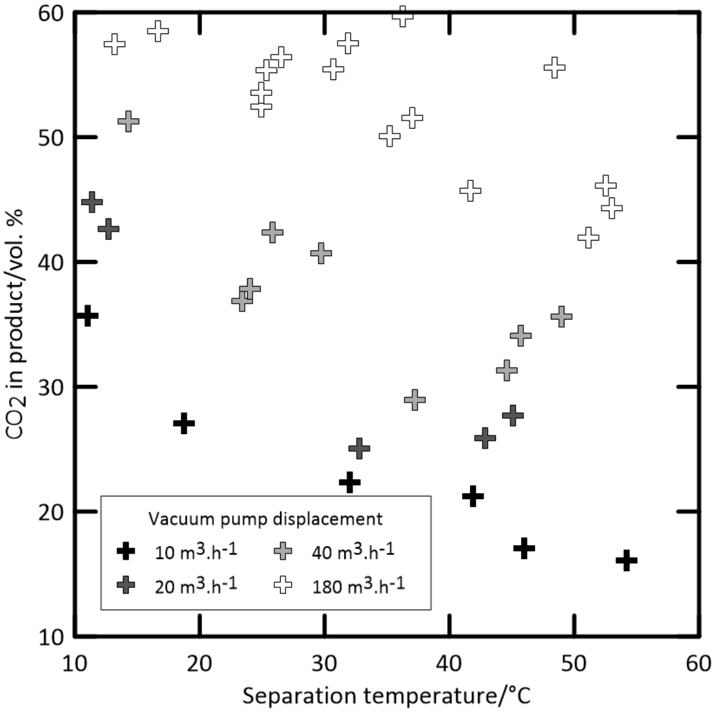

Figure 4. Dependence of CO_2 concentration in product based on the separation temperature

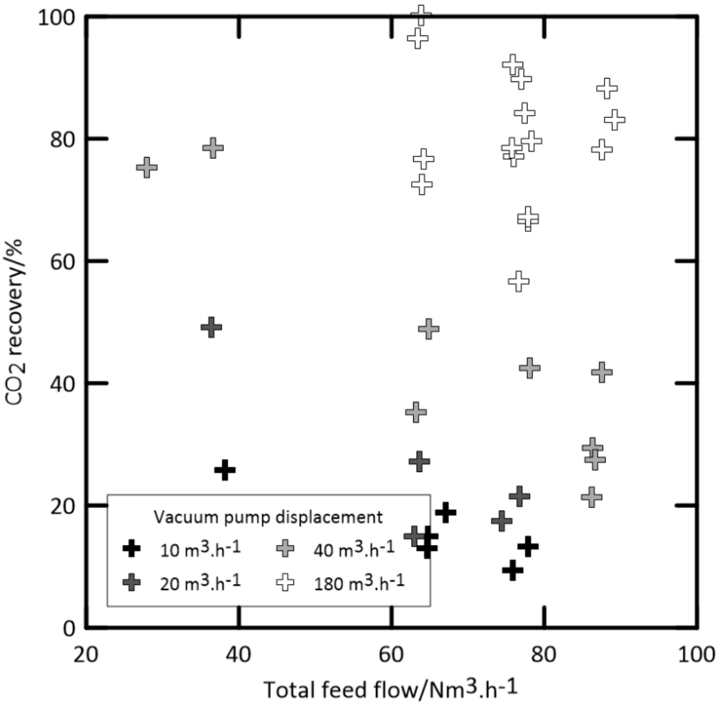

Figure 5. Total CO_2 recovery related to flue gas flow through the membrane

Figure 6 shows simulation data when extrapolating towards higher CO_2 concentrations in flue gas from 6.7 to 11.9 vol. % in dry gas. The higher value represents stoichiometric burning of natural gas (CH_4) in air without any air excess, while the lower value represents burning with 70% excess of air. The simulations were carried with regards to minimizing the number of membrane modules, energy consumption and CO_2 recovery of at least 67%.

This means that the flue gas blower discharge pressure is 1.1 bar(a) and separation temperature is 45 °C, vacuum pressure is 0.05 bar(a). It was shown that the fact that there is less ballast gas in the higher CO_2 concentration flue gas causes lower specific separation energy while increasing CO_2 concentration in product. The drop in specific separation energy is considerable (from >0.9 kWh $kgCO_2^{-1}$ to <0.6 kWh $kgCO_2^{-1}$), suggesting more economic opportunities for flue gas sources with higher CO_2 content are possible. This will be validated by more pilot testing at locations with higher CO_2 concentration in flue gas in the future. For now, we can say that the pilot testing fits the simulation at specific separation energy of >1 kWh $kgCO_2^{-1}$ for flue gas containing 6 % of CO_2. The CO_2 concentration also fits at around 50%. This is no surprise given that the pilot tests were the source data for the simulation.

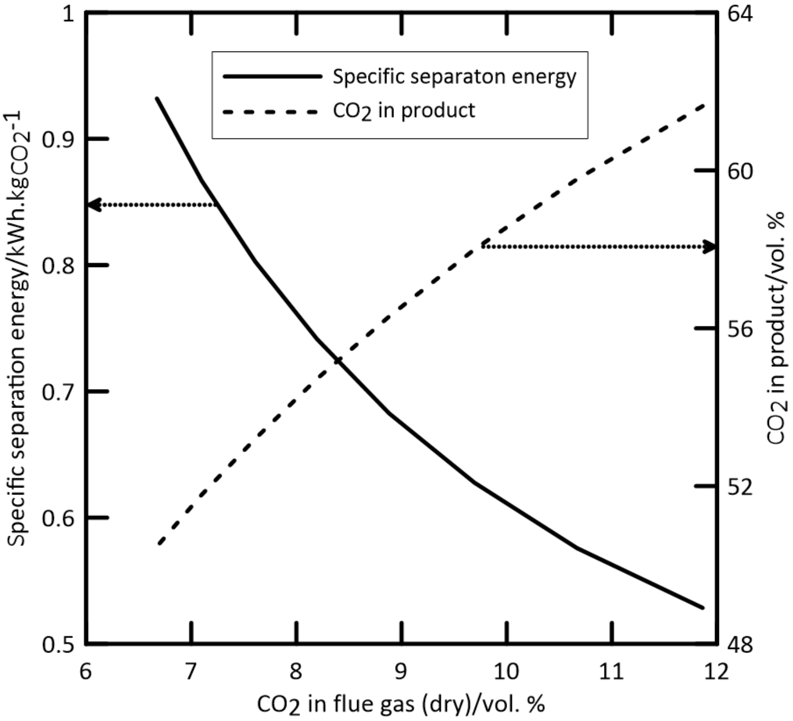

Figure 6. Simulation of separation characteristics extrapolated to higher flue gas concentration

Conclusion

It can be concluded that, implementing in-house python module for membrane separation in DWSIM software, a “digital twin” of pilot unit for separation of CO_2 from flue gas was created. A direct comparison between pilot testing and simulation is not yet possible in a wider flue gas CO_2 concentration interval due to the lack of higher CO_2 flue gas source. Further pilot testing will be carried out to verify simulation results. Suspected commercial viability is higher for flue gas sources containing more CO_2, concentrations of 12% are expected to lead to energy requirements for separation 0.6 kWh $kgCO_2^{-1}$ or lower. Pilot tests have shown ways to optimize CO_2 separation by varying process parameters such as flue gas flow rate, separation temperature, vacuum pressure and others. It was shown that operating with high flue gas flow rate, high separation temperature (45 °C) and low vacuum pressure (0.05 bar(a)) was the best for minimizing specific separation energy. The limit of membrane module performance was not reached (indicated by extremely high CO_2 recovery of >90%).

Acknowledgement

This work is supported by TACR TK02030155 using the infrastructure of the Membrane Innovation Centre.

References

1. Pourafshari Chenar M., Soltanieh M., Matsuura T., Tabe-Mohammadi A., Feng C.: Sep. Purif. Technol. 51, 359 (2006).

TESTS OF PILOT MEMBRANE SEPARATION OF CO_2 FROM FLUE GASES

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Abstract

To separate CO_2, several technologies are verified and used in the world, mainly chemisorption with absorption agents MEA (monoethanolamine), DEA (diethanolamine), MDEA (methyldiethanolamine), absorption with the agent Rectisol (methanol) or Selexol (dimethyl ether polyethylene glycol), adsorption on molecular sieves, membrane separation and possibly other special processes, such as cryogenic separation. Increased attention to the use of CO_2, or the reduction of its emissions, is mainly due to the EU's efforts to decarbonize existing industrial processes, or other activities of human society.

Introduction

During September 2023, the pilot was installed and connected to the flue gas pipe of boiler No. 1 at the company site of Českolipská teplárenská a.s. (ČLT). Operational tests of CO_2 membrane separation took place from October to November 2024. The goal was to verify the separation properties of the used membrane module in real operation. Electricity consumption was also recorded during operation, which is crucial for finding optimal operating parameters. The operating cost of the technology for separation of CO_2 from flue gases is most affected by the concentration of CO_2 in flue gas and also by the consumption of electricity, its price. During the tests, the were changed flow of flue gas and its pressure, separation temperature and vacuum on the permeate side.

Experiments

Description of the CO_2 membrane separation pilot unit

The entire technology, including process control is placed in the ISO 20 container with dimension of 6 × 2.5 × 2.5 m. The unit consists of three exchangers – in the first exchanger, the flue gases are cooled to approx. 65 °C, this exchanger is cooled using an atmospheric cooler located on the roof of the container. In the second exchanger, which has a cooling circuit connected to a chiller located outside the container on the left next to the main entrance door, cooling takes place well below the dew point and the flue gases are cooled to approx. 5–8 °C. The temperature of the flue gas downstream of the blower is regulated by the third exchanger. After separating the condensate, the flue gas passes through the membrane module, where the flue gas is separated into a component enriched with CO_2 and waste gas, which mainly contains nitrogen. The flue gas inlet (Feed) comes through a stainless-steel flexible pipe to the first cooler. After quality verification, the gas stream enriched with separated CO_2 (permeate) is mixed with the waste gas stream (retentate) and discharged together through a chimney opening 1 m above the roof of the container. The required flow rate and pressure of the flue gas is ensured in the pilot unit by a blower controlled by a frequency converter.
Main parts of the device:

- Atmospheric cooler (located on the roof of the container)
- Heat exchangers, 3 pcs
- Chiller (placed next to the short side wall of the container)
- Blower
- Cooling circulation pump
- Membrane module
- Control panel with electrical switchboard and M+R
- Flue gas analyzer, switch and gas sample cooler
- Condensate pump
- Condensate neutralization tank
- Chimney for exhaust gases
- Container air conditioning unit

The electrical connection of the container is 400 VAC, 30 A, the flue gas flow for CO_2 separation is 60–100 Nm3/hour.

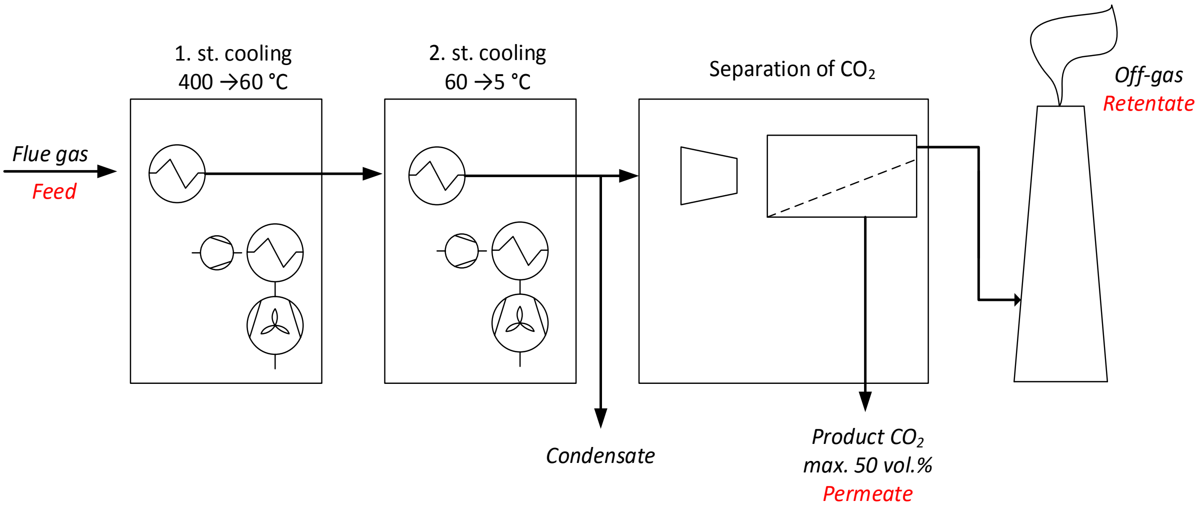


Figure 1. Technological scheme of the CO2 separation pilot unit

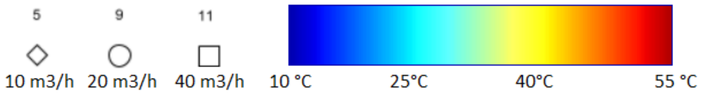
Table I
Range of tested parameters

Parameter	Min.value	Max.value	Unit
Feed temperature	30	60	°C
Volume flow	28	88	Nm^3/hod
Feed pressure	1.05	1.13	bar(a)
Separation temperature	11	54	°C
Permeate vacuum	0.13	0.45	bar(a)

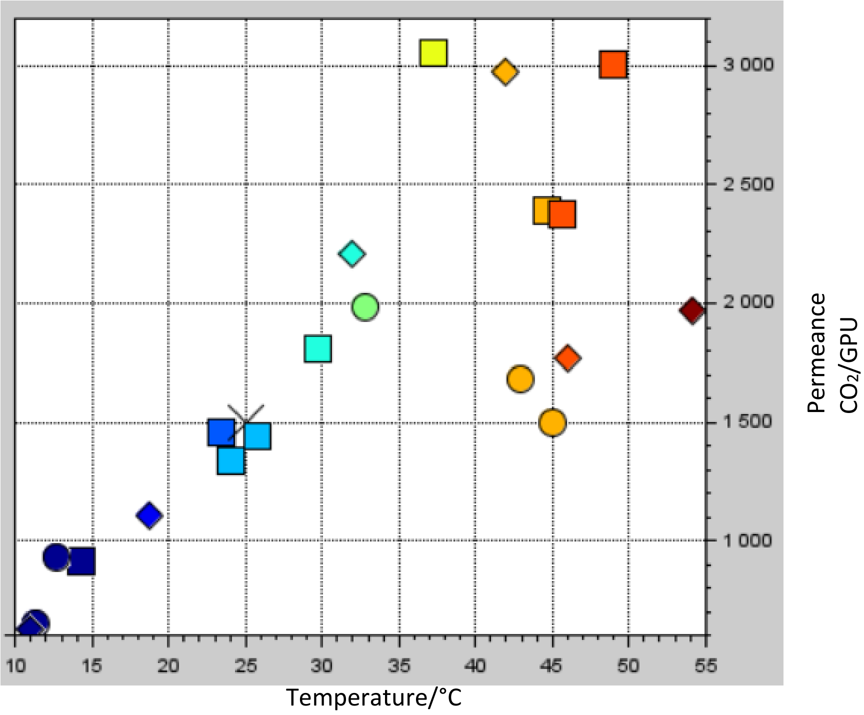
Figure 2. Photo of location of the pilot unit on the ČLT a.s.

Discussion and result of operational parameters achieved

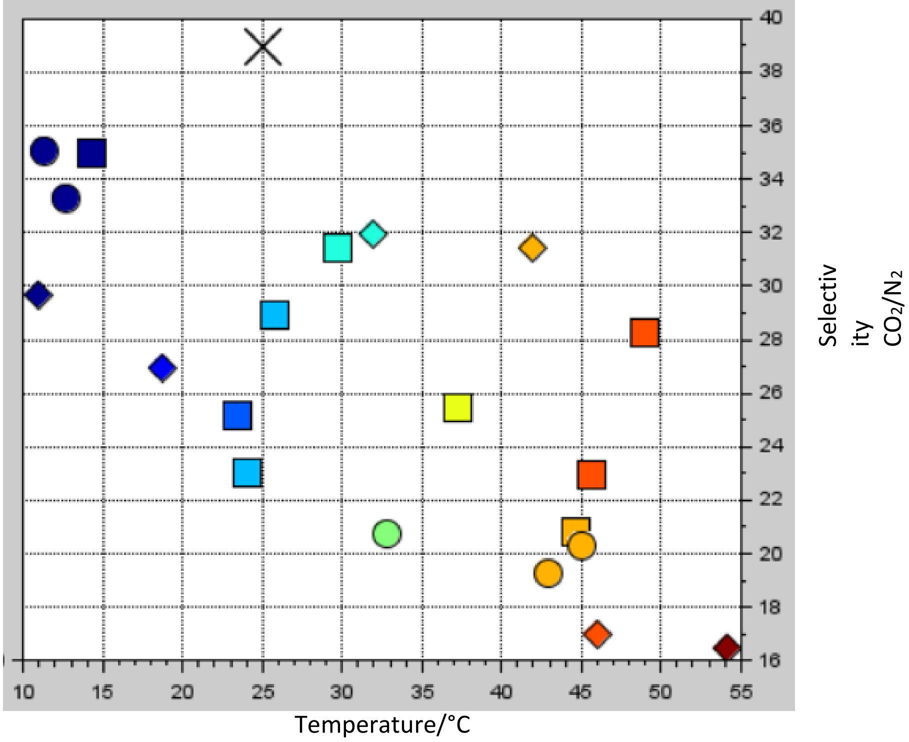
Tests of the pilot unit were carried out in the period September – November 2023. The process parameters are shown in the following graphs 1–3.



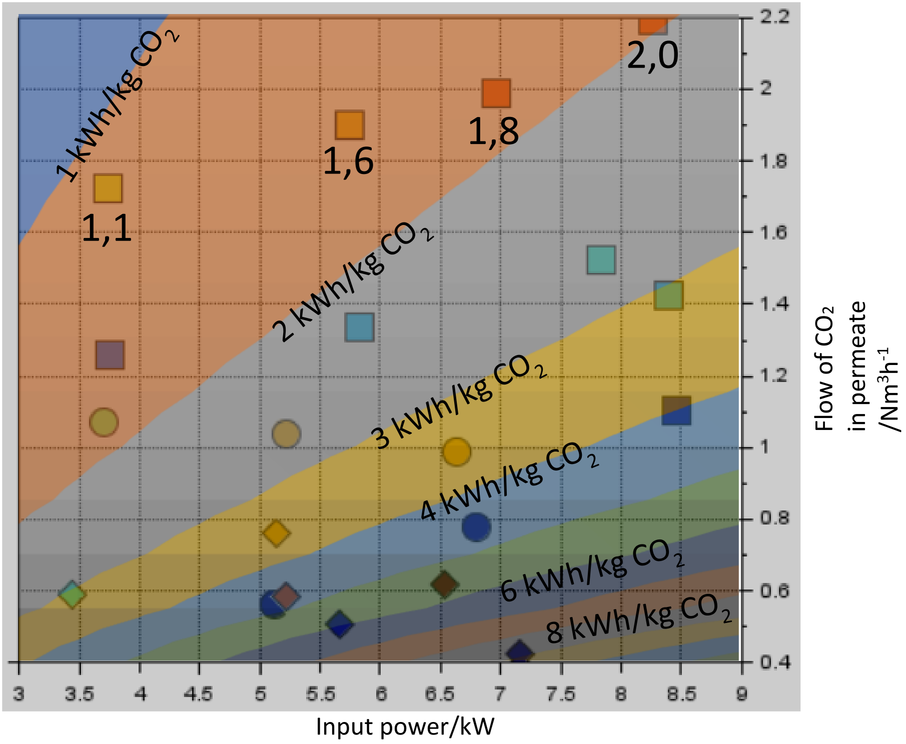
Legend to graphs



Graph 1. Dependence of CO_2 permeability on separation temperature



Graph 2. Dependence of CO_2/N_2 selectivity on temperature



Graph 3. Dependence of the flow CO_2 in the permeate on the electrical input

The pilot unit produced 6,5 l/h of condensate during flue gas cooling. Analysis of condensate is in following table. The condensate was alkalized before entering the sewage system.

Table II
Analysis of condensate

Parameter	Unit	Average value
Cu	[mg/l]	1.410
Fe	[mg/l]	0,055
Mn	[mg/l]	0,551
Na	[mg/l]	<0,100
Ni	[mg/l]	0.251
Zn	[mg/l]	0.276
Chlorides	[mg/l]	0.151
Nitrites	[mg/l]	8.91
Nitrates	[mg/l]	1.58
Phosphates	[mg/l]	<0.050
Sulfates	[mg/l]	5.90
pH		3.86
Temperature	°C	24.5

Problems during tests
During the pilot operation, several problems with the pilot unit were identified:

- The first problem was with an undersized vacuum pump. Only a diaphragm pump with a pumping capacity of 12 m^3/h was purchased for the pilot unit. The permeate flow rate was originally considered to be 4 Nm^3/h, which, however, at the required pressure of 0.05 bar(a), corresponds to a pumping capacity of 80 m^3/h. For that reason, additional pumps were subsequently included in the technology with the aim of increasing the pumping capacity as much as possible. A spiral vacuum with a capacity of 10 m^3/h and finally a rotary vacuum with a capacity of 33 m^3/h were added to the membrane vacuum. The vacuum pumps were always operated at 100% of their capacity, yet the average vacuum during the tests was 0.3 bar(a). When connecting all three vacuum pumps, an average vacuum of 0.23 bar(a) was achieved, which was close to the calculated values at 0.2 bar(a).

- The second problem was with the absence of independent heating between the blower and the membrane module. In cases where the technology was operated with a low Feed flow, the blower itself was not able to heat the gas to the required temperature of up to 55 °C, but only to, for example, 30 °C. This made it impossible to perform measurements at low flow rates and high separation temperatures.

Conclusion

The test results confirmed the permeability of the membrane, the selectivity is lower than expected. For industrial use, it is necessary to achieve a CO_2 permeability of at least 1500 GPU and a CO_2/N_2 selectivity of 40. At the same time, the consumption of electrical energy is very important. The lowest electricity consumption achieved was 1.1 kWh/kg CO_2 at an inlet gas temperature of 40 °C. It should be added that the pilot unit did not include a recuperation exchanger behind the condensation, in which the Feed would be pre-cooled and thus the resulting energy consumption would be lower. For industrial use, it is necessary to achieve a maximum energy consumption of 0.6 kWh/kg CO_2. At a low CO_2 content (below 6 vol.% on ČLT) in the flue gas, the results show that achieving low electricity consumption for CO_2 separation will be very difficult. Low electricity consumption during the combustion of natural gas will not be achieved only by the efficiency of the separation process, but also by other modifications of the combustion process itself, such as the excess amount of air during combustion, the use of "air sweep", or by dosing pure oxygen into the combustion process.

Acknowledgement

This work is supported by TAČR TK02030155 using the infrastructure of the Membrane Innovation Centre.

ECONOMICS OF CHEMICAL INDUSTRY

DIGITAL WELL-BEING AND THE TOOLS TO MAINTAIN IT

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Abstract

Occupational health and safety is an issue that every company in the European Union has to address. In the Czech Republic, this is an area on which over 70 laws, decrees, and government regulations have been published since 2000 alone. While the original focus of OSH was mainly on the protection of physical health, over time it has also become oriented towards mental health. In 2018, ISO 45 001 came into force, which added physical and mental well-being into the OSH management system. However, digital wellbeing, i.e. the ability to use digital tools and social networks in a way that does not limit one's personal life in the real world, has not yet been considered.

This paper focuses on defining the concept of digital wellbeing, the requirements for its legislative anchoring or inclusion in company regulations and introducing selected tools for maintaining digital wellbeing.

The paper is based on a search and analysis of mainly legislative documents and standards valid in the Czech Republic and the EU. The need for more precise anchoring of digital wellbeing was monitored in an international questionnaire survey and the obtained outputs were refined by in-depth interviews.

Neither the ISO 45 000 series nor other applicable legislative documents in the Czech Republic explicitly mention digital wellbeing. However, there are already several countries in the EU that have legislated the right to disconnect (one of the essential components of digital wellbeing). Maintaining digital wellbeing is therefore currently dependent on informal agreements or formalised policies that each company sets at its own discretion. Digital wellbeing is likely to be one of the areas of focus for OSH in the near future. It is therefore worthwhile to start addressing it in workplaces of all kinds, especially in positions where hybrid working is possible.

Introduction

Occupational health and safety (OSH) is one of the areas that every company must address. This does not only apply to companies with intense physical labour, such as those in manufacturing and warehouse management, or those dealing with complex and potentially dangerous chemicals and hazardous materials, for example, but also to industries not commonly associated with issues related to workplace safety, such as consulting companies or educational facilities. Originally, OSH was mainly concerned with physical health, however, this later went on to include mental health and, especially, psychosocial risks. Digital wellbeing is likely to be another area of OSH concern, although it has not yet appeared in any OSH legislation.

The main standard that defines OSH in the Czech Republic is the Labour Code, i.e. Act No. 262/2006 Coll[1]. The issue of OSH is dealt with in Part 5 of the code and is mainly concerned with risk prevention and the obligations and rights of employers and employees. Detailed requirements for employers are contained in Act No. 309/2006 Coll[2]. on ensuring that other conditions of occupational safety and health are met. However, these requirements are often very general, e.g. section 4 which states that "machinery must be equipped with protective devices that protect the life and health of employees". More specific descriptions of what constitutes an OSH offence and the relevant penalties are given in Act No. 251/2005 Coll., on Labour Inspection, in section 4. Offences[3].

However, the employer is also obliged to comply with the relevant requirements of all other laws, decrees, regulations and standards concerning employment, of which there are hundreds in Czech law, including:

- Government Regulation (GR) No. 176/2008 Sb. on technical requirements for machinery.
- GR No. 378/2007 Sb. laying down more detailed requirements for the safe operation and use of machinery, equipment, appliances and tools.
- GR No. 361/2007 Sb. laying down conditions for the protection of OHS.
- GR No. 201/2010 Sb. on the way of recording accidents, reporting and sending of an alert record.
- Act No. 59/2006 Sb. on prevention of major accidents caused by selected hazardous chemicals.
- GR No. 101/2005 Sb. on more detailed requirements for workplace and work conditions.
- GR No. 362/2005 Sb. on more detailed OSH requirements in workplaces with the danger of falling from a height or depth.

- GR No. 406/2004 Sb. on more detailed requirements for the provision of health and safety at work in potentially explosive atmospheres.
- GR No. 11/2002 Sb. on the appearance and location of security signs and the introduction of signals.
- GR No. 168/2002 Sb. which determines the approach of work organization and working procedures, which the employer is obliged to ensure during transportation by means of transport.
- GR No. 495/2001 Sb. laying down the scope and details of the provision of personal protective equipment, washing, cleansing and disinfectants.
- Act No. 258/2000 Sb. on public health protection.

It can be said that there are two main sets of obligations in OSH, the first of which is focused on employees. It is necessary to protect their lives and health through a whole set of measures. The second set is focused on employers and deals with the measures, tools and processes which they have to accept in order to maintain compliance as well as the maintenance of the necessary documentation.

ISO 45000

As previously mentioned, the OSH area is also underpinned by certain standards. In particular, the ISO 45001 standard, which was published on March 12th, 2018 and is valid since November 2018[4]. This standard supersedes the previously used OHSAS 18000 series and addresses the issue of occupational health and safety management systems more broadly than its predecessors did. It is a document which specifies requirements for an occupational health and safety (OH&S) management system and gives guidance for its use in enabling organizations to provide safe and healthy workplaces by preventing work-related injury and ill health, as well as by proactively improving its OH&S performance[4]. This document allows an organisation to integrate other aspects of health and safety, such as the physical/mental well-being of workers, through its OH&S management system (p. 10)[4]. However, mental well-being is not discussed in detail.

The first 18 pages define the terms used. Requirements are then listed but do not cover digital wellbeing and mental health[4].

Information on how to implement ISO 45001 is contained in ISO 45002, the latest update of which is dated 2023. The word “wellbeing” does not appear in it. Other standards in the ISO 45000 series are[4]:

- ISO 45003 Occupational health and safety management – Psychological health and safety at work – Guidelines for managing psychosocial risks. It defines what psychosocial risks are and how to identify them, including the risks of working from home.
- ISO 45004 Occupational health and safety management – Guidelines on performance evaluation.
- ISO 45005 Occupational health and safety management – General guidelines for safe working during the COVID-19 pandemic. This document gives guidelines for organizations on how to manage the risks arising from COVID-19 to protect work-related health, safety and well-being. Mental well-being is the subject of Chapter 6. The standard is divided into ten articles. It contains a number of inspirational guidelines. It is intended to help employers eliminate the possibility of stress, burnout or reduced performance in their employees, as well as reduced creativity or increased turnover due to psychosocial risks. It offers examples of effective – often simple – measures to manage them and improve employee wellbeing. It focuses on three groups of stressors: work organisation, social factors and work environment, infrastructure and hazardous work. The Social Factors section includes work-life balance, e.g. taking work home. However, digital wellbeing is not addressed.
- ISO 45006 Occupational health and safety management – Guidelines for organizations on preventing, controlling and managing infectious diseases.

Standards in the working draft stage are[4]:

- ISO/AWI PAS 45007 Occupational Health and Safety Management – OH&S risks arising from climate change and climate action – Guidelines for organizations.
- ISO/AWI 45008 Occupational health and safety management – Guidelines for remote work.
- ISO/AWI 45009 Occupational health and safety management – Governance and Leadership Top Management requirements for ISO 45001:2018.
- ISO/AWI 45010 Menstruation, menstrual health and menopause in the workplace – Guidance.

It is possible that digital wellbeing will be part of the forthcoming ISO 45008 standard. However, this is currently an area that is not yet addressed in any directive or standard in the Czech Republic nor in any EU directive. However, some countries have already issued their own pertinent legislative documents to address issues related to digital wellbeing and several projects on digital wellbeing have been addressed within Erasmus+ projects.

Digital wellbeing in the EU

Digital wellbeing became more of an issue with the significant increase in telework during the COVID-19 pandemic. Remote work is not regulated at an EU level through hard law mechanisms. However, several directives and regulations address relevant issues to ensure good working conditions for teleworkers. These include directives on ergonomics, the creation of a suitable home workspace, and rules on working hours and breaks, etc. (see above). It is therefore up to individual EU countries to develop national legislation to ensure workers' rights in relation to the potential harmful effects of teleworking. However, there are large legislative differences between Member States.

For example, there are different definitions regarding what constitutes "remote work" – some national laws, such as the Czech Republic's, do not mention the use of digital technologies at all, while others have specifications for regular and temporary telework, each of which is covered by a different legal framework. However, it is generally agreed that teleworkers have the same legal status as on-site workers. However, this standard is difficult to enforce. Moreover, it concerns mainly technical aspects, ergonomics, breaks, compensation, etc. One of the new aspects of telework that has recently become the subject of national legislative interest is technostress. This has been addressed through legislation on the right to be disconnected. The expectation of constant availability by companies or clients has led some countries to regulate the right of disconnection, which includes agreements on the scheduling of working hours, limitations on availability and breaks. Although a legislative initiative of the European Parliament was adopted in 2021 calling on the Commission to propose a law aimed at recognising the right to disconnect, currently the only legal mechanism regarding the right to disconnect is legislation at national level, where there is a great deal of diversity:

- Italy – Employees are obliged to comply with the rules on rest periods and breaks laid down by law. During these rest and break periods, employees must switch off their work equipment.
- Luxembourg – Telework legislation states that employers should ensure that measures are taken to prevent teleworkers from becoming isolated from their colleagues in the office.
- Portugal – Labour law requires the employer to encourage regular contact between the teleworker, the company and other workers to prevent isolation.
- Slovenia – Employers must take into account factors such as stress and mental well-being.
- The Netherlands – Legislation requires the assessment and prevention of psychosocial risks associated with teleworking.
- Ireland, Slovakia, Belgium, France and Spain have also adopted legislation that allows teleworkers to disconnect from the internet.

Thus, although digital wellbeing is not anchored in legislation and does not even have a single definition, there are already at least some projects and studies that address it. The basis for concern is usually technostress. This term was used as early as 1984 and it is now generally accepted that it has five main causes[5]: Techno-overload, Techno-invasion, Techno-complexity, Techno-uncertainty, and Techno-insecurity.

In addition to technostress, the (anticipated) expectation of employers that their employee will be permanently prepared to deal with work tasks, in particular responding to emails, is usually added to the assessment of digital wellbeing.

Digital wellbeing is a phenomenon that is part of an individual's overall wellbeing. It is "a term used to describe the impact of technology and digital services on people's mental, physical, social and emotional health"[6]. However, one of the key challenges is that digital wellbeing is not yet widely identified and recognised as a distinct area of wellbeing in the workplace. The concept of digital wellbeing is still poorly understood and there are many different definitions for it[7]. However, these definitions usually point to a state of balance between online and offline activities and an awareness of the impact of digital technologies (both positive and negative) on overall well-being. Digital wellbeing represents the effective use of digital technologies for teaching and learning, digital literacy, digital agency and all areas that offer different perspectives[8]. Digital well-being focuses primarily on incorporating and adapting personal technology habits to meet essential goals[9].

Methodology and results

A questionnaire survey was used to collect data from partner countries (Czechia, Ireland, Finland, and Slovakia) involved in the Erasmus+ DWEL project (No 2021-1-SK01-KA220-HED-000032017). The respondents were all from higher education institutions. Six project partners (educational institutions) used their networks and asked respondents to re-send the link to their partners (a snowball sampling method). Unfortunately, the Irish and Finnish partners were only able to add a few respondents. For Czech and Slovak respondents, the questionnaire was translated into Czech and respondents received a link for it. The survey began on 1st June 2022 and finished on 30th June 2022. The survey included demographic questions which focused only on gender, the respondent´s position in the organization and country. The next group of questions asked the respondents about the digital tools and technologies in their educational practice. The third group of questions was focused on digitalization aspects and digital wellbeing. The survey included 22 multiple-choice questions and two open-ended questions which allowed respondents to answer in open text.

We received 38 responses from the Czech Republic, 25 from Slovakia (22 of them based on the Czech questionnaire), 13 from Finland, and 4 from other countries. Based on the collected data, we decided to analyse only Czech and Slovak respondents who used the Czech version of the questionnaire (38 from CZ and 22 from SK). A five-point Likert scale was used (from 1 = strongly disagree, to 5 = strongly agree). Wilcoxon signed rank in GRETL software was used to verify statistical significances. After the questionnaire, a 30-minute unstructured interview was carried out primarily on people who answered the questionnaire (however, this was not a requirement). Each partner conducted approximately 5 interviews with randomly selected respondents. In total, 27 interviews were conducted.

The results showed that digital wellbeing was not well taken into account in organisations. Only 6% of respondents strongly agreed that digital wellbeing is very well considered in the respondent's own organisation. This opinion was not significantly different between Czech and Slovak respondents. Other statements focused on digital wellbeing were not statistically different as well, as shown in Table 1.

Table I
Digital wellbeing focused statements

Questionnaire statements	Czech resp. (n=38)		Slovak resp. (n=22)		
	Average	St. der.	Average	St. der.	p-Value
The use of technology in teaching makes me feel technostress	2.16	0.987	2.18	1.58	0.493
Digitalization in my work has made me feel isolated	2.37	1.134	1.77	1.041	0.119
Increased digitalization has reduced the sense of community in my HEI organization	3.26	1.291	2.59	1.267	0.098
In my opinion, digital wellbeing is very well taken into account in my organization	2.84	1.113	3.14	1.254	0.218

As written above, a five-point Likert scale was used, with 1 = strongly disagree. The data show that the respondents do not feel a high level of digital stress independently of missing institutional support.

Based on the results, it can be interpreted that the problem is not so much the quality of digital tools or the lack of them. Rather, the obstacles are, on the one hand, the lack of skills to make full use of digital tools and, on the other hand, the lack of time to practice using them.

Discussion and result analysis

Although employees in our survey did not confirm high levels of digital discomfort or technostress, it is possible that they simply do not register their difficulties. We therefore consider it appropriate to report on the typical symptoms that indicate the need for a digital detox and, consequently, an increase in digital wellbeing. These are:

- Feeling anxious or tense when you can't find your phone.
- Checking your phone frequently, even every few minutes.
- Experiencing negative emotions such as depression, anxiety or anger after using social media.
- Obsession with likes, comments and sharing your posts.
- The constant fear of missing something if you don't check your device regularly.
- Changing your sleep schedule so you can spend more time on your phone.
- Difficulty concentrating with the urge to check your phone.

Tarafdar et al. proposed three categories for coping with technostress that make up seven strategies[5]:

Reducing IT-related emotions and stress.

- Venting: Expressing negative emotions.
- Executive Distancing: Moving away from the IT use situation.

IT capacity development

- Positive view of IT: Optimistic approach to technostress situations.
- Skills for using IT: Developing competence in using IT.

Developing the definition of IT use

- Autonomy in IT use: having control over IT use.
- Time allocation: setting aside specific time for certain types of IT use.
- Separation of work and non-work IT use: Definition of work and non-work IT use.

It is our opinion that maintaining digital wellbeing requires a bit more strategies and techniques. Therefore, we offer seven steps for maintaining digital wellbeing:

- Step 1 Evaluate and monitor your habits – take notice of any patterns that may hinder your digital wellbeing or increase your sense of technostress.
- Step 2 Set boundaries for use of digital technologies – Use the "do not disturb" or "away" features on your digital devices or establish (and maintain) a specific time when you will disconnect. Make sure to let others know when you will be offline.
- Step 3 Limit distractions realized by digital technologies – Turn off notifications and, if possible, separate work devices from personal devices.
- Step 4 Use self-control tools – Google and Apple devices have many built-in tools to help you be aware of your time online and relevant tools to help mitigate this.
- Step 5 Strengthen your privacy and security – Ask your company's IT department for help if necessary.
- Step 6 Pay attention to social networks – The potential danger of social networks is quite well-known nowadays.
- Step 7 Take care of your health – Mental health and wellbeing often directly correlates to one's own physical health, in both positive and negative ways.

Conclusion

Although there is currently no mention of digital wellbeing in current OSH regulations, recent OSH guidelines pertaining to mental health show that legislation is trending towards its inclusion. Furthermore, despite the absence of any Czech or EU directives pertaining specifically to digital wellbeing, a number of member states have taken the initiative in crafting their own national legislation to address the health and safety of its employees as it relates to digital wellbeing.

It is imperative that employees are aware of the symptoms of technostress and that employers take action to mitigate its onset. The post-pandemic shift towards hybrid work models and more digitized work environments has fostered in an era of new concerns as they relate to workers and their health. EU-wide legislation and accompanying OSH guidelines need to catch up to the demands currently put on workers as a result of the modern workplace. Until then, individual employees need to take action to alleviate (or avoid) technostress and employers need to ensure that an environment which fosters the digital wellbeing of their employees is maintained.

Acknowledgement

This work was supported by DWEL, Erasmus+ Project No 2021-1-SK01-KA220-HED-000032017.

References

1. Act No. 262/2006 Coll; Labour Code: https://www.zakonyprolidi.cz/translation/cs/2006-262?langid=1033.
2. Act No. 309/2006 Coll; Act on ensuring additional conditions for occupational safety and health: https://www.zakonyprolidi.cz/translation/cs/2006-309?langid=1033.
3. Act No. 251/2005 Coll., on Labour Inspection: https://www.zakonyprolidi.cz/cs/2005-251.
4. ISO Standards: https://www.iso.org/standards.html.
5. Hajduch M., Šarek J.: Triterpenoid derivatives. PCT Intl. Patent Appl. Publ. WO 0190136.

6. Tarafdar M., Tu Q., Ragu-Nathan B. S., Ragu-Nathan T. S.: The impact of technostress on role stress and productivity. J Manage Inform Syst, *24*(1), 301 (2007).
7. Digital crossroads. Digital wellbeing for enterprises, 2022 https://www.digitalcrossroads.eu/.
8. Themelis Ch., Sime J.: Mapping the Field of Digital Wellbeing Education: A Compendium of Innovative Practices and Open Educational Resources. Digital Wellbeing Educators. Lancaster University, UK 2019.
9. Passey D.: Digital Technologies - And Teacher Wellbeing? Educ. Sci. *11*, 117 (2021).
10. Dhyani A., Gaidhane A., Choudhari S. G., Dave S., Choudhary S.: Strengthening Response Toward Promoting Mental Health in India: A Narrative Review. Cureus. *14*(10), e30435 (2022).

COLLABORATION IN ENHANCING THE SUSTAINABILITY OF PACKAGING FOR CONSUMER CHEMICAL PRODUCT

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Abstract

The article focuses on the currently implemented forms of cooperation between manufacturers of consumer chemicals and their packaging partners. It presents the results of qualitative research conducted in three small enterprises using personal interviews. It specifies concrete ways and methods of cooperation in both the design and procurement of packaging from supplier companies. The article reveals that small enterprises primarily share information with their partners about legislative developments and new trends in packaging and collaborate mainly on changes in the overall design of packaging, solving technological issues related to the finishing production of primary packaging, and purchasing packaging based on common commercial operations. Since the studied companies do not apply any modern logistics technologies or advanced inventory management methods, the main recommendations for improvement are directed to this area. Additionally, it is desirable to develop cooperation with a broader portfolio of stakeholders and increase the complexity and systematic approach in managing collaboration.

Introduction

With growing environmental concerns and the future state of the environment, there is a significant shift towards sustainability. This shift affects not only consumers but also other microeconomic entities, especially businesses. Industrial companies, including those in the chemical industry, undertake various activities to increase the sustainability of their processes. Special attention is given to the area of packaging. Generally, there is a tendency to move away from plastic packaging and towards packaging based on circular economy principles. Innovations focus on selecting more sustainable packaging materials, changes in shape, and managing packaging flows. However, transitioning to more sustainable packaging requires considering not only ecological but also social and economic aspects. Sustainable packaging must meet the requirements of various stakeholders, including product manufacturers, intermediaries, consumers, recycling companies, and state institutions. Innovative packaging should ensure the smooth movement of goods in the logistics chain to the point of final consumption, prevent product damage, and inform customers about product characteristics[1]. They should be environmentally and socially friendly while being economically efficient for all parties involved in the supply chain, meaning the costs associated with packaging should be minimized, and resource utilization optimized[2].

Packaging innovations towards sustainability can be conducted independently at the enterprise level without direct collaboration with partners. However, cooperation can be developed vertically (in the supply chain with business partners) and/or horizontally (across the stakeholder network)[3]. Both types of cooperation allow combining the knowledge, experience, and capacities of the parties to achieve innovative and effective solutions[4,5]. Vertical and horizontal cooperation creates space for joint research and development activities, sharing technologies and know-how[4]. This facilitates achieving more favourable results concerning various sustainability dimensions. Establishing partnerships and coordination among different entities particularly helps comply with legislation[3], better identify the needs of individual stakeholders, uncover and solve problems, maximize resource utilization, reduce costs, distribute costs among different entities, and implement innovative and sustainable packaging solutions into practice[6,7,8].

Collaboration can be developed at both strategic and tactical-operational levels. At the strategic level, the concept of packaging and the concept of both direct and reverse physical flow of packaging can be jointly addressed. At the tactical-operational level, within the created concept, current physical flows can be jointly managed across and back in the chain. This collaboration can focus on packaging design, purchasing packaging, sorting and cleaning packaging after use, refilling, recycling, and disposal after the last use. Planning packaging supplies closely relates to inventory management, which should be initiative-taking. This will minimize storage and handling costs and losses due to obsolescence or non-use of packaging stocks. Effective inventory control improves the planning of the packaging purchasing process, minimizes excessive purchases, and increases efficiency in the use of financial resources[9]. Initiative-taking packaging inventory management thus contributes to minimizing overall costs and maximizing the efficiency of business processes[10], as well as further improving the environmental and social aspects of packaging and its supply.

Cooperation is also crucial for the efficient and sustainable processing of returned packaging and materials[8]. Its establishment in the area of reuse, recycling, and disposal of packaging after the last use can eliminate many obstacles that a single business entity would face alone. This mainly involves reducing costs for[7,11]:

- changing infrastructure for used packaging, such as changes to distribution centres, warehouses,
- acquiring or modifying equipment for cleaning and disinfecting packaging,
- purchasing new technologies and equipment,
- implementing effective flows within the circular economy of packaging (costs for systems enabling refilling, recycling, and disposal of packaging). Therefore, cooperation between manufacturers, distributors, and recycling companies can effectively improve reverse logistics[8].

It is clear that developing cooperation in the design, production, use, recycling, and disposal of packaging after the last use can significantly contribute to the sustainable behaviour of society as a whole and its individual entities. How this cooperation should look like is addressed by professional literature, but it has not been sufficiently clarified yet, especially in relation to packaging used for consumer chemicals[12]. Therefore, the research focused on this area. Its main purpose was to uncover the forms of cooperation used by small chemical companies with various partners in increasing the sustainability of packaging.

Simulation and experiment

The general objective of the primary research was to identify the nature of cooperation between small enterprises producing consumer chemicals and their suppliers and other stakeholders in the area of packaging. The specific objectives of the research were set as follows:

- Identify the enterprises where the research was conducted.
- Determine the process of partner selection for cooperation in packaging design and supply.
- Identify the areas and forms of cooperation in packaging design.
- Identify the methods applied in packaging design.
- Identify the strategies used in packaging procurement and analyse the process of securing packaging from supplier companies.
- Identify cooperation in securing packaging supplies.
- Uncover the use of modern information technologies in strategic and tactical-operational securing of packaging for consumer chemical products.

To achieve the above-mentioned objectives, qualitative research was conducted. Qualitative research was preferred over quantitative surveys to examine the issue in depth, especially to sufficiently understand the procedures and processes applied in strategic and tactical-operational management of cooperation in the respondent companies. The research was conducted in three small enterprises. All enterprises were manufacturers of consumer chemicals. Information about the enterprises where the research was conducted is displayed in Table I.

Table I
Research Sample

	Enterprise		
	A	B	C
Product portfolio	Consumer cosmetics – manufacturer of soaps, perfumes, natural balms, and candles	Consumer cosmetics and nutritional supplements – manufacturer of sunscreens	Consumer cosmetics and household chemicals
Length of business	Less than 5 years	5–10 years	More than 20 years
Number of employees	Less than 50	Less than 50	Approximately 50
Major markets	Czech and Slovak Republic	EU countries	Worldwide
Sales	Undetected information	Approximately 1 mil EUR	Approximately 7 mil EUR
Volume of packaging purchased	Approximately 7000	Approximately 120000	-

The basis for information gathering was an interview script developed based on a review of professional literature, particularly articles from the WoS database. The script was divided into several parts and designed to meet the general and specific objectives of the research. Employees from the procurement and packaging departments were interviewed. Several interviews were conducted in each company, each lasting an average of 60 minutes. The responses were recorded in written notes. Information was collected from March to April 2024, followed by content analysis processing. Comparing the results of the primary qualitative research with the professional literature allowed conclusions to be drawn about the forms of cooperation used and recommendations for improvement in this area to be formulated.

Discussion and result analysis

The results of the primary research concerning areas of cooperation between all three studied companies and their suppliers can be captured in the following Table II.

Table II
Areas of Collaboration for Increasing the Sustainability of Consumer Chemical Product Packaging

Areas of Collaboration	Enterprise			Frequency
	A	B	C	
Monitoring Packaging Legislation Developments		x	x	2
Information on New Trends in Packaging		x	x	2
Sharing Market Information			x	1
Changing Packaging Materials	x	x		2
Modifying or Designing the Overall Packaging Design		x		1
Design and Printing of Packaging and Labels	x	x		2
Purchasing Reusable Secondary Packaging	x			1
Returning Secondary Packaging	x			1
Production of Primary Packaging		x	x	2
Production of Secondary Packaging		x		1
Packaging-Free Sales	x			1
Collecting, Sorting, and Cleaning Returnable Consumer Packaging	x			1
Return Transport of Returnable Consumer Packaging	x			1
Cost Optimization for New Packaging	x			1
Planning and Implementation of Deliveries			x	1
Flexible Provision of Emergency Deliveries	x	x	x	3

Table II shows that companies mainly cooperate in sharing information about legislative developments and new trends in packaging and less frequently share market information. They are interested in cooperating with direct packaging suppliers, especially in changing the overall design of packaging and within that in the design or change of materials for packaging. If the packaging buyer (i.e., the consumer chemical manufacturing company) performs finishing operations of packaging production, the supplier of material for this production collaborates on solving technological issues.

Circular economy principles are reflected in packaging management, introducing the return of used primary and secondary packaging. Packaging-free sales are also applied but rather as a supplementary form of sales. Companies collaborate on packaging procurement based on common commercial operations, ensured by more or less formal agreements. Only one company uses automated ordering with the period-fixed model, but only with selected suppliers. Generally, the companies where the research was conducted rely on flexible adaptation and flexible exceptional deliveries from packaging suppliers when packaging needs change. No measures to facilitate this flexibility are applied. Modern logistics technologies for managing physical flows are not applied; physical and information flows are connected only for specific situations. Each partner keeps its own packaging stocks. None of the companies systematically manage the size of these stocks, i.e., neither the volume of financial resources tied up in stocks.

Based on the information obtained from the primary qualitative research, the main conclusions of the research can be formulated as follows:

- Even small companies producing consumer chemical products strive to increase packaging sustainability to a considerable extent.
- They cooperate in increasing packaging sustainability in various areas. However, their cooperation with different partners cannot be considered systematic and comprehensive. Cooperation relates more to selected areas and is also determined by the severity of the problem being addressed.

- They cooperate not only with direct packaging suppliers but also with other stakeholders, such as artists and designers of packaging visual aspects, companies providing packaging collection and cleaning, retailers, etc. It can be stated that increasing packaging sustainability is conducted more in a network of various stakeholders than in the supply chain.
- Cooperation is developed mainly at the strategic level, particularly in the area of packaging design.
- Cooperation at the tactical-operational level focuses on agreements and tools enabling more flexible packaging deliveries. More intensive cooperation based on logistics principles is not implemented. Modern logistics technologies such as Quick Response or Collaborative Forecasting, Planning and Replenishment are not utilized.
- Communication between companies and individual partners is conducted through unsophisticated methods such as phone communication, email communication, or tools like WhatsApp or MS Teams.
- Small companies do not integrate their information systems in increasing packaging sustainability with suppliers or other stakeholders, except for automated ordering of selected packaging from a few suppliers.

Conclusion

The primary research conducted revealed that even small enterprises producing consumer chemicals dedicate a relatively significant amount of attention to the packaging of their products and apply various tools to enhance their sustainability. In executing these activities, they collaborate with various partners, not only direct suppliers but also other stakeholders, especially artists and designers of packaging visuals, companies providing packaging collection and cleaning services, and retailers. However, this collaboration cannot yet be considered comprehensive and systematic, with notable gaps particularly in logistics management.

The development of cooperation with different types of stakeholders is undoubtedly hindered by the limited resources available to small consumer chemical manufacturing companies, including technical, human, knowledge, and financial resources. Therefore, it can be stated that the collaboration in the packaging sector between consumer chemical manufacturers and their suppliers and other stakeholders still has considerable potential for improvement. There is a relatively large scope for advancement in this area. Nonetheless, further progress in packaging sustainability through enhanced cooperation is at least partially determined by the ability to overcome existing limitations.

Next primary research should focus on medium and large enterprises. This would allow for a comparison with the results of the conducted research and help identify any specific characteristics of small enterprises in this area, as well as the feasible progress in sustainable packaging from the perspective of small consumer chemical manufacturers.

References

1. Koeijer B., Wever R., Henseler J.: Packag. Technol. Sci., 30, 443 (2016).
2. Yokokawa N., Amasawa E., Hirao M.: Sustain. Prod. Consump., 27, 1514 (2021).
3. Kleine Jäger J., Piscicelli L.: Sustain. Prod. Consump., 26, 733 (2021).
4. Bitzer V., Bijman J.: Br. Food J., 117, 2182 (2015).
5. Adomako S., Nguyen N.P.: Sustain. Dev., 31, 1735 (2022).
6. Brown P., Bocken N., Balkenende R.: Sustainability, 11, 635 (2019).
7. Accorsi R., Baruffaldi G., Manzini R.: Sustain. Prod. Consump., 24, 48 (2020).
8. Shi Y., Lin Y., Wang S., Wen H., Lim M. K., Tseng M.: Waste Manage., 161, 17 (2023).
9. Jiang Y., Shi C., Shen S.: Prod. Oper. Manag., 28, 2365 (2019).
10. Puspita F. M., Primadani N. A., Susanti E.: Advances in Economics, Business and Management Research, 142, 71 (2020).
11. Larsen S. B., Jacobsen P.: Int. J. Phys. Distrib. Logist. Manag., 46, 783 (2016).
12. Nilsson F., Göransson M.: J. Clean Prod., 296, 126471 (2021).

INFORMATION NEEDS OF SELECTED GROUPS OF EXTERNAL STAKEHOLDERS FOR ASSESSING THE REPUTATION OF A CHEMICAL COMPANY

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Abstract

The paper highlights the importance of targeted corporate communication to different stakeholder groups in creating a positive corporate reputation. The results of primary quantitative research are presented, the main objective of which was to find out what information is important for the public in the role of different groups of external stakeholders of a chemical company to assess the reputation of this company and what information channels are preferred by respondents to obtain this information. The research was prepared on the basis of a literature search mapping the expected sources or tools for building corporate reputation and also identifying the most used corporate communication channels for communicating with the public. The investigation confirmed the assumption that information needs differ between the different groups of external stakeholders studied. The results of the research provide chemical companies with effective guidance for specifically targeting their communications to different stakeholder groups using appropriate information disseminated by their preferred information sources.

Introduction

Chemical companies operating in an environment prone to environmental and safety challenges are particularly sensitive to the perception of their activities by external stakeholders. It is extremely important for these companies to monitor the overall awareness of their key stakeholders and to seek ways to best develop their communication and thus their own corporate reputation. Unfortunately, so far, chemical companies seem to be struggling to understand the information needs of their stakeholders. Therefore, this paper focuses on this issue and aims to identify and analyse the information needs of selected groups of external stakeholders in the context of assessing the reputation of chemical enterprises.

The paper summarizes the results of a primary quantitative research, the aim of which was to find out what types of information and what sources of information are preferred by respondents in the role of the general public, consumers, potential customers and the surrounding society to evaluate the reputation of chemical companies. The intention was to provide managers of chemical enterprises with the basis for making the right decisions about targeted communication towards different groups of external stakeholders in order to effectively build their relationships and promote a positive reputation of the enterprise by specific means of communication chosen directly tailored to the target audience and the chosen purpose. This leads to both maximising the target effect and saving resources.

Theoretical background

Corporate reputation is a very important phenomenon in today's markets, as it influences corporate success, which translates into firm value[1]. Its influence on various stakeholders, including customers, employees, investors, journalists, the general public, suppliers, the surrounding society and many others, is undeniable. A positive reputation of a company is a prerequisite for the emergence of a positive attitude of stakeholders, which is reflected in their increased willingness to form a relationship and interact with the evaluated entity[2]. In the case of a negative reputation, the opposite impact can be expected. Although the study of corporate reputation has received a great deal of attention and has been in the focus of the scientific community since the end of the last century, no consensus has yet been found and experts' opinions on the definition of corporate reputation still differ. One of the most cited definitions of corporate reputation is the one created by Fombrun back in 1996 when he argues that "corporate reputation is a perceptual representation of a firm's past actions and future prospects that describes the overall attractiveness of a firm to all of its key constituents relative to other leading competitors"[3]. Fombrun's ideas have subsequently been built upon by, for example, Gray and Balmer[4] and Gotsi and Wilson[5], who argue that corporate reputation typically develops over time as a result of consistent firm performance that is reinforced by effective communication. This idea is further developed by Barnett et al.[6], who offer a modern and analytical view of corporate reputation as "the collective judgment of observers about a corporation based on an assessment of the financial, social, and environmental impacts attributed to the corporation over time."This definition is particularly important because it seeks to specify the areas that are considered in the context of reputation assessment. Despite the fact that the specification of these factors is crucial for reputation management, their specification is not straightforward and has been examined from different perspectives. For example, Tejeras[7] in his research identified seven factors that most influence the formation of a company's reputation. These factors include: the quality of the products or services offered by the enterprise, the level of customer satisfaction with the products or services offered by the enterprise, the ethics and business practices of the enterprise, the way the enterprise communicates with its stakeholders, corporate social responsibility initiatives, financial stability and the performance of the enterprise[7]. It has been shown that a company's reputation is specific to different stakeholder groups[8]. Therefore, it is essential for a business to identify and understand what specific aspects play a role in establishing reputation with specific stakeholder groups and what their expectations are. This will enable the business to design strategies that will effectively shape and enhance its reputation. However, in order to differentiate communication and engagement with individual stakeholders[9], it is necessary to understand not only their specific information needs, but also their preferred communication channels. There are a number of different channels, each with its own advantages and disadvantages. It is therefore always necessary to carefully select the most appropriate channel depending on the target group and the communication purpose. According to the literature, the following communication channels and sources of information are among the most commonly used when a company communicates with external stakeholders: emails, television, radio, press, magazines, company trade register, company annual report, company employees (current and former), product packaging, websites, regular newsletters or bulletin emails, discussion forums and online community platforms, online search engines (List, Google, Bing...) or social networks (Instagram, Facebook, Network X, TikTok...)[10,11]. Communication with stakeholders is a key element of successful business management and reputation building. However, it is important to remember that each stakeholder is unique and has different preferences for the communication channels and types of information they prefer. Therefore, the information conveyed is tailored, and media are often combined for maximum effect.

Research methodology

The aim of the research was to find out what types of information and what sources of information are preferred by selected stakeholder groups for assessing the reputation of chemical companies. On the basis of a literature search and primary qualitative pre-research, which was conducted using 8 individual guided interviews based on a developed interview scenario, the aspects that appeared to be important for assessing the reputation of a chemical company in terms of the general public, potential employees, consumers and the surrounding society were identified. At the same time, the most desirable information sources where external stakeholders would probably look for or wish to find the necessary information were also identified. Following the qualitative pre-research, primary quantitative research was conducted using an electronic survey method. A total of 351 fully completed questionnaires were obtained. Although the aim was to obtain as wide a range of responses as possible from respondents of different genders and age groups, it was not possible to follow a quota sampling structure due to the involvement of students in the data collection and the selection can be rather characterised as random. In the statistical processing, the uneven selection of respondents had to be compensated for by weighting to simulate the structure of the Czech population resulting from the data on the age composition of the population by sex as of 31 December 2022 from the Czech Statistical Office with bound quotas by sex and age (CSO, 2023). The data were statistically processed using IMB SPSS Statistics software. Friedman's test and post-hoc were used for data validation and analysis. Based on the conducted investigation, it was possible to determine the importance of each proposed aspect for assessing the reputation of a chemical enterprise from the perspective of different selected groups of external stakeholders, as well as to identify the preferences of information sources enabling stakeholders to assess the reputation of a chemical enterprise.

Result analysis

The questionnaire was divided into four main parts, where respondents had to put themselves in the role of the selected external stakeholder (general public, potential employee, consumer and surrounding society). A four-point scale of 1 to 4 was used to rate the importance of each of the aspects of reputation assessed, where 1 = not at all important, 2 = rather not important, 3 = rather important and 4 = very important. Respondents then selected their preferred information sources from the defined response options, with no limit to the number of responses. Statistical data processing was always carried out separately from the perspective of the respondents in the role of a specific stakeholder group. When checking the differences in perceived importance of each proposed aspect of the chemical company's reputation assessment, in all cases, i.e. when examining the perspective of each stakeholder group, the significance of Friedman's test was less than 0.001. Thus, it can be said that respondents in the role of any stakeholder do not perceive all aspects as equally important and that there is a difference in perceived importance for at least one pair. After conducting post-hoc tests, the aspects from the perspective of each stakeholder group were separately compared from most to least important according to their weighted average ranking. In the same way, preferences for information sources were statistically evaluated separately for each group of external stakeholders. Table I summarises the results in terms of the presentation of the most important aspects of reputation and information sources for each group of external stakeholders. For each stakeholder group, the aspects of reputation and information resources are always ranked in descending order of perceived importance in the table.

Table I
Overview of the most important aspects of reputation assessment and the most important information sources for different types of stakeholders

Stakeholder type	**The most important aspect of reputation assessment**	**The most important information sources**
General public	Level of product quality, service and customer care	Television, radio
	Hazardous waste generation and disposal rates	City/municipality website
	Compliance with standards (certification)	Company website
	The company's relationship to the environment	Information from local residents
	Frequency of accidents	Internet search engine (Google, etc.)
Potential employees	Health risks	Labour Office
		Internet portals with job offers
	Amount of wage/salary	A person who has worked or is still working in the company
		Company website
Consumers	Overall quality of the company's products and services - level of customer satisfaction	E-commerce websites with user ratings
		Product packaging
		Company website
	Corporate interest in product composition and its impact on consumer health	Personal experience or experience of friends
		Internet search engine (Google, etc.)
Surrounding society	Health risks during normal operation (e.g. levels of exhalations, dust...)	City/municipality website
	Situation in terms of odour	Company website
	Level of pollution of water sources in the vicinity of the enterprise	Information from local residents
	Safety risks - danger of accident, explosion...	Internet search engine (Google, etc.)
	Noise status	Television, radio

As can be seen from Table I, each stakeholder group perceives the importance of different aspects of reputation assessment differently. Similarly, preferences for information sources vary according to the stakeholder group. These differences are due to the different stakeholder involvement, where the interests of each stakeholder differ in terms of the functioning, impact of the activities and existence of the firm.

The research also showed which of the selected information and which information sources are the least important or the most popular in terms of preferences of the monitored stakeholder groups for the assessment of the reputation of a chemical company. The results are summarized in Table II, where a descending order in terms of importance is observed, i.e. the information or resource ranked lowest is the least important for a given stakeholder group compared to other aspects.

Table II

Overview of the least important aspects of reputation assessment and the least important information sources for different types of stakeholders

Stakeholder type	**The least important aspect of reputation assessment**	**Least important information sources**
General public	Support for charitable or voluntary events Company size Activities of company employees	Instagram social network Company magazine or newsletter Social Network X (Twitter) TikTok social network
Potential employees	Company's position on the market	Trade register of companies
	The company's attitude towards ecology	Social network LinkedIn
	Production processes, technology used	Instagram social network Social Network X (Twitter)
Consumers	Problems of the company and ways of solving them	Instagram social network CTIA (Czech Trade Inspection) Social Network X (Twitter)
	Business result (level of profit or loss)	TikTok social network Social network Facebook
Surrounding society	Precise information on production and products manufactured	Association of the Chemical Industry of the Czech Republic
	Benefit of the enterprise for the surrounding communities	Instagram social network
	Appearance and neatness of the premises, including the exterior of the buildings	Register of companies
	Addressing the traffic situation in connection with the company's operations	Social Network X (Twitter)
		TikTok social network

Table II shows that even for the least important aspects of assessing a company's reputation or even for the least popular information sources, each stakeholder group has a different perspective. However, all stakeholder groups surveyed agreed that, from their perspective, the least preferred information channels were TikTok, X (Twitter) and Instagram.

Conclusion

The primary quantitative research was carried out in the Czech Republic and was open to people aged 18 years or older. The aim of the research was to find out the perceived importance of each proposed aspect for the assessment of the reputation of a chemical company and to identify the most preferred information sources from the perspective of different stakeholder groups. The research involved 351 respondents who answered from the perspective of the general public, potential employees, consumers and the surrounding society.

Research has shown that the specific information requirements of different stakeholder groups differ according to their different relationships with the company, but in principle it can be concluded that the most important parameters for assessing the reputation of a chemical company always include information on safety, health and socially responsible production aspects. The information is then mostly sought by stakeholders using the Internet, where the company's website is important for all stakeholders. Therefore, chemical companies should pay more attention to the content and updating of their websites. On the other hand, the least important attributes that respondents evaluate in terms of the reputation of chemical companies include in particular the area of information telling more about the internal affairs of the company (e.g. technology used, size, profitability, problems, etc.). The information requested is not usually sought by respondents using social networks.

The research provided evidence to help chemical companies communicate more effectively with selected stakeholder groups in their efforts to build positive reputations. The results of the research clearly indicate which specific types of information and which communication channels are most important to the public, potential employees, consumers and the surrounding community and which are not in high demand by these stakeholder groups in terms of assessing the reputation of chemical companies.

The random selection of respondents can be considered as a limitation of the research, which was compensated for by the above described recalculation in the analysis of the results, however, it would be advisable to verify the obtained results in the future by conducting a larger research using quota sampling. It would also be interesting to compare the results obtained for chemical industries with the views of stakeholders from other sectors. In terms of the analysis of the results, the findings could be complemented by a comparative analysis of the differences in the views of different groups of respondents according to their characteristics – e.g. age or education. This comparison has not been included in this paper due to its large scope.

References

1. Gatzert N.: Eur. Manag. J., *33(6)*, 485 (2015).
2. Bigus J., Hua K. P. M., Raithel S.: Account. and Bus. Res., 1 (2022).
3. Fombrun C. J.: *Reputation: Realizing Value from the Corporate Image, MA*: Harvard Business School Press, Boston 1996.
4. Gray E. R., Balmer J. M.: Lo. Ran. Plan., *31(5)*, 695 (1998).
5. Gotsi M., Wilson A. M.: *Cor. Comm.: An In. J.*, *6(1)*, 24 (2001).
6. Barnett M. L., Jermier J. M., Lafferty B. A.: Cor. Rep. Re., *9*, 26 (2006).
7. Tejeras D.: *What is Corporate Reputation Management and Why Does it Matter?* LindkedIn (2022).
8. Miles S.: J. Bus. E., *142*, 437 (2015).
9. Barney N., Holak B.: *What is a Stakeholder?,* TechTarget (2023).
10. Přikrylová J.: *Modern marketing communication: 2nd, completely revised edition*. Grada Publishing as, Prague, 2019.
11. Burešová J.: *Online marketing: from websites to social networks*. From Online Marketing to Online Marketing to Online Marketing, Praha 2022.

BRIDGING THE KNOWLEDGE GAP: ASSESSING COMPETENCIES AND SKILLS FOR TECHNICAL EMPLOYEES IN ECONOMIC AND MANAGEMENT SECTORS – A CASE STUDY OF CHEMICAL AND FOOD INDUSTRIES IN SLOVAKIA

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Abstract

This contribution aimed to determine the knowledge, abilities, and competency needed for employees in technical domains in the economy and management sector. The research concentrated on chemical production and the food business in Slovakia, monitoring three groups of employees: food production manager, chemical production manager, and operational section manager. The study began by studying state registries like the National System of Occupations and National System of Qualifications to determine the competencies, professional knowledge, and skills needed for certain occupations. It also examined whether university programs in these subjects met industry management and economics standards. The second section of the study examined business demands, focusing on medium-sized food companies. Over 32% of eligible food companies in Slovakia participated in the questionnaire. 43% of firms believe it is crucial for technically oriented individuals to possess fundamental understanding in economics, management, and marketing. The most commonly cited requirements were accounting, controlling, and budgeting.

Introduction

In the present day, it is nearly inconceivable that a university graduate lacks even rudimentary digital competencies[1,2,3]. This is particularly applicable to technical professionals who rely on computer technology to carry out their occupation. Furthermore, alongside digital skills, the so-called soft skills are becoming increasingly significant[4,5]. These talents are consistently featured in job adverts and CVs. Nevertheless, there are others as well. Unidirectional profiling of employees is frequently unsuccessful for employers. An employee who is profiled in this manner lacks the ability to comprehend wider business and contextual information, and hence cannot make appropriate judgments in their role. It is so fitting, and perhaps obligatory, for a professional of this nature to enhance their expertise in other domains, such as management, law, or economics[6,7]. By doing so, he can expand his opportunities and quickly become more advantageous for the organization. Employees with a university education frequently encounter challenges when it comes to overseeing many teams, handling reports and analyses. This can be particularly problematic if they lack fundamental expertise in business economics, entrepreneurship, and human management[8].

According to the Green Report 2022 published by the Ministry of Agriculture and Rural Development of the Slovak Republic[9], the food processing industry contributed 2.5% to total employment in Slovakia. Total revenues from the food processing industry were more than 6.1 billion euros in 2022. Companies in the industry generated a pre-tax profit of 294.3 million €. Of the aggregate branches of the food and beverage production sector, none made loss. Among legal entities in the food industry, limited liability companies continued to dominate, accounting for 95.7% of the total number of legal entities in the industry in 2022. The Table 1 show a total number of companies in the food processing industry according to economic activities.

Table I
Number of companies in the food processing industry according to economic activities[9]

Economic activity	**2021**	**2022**	**Index 2022/2021**
Manufacture meat and meat products	211	201	95.4
Processing of fish and fish products (incl. preservation)	2	3	171.4
Processing and preserving of fruits and vegetables	193	186	96.4
Manufacture of vegetable and animal oils and fats	26	25	96.2
Manufacture of dairy products	67	73	109.3
Manufacture of mill products, starch and starch products	80	75	93.5
Manufacture of bakery and farinaceous products	502	537	107.7
Manufacture of other food products	901	1 016	112.7
Manufacture of prepared animal feeds	232	239	103.1

Economic activity	**2021**	**2022**	**Index 2022/2021**
Manufacture of beverages	660	719	108.8
Manufacture of tobacco products	1	2	-
Registered natural persons	1 979	2 194	110.9
Legal persons, total	2 874	3 075	107.0
Total registered enterprises	**4 853**	**5 269**	**108.6**

Methodology and methods

The initial phase of the study focused on analyzing the essential competencies, professional knowledge, and skills needed for specific professions as outlined in state registers such as the National System of Occupations and National System of Qualifications. It also aimed to determine if university study programs in these fields have fully incorporated the requirements set by industry experts in management and economics. The research concentrated on chemical production and the food business in Slovakia, monitoring three groups of employees: food production manager, chemical production manager, and operational section manager. The data were obtained from publicly available database.

The second phase of the study involved analyzing the needs of the business environment, with a specific focus on medium-sized enterprises in the food industry. We surveyed organizations with a turnover exceeding €50 million using a systematic questionnaire to determine their specific labor needs, particularly focusing on economic and managerial expertise requirements.

Discussion and result analysis

The research conducted in both phases produced some intriguing discoveries, which served as the foundation for developing recommendations to enhance the curriculum of university study programs in order to align with industrial demands.

Requirements for Employees Identified by National Institutions

In this section of our study, we offer our research based on the data obtained from the state records. The research focused in detail on three categories of workers: manager of food production, and manager of chemical production, manager of the operational section.

The first register from which we obtained the data is the National Qualification System (NQS)[10]. NQS is a publicly accessible register that contains descriptions of distinguished and verified job positions in Slovakia. Its aim is to create a uniform and transparent system based on the assumption that the skills, knowledge and competences needed to obtain a qualification can be obtained through various paths of education and learning:

- formal education – takes place at school and leads to obtaining a diploma or certificate of education,
- informal education, which takes place on the grounds of various educational institutions outside of school education,
- informal learning – it takes place as a natural part of our lives anywhere, anytime and does not have to be intentional (e.g. learning in the family, at the workplace, as part of our hobbies, etc.).

The backbone of the NQS are qualification cards, in which the public can find the so-called qualification and evaluation standards:

- the qualification standard represents a summary of the knowledge, skills and competences that are necessary to acquire the relevant qualification,
- the evaluation standard represents a summary of criteria, organizational and methodological procedures, material, technical and spatial prerequisites for verifying the achieved qualification standards.

Each qualification is assigned to one of the eight levels of the Slovak Qualification Framework and the European Qualification Framework. These are tools that make qualifications more transparent and clear and allow us to compare our qualifications with qualifications abroad. A foreign employer who is not familiar with the Slovak education system will have a better understanding of the level of qualification. Therefore, this tool can also help people seeking employment on the European market.

The second state register is the National System of Occupations (NSO)[11], which is defined by Act no. 5/2004 Coll. on employment services as a nationwide, unified information system describing standard labor market requirements for individual jobs. The NSO determines the requirements for professional skills and practical experience needed to perform work activities on the labor market. Its center is the Employment Register made up of national employment standards, which describe employers' requirements for qualified employment performance. The Ministry of Labour, Social Affairs and Family of the Slovak Republic is in charge of managing the register.

In our research, we focused on knowledge, skills and competences in the field of management and economics for selected types of technically oriented occupations. To describe the required level of education of individual professions, we will use qualification frameworks, specifically the Slovak qualification framework (SQF) and the European qualification framework (EQF).

The SQF has 8 levels that are linked to the levels of the European Qualification Framework (EQF). The EQF is a common reference framework that helps to understand, compare and recognize qualifications obtained in the European Union. This interconnection enables the understanding of Slovak qualifications anywhere in the European Union.

Manager of food production

The position of manager of food production has a SQF/EQF level 7. Professional experience of 24 months is recommended for the performance of this job. The overview of the required qualifications for this position is shown in Table 2.

Table II

Overview of qualifications requirements for Manager of food production[10,11]

Description	National Qualification System	National System of Occupations
Knowledge		
personnel and process management	Yes	Yes
methods and procedures of human resource planning	Yes	Yes
economics and management of food production	Yes	Yes
quality management	Yes	Yes
marketing	Yes	Yes
labor and commercial law	Yes	Yes
methods of evaluating economic efficiency and return on investments and projects	No	Yes
Skills		
calculate production costs	Yes	Yes
analyze labor productivity	Yes	Yes
lead and motivate employees	No	Yes
Competencies		
ability to lead and motivate a team	Yes	Yes
communication competencies	Yes	Yes
economic and financial literacy	No	Yes
ability to make decisions and take responsibility	Yes	Yes

Manager of chemical production

The position of chemical production production has a SQF/EQF level 7. Professional experience of 24 months is recommended for the performance of this job. The overview of the required qualifications for this position is shown in Table 3.

Table III

Overview of Qualifications Requirements for Manager of chemical production[10,11]

Description	National Qualification System	National System of Occupations
Knowledge		
personnel and process management	No	Yes
methods and procedures of human resource planning	No	Yes
economics and management of chemical production	Yes	Yes
quality management	No	Yes
marketing	No	Yes
labor and commercial law	No	Yes
methods of evaluating economic efficiency and return on investments and projects	Yes	Yes

financial analysis, economic balances	No	Yes
Skills		
calculate production costs	No	Yes
analyze labor productivity	No	Yes
lead and motivate employees	Yes	Yes
conduct meetings effectively	Yes	No
plan and organize work	Yes	Yes
analysis of the company's economic results	No	Yes
analysis and forecasts of price conditions on the market	No	Yes
preparation of documents for planning, decision-making and management of chemical production	No	Yes
Competencies		
ability to lead and motivate a team	No	Yes
communication competencies	Yes	Yes
economic and financial literacy	No	Yes
ability to make decisions and take responsibility	Yes	Yes
presentation competencies	Yes	No
managerial skills	Yes	No

Manager of operational section

The position of the manager of operational section has an SQF/EQF level 7. Professional experience of 36 months is recommended for the performance of this job. The overview of the required qualifications for this position is shown in Table 4.

Table IV

Overview of Qualifications Requirements for Manager of operational section[10,11]

Description	National Qualification System	National System of Occupations
Knowledge		
personnel and process management	No	Yes
methods and procedures of human resource planning	No	Yes
economics and management production	No	Yes
quality management	Yes	Yes
business economics	No	Yes
labor and commercial law	No	Yes
project management	No	Yes
financial analysis, economic balances	No	Yes
methods and procedures of financial planning	No	Yes
pricing principles	No	Yes
supplier-customer relations	No	Yes
Skills		
calculate production costs	No	Yes
analyze labor productivity	No	Yes
lead and motivate employees	No	Yes
use of process management principles in management	No	Yes
plan and organize work	No	Yes
coordination of activities in the field of supplier and customer relations	No	Yes
participation in the planning and creation of operating department budgets	No	Yes
process analyzes in management	Yes	Yes
apply the principles of quality and quality management	Yes	Yes
Competencies		
ability to lead and motivate a team	No	Yes
communication competencies	Yes	Yes
economic and financial literacy	No	Yes
ability to make decisions and take responsibility	Yes	Yes

presentation competencies	Yes	No
the ability to solve conflict and stressful situations	Yes	No

Based on the data provided, it is evident that although though these positions are intended for technically skilled individuals who have received education at technical universities, it is imperative for these workers to possess at least fundamental understanding in the areas of management and economics. The three analyzed roles all required skills in managing, inspiring, and leading individuals, as well as knowledge of labor legislation and commercial code. Additionally, proficiency in controlling, various forms of financial analysis, and process analysis were also necessary. The position of manager of chemical production had the least number of requirements from the field of economics and management, while the post of manager of the operational department had the highest number of such criteria. Overall, the NSO had more economic and managerial demands compared to the NSQ.

Requirements for Employees Identified by Survey of Employers

This section of the manuscript contains the findings of our research into food processing industry corporations. Employers were sent a questionnaire containing inquiries regarding their criteria for technically-oriented employees. The majority of participants were companies of medium size with a turnover above 50 million €. According to data from Finstat[12], over 32% of companies in Slovakia that fulfilled the specified criteria answered to our inquiry. We are providing the findings obtained from these companies.

The legal structure of a joint-stock firm was reported by over 70% of the respondents. Each of them has been available on the market for over a decade. Only 28% of the respondents indicated that they exclusively operated within Slovakia or the V4 region, while the remaining respondents stated that they operated either globally or at least within the European Union. The majority of the examined organizations had a workforce exceeding 250 individuals.

Subsequently, companies were requested to assess the factors they deem most crucial when choosing a candidate for employment. A rating scale ranging from 1 to 5 was employed, where 5 denoted the highest level of importance and 1 indicated the lowest level of importance. The criteria for evaluation included the level of education attained, professional experience, prior employment history, pay expectations, personal impression, and proficiency in a foreign language. The evaluations for previous job experience (average 4.57), experience in the field (average 4.43), and acquired education (average 4.14) were the highest. They regarded proficiency in a foreign language as the least significant factor, along with pay expectations (average 3.29) and personal perception (average 3.71). Figure 1 depicts the arrangement of the responses to each specific question.

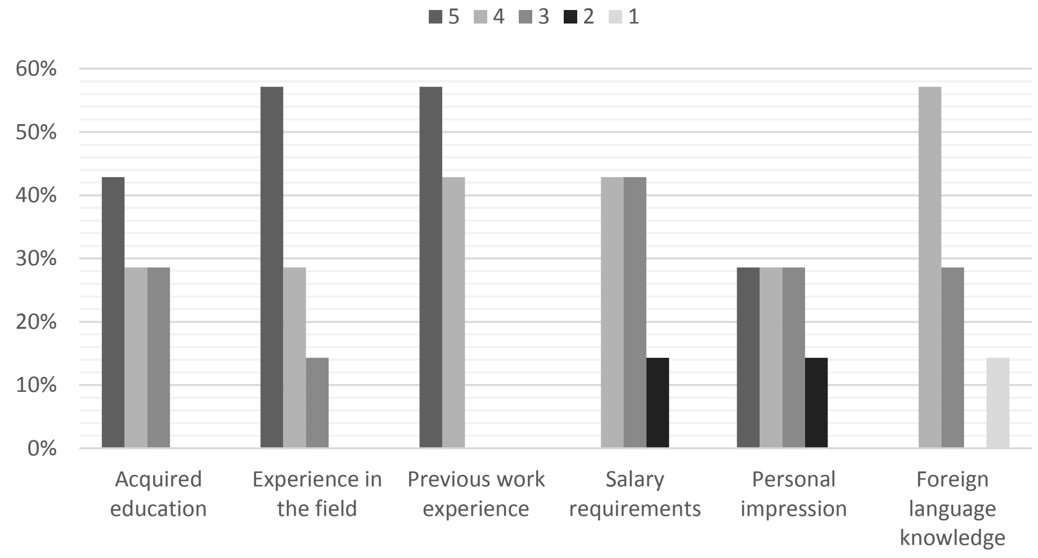

Figure 1. Evaluation criteria for selecting employees (5 – most important, 1 – least important)

When questioned about the significance of basic knowledge in economics and management for a technically skilled employee, 43% of companies responded affirmatively. The areas of budgeting, accounting, and controlling were identified as the most commonly referenced.

The final inquiry posed to the participants was regarding the typical duration required for training newly hired personnel. 43 percent of respondents indicated that the duration of new employee training ranges from 1 to

3 months. 29% of respondents indicated that they typically answer within a few days, whereas exactly 14% stated that it takes them more than 3 months to respond, or that it varies depending on their individual occupation.

Conclusion

Currently, we can observe a significant trend in the labor market in the gradual increase in demands for the so-called soft skills in employees. More and more employers state this in their job advertisements, which has gradually been transferred to approved requirements in national registers. This principle applies not only to management and commercial professions but is already expected for employees with technical backgrounds. Alongside soft skills, the certification cards of technically oriented personnel also include prerequisites for fundamental knowledge in economics and management. Among the professions we analyzed in the fields of economics and management, the most prevalent areas were human resources management, controlling, business economics, and the fundamentals of labor law. Upon investigation, we discovered that the National System of Occupation imposes more stringent economic and managerial criteria on technically skilled workers compared to the National Qualification System. A study conducted on a sample of medium-sized enterprises in the food processing industry, with a revenue over € 50 million, has found that having a certain level of education is a crucial factor in the hiring process for new employees. Approximately 50% of the participants indicated that they believe it is crucial for employees with technical expertise to possess a fundamental understanding of economics and management. Specifically, they highlighted budgeting, accounting, and controlling as the most significant domains. Based on this information, it may be inferred that technical universities should incorporate disciplines related to economics and management into their study programs. According to additional research[13], it is evident that the introduction alone may not suffice, highlighting the significance of promoting the topic among students. Many students are unaware that, although attending a technically focused university, acquiring expertise in economics and management would be advantageous for their career and is also a prerequisite for employers.

Acknowledgement

The contribution is a partial output of the KEGA research task no. 011STU-4/2022 "Creating a model of education supporting the increase of competencies of students of a non-economically oriented university in the field of innovative, entrepreneurial thinking and business support" conducted at the Institute of Management of the STU in Bratislava.

References

1. Karaköse T., Polat H., & Papadakis S. Examining teachers' perspectives on school principals' digital leadership roles and technology capabilities during the covid-19 pandemic. Sustainability 2021;13(23):13448. https://doi.org/10.3390/su132313448.
2. Sparks J., Katz I., & Beile P. Assessing digital information literacy in higher education: a review of existing frameworks and assessments with recommendations for next-generation assessment. ETS Research Report Series 2016;2016(2):1-33. https://doi.org/10.1002/ets2.12118.
3. Kaminski K., Switzer J., & Gloeckner G. Workforce readiness: a study of university students' fluency with information technology. Computers &Amp; Education 2009;53(2):228-233. https://doi.org/10.1016/j.compedu.2009.01.017.
4. Chytiri A., Bouranta N., & Tsirkas K. The gap in soft skills perceptions: a dyadic analysis. Education + Training 2020;62(4):357-377. https://doi.org/10.1108/et-03-2019-0060.
5. Villazon Montalvan R., Affonso Neto A., & Neumann C. Developing soft skills in the business classrooms of industrial engineering students in brazil. Journal of International Education in Business 2024;17(2):304-318. https://doi.org/10.1108/jieb-11-2023-0092.
6. Calabrò A., Torchia M., Gimenez-Jimenez D., & Kraus S. The role of human capital on family firm innovativeness: the strategic leadership role of family board members. International Entrepreneurship and Management Journal 2020;17(1):261-287. https://doi.org/10.1007/s11365-020-00657-y.
7. Adisaputra A. Analysis of financial services authority employees' competence in the regulation and supervision of financial institutions. JEMBA: Journal of Economics, Management, Business and Accounting 2023;1(1):59-68. https://doi.org/10.54783/jemba.v1i1.5.
8. Niazi A., Faraz H., Arshad B., & Asghar W. Impact of managerial competency and learning orientation on job performance. Journal of Accounting and Finance in Emerging Economies 2020;6(3):885-896. https://doi.org/10.26710/jafee.v6i3.1423.

9. Ministry of Agriculture and Rural Development of the Slovak Republic. Green Report 2022. 2024.
10. Národná sústava kvalifikácii. Čo je Národná sústava kvalifikácií (NSK)? [What is the National Qualifications System (NSK)?] https://www.kvalifikacie.sk/co-je-nsk.
11. Sústava povolaní. O projekte. [About Project. National system of occupations.] Národná sústava povolaní. https://www.sustavapovolani.sk.
12. Finstat.sk. Databáza finančných údajov [Database of financial data.].2024. https://www.finstat.sk.
13. Katrencik, I. and Zatrochova, M. Financial Literacy Of Technically Oriented Students In Slovakia: An Evaluation Of Fundamentals Of Financial Literacy. Valencia: IATED Academy. 2022. p.581. https://doi.org/10.21125/edulearn.2022.0173.

DEVELOPMENT OF THE CHEMICAL INDUSTRY (CZ-NACE 20) IN THE CZECH REPUBLIC FOR THE PERIOD 2020–2022

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Abstract

The position of the chemical industry (CZ-Nation 20) is exceptional in that its production reaches almost all sectors of the economy.

The chemical industry in the Czech Republic (CZ-Nace20) experienced a significant decline in performance in 2020, around 25.3% compared to 2019, in terms of production, related to the restrictions imposed to limit the spread of the SARS-CoV-2 virus. The industry experienced another significant decline in 2020, when it reported a loss of $2.96 million. This resulted in a loss of CZK 2.96 million. On the other hand, there is a slight increase in investments, with approximately 5.98% in 2020 compared to 2019. On the other hand, 2022 brings a turnaround, with production showing a significant growth of approximately 31.9% compared to 2021.

This paper focuses on the evolution of selected financial ratios and employment trends of the chemical industry compared to the overall manufacturing industry over the period 2020–2022.

Introduction

The Czech Republic is one of the second most industrialised countries in the European Union. In 2020, the chemical industry is expected to decline by 5.9% due to the SARS-CoV-2 virus pandemic and a decline in demand[6]. The chemical industry plays an important role in the economic environment. Its importance lies in the fact that it is involved in the production of components for electric cars, solar panels or wind turbines, among other things. Its share in the economic characteristics is between 2 and 4%.

It can be said that the chemical industry is one of the most energy-intensive sectors. For this reason, it is necessary to find ways to provide alternatives that help reduce the economic intensity of the chemical industry[3,4,6].

Not only the price of energy, but also the rising cost of raw materials is causing significant complications for companies in the chemical industry. Some companies are responding by optimising their production processes and looking for synergies between technologies where none existed before. In addition, chemical companies are trying to invest in securing their own renewable energy sources. In addition to direct investments, companies are entering into long-term agreements to purchase green energy.

The aim of this article is to assess the position of the chemical industry in the period 2020–2022 with the help of a graphical apparatus. The indicators used to assess the position and state of the chemical industry are the volume of production (in millions of CZK), profit, investments, gross value added, profitability of sales, gross wages and salaries and employment in the chemical industry[2,6,7].

Production of the chemical industry in the period 2020–2022

The output of the chemical industry changed significantly between 2020 and 2022. In 2020, compared to 2019, there is a significant decrease in the indicator of the annual percentage change in the total output of the chemical industry. This is a decrease to a value of – 23.52%. Figure 1 shows that the following year also sees a recovery in the production of the chemical industry. The year-on-year growth in production from 2020 to 2021 is 26.0%. The following year also brings an increase of around 6%.

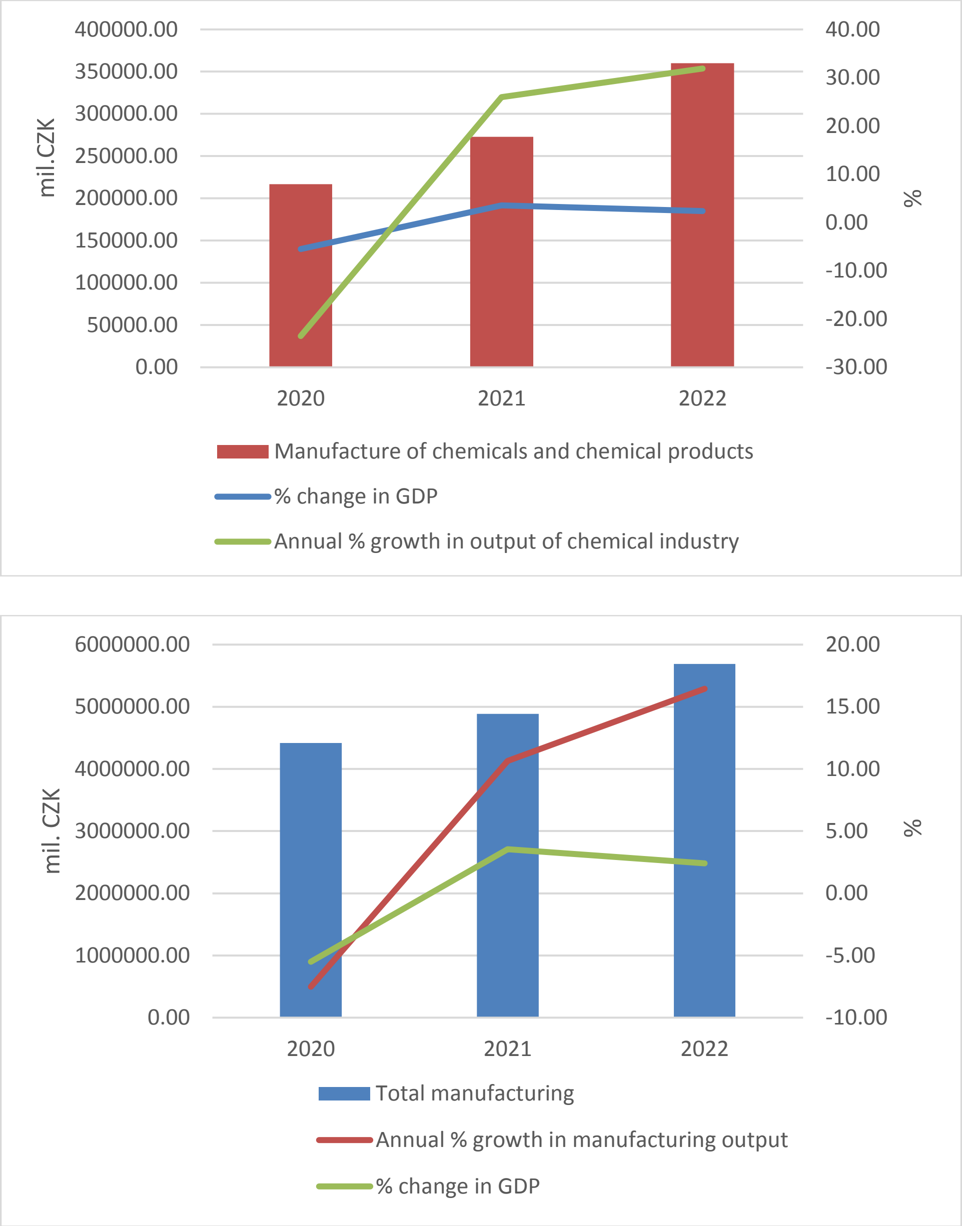

Figure 1. Evolution of production in the chemical industry in the period 2020-2022
Source: own according to CSO[1]

Compared to the total manufacturing industry (Figure 1), the production of the chemical industry reaches from about 4.9% to 6.3% of the total manufacturing industry. The highest share, 6.3%, is reached in 2022.

The output of the chemical industry achieves significant growth in the period 2020-2022. This growth is supported by an increase in the gross value added indicator from 2021 to 2022, with the change in this indicator reaching 93.6%. The volume of investments in the chemical industry remains almost unchanged, averaging around CZK 11,500 million. CZK. See Figure 2 for more details.

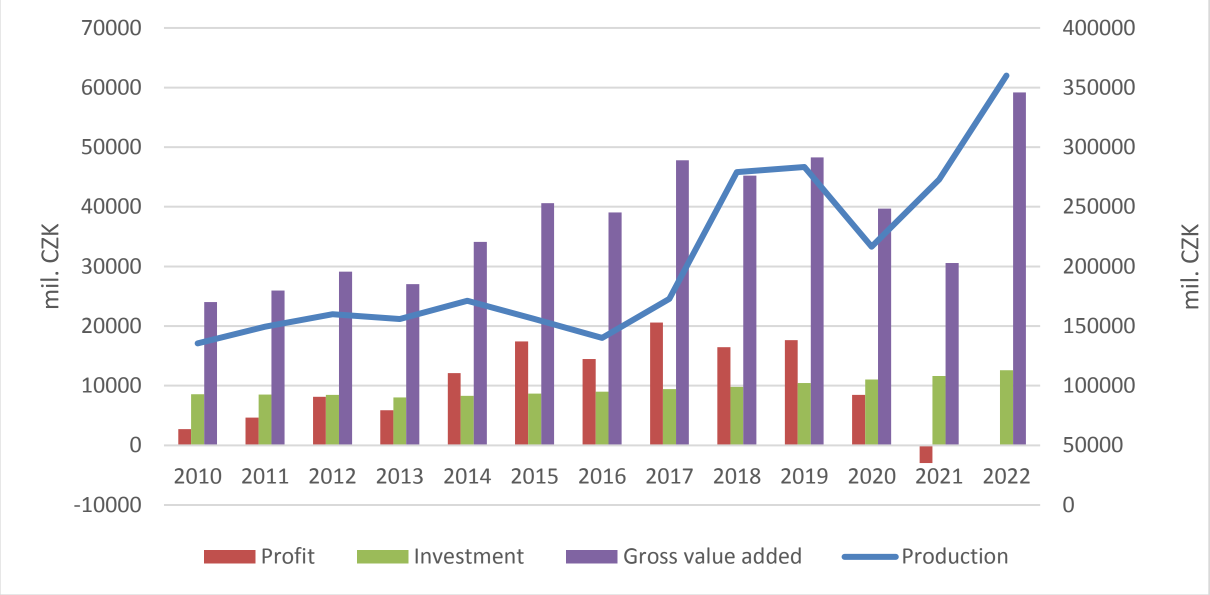

Figure 2. Evolution of selected indicators for the chemical industry
Source: own according to CSO[1]

Profitability of sales in the chemical industry
The profitability of sales (Figure 3) shows a decline over the forecast period 2019-2021. In 2019, the value of the profitability of sales indicator is 6.2%. In 2022, the value of this indicator turns negative due to the losses incurred by the chemical industry.

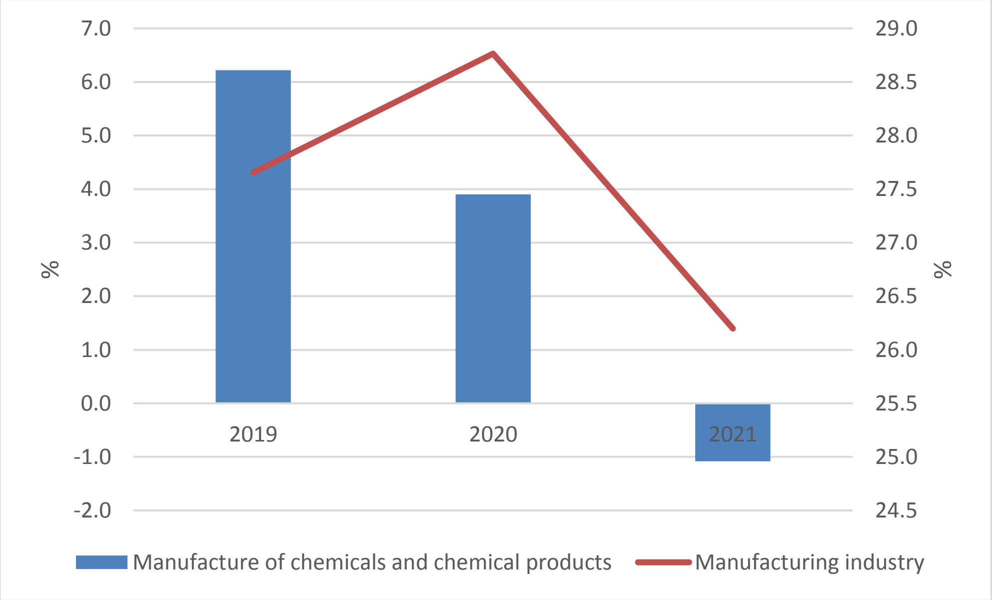

Figure 3. Profitability of sales in the chemistry industry
Source: own according to CSO[1]

Compared to the manufacturing industry as a whole, there is an interesting fact. In 2020, the profitability of sales in the chemicals industry will fall by around 3%, while it will rise by 1% in manufacturing.

Gross wages and salaries in the chemical industry in the period 2020-2022
Gross wages and salaries are expected to be around 2.7% year-on-year in 2020. The inflation rate during this period was 3.2%. The following year brings only a marginal increase in the value of the annual percentage growth rate. The year 2022 provides an interesting comparison with 2021. The annual growth of gross wages and salaries is 4.4%, but the inflation rate has increased by 11.3%. See figure 4 for a closer look.

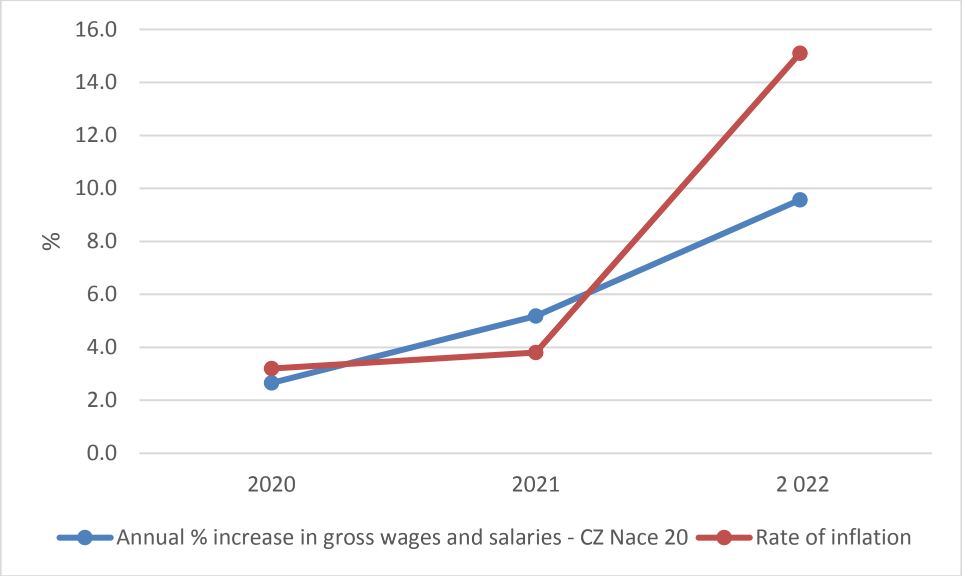

Figure 4. Gross wages and salaries in the chemical industry in the period 2020-2022
Source: own according to CSO[1]

The average monthly wage in the chemical industry will be CZK 60,456.7 in 2022. This is an increase of 9.5% compared to 2021.

Employment in the chemical industry in the period 2020-2022
Employment in the chemical industry remained almost stable at 33 thousand persons over the period. Compared with employment in total manufacturing, there was no fluctuation in the number of persons employed.

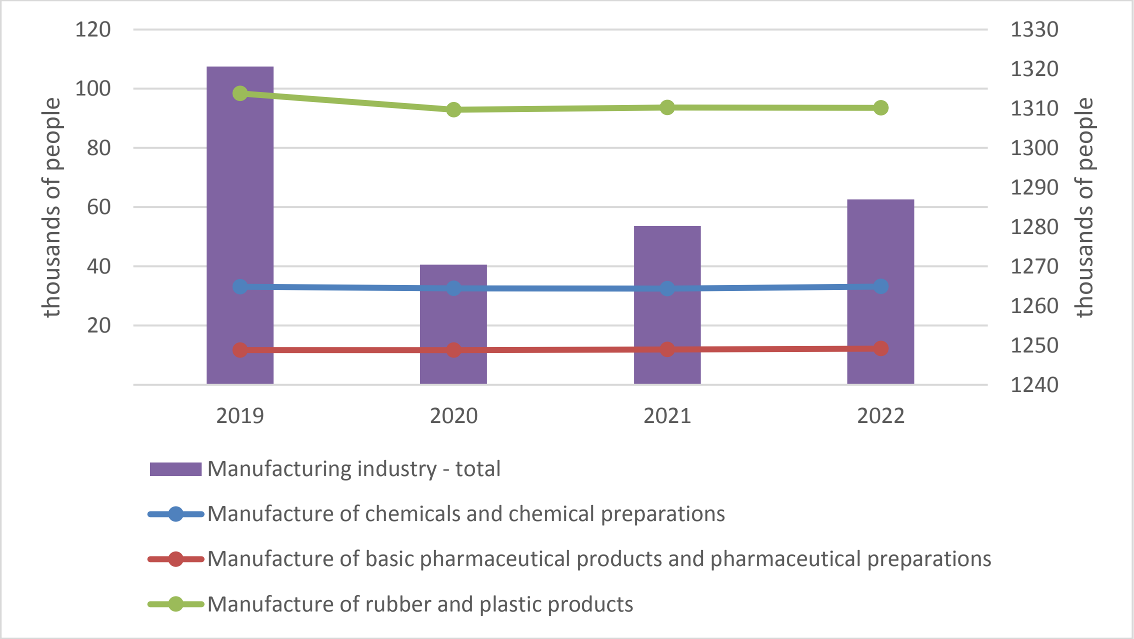

Figure 5. Employment in the chemical industry
Source: own according to CSO[1]

Conclusion

The position of the chemical industry (CZ-Nace 20) is exceptional in that its production reaches almost all sectors of the economy. The chemical industry in the Czech Republic (CZ-Nace 20) experienced a significant decline in performance in 2020, around 25.3% compared to 2019, in terms of production, which was related to the restrictions imposed to limit the spread of the SARS-CoV-2 virus.
The industry experienced another significant decline in 2020, when it reported a loss of CZK 2.96 million.

Conversely, there is a slight increase in investment, which is around 5.98% higher in 2020 than in 2019. However, it can be said that the chemical industry is more resistant to innovation. There are noticeable delays in responding to industrial trends, such as Industry 4.0.

Conversely, 2022 brings a reversal, with production showing a significant increase of around 31.9% compared to 2021.

In the atmosphere of the Green Deal, there is uncertainty and the chemical industry may not be as attractive to investors. But there is still opportunity for companies that make the right strategic decisions. That decision could be to introduce an alternative fuel into their production processes. This alternative fuel is seen as hydrogen, which can be produced in a cleaner way, for example by pyrolysis of methane. This would be a possible way of producing basic chemicals without emissions.

References

1. Český statistický úřad. [available online: https://www.czso.cz/][cit. 2024-04-10].
2. Eurostat database. [available online: https://ec.europa.eu/eurostat/data/database/][cit. 2024-04-10].
3. Kostalova, J., Bednarikova, M.: An Analysis of the Chemical Industry Labour Market in the Czech Republic. Chemicke listy. *113*, 691 (2019).
4. Krause, J., Špička, J.: Ekonomická analýza chemického průmyslu. Chemické listy. *107*, 563 (2013).
5. Lostakova, H., Jelinkova, M., Vlckova, V.: Assessment of employment attractiveness in the Czech chemical industry. Przemysl Chemiczny. *97*(11), 1945 (2018).
6. Ročenky 2020-2022. Svaz chemického průmyslu České republiky. Zprávy SCHP. [available online: https://www.schp.cz/info/zpravy-schp][cit. 2024-04-02].
7. Vlček, D., Kostalova, J.: Economic Analysis of the Chemical Industry of the Czech Republic in the Period of Economic Growth. International Scientific Conference on Hradec Economic Days (HED). *20* (2020).

ANALYSIS OF THE FOREIGN TRADE OF RAW MATERIALS OF THE CHEMICAL INDUSTRY OF THE CZECH REPUBLIC WITH THE SELECTED COUNTRIES FOR THE PERIOD OF 2020–2022

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Abstract

The foreign trade balance of the Czech Republic shows a passive balance over the forecast period. In 2019, the Czech Republic will have a passive balance with the EU countries of around minus CZK 97.1 bn, while in 2022 the balance will reach minus CZK 89.8 bn. The most significant decrease in the balance will occur in 2020. Germany is the most important and largest foreign trade partner of the Czech Republic, followed by China and France. Trade in oil, natural gas and basic metals, has a negative impact on the foreign trade balance.

The paper focuses on the analysis of foreign trade of raw materials of the chemical industry of the Czech Republic with selected countries for the period 2020–2022. The analysis focuses on year-to-year comparisons of important chemical industry commodities for foreign trade with Germany, Russia, China, Ukraine, Turkey and the Visegrad Four.

Introduction

The EU-27 countries remained the dominant area for exports and imports of chemical industry products to the Czech Republic in 2020–2022. The total external balance in 2021 will reach CZK -169.9 bn, a decrease of CZK 22.6 bn compared to 2020, i.e. a decrease of 15.4%. The passive balance with the EU-27 countries will decrease by about CZK 23 billion in the monitored period, with China and Germany, among others, having the greatest influence on its level. Among the selected countries, in 2022 we have a positive balance with Slovakia (+ CZK 14.9 bn), Hungary (+ CZK 4.4 bn), Austria (+ CZK 1.2 bn)[1,3,4,6].

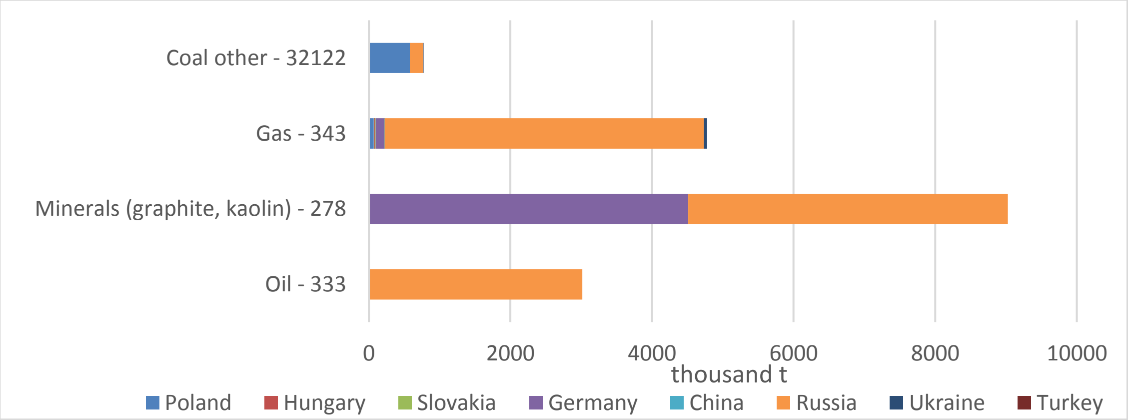
In 2022, exports to Germany, Slovakia and Poland will make a significant contribution to the export sector. On the other hand, only Russia and Germany can be mentioned on the import side.[4,6]

There is some potential in the area under consideration, namely in Turkey.

The data for the analysis were extracted from the public database of the Czech Statistical Office within the database of the cross-border movement of goods in the period from March to April 2024. The obtained data were transformed into a table in MS Excel.

Import status of the Czech Republic of selected chemical industry commodities in the period 2020-2022

Important import territories for the Czech Republic are Russia, Slovakia, Germany and Poland. In 2020, the most important imports from Russia were oil – crude oil (almost 3 013 thousand tonnes), followed by 278 – minerals – graphite, kaolin and 32122 – coal other. Germany is the second largest importer with 278 – Minerals and 573 – PVC. See Figure 1 for a closer look.



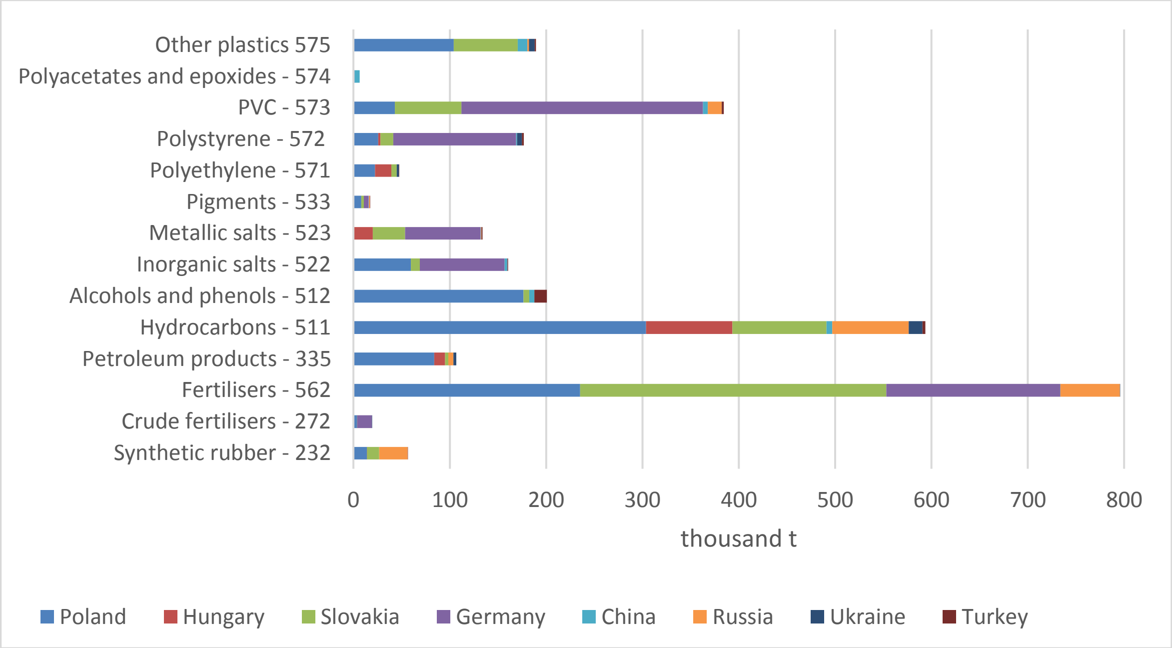


Figure 1. Import status of selected chemical industry commodities in year 2020
Source: own according to data ČSÚ[2]

In 2021, the import mix is almost unchanged, as shown in Figure 2. There is an increase in the volume of imports from Russia, namely 333 – oil (an increase of around 13%) and 232 – synthetic rubber (an increase of around 19%). The most significant increase in imports is expected for Slovakia in 2021, namely for 232 – synthetic rubber (an increase of 114%) and 562 – fertilisers (an increase of 100%).

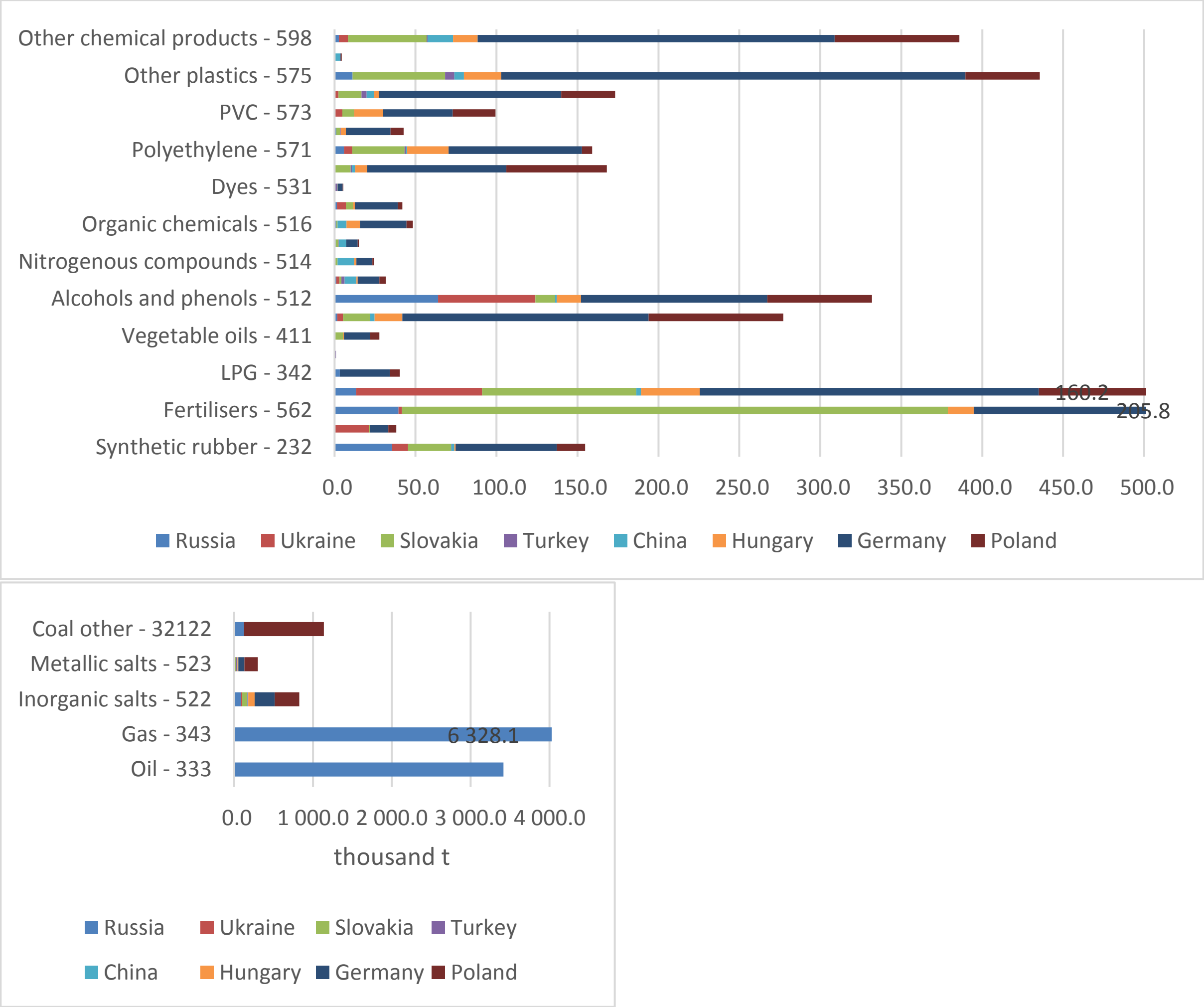


Figure 2. Import status of selected chemical industry commodities in year 2021

Source: own according to data CSO[2]

In 2022, the import structure is maintained. The volume of imported commodities has increased the most for Germany, imports of 32,122 – coal other increased from an original value of 0.5 thousand t to 10.6 thousand t (an increase of almost 2,100%). Other significant increases are recorded for imports from Turkey, namely 573 – PVC, an increase of 300% (from an original import value of 0.1 thousand t to 0.4 thousand t and 598 – other chemical product, an increase of 100% (from an original value of 0.6 thousand t to 1.2 thousand t).

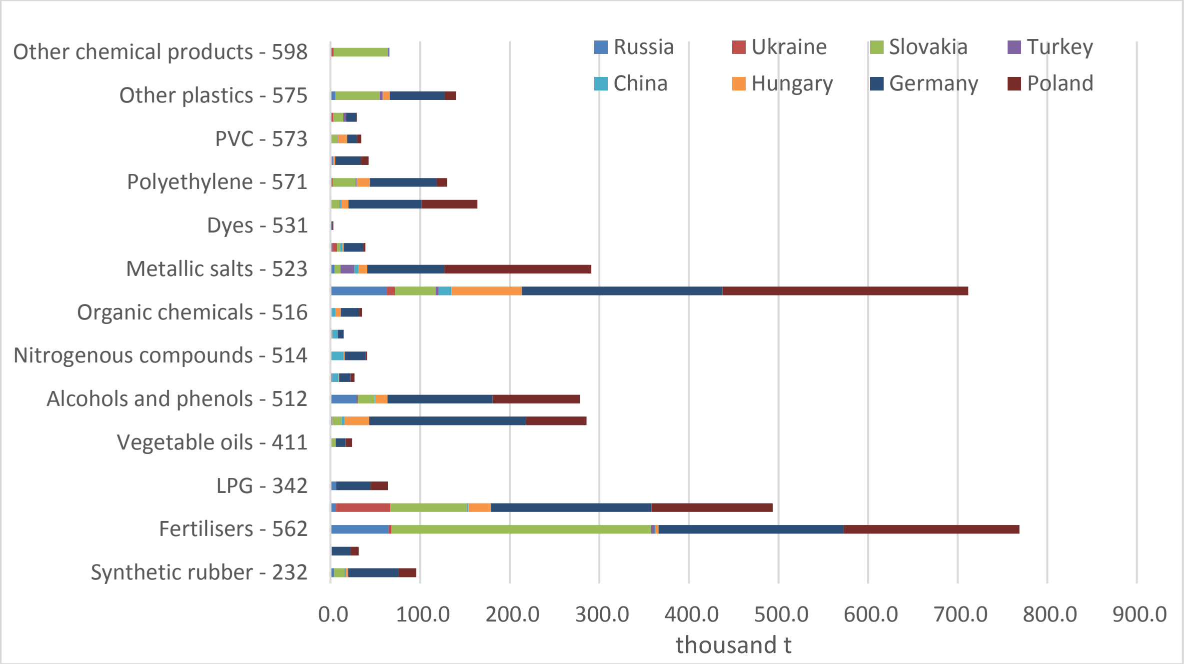


Figure 3. Import status of selected chemical industry commodities in year 2022
Source: own according to data CSO[2]

Imports to the Czech Republic in the period under review can be assessed in such a way that the largest imports came from Russia, namely 333 – oil, in a volume ranging from 3,013.5 to 4,161.5 thousand tonnes. In addition, imports of 278 – minerals (graphite, kaolin) were significant, namely from Slovakia and Germany in a volume of about 500 thousand tonnes. Here, the import volume ranges from 881.7 to 1,013.9 thousand tonnes, which is a significant decrease from the original import volume of 1,013.9 thousand tonnes to 881.7 thousand tonnes.

Export status of the Czech Republic of selected chemical industry commodities in the period 2020-2022
The Czech Republic's exports in 2020 were mainly to Germany, followed by Slovakia. Figure 4 shows that the most important exports to Germany in 2020 are 562 – fertilisers and 575 – other plastics. The most important exports to Slovakia are 278 – minerals (volume almost 742 thousand tonnes) and 575 – other plastics.

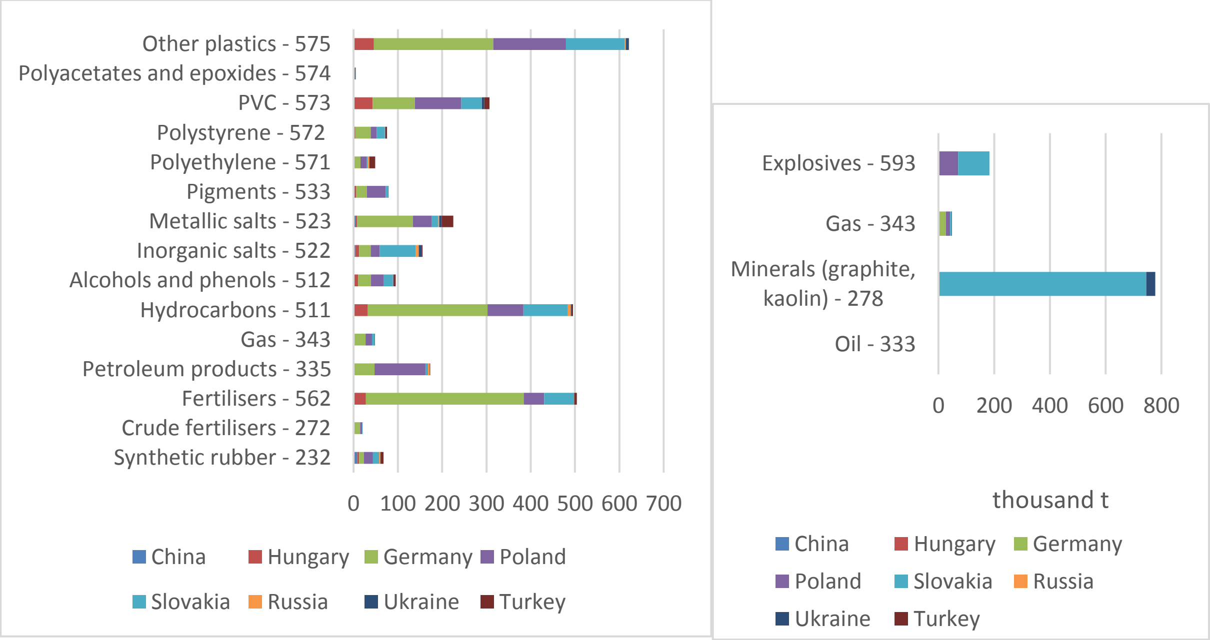


Figure 4. Export status of selected chemical industry commodities in year 2020
Source: own according to data CSO[2]

In 2021, Poland will join Germany and Slovakia. The most important export to Poland was 278 – Minerals (almost 785.6 thousand tonnes). Figure 5 shows that there was an increase in the volume of 562 – fertilisers exported to Germany (an increase of about 17%).

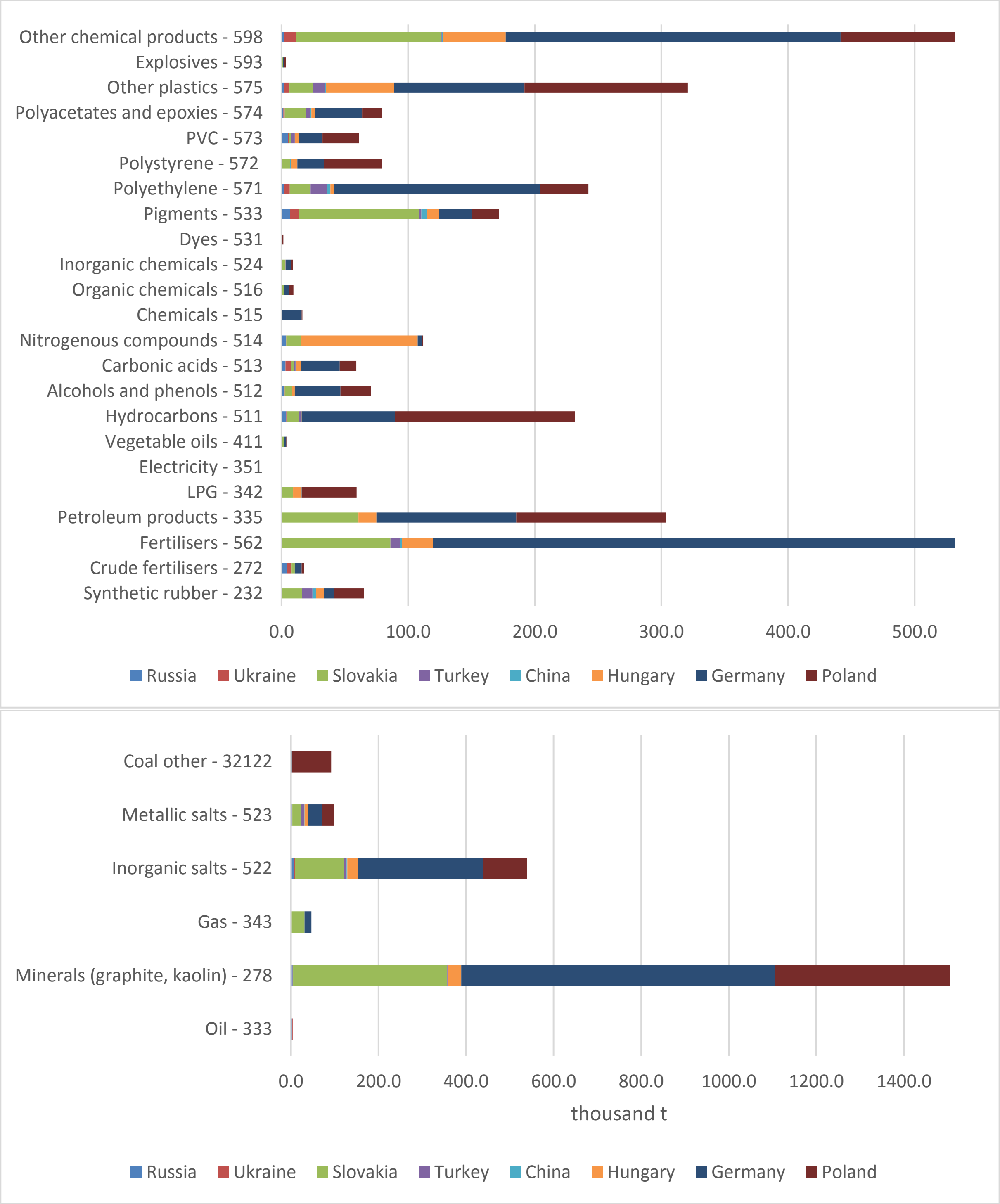


Figure 5. Export status of selected chemical industry commodities in year 2021

Source: own according to data CSO[2]

In 2022 there will be a significant increase in exports of around 2,500% for commodity 232 – Synthetic rubber to Turkey. If in 2021 the export volume was about 0.3 thousand tonnes, in 2022 it will be 7.8 thousand tonnes. Another significant increase occurs for commodity 278 – Minerals to Hungary. In this case there is an increase of about 1100% – the export volume is about 25.4%.

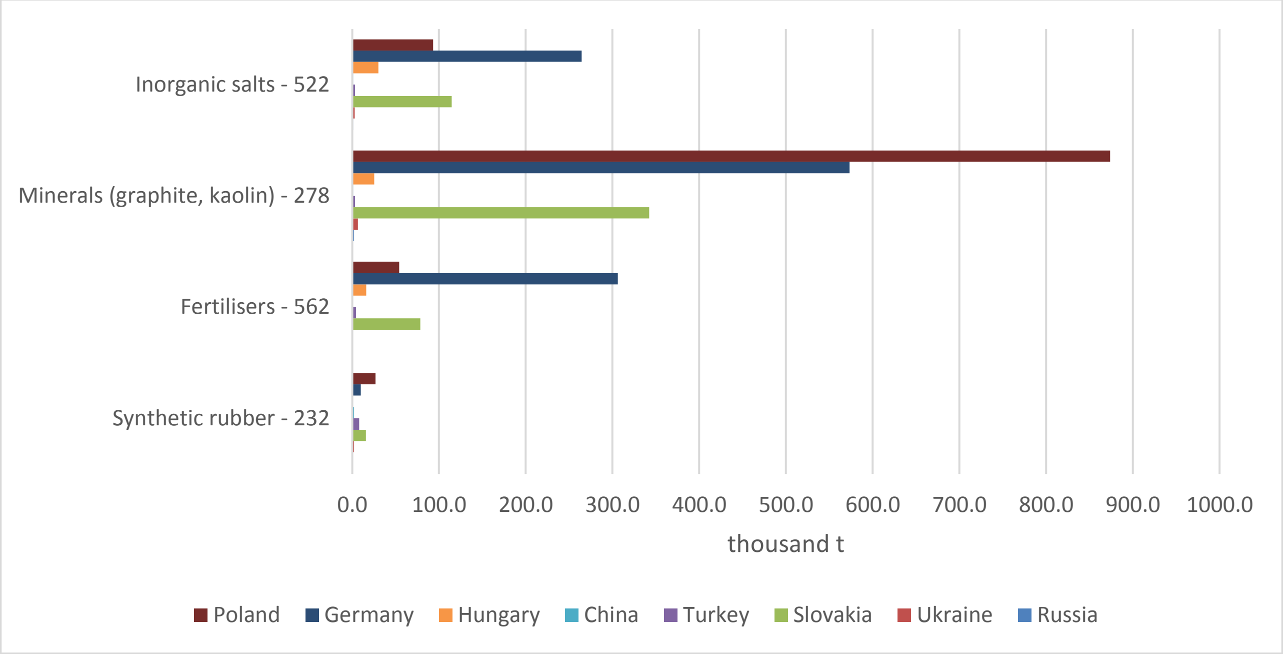


Figure 6. Export status of selected chemical industry commodities in year 2022
Source: own according to data CSO[2]

During the period under review, there was an increase in the volume of exports of all the main products of the chemical industry. Within the monitored commodities, the most important export commodity is 278 – minerals (graphite, kaolin), followed by 335 – petroleum products, 562 – fertilisers. The main export destinations are Germany, Poland and Turkey.

Conclusion

Germany plays a dominant role in exports to neighbouring countries. It is followed by Slovakia and Poland.
For imports, Germany is again the most important country. The second most important country for imports of products within the chemical industry is Poland.
In 2022, three commodities – LPG – 342, coal other – 32,122 and polyacetates and epoxies – 574 – have export values above 10 thousand tonnes. This is an increase compared to 2021, when these values were below 10 thousand tonnes.

References

1. Bergoeing, R., Kehoe, TJ, Strauss-kahn, V., YI, K.: Proč obchod s výrobou roste, i když produkce klesá? American Economic Review. *94,* 134 (2004).
2. Český statistický úřad. Databáze zahraničního obchodu se zbožím. [available online: https://www.czso.cz/][cit. 2024-04-10].
3. Eurostat database. [available online: https://ec.europa.eu/eurostat/data/database/][cit. 2024-04-10].
4. Ročenky 2020-2022. Svaz chemického průmyslu České republiky. Zprávy SCHP. [available online: https://www.schp.cz/info/zpravy-schp][cit. 2024-04-02].
5. Rojíček, M.: Konkurenceschopnost obchodu ČR v procesu globalizace. Politická ekonomie, *58*(2), 147 (2010a). https://doi.org/10.18267/j.polek.724.
6. Vokorokosová, R.: Komparatívne výhody zahraničního obchodu - indikátor konkurenční schopnosti Slovenskej republiky? Politická ekonomie, *51*(6), 851 (2003). https://doi.org/10.18267/j.polek.442.

HOW HOST AND HOME COUNTRY INSTITUTIONAL COMPLEXITIES INFLUENCE CSR ENGAGEMENT OF AN MNC: EVIDENCE FROM ESG DISCLOSURES OF A GERMAN MULTINATIONAL CHEMICAL COMPANY AND ITS INDIAN SUBSIDIARY

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Abstract

In this globalized free trade era, cross-border CSR engagements of multinational corporations have an overarching impact on societies, while ensuring their much-needed legitimacy in host and home markets. In international business and business ethics streams, many studies dealt with MNCs' responsibility practices and the challenges associated with the institutional duality they must address when operating in environmentally dispersed markets with the same set of parental business values. A micro-level study that discusses a particular MNC's difference in CSR engagement within its home and host country is relatively scarce. This study is organized into two parts, the first critically examines the institutional complexities prevailing in Germany and the Indian business environment that shape specific CSR engagements and states a few propositions based on that. In the next part, we test the validity of those propositions by pitching them against real-life CSR business practices. We examine how institutional factors influence the CSR engagement of a chemical company from Germany that has a fully-owned subsidiary in India. Content analysis is employed on respective ESG reports released by the MNC on their global website and the subsidiary's Indian website. A visible pattern and prioritization in ESG disclosure were found in both reports, complementing the propositions. The German parent company prioritized climate control, employee rights compared to its subsidiary in India, wherein the subsidiary gives more time, effort, and money to community development causes. This study provides practical CSR engagement insights for European chemical companies while operating in Indian markets.

Introduction

Corporate Social Responsibility is one of the most controversial and debated topic among business and ethics researchers[1]. However, researchers around the world agree that CSR is no longer an altruistic function but a strategic one that adds value to all its stakeholders[2]. Institutionalized (cognitive, normative, and regulatory) pressures explain the motivation of firms to engage in CSR activities that ensures social order and homogeneity[3]. When an MNC company operates across countries, then it has to comply with dichotomous institutionalized pressures from both home and host country[4]. These institutional differences forces MNC companies to customize their CSR activities across the globe so as to ensure legitimacy and for an MNC subsidiary, legitimacy from both parent and host country is significant. There are common norms in business which are universally accepted but the specific practices based on such norms are dependent function of the local society, national culture and economic and regulatory environment of the host country. If the MNC is operating in hazardous chemicals or associated industries, then such MNCs will be subjected to much harsher scrutiny and hence required to proactively provide evidence of minimizing negative impacts in comparison with their domestic industry peers.

CSR practices along with its communication constitute the CSR engagement of a company which helps consumers, governments, regulatory bodies, and other stakeholders to understand how effectively a company is managing its risk and opportunities associated with ESG dimensions and quantify their environmental and CSR efforts[5]. MNCs that are pro-sustainable will have different CSR priorities in specific markets and normally maintain separate ESG reports for the parent firm and for every subsidiary. By comparing ESG report of an MNC parent and that of its subsidiary, we could understand the difference in CSR priorities of both the entities with certain degree of conformity. Studies on relative difference of CSR engagement of the same MNC in a geographically dispersed settings are scarce and this paper intends to fill that research gap. This paper is organized as follows, with help of existing literature, we list out the institutional differences prevailing in two countries, Germany and India, with regards to cultural, economic and regulatory complexities and describes how those differences influence the CSR engagement of a subsidiary firm. Further to this, we test the practical validity by comparing the ESG report of a parent and subsidiary chemical MNC operating in those countries. For comparison a content analysis is employed on ESG reports available on their websites and discuss how the same aligns with the propositions we made earlier based on institutional complexities. As per Barlett and Ghoshal “MNCs are geographically dispersed inter organizational network that is embedded in an external network”[6]. In other words, MNCs are entities that shares a common DNA but geographically separated with different means and strategies leading to a common end. The host country institutional pressures in a subsidiary environment may not synchronize with the institutional environment of its parent and hence a particular institutional logic in one country becomes incompatible in another resulting in an institutional complexity[7]. The major institutional complexities that force subsidiaries to adopt a different CSR strategy than its parent firm is cultural complexity, economic complexity, and regulatory complexity which we analyze in this study separately.

Literature review

Cultural complexity

The cultural complexity implies that the national cultural environment prevailing in a host country could be different from its parent country. The national culture and its ethical determinants were studied by Hofstede and proposed the following dimensions given in the table 1 that are used by researchers extensively till date[8,9].

Table I
Hofstede's dimensions and CSR inclinations[8,9]

Hofstede's Dimensions	Societal Inclinations	Inclinations related to CSR
Individualistic Vs Collectivistic	IDV- Independent, Individual rights and growth, privacy. COL- Interdependent, common good, group cohesion and relationship	IDV-Career, personal growth, training, privacy. COL- Freedom of association, group rewards, community living.
Masculinity Vs Femineity	MAS-Success, assertions, competition. FEM-Compassion, modesty, sympathy	MAS-Work over family, Incentives, success. FEM-Work life balance, gender equality, employee relations
Uncertainty Avoidance index	Low UAI – Low anxiety, stress, comfortable with ambiguity, high score on health, dislike rules and other way round with high UAI	Short term career, high attrition, rule-based conformity, averse to organizational change for Low UAI and opposite with high UAI
Power Distance	Adult-children divide, power concentration on top, less communication, corruption, Un even income in high PD and reverse in low PD	Hierarchy, communication only on top, less grievance handling in high PD and the reverse in low PD
Long term and Short-term orientation	Heavy spending and consumption, traditions and cultural stringency in STO societies	Long term success and goals, more adaptive to suit long term changes, more sustainable practices in LTO organizations

Economic & regulatory complexity

The economic complexities of host country in which an MNC subsidiary operates, influences the CSR engagement. The economic complexity faced by a subsidiary could be, the varieties of capitalism framework such as Liberal Market Economies or Coordinated Market Economies, Developed or Developing/ Emerging economies, Welfare or non-welfare economies. Researchers opines that in LME countries, companies may not be aggressive with CSR especially in factors where the returns are not confirmed or immediate and In CME countries because of powerful institutions and coordination between them, firms from those companies will be aggressive in CSR[10]. In the case of developed and developing/emerging classification, the CSR aggressiveness is contested, some studies conclude that in developed nations CSR will be ceremoniously followed especially in climate, environment, human rights areas and on the contrary a few studies says that many CSR dimensions will be taken care by state in developed countries so the firms may care less about CSR[11]. Regulatory environment and related institutions in host country is one thing that forces subsidiaries to have a major overhaul in strategies that were followed back in their home country by its parent[12]. Regulations and related business laws helps to prevent companies from exploiting the local society for their selfish motives. Some countries have tighter environmental regulations and some others regulate more on human and employee rights regulations and few have community-based regulations that forces subsidiaries operating in those countries to comply irrespective of the CSR strategy of their parent MNC[13]. The absence of a well-defined business regulatory environment may result in subsidiary firms assuming a lower standard in responsible business practices. In developed nations regulations will be more in areas such as climate control, environment protection, human rights areas and in developing nations regulations can be more oriented towards pollution, employee rights, community expenditures[14]. In a developing or emerging country, the preferences should be in economic development and employment generations and such countries tend to keep environment and social factors less regulated to attract MNCs[15].

Research methodology

After reviewing the literature, we then verify it with a practical business case. We selected Germany and India for our case study because of the antithetical institutional complexities those countries have, which would readily be reflected in their CSR engagement differences. The relevant institutional complexities prevailing in those countries that could influence the CSR roadmap of subsidiary is listed in the Table.2 below. Source of cultural complexity dimensions of respective countries are from studies of national culture by Hofstede[8,9].

Table II
The specific institutional complexity prevails in Germany and India

Cultural Complexities	Germany	India
Individualistic Vs Collectivistic	Individualistic	Collectivistic
Power Distance	Low	High
Uncertainty Avoidance	High, Low probability of social protest	Low, High probability of social protest
Long Term Vs Short Term Orientation	Short term	Long term
Economic Complexities	Developed/ Coordinated	Developing/ Emerging
Regulatory Complexity	Regulated CSR - Based on EU Policies	Regulated CSR – Mandatory CSR, Companies Act 2013

Based on the above discussed specific cultural, economic and regulatory environment prevailing in Germany and India, we furnish six propositions as to the possible difference in CSR priorities by MNC and its subsidiary as given in Table.3

Table III
Six propositions to the possible difference in CSR priorities by MNC and its subsidiary

Relevant Complexity	Expected Engagement trend based on literature
Individualistic Collectivistic	**P1:** German parent aggressive in individualistic values and Indian subsidiary aggressive in collectivistic values.
Power Distance	**P2:** German parent aggressive in disclosures especially in equality and inclusion. Indian less aggressive in disclosures especially equality rights.
Uncertainty Avoidance	**P3:** German parent aggressive in disclosures especially in future risk factors and Indian not aggressive in risk, aggressive in social protest factors
Long term vs. Short term	**P4:** German less aggressive in CSR disclosures, especially in long term sustainability/climate factors. Indian subsidiary aggressive in sustainability.
Developed vs. Emerging	**P5:** German parent aggressive in climate, environment and human/employee rights. Indian subsidiary aggressive in social and community development
Environmentally regulated vs. Socially regulated	**P6:** German parent aggressive in climate related controls and disclosures. Indian subsidiary aggressive in community related practices

Once we drew the propositions, in order to understand the significant differences in engagement, we undertook a content analysis of the CSR/ESG reports available on the website of MNC parent company and the subsidiary. There are comparative studies in literature using interviews and surveys of persons concerned but in such studies honesty of assertions are doubtful due to desirability bias and for a content analysis study that can be overruled. Scholars take cues from web communications to arrive on conclusions regarding intensity and pattern for CSR practices[16]. In our context, German MNC has an integrated report and Indian subsidiary has a standalone sustainability report along with a business responsibility and sustainability report (BRSB). For this analysis we employ sixty seven most frequently used Keywords that represent various ESG factors globally and counted their occurrences in respective reports. For deriving meaningful information and classification purpose, we divide the environmental keywords into two subsections, climate control (9 Keywords) and environmental protection/pollution control (14 Keywords). The social aspect is classified into two further subsections human and employee rights (17 Keywords), and community development (15 Keywords). And finally for Governance (12 keywords) were used. While considering the level of recurrence of keywords as a pointer towards CSR commitment of a company towards CSR, we should also consider the possibility of CSR washing, discrepancy between what is being disclosed and what is followed. To circumvent that disability in our analysis, if the disclosure is backed up with quantitative or monitory data then we considered such disclosure as specific and assigned a multiplication value of two to those frequencies of occurrences. If it is general without the support of any specific quantitative data then we consider that keyword frequency as such without any multiplication factor to reach the final score.

Discussions and findings

Based on the frequency of keyword occurrences and the scores we obtained, we can clearly deduce a pattern as to where German MNC and Indian subsidiary gives priority and based on those priorities, we accept the validity of propositions we made earlier from the literature. Specific complexities, with relevant CSR factors influenced by those complexities and the inference on the propositions we made earlier were listed in Table 4.

Table IV
List of specific complexities, with relevant CSR factors and related inference on the propositions

CSR Engagement difference observed in content analysis	Author inferences
Human rights (DE&I), employee rights, career development & growth received priority in MNC report. Rights like sexual harassment protection and non-discrimination gets more weightage in subsidiary reports. Community and rural development get more weightage in Indian report which partly agrees with collectivistic culture in Indian context	In collectivistic values subsidiary is aggressive but both gives comparable weightage to Individualistic values so P1 is rejected.
Both countries are comparable. PD influencing factors like Human rights, Employee rights, Non-discrimination, governance etc. is comparable. Difference in aggressiveness not seen in factors except climate.	Both are comparable in disclosing factors crucial on power distance. So, P2 is rejected.
A visible priority in climate control and emissions in parent MNC report concluded from content analysis. Pollution control, waste management, energy consumption related disclosures comparable in both and reason can be fear of people protests due to high uncertainty tolerance in India.	Based on our analysis, UA tolerance influences the CSR engagement of MNC in the home and host country. So P3 is accepted
Parent MNC report aggressive in climate, emissions, environment, pollution control, all of which are LTO factors. Subsidiary report gives less space to LTO factors like climate but more prominence to STO social and community factors	STO & LTO have nil to negative relevance in CSR disclosure practices. P4 is rejected
MNC report aggressive in climate and employee rights, good in environment protection and pollution control, less in community. Indian subsidiary not aggressive in climate, environment. Comparable in pollution control. Aggressive in community and infrastructure development	Economic complexity has huge influence on deciding the priority of CSR in MNC and subsidiary. P5 accepted
German MNC is aggressive in climate control and environment protection, and employee rights but less aggressive community development and welfare. Indian subsidiary aggressive in pollution control and environment, energy management, waste recycling and human rights, community, education and development	Regulatory complexities have strong relevance in the difference of CSR engagement in the home and the host country. P6 accepted.

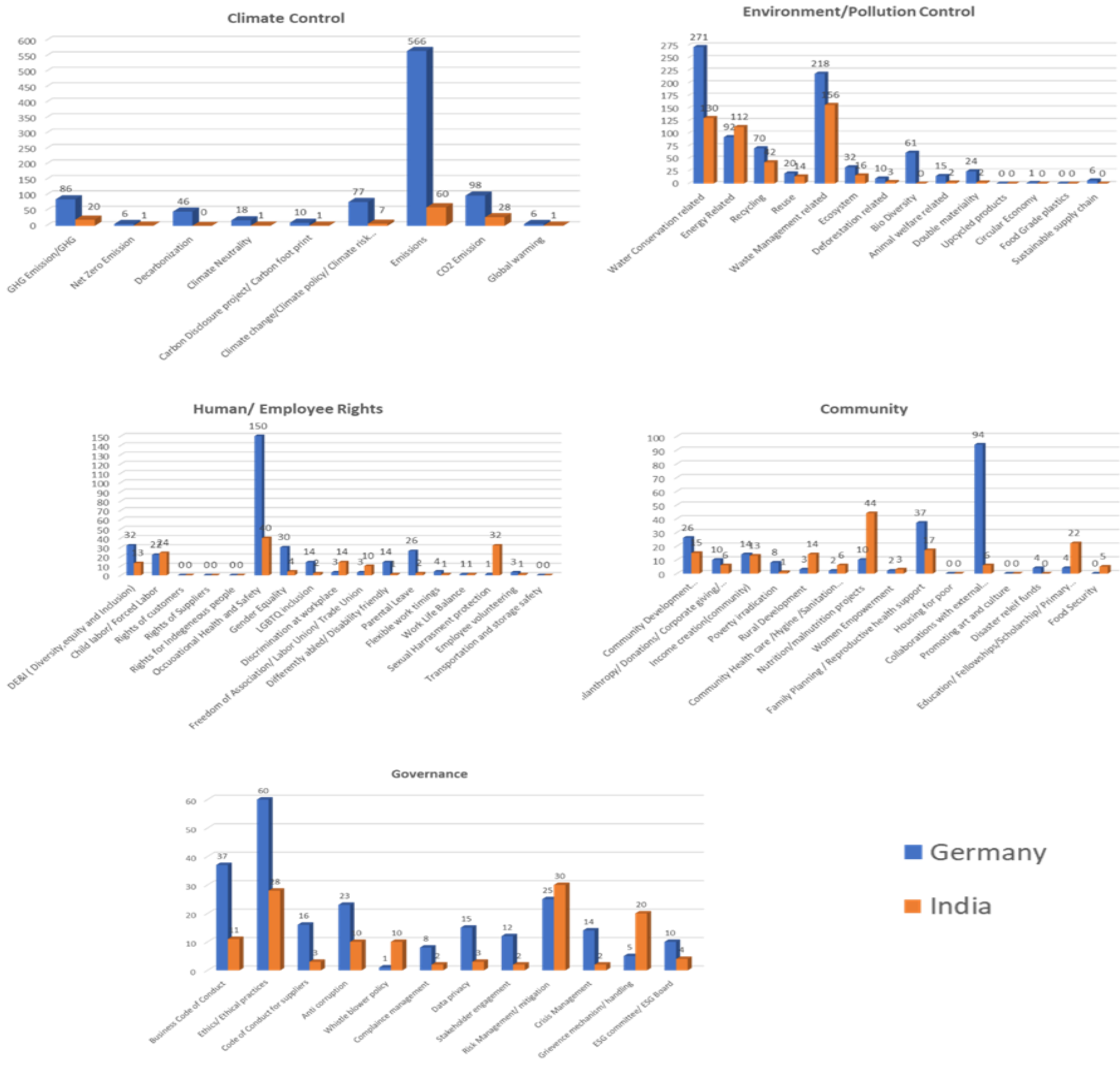

Figure1. Graphical representation of the results, where we can see some clearly observable priority in CSR engagement by MNC parent in the home country and its subsidiary in the host country.

Conclusion

From the visible difference of priorities as evidenced by the amount of space and importance given to factors like climate, environment, employee rights, human rights, and community development in disclosures, In our specific case we can say that climate control is one important CSR priority of MNC parent which they didn't transfer to its Indian subsidiary and conversely community and infrastructure development, which MNC parent itself is not following aggressively is a priority to subsidiary in India to ensure legitimacy in host country. Employee rights also reflect a slight aggression in parent MNC which didn't get transferred to subsidiary and for the rest of the factors like environment protection & pollution control, human rights, and governance, even though there is difference in visibility and exposure on certain individual dimension, when considering in their entirety, both parent and subsidiary gives almost similar level of priority. We can also conclude that one of the reasons for this difference in priority is institutional difference between parent and host country. From our case study we further conclude that economic and regulatory complexities are the two main factors that drives CSR. However, we can't generalise and apply our specific conclusions to all MNC- subsidiary CSR relations. There is also a possibility that MNC or subsidiary may follow an explicit – implicit strategy of CSR communication which may result in reaching wrong inferences[17]. Moreover, inference form just a single case cannot be considered universal, especially in a contested topic like CSR, where a lot of independent and dependent variables influences the premise, something that we cannot control or even identify. The CSR priority difference could also be a function of size, strength, autonomy, and other physical aspects of either MNC or subsidiary.

References

1. Dahlsrud, A. How Corporate Social Responsibility is Defined: An analysis of 37 Definitions. *Corp Soc Responsib Environ Manag* **15**, 1–13 (2008).
2. Du, S., Bhattacharya, C. B. & Sen, S. Maximizing Business Returns to Corporate Social Responsibility (CSR): The Role of CSR Communication. *International Journal of Management Reviews* **12**, 8–19 (2010).
3. DiMaggio, P. J. & Powell, W. W. The Iron Cage Revisited: Institutional Isomorphism and Collective Rationality in Organizational Fields. *Am Sociol Rev* **48**, 147–160 (1983).
4. Kostova, T. & Roth, K. Adoption of an Organizational Practice by Subsidiaries of Multinational Corporations: Institutional and Relational Effects. *Source: The Academy of Management Journal* **45**, 215–233 (2002).
5. Crane, A. & Glozer, S. Researching Corporate Social Responsibility Communication: Themes, Opportunities and Challenges. *Journal of Management Studies* vol. 53 1223–1252 Preprint at https://doi.org/10.1111/joms.12196 (2016).
6. Ghoshal, S. & Bartlett, C. A. The Multinational Corporation as an Interorganizational Network. *Academy of Management Review* **15**, 603–626 (1990).
7. Greenwood, R., Raynard, M., Kodeih, F., Micelotta, E. R. & Lounsbury, M. Institutional Complexity and Organizational Responses. *Academy of Management Annals* **5**, 317–371 (2011).
8. Hofstede, G. Cultural Differences in Teaching and Learning. *International Journal of Intercultural Relations* **10**, 301–320 (1986).
9. Hofstede, G. The Business of International Business is Culture. *International Business Review* **3**, 1–14 (1994).
10. Walker, K., Zhang, Z. & Ni, N. (Nina). The Mirror Effect: Corporate Social Responsibility, Corporate Social Irresponsibility and Firm Performance in Coordinated Market Economies and Liberal Market Economies. *British Journal of Management* **30**, 151–168 (2019).
11. Husted, B. W. & Allen, D. B. Corporate Social Responsibility in the Multinational Enterprise: Strategic and Institutional Approaches. *J Int Bus Stud* **37**, 838–849 (2006).
12. Wagner, M. Sustainability and Competitive Advantage: Empirical Evidence on the Influence of Strategic Choices Between Environmental Management Approaches. *Environmental Quality Management* **14**, 31–48 (2005).
13. Welford, R. Corporate Social Responsibility in Europe, North America and Asia. *Journal of Corporate Citizenship* **17**, 33–52 (2005).
14. Gjolberg, M. The Origin of Corporate Social Responsibility: Global Forces or National Legacies? *Socioecon Rev* **7**, 605–637 (2009).
15. Narula, R. & Pineli, A. Improving the Developmental impact of Multinational Enterprises: Policy and Research Challenges. *Economia e Politica Industriale* **46**, 1–24 (2019).
16. Maignan, I. & Ralston, D. A. Corporate Social Responsibility in Europe and the Insights from Businesses' Self-presentation. *J Int Bus Stud* **33**, 497–514 (2002).
17. Jackson, G. & Apostolakou, A. Corporate Social Responsibility in Western Europe: An Institutional Mirror or Substitute? *Source: Journal of Business Ethics* **94**, 371–394 (2010).

PROJECTS FULFILLING THE GOALS OF SUSTAINABILITY AND THE TRANSITION TO A CIRCULAR ECONOMY IN THE CONDITIONS OF THE CHEMICAL INDUSTRY

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Abstract

The term sustainable project has been commonly used for a very long time. However, a project focused on sustainability, i.e. the circular economy, is something else. In practice, this connection occurs for a significantly shorter period of time. And that is the focus of this post. In it, the authors build on their previous qualitative research characterizing the impact of the bio-base/circular economy on chemical companies. This contribution summarizes the findings of the transition from a linear to a circular economy with the aim of enhancing competitiveness for chemical enterprises. It will be a guide to the concept of a corporate project system focused on the principles of "green chemistry" and the process of integration into the circular economy.

Introduction

Today, sustainable business is the norm. For companies in the chemical industry, sustainability is even more critical[1], also with regard to the high barriers to entry into the industry, the cyclicality of industry development[2] and the current competitive environment. Doing business in accordance with the concept of sustainable development requires changes in all business processes and in the entire management of the company[3]. It is necessary to set goals and target values that will mean the achievement of sustainability. Companies in the chemical industry thus face a challenge focused not only on the circular economy, but also on sustainable projects[4,5] focused on the economic, environmental and social aspects of process management.

For the successful integration of circular ideas, it is necessary to set up a management system in accordance with the principles of continuous improvement[6] and it is necessary to emphasize the need to create a concept of a learning organization where proactive approaches will be supported and there will be a close link between personal goals and company values[7]. After all, a certain proposal for business management towards sustainability emerged from the authors' previous qualitative research and can be briefly summarized in the form of Table 1.

Business management towards sustainable performance has three problem areas[8]: how to establish individual indicators (indicators) of performance, how to set up a measurement system, and also how to set up relationships between the business system and the external environment. The entire implementation process should take place in the following logical steps[9]:

- Identification of environmental and social threats to business. In this step, it is necessary to identify those environmental and social aspects that are relevant for the given enterprise. There can be more of these factors and they can be different from company to company. It always depends on the company and its field of business, on the products, production processes, location of the company, etc. It is always necessary to select the important ones that would provide a basic overview of environmental and social problems. A matrix of aspects is drawn up, which should be structured according to the inputs used, environmental and social impacts and stakeholders.
- Analysis of the strategic importance of environmental and social aspects. In this step, it is necessary to identify strategically important environmental and social aspects – that is, a set of aspects that can potentially significantly affect the success of the business.
- Creating a strategic map of causes and consequences. This step reflects the link between strategically important environmental and social aspects and corporate goals and activities – their potential impact on business success is assessed. As part of this step, a strategic map is used as a tool.
- Defining key indicators and determining their measurement methods (the goal is to provide information about the company's performance with regard to sustainable development). Based on the previous step, goals for individual management levels, performance indicators and actions (activities) that should be implemented are set.
- Characteristics of key performance indicators, communication and reporting of business activities.

- System implementation, review and reporting of sustainable development indicators. It is necessary to ensure that the system is constantly reviewed in relation to the branch of the chemical industry and its specificities.

The implementation of the principles of the circular economy and social responsibility will therefore logically affect the economic performance of the company, and not only in the field of the chemical industry. However, the promotion of the concept brings certain indisputable advantages[10]. And there are several reasons for this:

- There is an increase in the economic-environmental efficiency of technological processes,
- negative impacts on health, the environment and property are mitigated,
- the company's relationship to sustainable development can be a "marketing" element that can contribute to improving economic results,
- the application of approaches that are in line with sustainable development means prevention against potential problems when dealing with state authorities, self-government and other representatives of civil society,
- the adoption of the principles of sustainable development increases the positive relationship of employees to the company and thus significant economic effects can be achieved,
- the attractiveness for potential investors and international cooperation increases.

Materials and methods

The qualitative research method, a semi-structured in-depth interview, was used to obtain data. The research took place in the second half of 2023. A conceptual framework was established and a framework scenario was created based on a literature search. The framework scenario was first verified in a pilot study involving two subjects from the study group. It turned out to be appropriate to add a short-structured questionnaire with the characteristics of the company's demographic data to the interview, which the respondents could fill out themselves before the interviewer's visit.

The research sample was selected using a purposeful, selective method. Representatives of companies from various sectors of the chemical industry participated in the research and respondents from a wide range of management areas were approached to understand the significance and context of BBE/CE for the activities of chemical companies as a whole. Initially, 45 respondents were contacted by email, 18 agreed, most of whom (14) stated that their company size was 50-249 employees, 3 respondents represented the company size category of up to 49 employees and 1 respondent represented a company with more than 250 employees. The respondents were then scheduled for a visit, during which they were provided with semi-structured interviews lasting 60-90 minutes. The interviews were conducted based on a framework scenario, which, due to the diversity of the issues under investigation, the researchers continuously supplemented according to the current direction of the interview. The interviews were always conducted in the respondent's parent company.

The interviews were subsequently analysed and completed with the results of the authors' previous research[11]. Thanks to this, more massive guidelines and recommendations in the field of environmental management of companies that are moving towards a circular economy could be adopted.

Results

The proposal for managing a company towards sustainability partly emerged from the authors' previous qualitative research, where the next phase of research was declared. After a critical evaluation of all available information, the authors present theses and principles for the environmental management of companies. These points are structured in the form of Table 1:

Table I

Business management towards sustainable development

Management phase	Intention
Vision (to define a vision for sustainable development and ensure leadership support)	• Subscribe to the principles of sustainable development and ensure that this commitment is accepted by senior management. • Identify stakeholders and initiate a dialogue with them about key impacts and proposed approaches to their resolution. • Formulate the corporate mission, vision and basic principles and strategies with regard to sustainable development and ensure their regular review.

	• To emphasize the need to be aware of the problems of sustainable development and their influence on business success (also with regard to the development of requirements in this area). • Ensure that the corporate culture supports development towards sustainability.
Planning (suggesting what needs to be done to improve business performance)	• Ensure the company's current performance with regard to sustainable development, legal requirements in this area and accept voluntary commitments. • Identify key issues and set priorities. • Develop strategic plans that are in line with the corporate vision and address all significant issues regarding sustainable development. • Plans to discuss with stakeholders. • Process tactical and operational plans that are in line with strategic plans and define goals, target values and responsibilities.
Implementation management (improve performance)	• Design programs so that they are in line with strategic plans and tactical-operational plans and corporate vision. • Ensure that individual actions (activities), impacts and results are managed (controlled and directed) and that they are in accordance with legal requirements and voluntarily accepted commitments. • Through strategies and action plans resulting from them, to improve the performance of the company with regard to sustainable development. • Influence suppliers and other business partners to respect the principles of sustainable development.
Monitoring and reporting (check business performance and report results)	• Monitor results and compare them with established goals and target values, analyse deviations and identify the causes of their occurrence. • Communicate with stakeholders through reporting and build feedback in order to create prerequisites for effective review of strategic and tactical-operational objectives and to implement corresponding changes.

The following section of our conclusions identifies problematic points in circular economy management. The identified theses are supported by further research into general knowledge.

The principles of the circular economy are associated with a number of benefits, but also barriers. Both are an important part of management for sustainability-focused companies.

Environmental benefits

Among the most frequently cited environmental benefits is a reduction in the number of raw materials used for production and, with them, a lower consumption of non-renewable resources[10,12]. Another obvious benefit is the minimization of waste generation along the entire life chain of materials or the products themselves[13]. Significantly lower carbon and greenhouse gas emissions compared to linear production. Another environmental benefit can be found in the area of water and its circulation.

Economic benefits

These benefits can result from savings on material inputs. According to the European Commission, more efficient use of raw materials and resources throughout the supply chain could reduce the need for new raw materials by up to 24% by 2030, with savings for European industry estimated at €630 billion per year. By cycling material flows, a lower dependence on imported raw materials will also be achieved[14]. Sources of reduced costs can come from savings in waste management[15], emission allowances and environmental taxes, or from energy savings. Companies can also achieve higher profits through higher income, for example, from sales of waste to other processors, from obtaining energy from waste. The circular economy will also have a significant impact on economic growth, which may increase to a value of 4.5 trillion dollars worldwide by 2030[16].

Benefits to society

In addition to the environmental and economic benefits, there is also much discussion about the benefits for society, which mainly result from the creation of new jobs. The European Commission points to the fact that the transition to non-linear production models will undoubtedly lead to the loss of jobs and the creation of new ones, with the new ones prevailing. According to the assessment of the European Commission, up to 178,000 new jobs could be created by 2030 in the area of waste management alone[14]. Linking between businesses to close the material flow leads to greater transparency and greater company involvement in the product chain, for example through recycling.

Operational benefits from the perspective of companies

This study[13] points to benefits in 4 areas, namely: environmental, economic, social and legislative. In the economic area, businesses value cost reduction through sustainable sourcing and supply chain management, revenue from waste sales, as well as creating new revenue streams through more efficient product life cycle management. In the environmental field, the most significant benefits are perceived as: increasing availability of green products, reduction of ecological pollution and prevention of the creation of toxic materials. Companies consider the improvement of awareness of environmental problems, the creation of new jobs and the improvement of relations between the industrial sector and local communities to be other benefits.

Cultural barriers

Cultural, or also social barriers, are defined as those limitations that result from customs, and to overcome them, a change in consumption habits and behavior of members of the distribution chain and end users is required[12]. The problem also lies in the fact that customers prefer new products to recycled products because they attach less value to them. Three of the five largest barriers are of a social nature[16].

Legislative barriers

Current legislation and regulations are more focused on a linear economy, although state and multinational bodies are gradually starting to take appropriate steps. As a result, some aspects of (national and European) legislation may hinder the transition to a circular economy. Legislative barriers also arise in the areas of ownership, finance, transport of waste across borders, input taxation mentioned[13].

Market barriers

Market barriers prevent the transition to a circular economy due to low prices of original materials, the costs of implementing new business models. Low raw material prices would make it impossible for circular economy products to outperform linear mass flow products[12].

Technological barriers

Ecodesign and recycling technologies are critical to implementing a circular economy. The way and the form in which the products are manufactured represent a significant problem for re-use, recycling and remanufacturing[15]. Life cycle costing analysis suggests that a large proportion of the opportunities to reduce the costs of projects or products can be found in their development phase.

Discussion and results analysis

The exhaustibility of natural resources and the limited assimilation capacity of nature in relation to emissions from the chemical industry are gradually forcing society to address the issue of applying the circular economy in the chemical industry sector. It is clear that even in this sector the linear way of production "take-make-dispose" must be replaced by closed-cycle solutions and zero-waste alternatives that can serve as a tool to solve global crises such as climate change, reduced biological diversity but also the lack of food, water and energy. The concept of green chemistry has become established among experts. The global green chemistry market is projected to reach USD 229.04 trillion in 2030, more than double that of 2021[13]. 12 principles of green chemistry are defined:

1. prevention – prevention of waste generation, when it is also more economically advantageous to focus on prevention than on subsequent disposal,
2. atomic economy – synthesis should be carried out at an optimal stoichiometric amount so that no waste is created,
3. safer synthesis – synthesis should be designed so that unusable or dangerous chemicals do not enter,
4. safer chemicals – the lowest possible toxicity of chemicals,
5. use of safer solvents – the use of organic solvents should be limited as much as possible,

6. design for efficient use of energy – design of processes so that they consume as little energy as possible,
7. use of renewable raw materials – whenever it is economically and technologically possible, renewable raw materials should be used instead of non-renewable ones,
8. reduction in the creation of derivatives,
9. catalysis – the use of as many selective catalysts as possible is preferred,
10. production of degradable products – creation of chemicals that break down into harmless products after use,
11. real-time process analysis – process monitoring must prevent the formation of dangerous chemicals,
12. minimization of potential accidents – the substances themselves, as well as the way they are used in the chemical process, should be chosen in such a way that they represent the least possible risk and thus prevent accidents and injuries.

Circular chemistry

The green chemistry framework can be considered suitable for the transition from linear to circular business models. Green chemistry develops innovative models that could easily be incorporated into the circular economy or industrial ecology. The poor definition of the relationship between these disciplines can also be the reason why studies related to green chemistry do not connect with circularity. How often these two terms are used can be seen from figure number 1. It also shows that the term green chemistry was used long before the concept of circular economy started to be talked about.

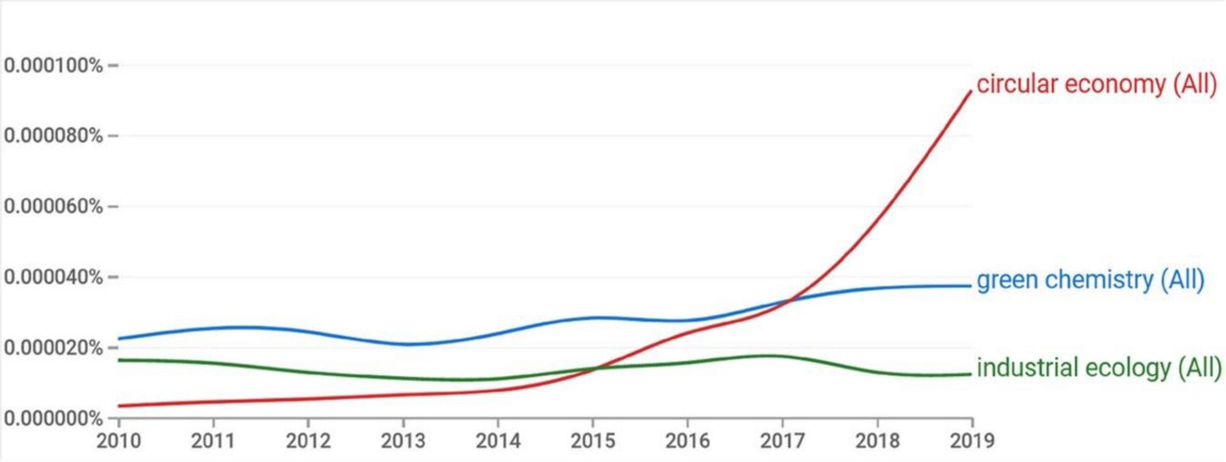

Figure 1. Popularity of terms (Google trends, b.r.)

Principles of circular chemistry based on the principles of green chemistry:

1. collect and use waste – waste is a valuable resource that should be transformed into products,
2. maximize the circulation of atoms – circular processes should aim to maximize the use of all atoms in molecules,
3. optimize resource efficiency – efforts should be made to support re-use and maintain the highest possible added value of products,
4. optimize energy use – energy efficiency should be maximized,
5. increase the efficiency of the process – innovation should constantly improve the possibilities of reuse and recycling during and after the process, preferably directly at the point of production,
6. no toxicity outside the plant – chemical processes should not release any toxic compounds into the environment,

7. focus on optimal design – the design of the product should be such that it allows the preservation of the highest possible value of the product,
8. assess sustainability – environmental assessment of the process (typically LCA) should become prevalent to identify chemical process inefficiencies,
9. apply the 9R framework – end-of-life products should be further used by a circular strategy placed as high as possible in the 9R hierarchy,
10. sell a service, not a product – manufacturers should use service-based business models, such as chemical leasing, that promote efficiency,
11. innovation environment – the business and regulatory environment should be flexible to enable the introduction of innovations,
12. unify the industry and establish a unified corporate policy – manufacturing and corporate policy should be unified to create an optimal environment enabling circularity in chemical processes.

Conclusion

The circular economy is gaining ground in Czech business and has become part of the government program. It is clear that there is no other alternative for reducing the environmental burden, improving energy efficiency and making better use of resources. The circular economy therefore represents a huge opportunity. An opportunity not only for the environment. At the European level, the circular economy is already one of the main priorities for efficient management of resources.

The gradual transition, also supported by legislation and environmental policy, leads to the fact that production begins to be oriented towards the efficient use of resources, the transition to renewable resources, the prevention of waste and the design of products in such a way that they can return to circulation, that is, circulate. So, the goal of all companies, not just chemical companies, should be to achieve such a level of process control that all resources circulate in the highest quality for as long as possible. It's about overcoming all the barriers and taking advantage of all the expected benefits. These are the main ideas of the circular economy. we live in a time when economic development must go hand in hand with ecological aspects.

References

1. Ameer, R., Othman, R.: Sustainability Practices and Corporate Financial Performance, A Study Based on the Top Global Corporations. *Journal of Business Ethics*. 108, 61-79 (2017).
2. Lanolizelee, F. Q.: Are Competition and Corporate Social Responsibility Compatible? *Society and Business Review*. 6 (1) (2019).
3. James, P., Wehrmeyer, W.: Environmental Performance Measurement. In: Groenewegen, P., Fischer, K., Jenkins, E.G., Schot, J.E., eds. The Greening of Industry Resource Guide and Bibliography. Washington DC: Island Press, s. 111-136 (2016).
4. Cordasco, P.: Consumers Continue to Prioritize Social Responsibility. Across Business Sectors, Despite Recession [online]. [ac. 2024-04-16]. Available: http://www.burson-marsteller.com/newsroom/lists/Press Releases.
5. Bierma, T.J., Watterstraat, F.L.: Chemical Management: Overcoming Barriers to Diffusion [online]. Waste Management and Research Center Report, RRE87 [accesed 2024-05-06]. Available: http://www.istc.illinois.edu/info/library_docs/rr/RR87ChemicalManagement.pdf.
6. Henriques, I., Sadorsky, P.: The Relationship between Environmental Commitment and Managerial Perceptions of Stakeholder Importance. Academy of Management Journal. 42 (1), 87-99 (2022).
7. Schaltegger, S., Wagner, M., 2006. Managing Sustainability Performance Measurement and Reporting in an Integrated Manner. In: Schaltegger, S., BEennett, M., Burritt, R., eds. Sustainability Accounting and Reporting. Dordrecht: Springer, s. 681–697 (2017).
8. Bansal, P., Roth, K.: Why Companies Go Green: A Model of Ecological Responsiveness. Academy of Management Journal. 43 (4), 717-736 (2018).
9. Asif, M.: An Integrated Management Systems Approach to Corporate Sustainability. European Business Review. 23 (4) (2021).

10. Robins, F.: Why Corporate Social Responsibility Should Be Popularized but not Imposed. Corporate Governance. 8 (3), 330-341 (2018).
11. Kutnohorská, O., Strachotová, D. Cirkular economy in enterprises of the czech chemical industry. In: PROCEEDINGS of the 10th International Conference on Chemical Technology (2023).
12. Baars, J., Domenech, T., Bleischwitz, J., Melin, H., J, Heindrich, O.: Circular economy strategies for electric vehicle batteries reduce reliance on raw materials. Nature Sustainability [online]. 4(1), 71-79 [ac. 2024-02-02] (2021).
13. European Comission, 2020. Circular economy action plan. European comission [online]. Brusel: European union, 2020 [ac. 2024-01-31]. Available: https://environment.ec.europa.eu/strategy/circular-economy-action-plan_en (2024).
14. Howard, H., Yan, M., X., Mustafee. N., Charnley, F., Böhm, S., Pascucci, S.: Going beyond waste reduction: Exploring tools and methods for circular economy adoption in small-medium enterprises. Resources, Conservation and Recycling [online]. 182 [ac. 2024-02-02] (2022).
15. Esmaeili, M., Allameh, G., Tajvidi, T., Using game theory for analysing pricing models in closed-loop supply chain from short- and long-term perspectives. *International Journal of Production Research* [online]. 54(7), 2152-2169 [ac. 2024-02-03] (2015).
16. Lacy, P., Long, J., Spindler, W.: The circular economy handbook: realizing the circular advantage. 1. London: Palgrave Macmillan (2020).

IMPACTS OF CLIMATE CHANGE ON CHEMICAL ENTERPRISES

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Abstract

Climate change is becoming an undeniable fact and affects every individual, the public and industrial enterprises. Rising temperatures caused by greenhouse gas emissions create several direct impacts on the operations of industrial enterprises and force them to respond to changing climate conditions. Deterioration of access to quality water, protection against extreme manifestations of climate change in the form of floods, extreme wind or long-term tropical temperatures, forces management to introduce mitigation and adaptation measures to climate change at the corporate level. In addition to the costs of decarbonisation of industry and the obligation to purchase emission allowances, a considerable part of the funds must therefore be spent on the direct effects of climate change. The degree of threat from climate change and the impact of adaptation measures on the economic performance of industrial enterprises was mapped by qualitative research in a selected chemical enterprise. The fundamental consequences of climate change for industrial enterprises were identified, as well as the adaptation and mitigation measures being adopted.

Introduction

Climate change represents one of the most important global challenges of the present, but also of the future, it has a significant impact on the environment, the economy and society. Even industrial enterprises are becoming one of the key actors that are confronted with the consequences of these changes. Industrial enterprises not only represent the cornerstones of the economy but are also important players in shaping our society. In connection with climate change, industrial enterprises find themselves in an environment of constant changes and challenges. They are forced to adapt their production processes and business strategies to minimize the negative impacts of climate change while taking advantage of opportunities for innovation and sustainable development. This dynamic creates space for the implementation of new approaches and technologies that will enable industrial enterprises to successfully respond to the challenges related to climate change and at the same time strengthen their competitiveness.

The impacts of climate change on society and their perception were investigated at the global level by Leiserowitz et al.[1] and consistent with previous research Brechin and Bhandari[2] confirmed, climate change is perceived as a serious social problem. Currently, the main cause of climate change is mainly human activity, which causes an increase in greenhouse gases in the atmosphere, which Barros[3] identified in his research. Related negative scenarios of lack of raw materials and resources (especially water) for society and industry were also published by Wilhite[4], the necessity to develop crucial drought mitigation strategies was formulated by Serraj et al.[5], suitable measures for Europe in this regard were formulated by Vogt & Somma[6].

After the general agreement of the developed countries of the world that climate change is indeed occurring because of human activity, there is also an agreement that it is necessary to react to phenomena already underway, which are practically impossible to reverse, but especially to try to treat future threats of much more serious changes. In particular, the previously mentioned anthropogenic factors need to be addressed, which should be the primary goal of future climate action. In addition to the mentioned factors causing climate change, it is also essential to find out what all can be included among the consequences, i.e., climate manifestations and what affects individual stakeholders because of the greenhouse effect, and then to define the consequences for businesses. Manifestations of climate change cause a variety of consequences, some of them are directly evident, such as an increase in air temperature, warming of the oceans, melting of glaciers, rising ocean levels, others less causal and obvious, such as soil erosion, torrential rains, less snow, warmer winters and long periods of drought, which also have negative impacts and affect many fields, e.g. agriculture, medicine, energy and, last but not least, industry[7].

The potential serious effects of climate change on competitiveness are mentioned by Kee et al.[8], and the necessary management skill to efficiently use its resources in the conditions of climate change is demonstrated by Ullah et al.[9]. Individual climate manifestations have different risks for businesses and therefore require a holistic and diversified approach. In addition to the direct climatic effects, the secondary consequences on the

European market with emission allowances and the CBAM system, which have direct impacts on the energy management of enterprises and the overall competitiveness of corporations, are also essential.

Climate manifestations and their impacts

Changes in the climate system, according to the Intergovernmental Panel on Climate Change, can be observed since the 1950s. Since then, the atmosphere and ocean have been warming, the amount of snow is decreasing, and the ocean level is rising. According to the authors of the study European climate of the past 500 years[10], the European climate is characterized by regional variability, the main influence on it is atmospheric circulation. When comparing the European climate to the global one, the European climate change is up to half as high, with the greatest warming observed in summer and the least in autumn. However, Europe is characterized by extreme high temperatures rather than cold extremes[10].

Climate change is not just about changing temperatures, but also changing precipitation patterns, melting glaciers, and rising sea levels. As a result of temperature changes, there are increased dry periods, when the combination of increasing water temperature and increasing dry periods, water quality is reduced, a greater occurrence of sudden extreme rains also contributes to the deterioration of water quality, a change in the volume of snow and glaciers can negatively affect inland shipping and hydropower production. As a result of the above-mentioned phenomena (dry periods, increased air temperature, extreme temperatures, or increased rainfall variability), other manifestations occur that affect not only businesses, but also society, such as floods or vegetation fires. Consider the following as the main phenomena of climate change: increased air temperature, extremely high temperatures, variability of precipitation totals, floods and flash floods, dry periods, vegetation fires, snow characteristics, and extreme wind.

While so far research initiatives have focused mainly on the influence of climate change on the cultivation of various crops with an impact on the food or textile industry[11,12], the influence of climate change and climate manifestations on industrial production has not been given significant attention. In doing so, it is possible to identify several impacts of climate phenomena on industrial enterprises. Rising temperatures cause insufficient cooling consequences for production itself, e.g., production slowdown, affecting the stability and reactivity of chemical substances, change in the rate of chemical reactions, increase in wastewater temperature, wear, and tear of production equipment and at the same time increase in greenhouse gas emissions. Extremely high temperatures also have negative effects on the health of employees with the consequences of shortening work shifts, increasing the number of breaks, installing additional sources of cooling (fans, air conditioning) and ensuring enough fluids protective clothing. Drought seasons and areas cause not only a lack of water, but also drying of material and product and increasing the risk of fires. Floods and flash floods cause flooding of production areas, damage to buildings, damage to production equipment, infrastructure damage, destruction of stocks and products and can subsequently cause leaching of dangerous and toxic substances and production failures. Fires and extreme wind can cause similar damage to property, equipment, facilities, and infrastructure like floods, as well as leaching of dangerous and toxic substances and production failures.

In addition to direct climate impacts, industrial enterprises are also indirectly affected by the policy of the European Union, which, under the influence of the Paris Agreement and the Green Deal, adopted trading system of Emissions allowances (EU ETS), which are a fundamental tool for regulating emissions on EU territory. However, their high prices have a noticeable impact on production costs, they encourage speculative purchases, which bring difficulties for companies due to price fluctuations of these allowances[13]. Complementing the EU's emissions trading system, the European Commission has proposed a Carbon Border Adjustment Mechanism (CBAM) that would apply a carbon price to import-related emissions, another climate change adaptation measure with an impact on the business activities of industrial enterprises[14].

Finally, climate change has an impact on employees, who must deal with climate change, implement adaptation and mitigation measures, and continuously educate themselves to increase awareness of the risks of climate change and climate manifestations.

Research methodology

To confirm the theoretical basis of the impacts of climate change on industrial enterprises, a qualitative pilot study was used to map the degree of threat from individual manifestations of climate change in a chemical company, in particular, attention was paid to the extent of corporate measures caused by climate change and the impact of adaptation measures on the economic performance of industrial enterprises.

Academic research and studies from the relevant fields of research, climate change, climatic phenomena, climatic manifestations, and adaptation and mitigation measures are used to address the validity of theoretical assumptions regarding the formulation and implementation of relevant managerial decisions in business practice.

A form of qualitative research with representatives of a large chemical production company was chosen for the research itself. The intention was to address representatives of a multinational corporation with demonstrable experience with the implementation of measures against climate change. The pre-selection was made based on press releases and regular environmental reports, on the assumption that a large multinational company has sufficient resources to identify, classify, diversify, and make decisions on adaptation and mitigation measures at the corporate level.

Based on a theoretical basis qualitative research was carried out as structured one-to-one interviews with managers of a chemical company producing basic chemical acids and nitrogen fertilizers. The respondents were the company managers co-responsible for taking relevant measures to reduce energy consumption, protect property and comply with health and safety principles at work. The research was carried out in the period January 2024 – April 2024. Information obtained was processed using content analysis. The first set of questions investigated the company's general approach to climate change and related measures taken by the company in relation to individual climate manifestations. The second set of questions investigated the measures taken in connection with emission limits and emission allowances. The third set of questions was focused on the impact of climate change on internal stakeholders, especially employees.

Research findings

The first set of questions first confirmed that the representatives of the company do not perceive the direct manifestations of climate change as a fundamental critical factor threatening the competitiveness of the company and consider the problem of high prices of emission permits to be much more serious, which, on the contrary, they consider to be a threat to competitiveness. Furthermore, it was confirmed that they apply a differentiated approach to individual manifestations of climate change regarding the risks that could arise in the wake of individual climatic manifestations. Table 1 shows the breakdown of the risk of individual climatic manifestations.

Table I

Significance of individual climatic manifestations

High	Moderate	Low
Rising temperatures	Extremely high temperatures	Drought seasons and areas
Floods and flash floods	Variability of precipitation	Snow characteristics
		Extreme wind & Fires

The main consequences that a business faces in relation to climate phenomena are property damage, possible increase in operating costs, and production interruptions, which ultimately will always threaten the company's financial performance, long-term sustainability, and competitiveness in the market. The company therefore deals with high- and medium-risk climate events and invests in security and the implementation of preventive measures to minimize their impact.

The second part of the questioning showed that the management perceives the consequence of the rising prices of emission allowances in the EU ETS system as essential, which results from the nature of production, which is highly energy-intensive and therefore the price of emission allowances is a significant cost item. Therefore, the company pays considerable attention to sources of emissions and waste. It measures the company's carbon footprint at the Scope 1 and Scope 2 levels, and sets strict targets for reducing direct emissions, especially with the promise of cost savings. Implement dozens of clean technology and innovation projects. The issue of the carbon duty (CBAM) does not currently directly concern the company. The company is not currently forced to import materials and intermediate products from outside the EU, so it does not expect the carbon duty to have any major role in the cost of purchase or trade. Other adaptation or mitigation system measures do not have a significant effect on the company's competitiveness.

Based on the third part of the research, it was found that although significant risks of climate manifestations are not perceived, the company adopts some adaptation measures. A responsible approach to reducing emissions is already part of the company's strategic goals and they have the full support of the company's management. The current level of education of employees in climate change and adaptation issues is usually limited only to mandatory EMS and OHSAS training. Employees could actively participate in proposals and innovations in the areas of environmental protection, emissions and energy, and the direction of their development is mainly in the environmental dimension.

Discussion and result analysis

Research has confirmed that one of the key climate phenomena that has a significant impact on the operation of industrial enterprises is the increase in air temperature. This climatic phenomenon brings with it several challenges that are reflected in the day-to-day functioning of the company. If the air temperature rises to unexpectedly high values, industrial equipment faces considerable difficulties, especially in cooling and maintaining optimal working conditions. This phenomenon not only creates logistical obstacles and technical complications, but also increases demands on energy consumption, which can have a significant impact on the overall efficiency of operation and financial performance of the company. Rising air temperatures influence the reactivity of chemical substances in industrial processes. Although it is not a significant risk factor, it is considered that increasing the temperature can affect the behavior and stability of materials, semi-finished products, and final products. Finally, high temperatures can lead to discomfort and fatigue of employees, which can reduce their productivity and increase the risk of occupational accidents.

The management of the company confirmed the increased risk of floods and flooding, which is caused by the strategic, but risky geographical location by a large river. In the past, the company had to deal with the consequences of two serious floods. Extensive damage to the property and infrastructure of the company and led to a temporary stop of its operation, significant financial losses, and loss of market share. Therefore, the company makes strategic investments for property protection, developed, and implemented preventive measures and crisis management plans that allow it to better respond to future floods and minimize their negative effects on the operation and financial stability of the company.

Intense rainfall represents a medium-evaluated risk, while the fundamental problem is the potential exceeding of the capacity of treatment and purification of wastewater with risks of dangerous substances being washed into the surroundings of the company. The increase in the number of extremely hot days is mainly negative from the perspective of employees, who may suffer from unpleasant conditions in the working environment and may struggle with fatigue and impaired work performance, which the company solves with operational measures to adjust working hours, increased frequency of breaks and adherence to drinking regime.

The company perceives as insignificant the risks associated with periods of drought (strategic position near a large river), occurrence of fires, extreme wind (low probability of occurrence) or changes in snow characteristics (does not affect the production process).

Current legislation, especially integration into the EU ETS system, creates a significant regulatory and administrative burden for the company. Not only emissions allowance prices, but also environmental legislation limit emissions and require effective management and monitoring of emission factors.

The company therefore perceives the volume of emissions and emission allowances as an important factor affecting economic stability and will continue to support the implementation of measures to reduce the carbon footprint, the introduction of emission-free technologies and the implementation of projects and investments to fulfill the Green Deal goals.

The amount of investments and the number of implemented projects proves that the company actively responds to challenges and requirements related to sustainable development and environmental protection, but at the same time uses these opportunities to strengthen its position on the market and for long-term sustainable growth. Finally, the company also supports ESG and environmental protection activities with the secondary goal of increasing the company's reputation and image.

The company has plans and guidelines that monitor and evaluate the implementation of selected climate change related adaptation and mitigation measures both internally within the concern and in accordance with legislative requirements. However, the systematic education of employees on how to proceed correctly in the event of extreme climatic manifestations and how to minimize risks to their health and safety in the company is not yet sufficiently promoted. Emergency plans are formulated in the event of a fire, but there are no alternative instructions in the event of service interruption due to floods or extreme winds. These plans would allow the company to prepare for possible unforeseen events and would minimize adverse effects on the business's operations and stability.

Conclusion

Based on the content analysis of the obtained information, it is possible to evaluate the company's proactive approach to the issue of climate change. The company rationally implements measures related to risky climatic manifestations, such as rising air temperature and the risk of inundation of the premises during floods and flash floods, where it does not hesitate to invest. Conversely, for less risky climate manifestations, the company does not spend significant investments.

The conducted pilot research cannot be generalized, as the company's approach to climate change and climate manifestations is highly dependent on the geographical conditions in which the company or production plant is located. While the lack of water is not a significant factor in the investigated enterprise, for other industrial enterprises located outside of sufficient sources of high-quality water, they can evaluate this as a very essential and risky factor. It is therefore desirable to approach adaptation and mitigation measures based on a thoroughly performed risk analysis, SWOT analysis and apply a diversified approach to the implementation of meaningful measures.

Other variables that can influence management's approach in taking measures due to climate change are the climatic conditions in the area of operation, the energy intensity of the industry, the energy intensity of the production process itself, the availability of alternative sources of energy and water or the level of emissions released by the company. Finally, the proactive approach of the management in promoting the strategic goals of the company in connection with the promotion of the goals of the Paris Climate Agreement and a responsible approach to solving climate change on Earth.

Acknowledgement

This work was supported by project “Research into modern methods and processes of environmental and chemical engineering and sustainable process operations management” No. SGS_2024_003.

References

1. Leiserowitz A., Carman J., Buttermore N., Neyens L., Rosenthal S., Marlon J., Schneider J., Mulcahy K.: *International Public Opinion on Climate Change,* Yale, New Haven, CT 2022.
2. Brechin S. R., Bhandari M.: WIREs Clim Change, *2,* 871 (2011).
3. Barros V.: *El Cambio Climatico Global*. Buenos Aires: Libros del Zorzal 2021.
4. Wilhite A. D.: *Drought and water crises: Science, technology, and management issues,* Crc Press, Taylor & Francis Group, Abingdon, UK 2005.
5. Serraj R., McNally K. L., Slamet-Loedin I., Kohli A., Haefele S. M., Atlin G., Kumar A.: Plant Prod. Sci. *14(1)*, 1 (2011).
6. Vogt J. V., Somma, F.: *Drought and drought mitigation in Europe (Vol. 14)*. Springer Science & Business Media 2013.
7. Schreurs M. A. Politics Gov, *22(3)*, 344 (2011).
8. Kee H. L., Ma H., Mani M.: World Econ. *33(6)*, 820 (2010).
9. Ullah G. M. W., Khan I. Abdullah M.: Int J Manag Financ., *20(3)*, 651 (2024).
10. Brázdil R., Dobrovolný P., Luterbacher j., Moberg A., Pfister Ch., Wheeler D., Zorita E.: *European climate of the past 500 years: new challenges for historical climatology. Climatic Change,* Springer, 2010.
11. Singh R. P., Prasad P. V. V., Reddy K. R.: Adv Agron, *118*, 49 (2013).
12. Barlow K. M., Christy B. P., O'Leary G. J., Riffkin P. A., Nuttall J. G.: Field Crops Res. *171*, 109 (2015).
13. Wang M., Zhou P.: Energy J. *41(6)*, 215 (2020).
14. Kuehner A. K., Jakob M., Flachsland C.: Environ. Res. Lett., *17(12)*, 124007, (2022).

INORGANIC TECHNOLOGY

PHOSPHATE ASH AS AN ALTERNATIVE WASTE SOURCE OF PHOSPHORUS FOR FERTILIZER PRODUCTION

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Abstract

Production of fertilizers containing phosphorus often involves processing phosphates from phosphate rock. Phosphate rock is a natural source of phosphorus, a crucial nutrient for plant growth.

In 2014, the EU classified phosphate rock as a critical raw material, and in 2017, phosphorus as an element was added to the list[1,2]. Typical phosphate rock contains phosphate expressed as P_2O_5 at a concentration of 25–40%. The extraction of phosphorus from waste sources gains increasing attention because phosphate rock resources are depleting. One alternative waste source of P is ash from sewage sludge after thermal treatment. Phosphate ash contains phosphorus compounds which can be biologically utilized by plants. The phosphorus content, expressed as P_2O_5, in sewage sludge ash can range from 6–25%[3]. Phosphate ash is also enriched with other nutrient components such as Ca, Mg, and possibly K. The exact composition of phosphate ash may vary depending on the specific production process and raw materials used.

Industrial technologies using sewage sludge ash as a raw material demonstrate high efficiency and utilization with lower environmental impact. Raw phosphate ash is often processed into fertilizers or can be used as an industrial additive to improve soil properties.

This contribution describes the direct application of phosphate ash after thermal processing of sewage sludge in the production of granulated fertilizers, considering not only nutrient content but also heavy metals in accordance with EC regulation[4].

Introduction

The resulting ash from the combustion of sewage sludge can contain various useful substances, such as the already phosphorus, but also hazardous substances that threaten (pose a threat to) the environment. Organic pollutants are destroyed by combustion, but heavy metals remain in the ash or, if not captured, are released into the atmosphere (e.g., toxic Pb, Cd), depending on their type and quantity, the composition of the sludge, and the settings of the process[5].

A disadvantage of sewage sludge and other sources containing phosphates, such as ash, is that the phosphorus contained is only partially in a citrat-soluble form, which makes it accessible to plants when fertilizing. A couple of methods have been developed to convert phosphorus into a water-soluble form and reduce the concentration of heavy metals in the final product: thermochemical treatment or wet extraction. The advantages of thermochemical solutions are the 98% phosphorus recovery potential and the low chemical consumption. On the other hand, investment costs, energy costs, and proper ash composition in some solutions must be considered and compensated by the size of the equipment. More flexible methods of phosphorus recovery are wet methods using acidic solutions for leaching sewage sludge ash. Extraction methods can be divided into the following groups: acid leaching with H_2SO_4, HNO_3, HCl, H_3PO_4, citric acid, and oxalic acid[6]. Less popular is the use of bases as extractants, bioextraction, or supercritical fluid extraction and wet oxidation of ash from supercritical water oxidation[6].

The aim of the work, considering the relatively high content of citrate-soluble phosphorus in the phosphate ash samples, was its direct incorporation in its raw state in the production of granulated fertilizers. In laboratory conditions, the decomposition of phosphate ash was carried out using sulfuric acid and nitric acid.

Characteristics of phosphate ash samples

The phosphorus content in the phosphate ash samples was determined in both total and citrate-soluble forms, with the latter form containing more than 75% of the total phosphorus content. Due to the relatively high content of citrate-soluble phosphorus (>75%), waste phosphate ashes were directly incorporated into the fertilizer in their raw state.

Table I
Chemical analysis of phosphate ash

Sample of phosphate ash	Ptotal %	Pcitrate %	P_2O_5total %	P_2O_5 citrate %	Pcitrate/Pcitrate*100 %
Sample No. 1	6.75	5.09	15.47	11.66	75.41
Sample No. 2	5.01	4.39	11.48	10.06	87.62

Table II
Qualitative analysis results Phospate ash – sample No.1

Phase name	Formula %
Hematite	Fe_2O_3
Quartz alpha, alpha$_2$	SiO_2
Calcium Iron Phosphate	$Ca_9Fe(PO_4)_7$
Stanfieldite, syn	$Mg_3Ca_3(PO_4)_4$
Sarcopside, syn	$Fe_3(PO_4)_2$

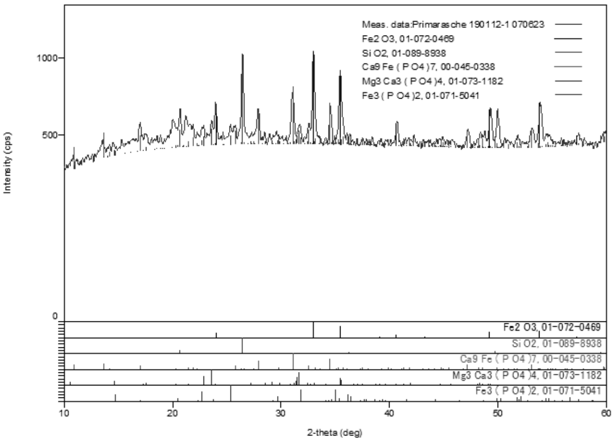

Figure 7. XRD – phase analysis – Phosphate ash – sample No.1

Figure 8. Phosphate ash sample No. 1

XRD phase analysis of the ash sample revealed the presence of hematite, quartz, calcium iron phosphate, stanfieldite – calcium magnesium phosphate, and sarcopside – iron phosphate.

Table III
OES – ICP analysis of phosphate ash, heavy metal content

Sample of phosphate ash	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	As	V	Hg
	ppm							%	ppm		
Sample No. 1	3.7	9.5	48.3	854	795	38.7	38.8	0.21	< 0.1	-	0,055
Sample No. 2	<0.1	11.8	160	750	898	48.3	56.6	0.22	< 0.1	-	0,061

The total Cr content in sample of phosphate ash No. 1 is 68 mg/kg of dry matter, with hexavalent chromium content at 0.220 mg/kg. The total Cr content in sample No. 2 is 202 mg/kg of dry matter, with hexavalent chromium content at 0.600 mg/kg. Both samples meet the conditions for hexavalent Cr content according to European regulations.

Granulated fertilizer NSP on base ammonium sulfate with phosphate ash

Quarter-plant scale plate granulation) on the ERWEKA AR 403 device was used to prepare NSP granulated fertilizer with the addition of phosphate ash. The granulation process itself went without problems, and the finished product has a brown – purple colour. Granulation is performed with steam, and the remaining part of the input mixture is gradually added until the entire quantity is incorporated. The wet granulate is dried in an oven for 2 hours at a temperature of 110 °C.

Figure 9. Laboratory plate granulator ERWEKA AR 403

Figure 10. Granulated fertilizer NSP with phosphate ash (brown – purple colour)

Table IV
Physical and chemical properties of fertilizer after production

Samples	H_2O Wet granules %	H_2O Final product %	Caking N	Granule strength N
NSP sample No. 1	8.27	0.48	6.3	53.81
NSP sample No. 2	6.03	0.38	3.8	73.49

Table V
Chemical analysis of fertilizer

Samples	N Ammon	N Total	Ca Total	CaO	Mg Total	MgO	S Total	Fe Total
					%			
NSP sample No. 1	11.90	14.40	6.42	8.98	0.53	0.88	12.20	4.48
NSP sample No. 2	1.50	14.20	6.02	8.42	0.53	0.88	12.30	4.00

Table VI
Chemical analysis of fertilizer – phosphorus content

Samples	Ptotal	P_2O_5total	Pwater	P_2O_5 water	Pcitrate	P_2O_5citrate	Pwater/Ptotal *100	Pcitrate/Ptotal *100
					%			
NSP sample No. 1	2.79	6.39	0.12	0.27	1.67	3.83	4.30	59.86
NSP sample No. 2	2.79	6.39	0.11	0.25	1.74	3.99	3.94	62.37

Table VII
OES – ICP analysis of fertilizer, heavy metal content

Samples	Cd	Pb	Hg	As	Cr	Ni	Se	V	Co
					ppm				
NSP sample No. 1	1.23	15.8	0.019	7.1	55.4	18	< 0.1	12.8	2.6
NSP sample No. 2	1.14	14	0.020	7.6	47.3	15.5	< 0.1	13.3	2.0

Fertilizer NSP with a phosphate ash content of 30% complies with the regulation regarding heavy metal content.

Granulated fertilizer NSP 19-10-6

NSP 19-10-6 type fertilizer with the addition of powdered phosphate ash was also prepared by quarter-plant scale plate granulation. The produced fertilizer has had a burgundy – brown colour and standard physicochemical properties suitable for quarter-plant scale research. The content of heavy metals has met the legislative requirements.

Table VIII
Physical and chemical properties of fertilizer NSP 19-10-6

Samples of the fertilizer	H_2O Final Product %	Granule strength N	Dustiness %	Abrasion %	Caking N
Sample No. 1	0.960	42.79	0.13	0.86	196.2
Sample No. 2	0.785	62.27	0.14	0.2	183.1
Sample No. 3	1.014	74.33	0.14	0.15	234.8

Figure 11. Granulated fertilizer NSP 19 -10 - 6 + 4,5 CaO
(burgundy – brown colour)

Table IX
Chemical analysis of fertilizer

Sample	N total	Ca	CaO	S	P total	P_2O_5 total	P citrate	P_2O_5 citrate	P citrate/P total *100
						%			
Sample No. 1	18.89	3.29	4.60	9.82	2.58	5.91	2.36	5.41	91.47
Sample No. 2	19.10	3.08	4.31	9.61	2.43	5.57	2.31	5.29	95.06

Table X
OES – ICP analysis of fertilizer, heavy metal content

Samples	Cd	Pb	Hg	As	Cr	Ni	Se	V	Co
					ppm				
NSP sample No. 2	0.1	1.8	51	210	273	19.3	15.9	690	5.1

Decomposition of phosphate ash

The decomposition of phosphate ash under laboratory conditions was tested using sulfuric acid and nitric acid. After adding sulfuric or nitric acid to the ash suspension in water, phosphorus is displaced in the form of phosphoric acid. Calcium sulfate is formed during the reaction of sulfuric acid with calcium magnesium iron phosphate. Part of it is dissolved in the filtrate, part is precipitated as a solid, what increase the weight of the filter cake.

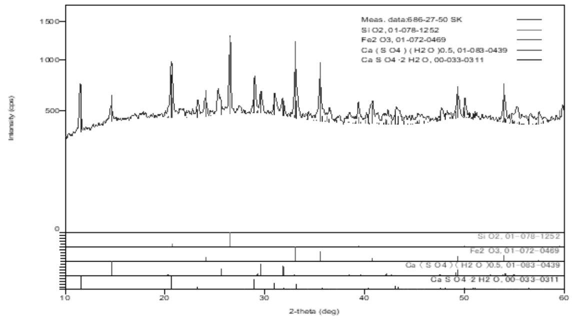

Figure 12. XRD – Phase analysis – Dry filter cake after decomposition P – ash with H_2SO_4

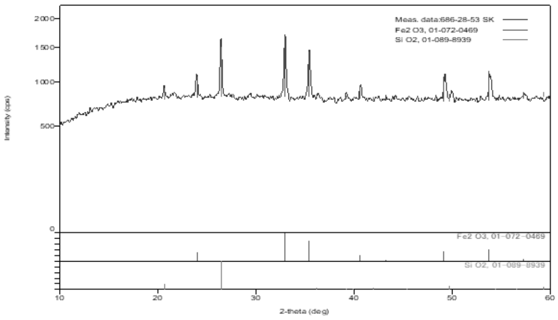

Figure 13. XRD – Phase analysis – Dry filter cake after decomposition P – ash with HNO_3

XRD – phase analysis of the dry filter cake after decomposition of the ash by sulfuric acid demonstrated the presence of quartz, hematite, bassanite, and gypsum (Fig. 6.). XRD – phase analysis of the dry filter cake after decomposition by nitric acid demonstrated the presence of only quartz and hematite (Fig. 7.).

Phosphorus was separated in the filter cake after neutralization by ammonia solution as low – soluble phosphate – $MgNH_4PO_4.6H_2O$.

Figure 14. Neutralization of the filtrate after decomposition of P – ash

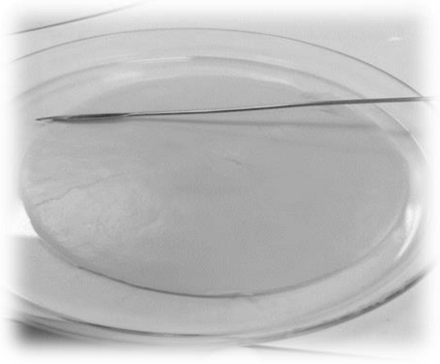

Figure 15. Dry filter cake after the neutralization of the filtrate – struvite

Conclusion

The aim of the work was the direct application of raw ash in the production of granular fertilizers. Experiments were evaluated by determining physicochemical parameters, phosphorus content, micronutrient content and heavy metal content. In laboratory conditions, the decomposition of phosphate ash was made with sulphuric acid and with nitric acid.

- Incorporation of raw phosphate ash into the production of granular fertilizers (P content in waste phosphate ash is set above 5%, of which ¾ is in the form soluble in citrates) is possible. The result is a NSP fertilizer with a suitable nutrient ratio. Fertilizers met the legislative requirements in regard to the content of heavy metals.
- By decomposing the phosphate ash with H_2SO_4, the highest conversion of P was achieved, more than 97%.
- By decomposing with HNO_3, the conversion of 86 % was achieved
- After phosphate decomposition, precipitation of struvite was made by the use of the ammonia solution.

References

1. EC. Report on critical raw materials for the EU. In Report of the Ad-Hoc Working Group on Defining Critical Raw Materials; EC: Brussels, Belgium, 2014; p. 41.
2. EC. Study on the Review of the List of Critical Raw Materials; European Commission: Luxembourg, 2017; p. 93.

3. EP3495323A1 A Process for obtaining a soluble phosphate fraction from phosphate containing ash, Bulletin 2019/24.
4. REGULATION (EU) 2019/1009.
5. Matis at all, Mud over gold – Institute of circular economy, Bratislava 2023.
6. Gorazda et all: Fertilisers production from ashes after sewage sludge combustion – A strategy towards sustainable development, Environmental research, 2017/154., p.171-180.

ZEOLITES IN FERTILIZERS

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Abstract

Natural zeolite – clinoptilolite is a hydrous aluminosilicate of cations of alkali metals and alkaline earth metals from the heulandite group, which have the ability to exchange their exchangeable cations for others. The three-dimensional lattice of zeolites generally contains holes forming channels in which cations or molecules, for example water, are adsorbed[1].

The multidirectional use of zeolites in agriculture results primarily from their high porosity, sorption-ion-exchange capacity and well-developed specific surface area. Their direct application to the soil not only has a beneficial effect on the soil sorption capacity, but also reduces soil acidification and increases the efficiency of nutrient use. Better utilisation of nutrients from fertilisers gives higher yields and reduces nutrient dispersion in the environment[2].

Zeolite as an additive to ammonium nitrate affects the phase transition temperature of crystal modification IV, which is a stable form during storage. A typical phase transition temperature of IV-III is 32 to 34 °C[3]. Modified ammonium nitrate has a higher transition temperature, depending on humidity, preparation method and the presence of additives.

Each phase transition causes the degradation of granular fertilizer, reduces mechanical strength, increases dustiness and hydrophilicity.

The contribution is devoted to the research of granular fertilizer based on ammonium nitrate with zeolite. The raw material is zeolite – clinoptilolite from Nižný Hrabovec on the east of Slovakia, mined by Zeocem j.s.c. Bystré.

Introduction

The literature describes the use of many materials that have been tested alone or in combination with other materials, such as natural phosphates, potassium metaphosphate, mono and diammonium phosphate, sulphates (ammonia, calcium, potassium), potassium chloride, magnesium salts, calcium salts, sodium silicate, clays, sodium-calcium and potassium nitrates, iron cyanides and copper oxides. Porous inorganic substances with a particle size of < 100 µm such as aluminium gel, silica gel, bentonite, attapulgite, zeolites, montmorillonite are often used to increase particle strength and improve transition resistance[4]. Degradation and caking are the most important problems during storage for prilled and granulated fertilizer. It's clear that in the final stored product, depending on the air humidity and temperature, any phase change in the structure causes caking. Depending on the phase change, the fertilizer particles adhere to each other, which leads to greater caking. The article describes the effect of the addition of zeolite on the qualitative parameters of the fertilizer and also on the resistance of ammonium nitrate to thermal stress.

Characteristics of zeolite

Powdered zeolite was added to the fertilizer containing ammonium nitrate. The average size of the zeolite particles was 17.29 mm. The average size of the dolomite particles was 27.41 mm. X-ray diffraction analysis of zeolite and dolomite is in Figure 1.

Zeolite as a natural raw material comes from Nižný Hrabovec locality in Slovakia. Based on XRD – phase analysis, the following components were identified in the zeolite:

clinoptilolite-Ca $(Na_{1.32}K_{1.28}Ca_{1.72}Mg_{0.52})(Al_{6.77}Si_{29.23}O_{72})(H_2O)_{26.84}$ and cristobalite-beta SiO_2. Phases were identified in ground dolomite: dolomite $CaMg(CO_3)_2$, calcite $CaCO_3$ and quartz SiO_2.

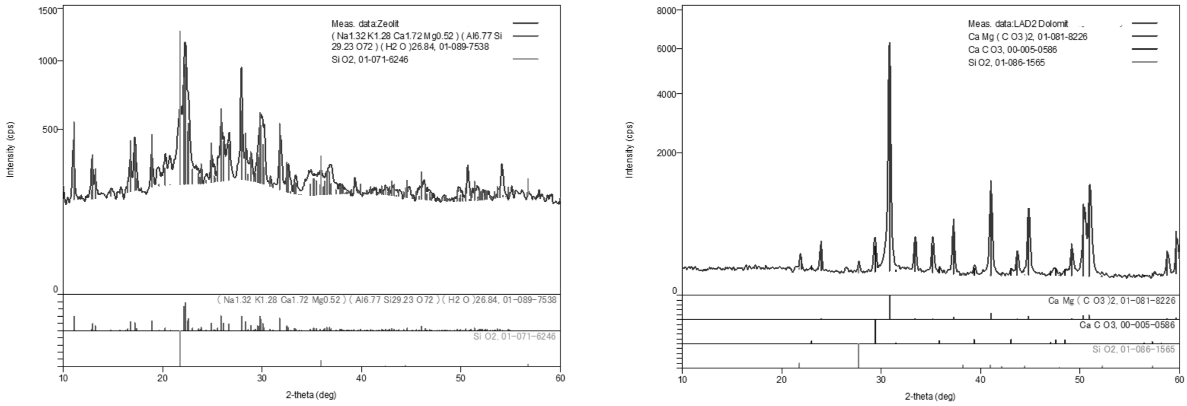

Figure 1. X-ray diffraction analysis (XRD) of zeolite (on the left) and dolomite (on the right)

Used ammonium nitrate was with a concentration of 98%. The ground zeolite and dolomite were applied for preparation of the fertilizer, where the particle size distribution was measured.

Laboratory preparation of fertilizers

Granulated fertilizers ammonium nitrate with dolomite (CAN), a combination of zeolite plus dolomite (CAN + Z) and fertilizer with only zeolite (ANZ) contain 27% nitrogen. The samples were prepared by screw granulation of the melt and the recycle. The concentration of used ammonium nitrate was 98%. The temperature of the melt before granulation was 150 °C. Granulation of the melt with recycle was followed after the addition of dolomite or zeolite. Drying of the granulate was at a temperature of 105 °C for the same time of 60 minutes. It is important to compare the physicochemical parameters of the zeolite – containing fertilizer with the quality of CAN which corresponds to the standard product. The physicochemical parameters of prepared fertilizers are in Table I.

Table I
Qualitative parameters of fertilizers

Quality parameter	Samples					
	CAN 27 / 1	CAN 27 / 2	CAN 27 +11 % Z /1	CAN 27 +11 % Z /2	ANZ 27 +21 % Z /1	ANZ 27 +21 % Z /2
H_2O, %	0.20	0.12	1.58	1.29	3.15	1.81
Dust, %	0.02	0.03	0.86	0.35	0.95	0.42
Abrasion, %	0.71	0.96	0.66	0.31	0.98	0.65
Crash point, N	63.90	73.70	63.70	73.00	68.20	74.20
Caking, N	174.50	142.00	175.20	165.00	169.30	161.00

The physicochemical parameters of the fertilizer containing zeolite indicate a comparable quality of the product, despite the high water content. No difference was noted in the granulations, despite the fact that a different filler was used.

Thermal cyclization of fertilizers

For testing the fertilizer against temperature fluctuations during storage, the procedure for thermal stress cycles for fertilizers with a high nitrogen content according to regulation (EU) 2019/1009[5] was applied. The tests are carried out at the temperature of 50 °C. The fertilizer is placed in a closed container, the influence of external moisture has been excluded.

In the samples of prepared ammonium nitrate standard (with additives and without) the equilibration during phase transformations in tenths of seconds. Transition III-IV is accompanied by a relative variation of density more than 3.5%, reduces mechanical strength, increases the dustiness and hydrophilicity (increased surface area), and finally, at a humidity higher than the critical value the reflow of fertilizer occurs[3].

Table II
Phase transitions of ammonium nitrate, temperature and related changes in volume[3]

Changes	Phase transition				
	Liquid -> I	I →II	II →III	III → IV	IV → V
Temperature, °C	169.9	125.2	84.2	32.3	-16.9
Volume change, %		1.9-2.1	1.3-1.6	3.4-3.6	0.9-2.9
ΔH, $J.g^{-1}$	73.7	52.6	15.5	18.4	5.9
Direction of volume change		Decrease	Increase	Decrease	Increase

100 g of fertilizer was poured into a 250 ml Erlenmeyer flask. The granulometry of the used fertilizer is 3.15 mm and 4 mm in a weight ratio of 1:1. The flasks with fertilizers were placed into a drying oven with a temperature of 50 °C for 2 hours, then were taken out and cooled down at a temperature of 25 °C. The procedure was repeated 6 times. 1 cycle lasts 4 hours (2 hours heating, 2 hours cooling). The granulometry and abrasion were measured after thermal cycling test of samples.

Table III
Sieve analysis of granular fertilizer before and after CAN fertilizer thermal cycling test

The content of the faction on the site, %	Fertilizer samples			
	CAN 27 / 1		CAN 27 / 2	
Number of cycles	0	6	0	6
The bottom	0.00	0.17	0.01	0.15
0.560 mm	0.00	0.08	0.00	0.07
1 mm	0.00	0.16	0.00	0.20
2 mm	2.00	1.22	3.49	2.44
3.15 mm	48.48	42.95	48.95	47.95
4 mm	48.29	47.84	47.05	46.96
Over the sieve 5 mm	1.23	7.58	0.50	2.23
Under the sieve 2 mm	0.00	0.41	0.01	0.42

Table IV
Sieve analysis of granular fertilizer before and after thermal cycling test of CAN fertilizer with half replacement of dolomite by zeolite

The content of the faction on the site, %	Fertilizer samples			
	CAN 27+11 % Z / 1		CAN 27+11 % Z / 2	
Number of cycles	0	6	0	6
The bottom	0.20	0.34	0.10	0.30
0.560 mm	0.00	0.01	0.01	0.05
1 mm	0.00	0.00	0.00	0.27
2 mm	3.43	0.47	0.36	0.38
3.15 mm	50.49	44.66	46.00	48.15
4 mm	45.04	46.96	50.93	48.47
Over the sieve 5 mm	0.84	7.56	2.60	2.38
Under the sieve 2 mm	0.20	0.35	0.11	0.62

Table V
Sieve analysis of granular fertilizer before and after thermal cycling test of ANZ fertilizer with complete replacement of dolomite by zeolite

The content of the faction on the site, %	Fertilizer samples			
	ANZ 27 21 % Z /1		ANZ 27 21 % Z / 2	
Number of cycles	0	6	0	6
The bottom	0.24	0.23	0.04	0.04
0.560 mm	0.00	0.01	0.00	0.01
1 mm	0.00	0.00	0.00	0.01
2 mm	3.60	2.21	0.16	0.10
3.15 mm	49.31	48.23	43.93	43.09
4 mm	46.22	45.70	53.37	54.15
Over the sieve 5 mm	0.63	3.62	2.50	2.60
Under the sieve 2 mm	0.24	0.24	0.04	0.06

The presence of zeolite improves the resistance of the fertilizer containing free ammonium nitrate to thermal attacks, to which the fertilizer is exposed during storage and especially during transportation, despite the incomparably higher water content in the product. Water is part of the zeolitic structure. It's necessary to respect in view of the overall stability of the product. Fertilizer containing zeolite is more resistant to abrasion.

Table VI
The results of abrasion of CAN fertilizer without and with zeolite after thermal cycling test, content of the shares under sieve 0.560 mm and 1 mm

Abrasion of fertilizer, %	Fertilizer samples					
	CAN 27 / 1	CAN 27 / 2	CAN 27 +11 % Z /1	CAN 27 +11 % Z /2	ANZ 27 +21 % Z /1	ANZ 27 +21 % Z /2
Under the sieve 0,560 mm	4.72	2.39	0.45	1.7	0.16	0.08
Under the sieve 1 mm	4.92	2.56	0.46	1.78	0.16	0.10

Comparison of CAN vs ZENFERT fertilizers resistance to thermal cyclization

The effort to maximize the zeolite content in fertilizers while respecting the final quality of the product has led to the operational production of granular fertilizer with a zeolite content of 30%. The nitrogen content in this case is 24 %. The resistance of the fertilizer to thermal cycling was determined in comparison with the standard CAN granular fertilizer with a nitrogen content of 27%. How many thermal cycles does the fertilizer last?

Figure 2. Sieve analysis of CAN 27 fertilizer after thermal cyclization 18×

Figure 3. Sieve analysis of CAN 27 fertilizer after thermal cyclization 24×

Figure 4. Sieve analysis of Zenfert 24 fertilizer after thermal cyclization 24×

Fertilizer containing zeolite didn't decompose even after 24 thermal cycles and minimally changed its granulometry. The standard CAN was also of excellent quality, but after the 12th thermal cycle it significantly deteriorated. The fertilizer after the 18th thermal cycles was unmanipulable. The fertilizer disintegrated into dust after 24th thermal cycles.

The granular fertilizer ammonium nitrate with zeolite and with the nitrogen content 24% is resistant to thermal cyclization.

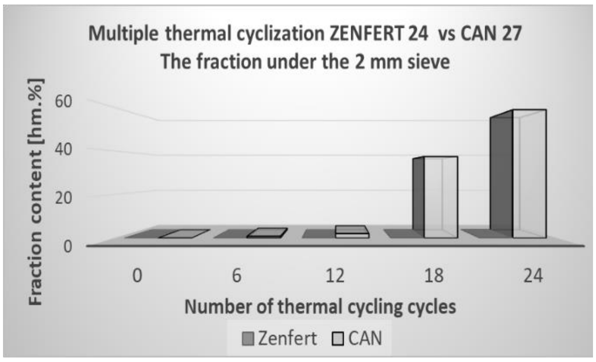

Figure 5. The content of the fraction under the 2 mm sieve after multiple thermal cyclization of fertilizers

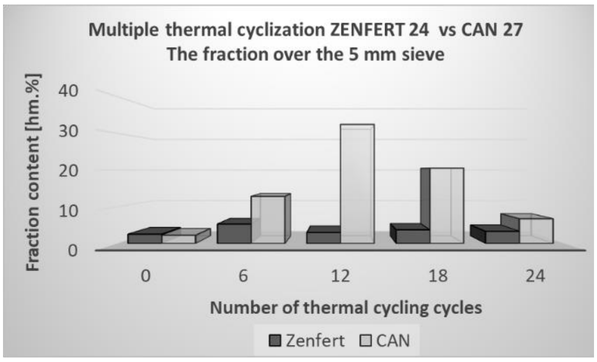

Figure 6. The content of the fraction over the 5 mm sieve after multiple thermal cyclization of fertilizers

Discussion and result analysis

The effect of thermal stress at a temperature of 50 °C on the quality of fertilizer with the addition of zeolite, which partially or completely replaced dolomite, was tested on the samples of fertilizer containing free ammonium nitrate. An increase in the volume of granules occurs during temperature changes and phase transitions. A significant difference in the increment of fraction under the 2 mm sieve is visible. The addition of zeolite to the fertilizer in the combination with ammonium nitrate significantly affects the resistance to temperature changes that accompany the fertilizer during storage and especially during transport. Physicochemical parameters are comparable despite the high water content in the product. The improved abrasion resistance of the fertilizer with the addition of zeolite is noted significantly after thermal cyclization. The operational production produced a fertilizer of excellent quality with excellent storage properties.

Conclusion

Zeolite – clinoptilolite from Nižný Hrabovec on the east of Slovakia, was applied. In combination with mineral fertilizers, zeolite helps the sorption of cations and leads to a reduction of nutrient losses through leaching.

Ammonium ions NH4+ and water H2O show the greatest affinity for binding to clinoptilolite. This property of zeolites can increase soil water capacity and improve soil hydraulic conductivity with long-term use of zeolite-containing fertilizers. In addition to the mentioned benefits, zeolite improves the qualitative properties of fertilizers and their storage properties.

References

1. M. Főldesová, P. Hudec: Štúdium povrchových vlastností slovenského prírodného zeolitu – klinoptilotitu fyzikálnou adsorpciou dusíka, Petroleum & Coal 49 (1), 34-40, 2007.
2. R. Jarosz, J. Szerement, K. Gondek, M. Mierzwa-Hersztek: The use of zeolites as an addition to fertilisers – A review, Catena, Volume 213, June 2022.
3. H. Kiiski: Properties of Ammonium Nitrate based fertilisers, University of Helsinki – Finland, Helsinki 2009.
4. Bernard Laurent, Kemira S.A., Belgium, Straight ammonium nitrate fertilizer granule – prill stabilization: Theoretical possibilities.
5. Regulation (EU) 2019/1009 of the European Parliament and of the council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003.

MATERIALS ENGINEERING

HEAT TREATMENT OF ADDITIVELY MANUFACTURED HIGH-STRENGTH MARAGING STEEL

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Abstract

Maraging steels are materials with superior strength and ductility, which they achieve through precipitation hardening during martensite aging. The 1.2709 maraging steel is also among the alloys frequently used for additive manufacturing. In this work, the effects of aging at 3 temperatures (440, 490 and 540 °C) and for 5 exposure durations (2, 4, 6, 8 and 10 h) on microstructure, phase composition, and microhardness of the 1.2709 maraging steel were mapped. For this purpose, steel additively manufactured by Laser Powder Bed Fusion was aged both in as-printed and post-print solution-annealed (820 °C/1 h) default states. Austenite reversion in the martensite matrix–having a detrimental effect on the mechanical properties–was observed and found to be related to both the manufacturing and the heat treatment processes. Solution annealing proved beneficial for the hardening process, minimised the retained austenite content, and helped to achieve the maximum microhardness of (620 ± 8) HV 0.1.

Introduction

Additive manufacturing (AM, i.e., 3D printing) is a modern process offering a fast and easily repeatable production of complex and detailed parts including unique customised parts[1,2]. As opposed to subtractive or formative manufacturing ways, the additive approach builds up each part layer by layer according to its CAD model. Laser Powder Bed Fusion (L-PBF) and Laser Direct Energy Deposition (L-DED) are the main metal additive manufacturing techniques. In both methods, the metal powder feedstock is completely melted by a laser energy source during printing[1,3,4]. Each system has some advantages, such as better resolution and precision in the case of L-PBF, or possible site-specific part repairs and composition gradients for L-DED[1,5,6]. In either case, 3D-printed metallic materials typically showcase characteristic layered, fine microstructures compared to conventionally manufactured parts[3,5,7].

Generally, the L-PBF – to which this work is dedicated – remains the most widely used method for AM of metallic materials[5,6]. In powder bed fusion processes, each part's layer profile is selectively melted in a coherent powder layer. Therefore, the whole part essentially becomes sunk in the volume of unused powder which works as a good heat conductor supporting already very high cooling rates (up to 10^8 K s^{-1} for L-PBF[7]) and the consequent appearance of a very fine microstructure[6,7].

Maraging steels are among the materials well-proven for AM with the model marked as EN 1.2709 (i.e., AISI 18Ni-300) being one of the most prominent[5,6]. The properties that allow successful and high-quality 3D printing of maraging steels are their thermal shock resistance, dimension stability, low reflectivity of laser wavelengths, and good wettability by the melt. For instance, the resistance to thermal shocks ensures the material is not so vulnerable to cracking during rapid cooling. Furthermore, good wettability prevents the formation of solid metal balls which tend to limit the fusion of consecutive layers, and therefore deteriorate the inter-layer adhesion and material coherency[8–10].

Maraging steels are considered a few of the strongest metallic materials while also disposing of great toughness. Their high mechanical properties can be achieved through a simple and short heat treatment (usually at around 490 °C) which induces the so-called martensite aging (hence "maraging"). During aging, precipitation hardening occurs with nanometric intermetallic precipitates such as Ni_3X (X = Mo, Ti, Al), Fe_2Mo and Fe_7Mo_6 forming in the martensite matrix. For this reason, the 1.2709 steel is highly alloyed with Ni, Co, Mo and Ti[11–14].

This work aims to evaluate the influence of heat treatment on the microstructure and mechanical properties of the additively manufactured maraging steel. The possibility of improving the hardening process by introducing solution annealing before aging is also studied.

Experiment

The object of interest was precipitation-hardenable, high-alloyed, low-carbon maraging steel 1.2709. L-PBF additive manufacturing method was used to print the material, specifically the SLM Solutions 280HL machine

(NETME Centre, Brno, Czech Republic). The tested specimens were printed into a flat tensile test shape – as depicted in Figure 1 – from a ready-made alloy powder. The chemical composition of the powder was analysed for the work of Strakosova et. al.[15] using X-ray fluorescence analysis (XRF) on an ARL 9400 spectrometer. The analysis results can be seen in Table I. As a reference material for microstructure studies in the as manufactured condition, maraging steel 1.2709 originally forged into the shape of a rod has been used.

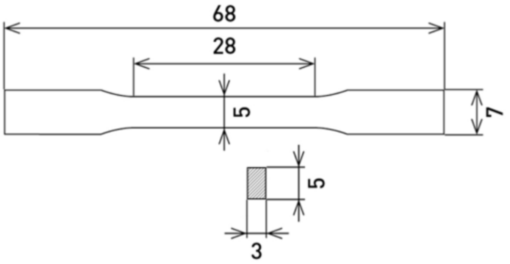

Figure 1. Dimensions of the studied L-PBF-printed specimens[15]

Table I
Chemical composition of the alloy powder used for L-PBF printing[15]

Element content, wt.%								
Fe	Ni	Co	Mo	Ti	Al	Si	Cr	Mn
Bal.	19.0	9.3	5.0	0.6	0.06	0.07	0.08	0.04

The influence of solution annealing at 820 °C for 1 h (air-cooled) on the L-PBF-printed steel was observed as it was implemented as the first step of heat treatment. The samples were divided into two groups–the first in the as-printed (AP), and the second in the solution-annealed (SA) condition–giving two possible default states for aging treatment. Both groups were followingly aged under three different temperatures – 440 °C, 490 °C and 540 °C – and five different durations – 2, 4, 6, 8 and 10 h – to map the influence of the aging conditions (water-cooled). All heat treatment steps were performed in Martínek MP 05-1.1 electric resistance furnace.

Individual samples were characterised using optical (OM, Nikon Eclipse MA200) and scanning electron microscopy (SEM, TESCAN VEGA 3 LMU). In both cases, the surfaces were ground on SiC papers from P240 to P4000, polished using 2 µm diamond paste, finished with Eposil F suspension, and etched using Nital 2. In as-printed condition, cuts both parallel and transverse to the printing direction were documented. After heat treatment, parallel cuts were considered representative and were documented exclusively.

Furthermore, X-ray diffraction analysis (XRD, PANalytical X'Pert PRO) was performed on samples in the default states and after 10 h aging to establish the phase composition. The analysis was done using a Co anode, 40 mA current and 35 kV voltage, while the measurement progressed in the 6–110° 2θ range with a 0,039° step. Samples for XRD analysis were ground on papers from P240 to P2500.

All samples in the default states and after heat treatment were mechanically tested using a Vickers microhardness tester (HV, Future Tech FM-700) with 0.1 kg load and 10 s indent duration obtaining HV 0.1 values. In each case, 10 indents were measured and the mean value with a 95% confidence interval was calculated.

Results and Discussion

Microstructure of the Default States

Firstly, the microstructure of the steel in the condition as printed by L-PBF has been documented. Figure 2 offers a side-by-side comparison with the same maraging steel 1.2709 conventionally manufactured by forging. In Figures 2a and 2d, a fully martensitic microstructure composed of pronounced laths is visible in the micrograph. On the other hand, additive manufacturing–owing to the layer-by-layer nature of the process and the selective melting in the programmed tracks–creates characteristic microstructures with specific features[3,5,7,9]. On the cut parallel (Figure 2b) and transverse (Figure 2c) to the printing direction, it is possible to see the individual layers, melt pools and scanning tracks in the printed microstructure. In all cases, well-defined boundaries can be observed around the mentioned features.

Unlike in the forged material (Figure 2d), martensite inside the melt pools–regardless of printing direction and melt pool shape–is found to be in the form of elongated micrometric cells instead of laths (Figures 2e, 2f). These cells were observed to have only around 1 µm in diameter[16] in the case of L-PBF. The cells keep the same orientation in certain areas that can be considered individual martensitic grains. The printed microstructure seems therefore noticeably finer, which may lead to improved mechanical properties compared to forged steel. Formation of the fine microstructure is caused by rapid cooling during the printing[5,7,8]. In fact, PBF processes achieve particularly high cooling rates among metal additive manufacturing techniques e.g., compared to Direct Energy Deposition–due to the compact volume of powder permanently surrounding the printed part[6,7].

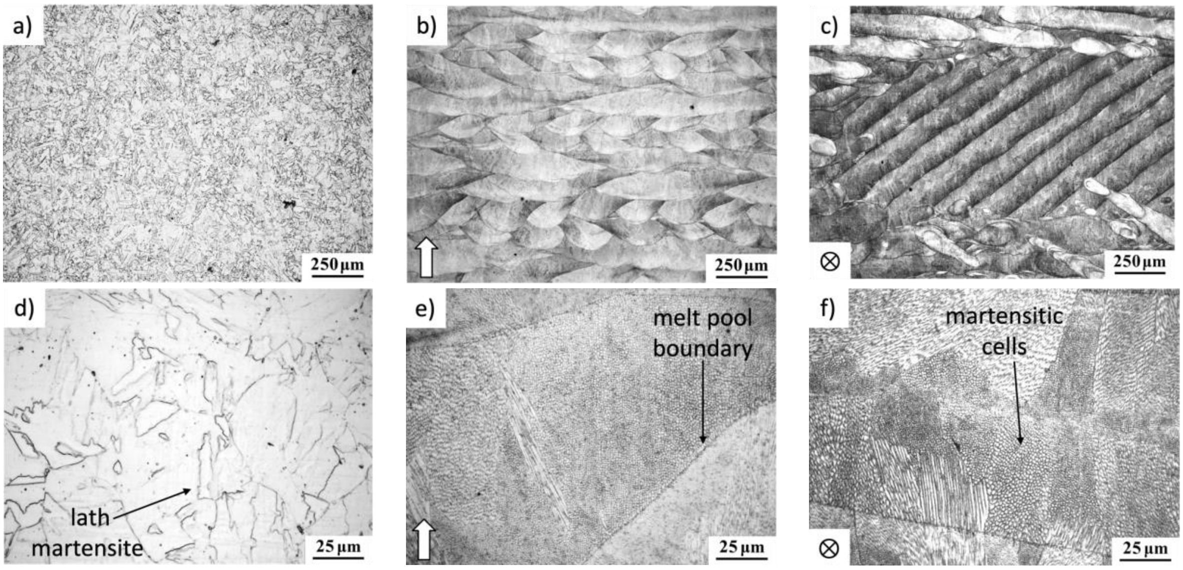

Figure 2. OM images of the microstructure of maraging steel manufactured by: a, d) forging; b, e) L-PBF – parallel cut; c, f) L-PBF – transverse cut; ⇧ and ⊗ symbols show the printing direction

As the optional first step of heat treatment, solution annealing at 820 °C for 1 h has been carried out. During SA, the steel is heated to a temperature where austenite is fully stable[8,11,17]. The goal is to improve chemical homogeneity with a better dissolution of alloying elements in the matrix and release residual stresses developed during printing. The resulting microstructure of the steel after the SA compared to the AP state is shown in Figure 3. As can be seen in Figure 3b, the major portion of the microstructure is still composed of cells in the solution-annealed state; the only difference is a slight softening of the cell boundaries and partial dissolution of the melt pool boundaries. Moreover, it is also possible to notice subtle contours of new laths after SA, suggesting the onset of martensite transformation. These findings suggest the length of this heat treatment step alone is insufficient for more significant morphological microstructure changes.

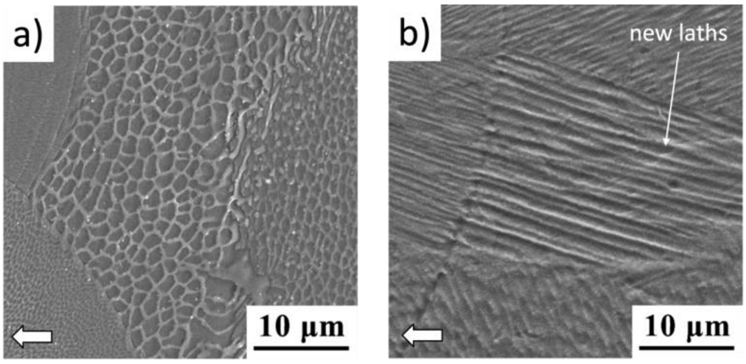

Figure 3. SEM micrographs of maraging steel in condition: a) as-printed, b) solution-annealed; arrows show the printing direction

Microstructure after aging

Aging treatment is an essential step for precipitation hardening, which is necessary for the maraging steel to achieve its excellent toughness and hardness[8–11,13–17]. Aging at three temperatures has been studied on samples with and without pre-aging solution annealing. The microstructures were documented after the longest exposure of 10 h to evaluate the strongest effect of a given aging temperature. The micrographs are presented in Figure 4. These micrographs show that aging treatment alone (Figures 4a, 4b, 4c) does not lead to definitive melt pool boundaries dissolution, even when 10 h exposure and the highest temperature of 540 °C are used. Besides that, cellular microstructure remains distinctive in the samples aged from the as-printed default state. On the contrary, the combination of both the solution annealing and the aging treatment (Figures 4d, 4e, 4f) can lead to a complete dissolution of the original printed microstructure with melt pools and cells. After SA + 490 °C/10 h aging (Figure 4e), a homogeneous microstructure compounded of newly formed, pronounced lath martensite is apparent. Micrographs taken after aging at 540 °C (Figure 4c, 4f) suggest that increased austenite reversion occurs at high temperatures as small new bright grains are noticeable in both microstructures.

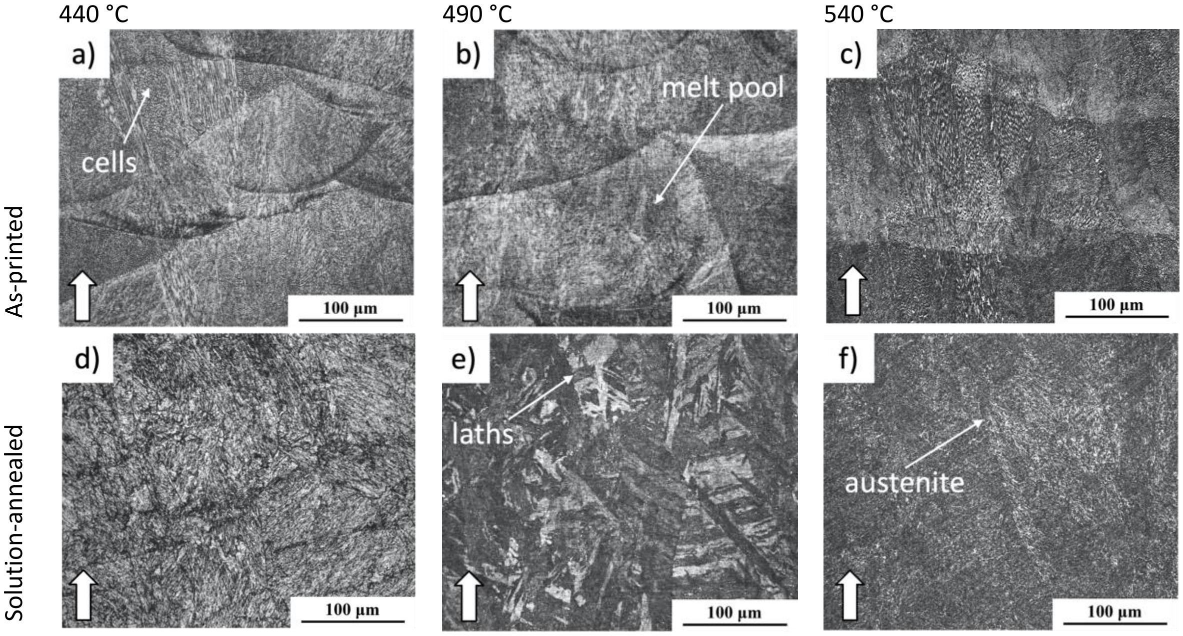

Figure 4. OM images of the maraging steel microstructure after 10h aging at different temperatures: a, d) 440 °C; b, e) 490 °C; c, f) 540 °C; arrows show the printing direction

Lastly, the influence of the standard two-step heat treatment (SA: 820 °C/1 h + aging: 490 °C/6 h) industrially prescribed for maraging steel 1.2709 was studied. The micrographs are shown in Figure 5. This heat-treated state manifests as an intermediate stage in the martensite shape transformation. Concurrently, the fragments of the original melt pool structure (Figure 5a) with very fine cells can be observed along the clear laths (Figure 5b) formed later during the heat treatment. Features of the printed material are therefore not fully dissolved after 6 h aging at this temperature, unlike after 10 h (Figure 4e).

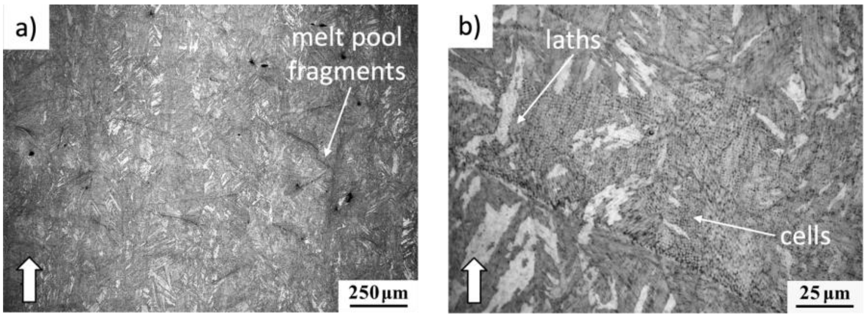

Figure 5. OM images of the microstructure of maraging steel after two-step heat treatment of SA 820 °C/1 h + aging 490 °C/6 h; arrows mark the printing direction

Phase Composition

The semiquantitative XRD phase composition analysis has been performed along the microstructure documentation on the samples in the default states (Figure 3) and the 10h-aged samples (Figure 4). The percentual contents of the observed martensitic α-phase and the austenitic γ-phase in the aforementioned samples are presented in Table II. The first result to highlight is that solution annealing proved beneficial in terms of retained austenite transformation to martensite. Microstructure after SA thus consisted almost exclusively of martensitic phase (as far as the resolution of XRD analysis allows to assess).

Table II
Phase composition in the default states and after 10h aging at different temperatures as obtained by XRD analysis

Phase	Phase content, %							
	As-printed	AP + 440 °C	AP + 490 °C	AP + 540 °C	Solution-annealed	SA + 440 °C	SA + 490 °C	SA + 540 °C
Martensite (BCC)	98	97	95	84	100	100	98	87
Austenite (FCC)	2	3	5	16	0	0	2	13

Consequently, all of the samples that were solution-annealed prior to aging treatment come with lower austenite content (by the amount equal to the retained austenite portion found in the as-printed condition). Secondly, the influence of the temperature is more significant than the exposure duration. As can be seen in Table II, samples aged at 440 °C do not show any more austenite compared to the default state even after 10 h. On the contrary, after aging at 540 °C – though after the same 10h exposure – a large increase in the austenite content was registered.

The XRD analysis results (Table II) also confirm the presence of austenite reversion during the aging treatment. This phenomenon means the transformation from austenite to martensite – which happens while cooling during the print and after solution annealing – takes place in the opposite direction[8,11,17]. Starting from the aging temperature of 490 °C, a slight increase in the austenite content is evident after 10 h. However, at further increased aging temperatures–specifically over 500 °C – the scale of austenite reversion is considerably larger. This effect is generally called over-aging and is linked to decreased mechanical properties, but enhanced plasticity[17].

Microhardness

Microhardness of both the as-printed (AP) and the solution-annealed (SA) series was mapped depending on the aging temperature and exposure duration. The values for the aged samples are plotted in Figure 6 along with both default states. The significant hardness drop is visible between the AP and SA default states – from (367 ± 5) HV 0.1 to (321 ± 4) HV 0.1 (Figure 6) – and is mainly connected to the release of the print-induced residual stresses[18]. The highest microhardness value of (620 ± 8) HV 0.1 was measured after the combined heat treatment of 820 °C/1 h + 490 °C/6 h (Figure 6b). The microstructure of the said state is documented in Figure 5. This result confirms the regularly prescribed heat treatment is appropriate for the printed maraging steel as well.

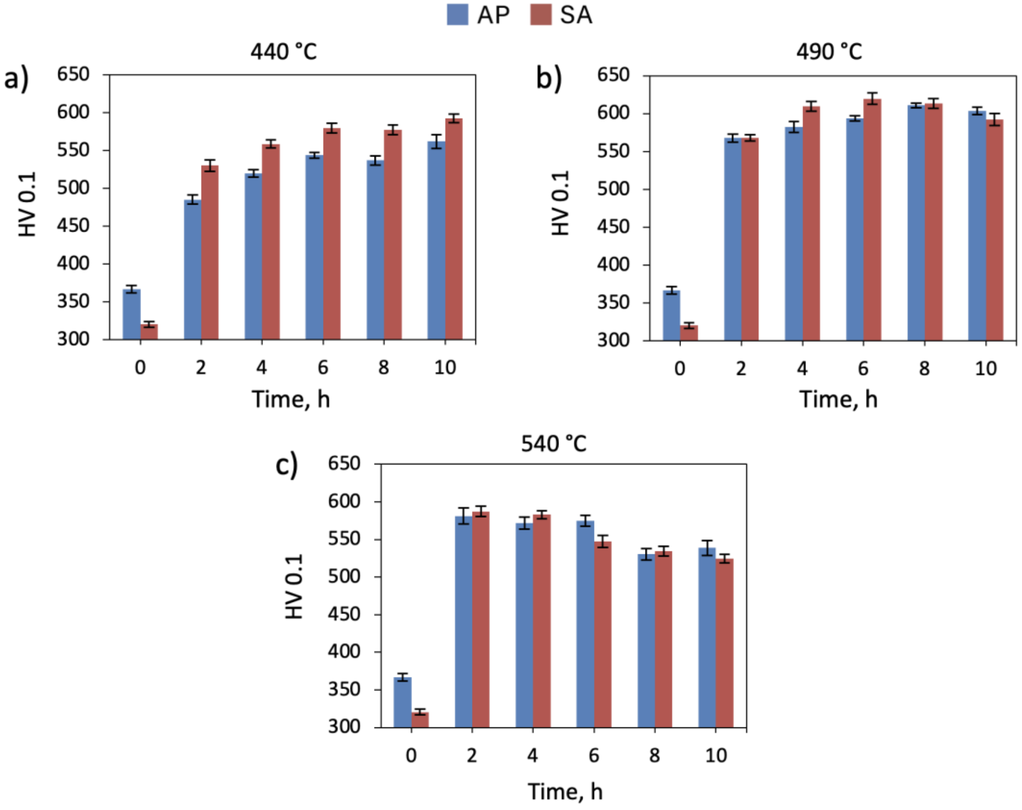

Figure 6. Dependence of maraging steel microhardness on aging temperature: a) 440 °C, b) 490 °C, c) 540 °C

Generally, two phenomena are apparent concerning aging temperatures. While the microhardness maximum was achieved at 490 °C (Figure 6b), the lower temperature is insufficient for hardening of the same scale during the 10 h exposure (Figure 6a). The temperature of 440 °C leads to an effect called under-aging. On the other hand, even the shortest exposure does not avoid the loss in hardness at the highest temperature (Figure 6c). The temperature of 540 °C causes an effect called over-aging. The over-aging phenomenon – during which the hardening degrades – is linked to the coarsening of the intermetallic precipitates and the earlier described austenite reversion[8,11,17]. Guo et al.[8] also explained that the Ni-containing precipitates decompose during high-temperature expositions releasing the austenite-stabilising Ni, hence the austenite reversion support. Based on the presented results, it is possible to see the correlation between the content of austenite in the microstructure and changes in hardness values. For high-temperature applications, over-aging may be induced on purpose in order to avert the decrease in mechanical properties during use. In the case of the aging temperature of 540 °C, the exposure time of at least 8 h would be necessary according to the results plotted in Figure 6c.

Lastly, adding solution annealing to the heat treatment supported the hardening effect. Considerably higher microhardness values were achieved thanks to SA and the initial growth is more intense than with the samples aged in the as-printed state. Similarly, the over-aging is sped up and starts earlier as well, as can be observed in Figure 6c and at the longest exposure times in Figure 6b.

Conclusion

The 1.2709 maraging steel additively manufactured by Laser Powder Bed Fusion was studied in terms of changes in microstructure and microhardness depending on the application of different heat treatments. The following conclusions can be drawn:

- The temperature of 490 °C was confirmed to be the most favourable for obtaining the highest microhardness values of the additively manufactured maraging steel.
- The highest hardness of (620 ± 8) HV 0.1 has been measured after the two-step heat treatment combining solution annealing at 820 °C for 1 h and aging at 490 °C for 6 h. The resulting microstructure exhibited a combination of fragments of melt pools with cells formed during the print and newly formed laths.
- The lower temperature of 440 °C led to under-aging and insufficient hardening, whereas the higher temperature of 540 °C led to over-aging including loss of hardness and increase in austenite content.
- Solution annealing proved to be an efficient heat treatment for retained austenite reduction.

Acknowledgement

This work was supported from the grant of Specific university research – grant No. A1_FCHT_2024_007.

References

1. Cai C., Zhou K.: Digital Manufacturing, 247 (2022).
2. Ngo T. D., Kashani A., Imbalzano G., Nguyen K. T. Q., Hui D.: Composites Part B-Engineering, *143*, 172 (2018).
3. DebRoy T., Wei H. L., Zuback J. S., Mukherjee T., Elmer J. W., Milewski J. O., Beese A. M., Wilson-Heid A., De A., Zhang W.: Progress in Materials Science, *92*, 112 (2018).
4. Bajaj P., Hariharan A., Kini A., Kürnsteiner P., Raabe D., Jägle E. A.: Materials Science and Engineering A, *772* (2020).
5. Svetlizky D., Das M., Zheng B. L., Vyatskikh A. L., Bose S., Bandyopadhyay A., Schoenung J. M., Lavernia E. J., Eliaz N.: Materials Today, *49*, 271 (2021).
6. Blakey-Milner B., Gradl P., Snedden G., Brooks M., Pitot J., Lopez E., Leary M., Berto F., du Plessis A.: Materials & Design, *209* (2021).
7. Herzog D., Seyda V., Wycisk E., Emmelmann C.: Acta Materialia, *117*, 371 (2016).
8. Guo L. L., Zhang L. N., Andersson J., Ojo O.: Journal of Materials Science & Technology, *120*, 227 (2022).
9. Conde F. F., Escobar J. D., Oliveira J. P., Jardini A. L., Bose W. W., Avila J. A.: Additive Manufacturing, *29* (2019).
10. Yin S., Chen C. Y., Yan X. C., Feng X. H., Jenkins R., O'Reilly P., Liu M., Li H., Lupoi R.: Additive Manufacturing, *22*, 592 (2018).

11. da Fonseca D. P. M., Feitosa A. L. M., de Carvalho L. G., Plaut R. L., Padilha A. F.: Ibero-American Journal of Materials, *24* (2021).
12. Chen B., Huang Y. H., Gu T., Tan C. W., Feng J. C.: Rapid Prototyping Journal, *24*, 964 (2018).
13. Ronda N., Grzelak K., Polanski M., Dworecka-Wójcik J.: Materials, *15* (2022).
14. Yao Y. Z., Huang Y. H., Chen B., Tan C. W., Su Y., Feng J. C.: Optics and Laser Technology, *105*, 171 (2018).
15. Strakosova A., Kubasek J., Michalcova A., Prusa F., Vojtech D., Dvorsky D.: Materials, *12* (2019).
16. Kvapil D.: *Structure and properties of high-strength steel manufactured by Direct Energy Deposition 3D printing process*, VŠCHT Praha, Prague, 2024
17. Rohit B., Muktinutalapati N. R.: Materials Science and Technology, *34*, 253 (2018)
18. Bai Y. C., Wang D., Yang Y. Q., Wang H.: Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, *760*, 105 (2019).

PROPERTIES OF A NOVEL LIGNIN-BASED UREA FORMALDEHYDE RESIN AS AN ADHESIVE FOR WOOD AND WOOD COMPOSITES

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Abstract

Lignin, produced in pulp mills around the world, is primarily used as a source of energy. Due to its chemical properties, there is potential for developing lignin-based materials. The current focus is on the development of adhesives from lignin, with an emphasis on lignosulfonate due to its superior reactivity compared to kraft lignin. However, kraft lignin is much more widely produced worldwide.

In this study, kraft lignin was used as a partial replacement for preparing urea-formaldehyde resin (UF) for bonding wood and wood-based composite materials. UF resins with 0 to 50% lignin replacement were prepared. The tensile shear strength of glued joint on high density fibreboard (HDF) samples was tested for the developed resins. The shear strength results show that the shear strength decreases with increasing lignin content. At the same time, a significant decrease occurred with the addition of 50% lignin due to too high viscosity of the prepared resin. After the test, the failure condition of the glued joint was visually evaluated.

Introduction

Lignin is the second most abundant biopolymer in nature after cellulose. Lignin is an aromatic, amorphous phenolic polymer found in vascular plants. It has a very complex branched structure, which is composed of phenolic units[1]. The representation of lignin in wood varies between 20–30% and is variable on the type of tree species, with broadleaved species generally containing a higher proportion of lignin than coniferous species [2].

The largest production of technical lignins occurs in the paper industry, where they are a by-product of delignification in the production of pulp for paper production [3]. Lignin and other substances give wood its colour, which is undesirable in paper production, so the aim of pulp production is to separate white cellulose fibres from lignin and other non-fibrous compounds[4].

Even nowadays, despite many expert studies, lignin is still considered as a waste by-product of the paper industry used for thermal energy production and only one percent of lignin is used in other applications with higher added value[5].

The attractiveness of lignin as a substitute in wood adhesives lies in its natural origin, its phenolic nature, high availability and low cost[6].

Urea-formaldehyde (UF) resins are synthetic resins formed by reacting urea with formaldehyde[7]. UF resins are the most widely used adhesive used for wood composite materials, with this segment of the industry accounting for 95% of the total UF resin consumption[8]. A major disadvantage of UF resins is their low moisture resistance, therefore products bonded with UF resin are mainly intended for interior applications.

The addition of lignin to UF resins could enhance their environmental performance, among others, also giving the products higher moisture resistance, higher thermal stability, while achieving the same or even slightly higher mechanical properties as untreated UF[9,10].

Materials and methods

Commercial UF resin Chemcol U100 was used to prepare the adhesive mixture. To this resin was added 0–50% hardwood kraft lignin (on a dry weight basis), obtained by precipitation from black liquor using sulfuric acid and subsequent neutralization (lignin isolation scheme in Figure I).

The resulting mixture was first mixing by an anchor stirrer (300–500 rpm, 10 min) and then to achieve a homogeneous mixture dispersing the mixture on a Yellow line DI 25 basic disperser (IKA, Germany) at 4000–5000 rpm for 5 min. Subsequently, the Diakol R 60 hardener required to cure the UF resin was added.

As adherent HDF with a raw or varnished surface of 110 × 25 mm was used. The adhesive mixture was applied to a 25 × 25 mm glued surface with a 0.12 mm application thickness secured with a spacer wire. The test samples were placed in a special mould and loaded with a force of 40 N. Curing was carried out at laboratory temperature for 48 hours.

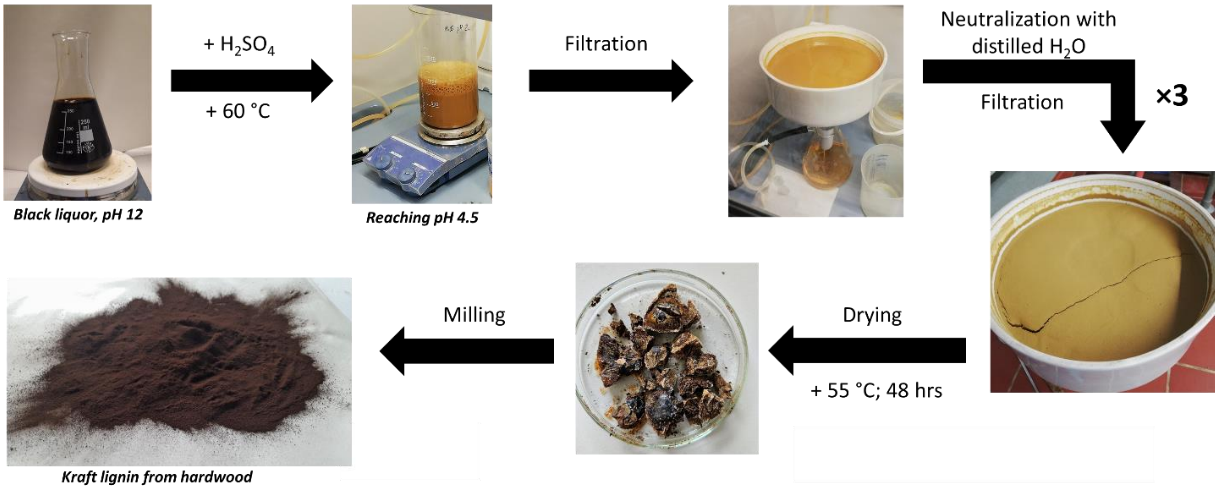

Figure 1. Scheme of kraft lignin preparation

Viscosity of resins

The two-plate model was selected to measure the viscosity of the resins. The measurements were conducted using a Malvern Kinexus lab+ rheometer (Malvern, UK) at 25 °C.

Tensile shear strength

The tensile shear strength (TSS) of the bonded joint was measured using a Shimadzu AGS-X testing machine (Shimadzu, Japan). The TSS was calculated according to:

$$TSS = \frac{F}{S}\ (MPa)$$

where F is the maximum force in N and S is the area of the bonded joint in mm^2.

After the TSS test, a visual assessment of the failure character of the bonded joint was made on the tested specimens.

Scanning Electron Microscopy (SEM)

SEM analysis was performed on the cured resin samples using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage at 20 µm resolution.

Discussion and results analysis

Viscosity of resins

Figure II clearly shows that the viscosity of the resulting adhesive mixtures increases exponentially with increasing lignin content. At a lignin content of 50% in the resin mixture, the viscosity was already too high to be measured by the chosen method.

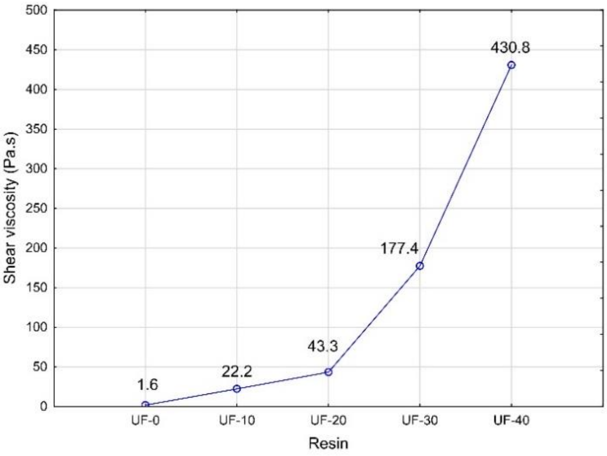

Figure 2. Shear viscosity of resins

The increasing viscosity of UF resins has a negative effect on the wood bonding itself, specifically on the depth of penetration, the interfacial area and its filling or the filling ratio of individual rays and lumens. These parameters further affect the strength of the bonded joint itself[11].

Tensile shear strength

The TSS results are shown in Figure 3. From the TSS results on the raw surface of HDF (Figure III.A), it can be observed that there was a decrease in stress with the addition of lignin, but this decrease was not statistically significant between the lignin content in the range of 5–40%. Subsequently, there was a significant decrease in strength for the resin variant with 50% lignin addition, which can be attributed to the already too high viscosity of the adhesive mixture, which caused an imperfect bond and failed to interlock with the HDF structure.

Similar TSS results were obtained for the varnished surface of the HDF (Figure III.B) where again there was a decrease in strength with the addition of lignin compared to the commercial UF resin, but there was no statistically significant difference between the TSS values for the samples bonded with resin containing 5–40% lignin.

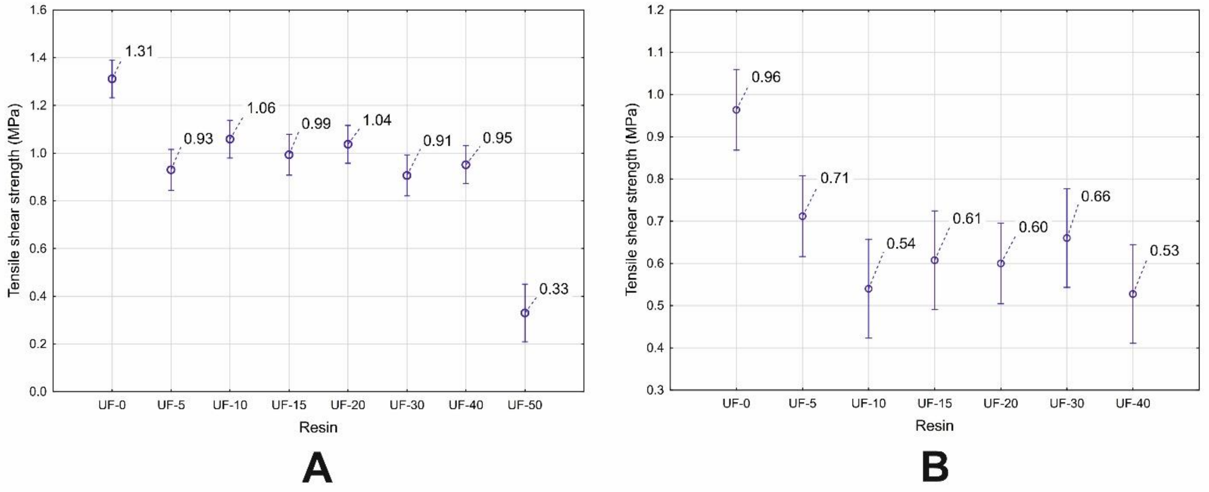

Figure 3. Tensile shear strength on HDF adherent; raw surface (A) and varnish surface (B)

The results of the visual assessment of the failure character of the bonded joint are shown in Table I. In the majority of cases, there was a cohesive failure of adherend or, in the case of a painted HDF surface, an adhesive failure between varnish and HDF. Only in specimen UF-50 on raw surface and UF-40 on varnish surface there was adhesive failure between resin and adherend which is unacceptable from the point of view of design and assessment of glued timber structures and wood-based materials[12].

Table I

Visual assessment of the glued joint failure

RESIN (LIGNIN CONTENT)	0%	5%	10%	15%	20%	30%	40%	50%
HDF (RAW SURFACE)	CA	CA	CA	CA	CA	CA	CA	AR
HDF (VARNISH SURFACE)	CA	CA	AV	AV	AV	AV	AR	–

Scanning Electron Microscopy (SEM)

In the SEM images of the cured resins (Figure IV), it can be observed that the addition of lignin to the adhesive mixture resulted in the creation of air bubbles in these resins. As the lignin content increased, the representation of these formations also increased (indicated by the yellow arrow). Since the reference UF resin was also mixed to add hardener, we do not assume that this is due to the mixing of the adhesive mixture itself. It is these air bubbles that could have influenced the reduction in TSS when lignin was added to the UF resins.

Furthermore, regions where lignin particles can be observed in cured resins containing lignin (marked in red) were identified. These areas indicate that lignin has been mixed with the UF resin but not dissolved.

Thus, from our results, it can be concluded that lignin in this application behaves only as a filler for the developed adhesive mixtures.

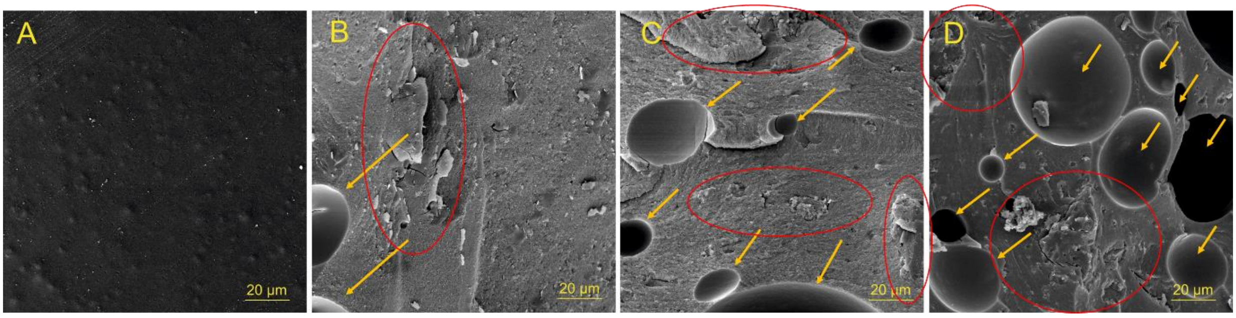

Figure 4. SEM images of surface of cured adhesive UF-0 (A), cross section of cured adhesive UF-10 (B), UF-20 (C) and UF-40 (D)

Conclusion

For the purpose of the research, a UF-based adhesive blend with lignin addition from 0 to 50% was used. The prepared adhesives were tested for their viscosity, Tensile shear stress of glued join on HDF and cured resins were analyzed by microscopic analysis.

The results show that the viscosity of the prepared blends increases exponentially with increasing lignin content. This increase further negatively affected the bonding and properties of the resins themselves.

Tensile shear stress results in both tested cases showed a decrease in bond strength of the resins with lignin addition compared to the reference UF resin. No statistically significant difference was found between resins with lignin content between 0–40%. A significant decrease was observed only when resin with lignin content of 50% was used, when adhesive failure between resin and adherend was occurred.

SEM images of the cured resins showed the presence of air bubbles in the lignin-containing blends, which probably contributed to the reduced strength of these resins. Furthermore, there were areas of visible lignin particles in the cured resins, indicating that lignin was used as a filler in this application.

From the results it can be concluded that the kraft lignin content between 5% and 40% can be effectively considered for replacing a larger amount of resin for the production of adhesives for the bonding of wood and wood-based materials.

Acknowledgement

This research was supported by the Faculty of Forestry and Wood Sciences of the Czech University of Life Sciences Prague (Internal Grant Agency, Project No. A_03_23) and for the support by the European Liaison Committee for Pulp and Paper through an EUCEPA Student Grant

References

1. Norgren M. and Edlund, H.: Current Opinion in Colloid & Interface Science *19*, 409 (2014).
2. Požgaj A., Chovanec D., Kurjatko S. and Babiak M.: Štruktúra a vlastnosti dreva. Bratislava: PRÍRODA 1997.
3. Becker J. and Wittmann Ch.: Biotechnology Advances *37*, 107360 (2019).
4. Thébault M., Müller U., Kandelbauer A., Zikulnig-Rusch E. and Lammer H.: European Journal of Wood and Wood Products *75*, 853 (2017).
5. Xu Ch. and Ferdosian F.: Conversion of Lignin into Bio-Based Chemicals and Materials. Springer-Verlag 2017.
6. Karthäuser J., Biziks V., Mai C. and Militz H.: Molecules *26*, 2533 (2021).
7. Gonçalves D., Bordado J.M., Marques A.C. and Dos Santos R.G.: Polymers *13*, 4086 (2021).
8. Carvalho L.H., Magalhães F.D. a Ferra J.: Formaldehyde: Chemistry, Applications and Role In Polymerization. New York: Nova Publishers, 2012.
9. Antov P., Savov V., Trichkov N., Krišťák Ľ., Réh R., Papadopoulos A.N., Taghiyari H.R., Pizzi A., Kunecová D. and Pachikova M.: Polymers *13*, 2775 (2021).
10. Natarelli, C.V.L., Lemos, A.C.C., de Assis, M.R., Tonoli G.H.D., Trugilho P.F., Marconcini J.M. and de Oliveira J.E.: Journal of Thermal Analysis and Calorimetry *137*, 1537 (2019).
11. Gavrilovic-Grmusa I., Dunky M., Miljkovic J. and Djiporovic-Momcilovic M.: Holzforschung *66*, 849 (2012).
12. Lukowsky D.: *Failure Analysis of Wood and Wood-Based Products*. McGraw-Hill Education, New York 2015.

INFLUENCE OF SOLUTION COMPOSITION AND IN VITRO TEST ARRANGEMENT ON THE RESULTS OF POTENTIAL BIOACTIVITY OF BIOACTIVE GLASS 45S5

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Abstract

This study investigates the dissolution behaviour of Bioglass 45S5 in simulated body fluid (SBF) solutions with varied compositions. Bioactive glass samples were exposed to different SBFs to analyse their interactions. The experimental setup included static-dynamic conditions and buffered SBF (ISO 23317:2014), non-buffered SBF without TRIS, and non-buffered SBF with adjusted hydrogen carbonate ion concentration. Monitoring pH level changes and weight loss over four days provided insight into the dissolution kinetics of the glass. Additionally, the formation of calcium-phosphate layers was examined using SEM imaging and XRD analysis. The study underscores the influence of SBF composition on the bioactivity of bioactive glass.

Introduction

Bioactive glasses, exemplified by Bioglass 45S5, have emerged as pivotal materials in biomedical applications due to their ability to integrate with bone tissue, promoting osseointegration. These glasses are renowned for their biocompatibility and bioactivity, characterized by the formation of a hydroxyapatite layer upon exposure to physiological fluids, which facilitates their bonding with bone[1,2].

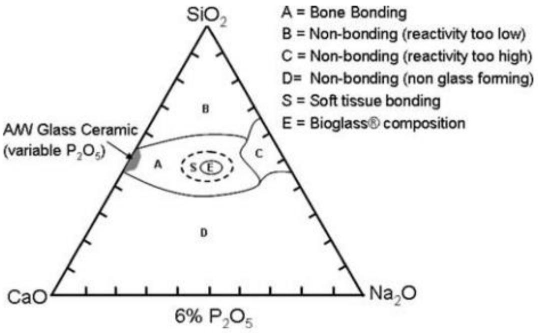

Figure 1. A diagram illustrating how the composition of Bioglass influences its capacity to form bonds with human bone[3]

Simulated body fluid (SBF) has become a standardized medium[4] for assessing the bioactivity of biomaterials, as it mimics the chemical composition of human blood plasma[5]. However, variations in SBF composition, particularly the concentration of buffering agents such as TRIS and the $(HCO_3)^-$ ion, significantly influence the dissolution kinetics and bioactive behaviour of bioactive glasses[2,6-8].

Research by Kulhánková et al. investigated the role of bicarbonate ions ($(HCO_3)^-$) in SBF and their impact on the dissolution behaviour of bioactive glass-ceramic scaffolds made from 45S5 bioactive glass. Their findings demonstrated that higher concentrations of $(HCO_3)^-$ ions in non-buffered SBF solutions increased the dissolution rate of the glass-ceramic material, suggesting that the concentration of these ions plays a crucial role. Variations in $(HCO_3)^-$ ion concentrations can alter the dissolution rates of bioactive glasses, affecting their suitability for specific biomedical applications. Additionally, they determined that $(HCO_3)^-$ concentrations of 20 and 27 mmol·dm^{-3} in SBF are too high for accurate in vitro testing due to the instability of such solutions. Recommending a concentration of around 15 mmol·dm^{-3}, which is half the amount found in human blood plasma, may be more suitable[6].

This study aims to design new conditions for the evaluation of bioactive glass materials, potentially contributing to the development of a new ISO standard. Specifically, the research focuses on two primary objectives: first, to study the behaviour of bioactive glass in different formulations of SBF, including non-buffered SBF without TRIS (SBFnoTRIS) and non-buffered SBF with modified $(HCO_3)^-$ ion concentration (SBF15); second, to investigate the effect of these modified SBFs on the dissolution behaviour and bioactivity of Bioglass 45S5. By addressing these aims, this study seeks to provide a comprehensive understanding of how these SBF variations influence the interaction between bioactive glasses and physiological fluids, thereby informing the tailored design and evaluation of bioactive materials for biomedical applications.

Experiment

Testing material

Bioactive glass samples based on Bioglass 45S5 as the most used type of bioactive glass were prepared by melting of the basic glass batch at 1300 °C for 3 hours. The finished homogeneous glass was then cast, tempered at 500 °C for one hour and cooled until next day. The bulk sample of bioactive glass (Figure 2) was crushed and sieved to obtain the grain size 0.3–0.5 mm. Crushed samples were ultrasonically cleaned in ethanol three times for 10 minutes and dried at laboratory temperature.

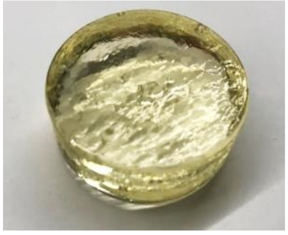

Figure 2. Prepared bioactive glass bulk sample

Table I

Bioactive glass composition (XRF) wt. %	
SiO_2	42.3
Na_2O	25.2
CaO	26.3
P_2O_5	5.7

In vitro bioactivity test

The *in vitro* tests of bioactivity were performed in three different testing SBF solutions. First solution was the buffered SBF prepared according to the ISO standard labelled as **SBF**, second was non-buffered simulated body fluid labelled as **SBFnoTRIS,** and third solution was non-buffered SBF with a modified concentrations of $(HCO_3)^-$ labelled as **SBF15**. The composition of individual test solutions and human blood plasma is shown in Table II. It is obvious that they exhibit substantial similarities, however, discernible differences persist, notably in the levels of chloride and hydrogen carbonate ions, as well as the presence of TRIS buffer.

Table II

Ionic composition of testing solutions and blood plasma[4]

[mmol·dm^{-3}]	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}	TRIS
SBF	142.0	5.0	1.5	2.5	**185.0**	**4.2**	1.0	0.5	50.0
SBFnoTRIS	142.0	5.0	1.5	2.5	**149.3**	**4.2**	1.0	0.5	-
SBF15	142.0	5.0	1.5	2.5	**137.3**	**15.0**	1.0	0.5	-
BP	142.0	5.0	1.5	2.5	**103.0**	**27.0**	1.0	0.5	-

The *in vitro* tests lasted for four days, and eight sampling times were selected. Testing took place in the temperature of 36.5 °C under static-dynamic conditions with refreshing the testing solution each 24 hours (Figure 3) and used S/V ratio was 0.1 gram of bioactive glass particles per 10 ml of testing solution.

Figure 3. Scheme of static-dynamic test for four days

Experiment evaluation

The experimental assessment encompassed analyses of leachates, involving pH measurement followed by determination of silicon, calcium, and phosphate ions concentration by ICP-OES method. Additionally, material analyses were conducted, including the monitoring of sample weight changes, surface morphology observation via scanning electron microscopy with an energy-dispersive X-ray spectroscopy (SEM/EDS), and X-ray diffraction (XRD) analysis was performed to determine the mineralogical composition of newly formed phases. These comprehensive analyses provided valuable insight into the monitoring and understanding of the processes taking place during the in vitro bioactivity testing of reactive glass materials in SBF solutions with different composition.

Discussion and results analysis

The graphs presented in Figure 4 illustrate the changes in pH of the solution and weight of the samples over a period of four days of experiment. Monitoring the pH changes provides insight into the interaction between the material and the solution. It is noteworthy that, despite the SBF solution prepared according to the ISO standard containing TRIS buffer, it does not maintain the desired pH throughout the experiment. The second graph shows a significant decrease in the weight of samples exposed to buffered SBF compared to samples in non-buffered SBF solutions. This finding demonstrates the interaction of TRIS with the samples and the dissolution of glass materials.

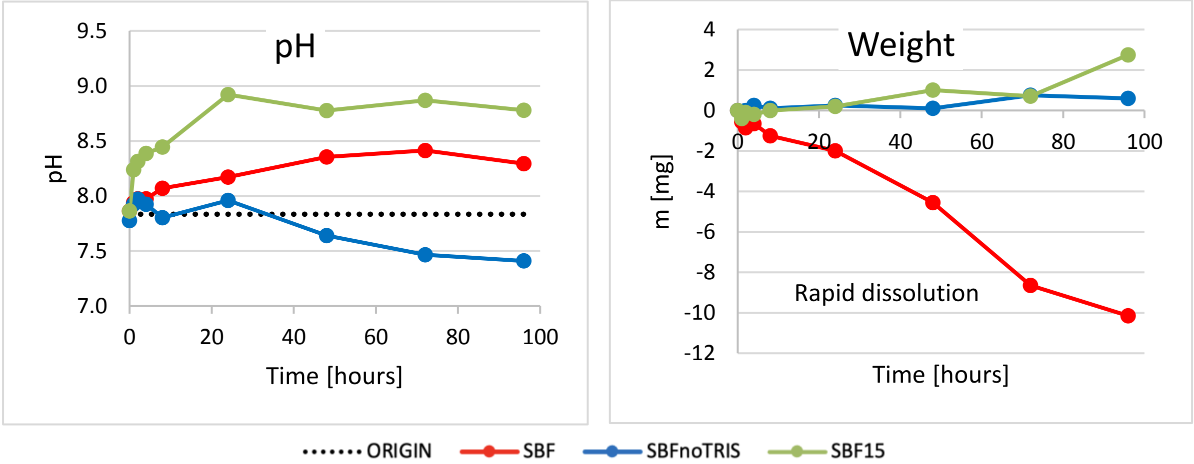

Figure 4. pH levels and weight changes of bioglass particles during the 4-day exposition in different SBFs

The concentration of silicon, calcium, and phosphate ions measured in eluates throughout the experiment are shown in Figure 5. The first graph of silicon concentration corroborates the previous weight graph, confirming that samples exposed to buffered SBF experience substantial dissolution. Conversely, in non-buffered solutions, there was almost no release of silicon, indicating minimal dissolution of the bioactive glass.

An increase in the concentration of calcium and phosphate ions in the solution indicates material dissolution, while a decrease suggests the depletion of elements from the solution and possible precipitation of a new layer – in this case, a calcium-phosphate layer. The graphs in Figure 5 further substantiate that glass samples dissolution occurred only in buffered SBF. However, based on these graphs, precipitation could also be expected on samples exposed to non-buffered SBF solution.

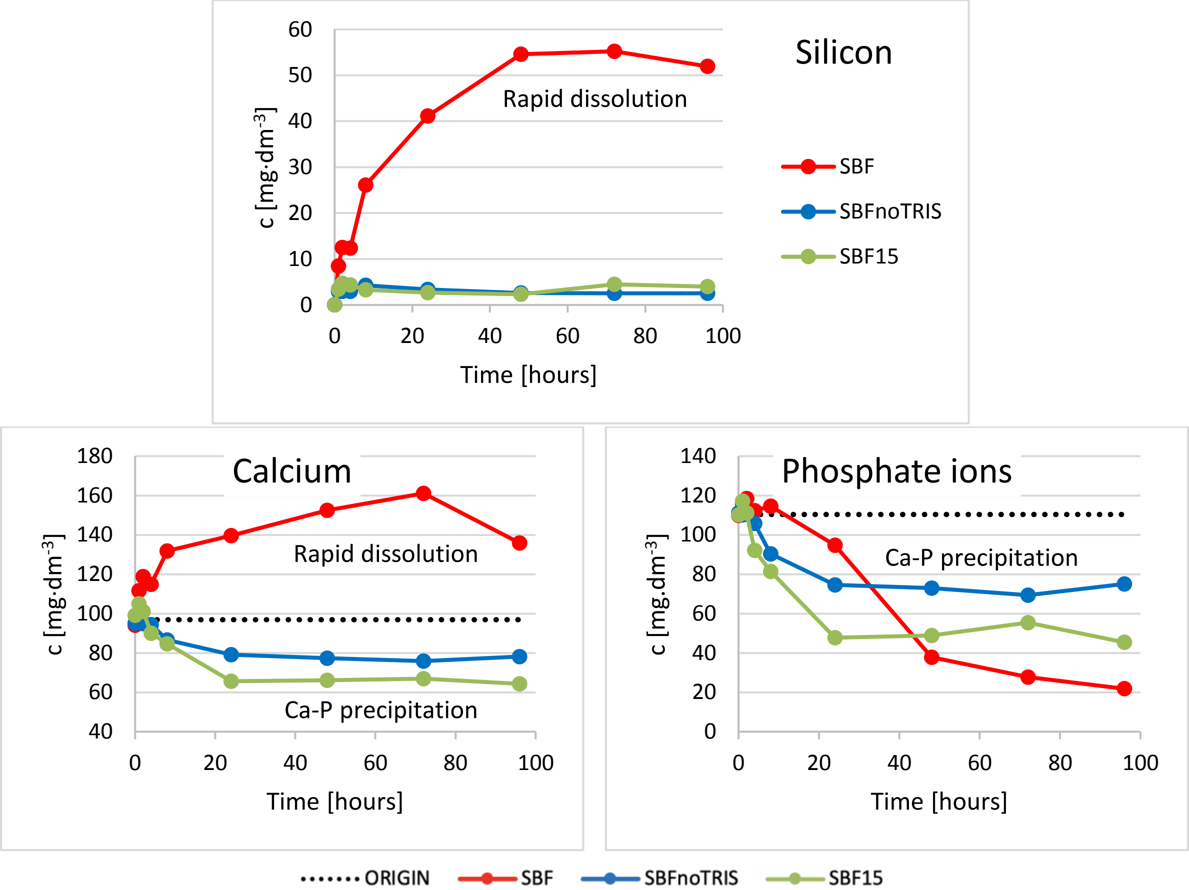

Figure 5. The concentration of silicon, calcium, and phosphate ions during the 96 hours interaction

The SEM images of samples' cross-sections, shown in Figure 6, indicate that glass particles exposed to non-buffered SBF solutions exhibit no change compared to the basic glass prior to the experiment. In contrast, new layers are observed on the surface of particles exposed to SBF containing TRIS. These include a layer of original glass, a silica-rich layer, and a newly precipitated Ca-P layer.

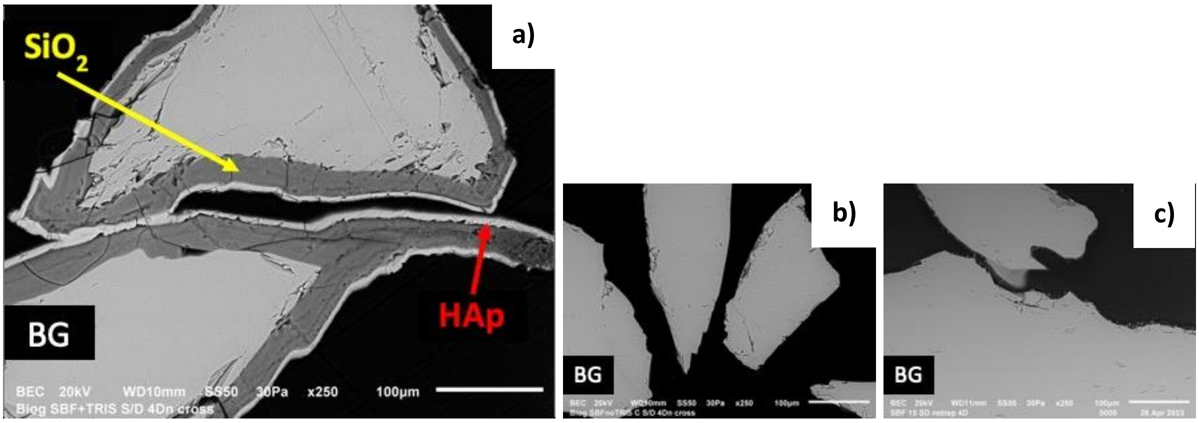

Figure 6. Cross-sectional images of bioactive glass particles exposed to different SBFs - 4th day a) SBF, b) SBFnoTRIS, c) SBF15

Furthermore, SEM images showing surface morphology, depicted in Figure 7, revealed that, although no significant difference was apparent in the cross-section images of samples exposed to SBF with adjusted hydrogen carbonate ion concentration, very fine precipitates, likely of amorphous calcium phosphate, were observed on the surface.

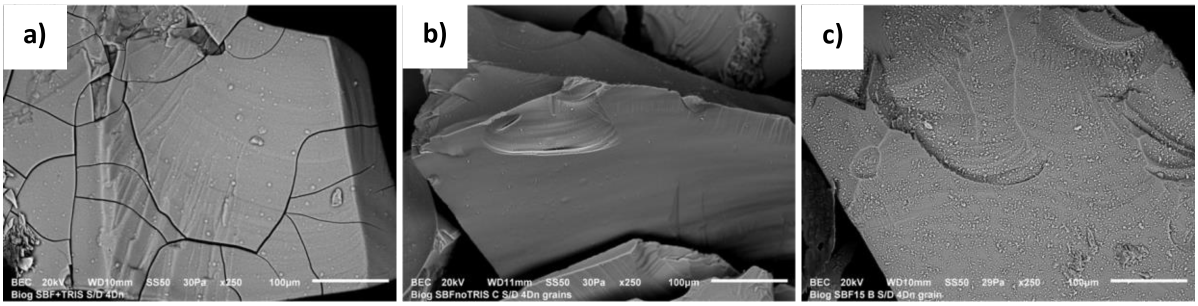

Figure 7. Surface morphology of bioglass samples after 4th day exposition to different testing SBF solutions a) SBF, b) SBFnoTRIS, c) SBF15

XRD analysis did not detect any crystalline phase in samples exposed to non-buffered SBF with adjusted hydrogen carbonate ion concentration (SBF15), not even in those exposed to SBFnoTRIS. Conversely, the presence of hydroxyapatite was confirmed in samples exposed to buffered SBF, as shown in the XRD spectra presented in Figure 8.

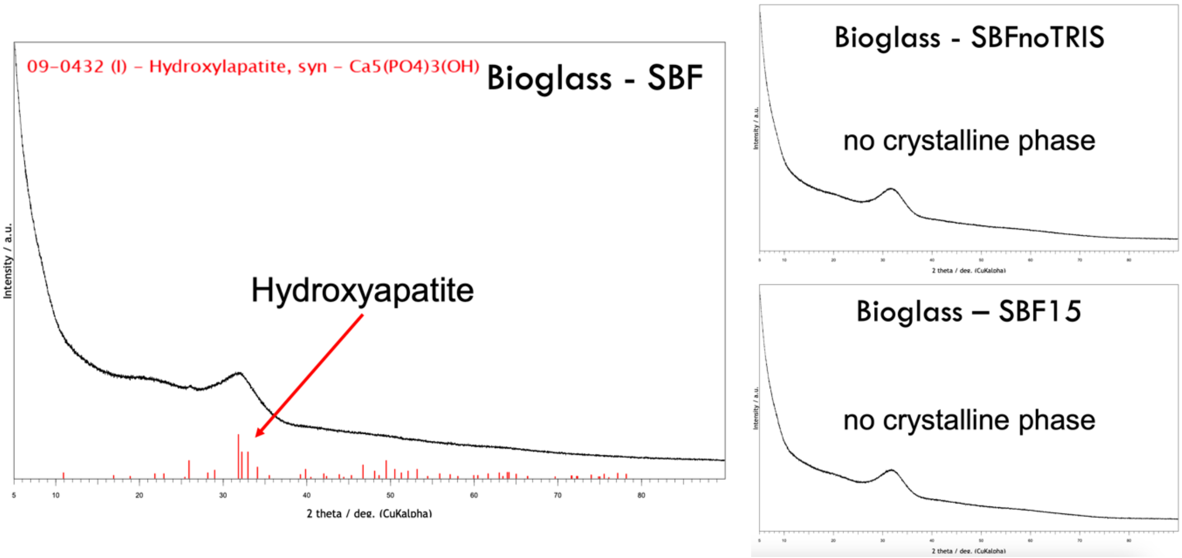

Figure 8. XRD analysis of samples exposed to different SBFs for 4 days

Conclusion

This study shows relationship between reactive glass materials and simulated body fluid (SBF) solutions with different compositions. It was observed that the bioglass dissolution rate was significantly accelerated in buffered SBF, attributed to the presence of TRIS, which is clearly not an inert buffer. Samples exposed to both non-buffered SBFs showed minimal dissolution. Additionally, in buffered SBF, we observed a swift growth of hydroxyapatite (HAp) layer, indicating heightened bioactivity. In contrast, only slight changes, primarily in the form of amorphous calcium-phosphate phases, were observed on samples exposed to non-buffered SBF with modified concentration of hydrogen carbonate ions (SBF15). Interestingly, for samples exposed to non-buffered SBF (SBFnoTRIS), no changes were observed.

These results emphasize the significant influence of SBF solutions composition on dissolution kinetics and bioactive properties of reactive glass materials. Furthermore, it underscores the need for customized testing protocols to accurately evaluate the performance of such materials in biomedical applications.

Acknowledgement

This work was supported from the grant of Specific university research – No. A2_FCHT_2023_042 and No. A2_FCHT_2024_045.

References

1. Krishnan V., Lakshmi D.: J. Adv. Pharm. Technol. Res., *4*, 78 (2013).
2. Kokubo T., Takadama H.: Biomaterials, *27*, 2907 (2006).
3. Hench L. L.: J. Mater. Sci. Mater. Med, *17*, 967 (2006).
4. ISO 23317:2014(E) (2014).
5. Kokubo T.: Biomaterials, *12*, 155 (1991).
6. Kulhánková J., Rohanová D., Horkavcová D., Bezdička P., Boccaccini A. R.: Mater. Today Chem., *28*, 101367 (2023).
7. Rohanová D., Boccaccini A. R., Yunos D. M., Horkavcová D., Březovská I., Helebrant A.: Acta Biomater., *7*, 2623 (2011).
8. Rohanová D., Horkavcová D., Paidere L., Boccaccini A. R., Bozděchová P., Bezdička P.: J. Biomed. Mater. Res. B Appl. Biomater., *106*, 143 (2018).

DEGRADATION OF A NEW CLINKER-FREE SULFOCALCIC BINDER 3C DUE TO FREEZING AND THAWING

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Abstract

Due to today's global need to reduce CO_2 emissions, there have been attempts to create new hydraulic binders with the potential to replace Portland cement in the future. Clays calcined in the range of 500-900 °C are a promising low-emission source of pozzolans, which can significantly contribute to further reducing the impact on the environment. The combination of calcined clays with calcium sulfate and lime creates a new stable calcium sulfate hydraulic binder called 3C with suitable cement-like mechanical properties. However, for a new binder, it is necessary to observe its behavior in corrosion conditions, which are one of the most important properties for the construction industry. The aim of this project was to describe the behavior of the 3C binder under conditions of alternating freezing and thawing (FT) in the presence of water or chemical de-icing agents according to the ČSN EN 73 1326, Z1 standard. First, a set of slurries and mortars of the 3C binder with different ratios of components was prepared. A constant water to binder ratio as well as plasticizer addition were used. Cylindrical samples with a minimum height of 50 mm were prepared using polypropylene pipes with a diameter of 100 mm. After a month of curing, water or a 3% NaCl solution was poured onto the sample surface. Subsequently, the samples were cycled at alternating temperatures according to ČSN EN 73 1326, Z1. After every 25 FT cycles, the amount of surface waste was weighed. The selected samples were analyzed from the point of view of phase changes by the XRD method. The results were compared with reference cement samples prepared with the same water to binder ratio.

Introduction

Due to the tendency to reduce CO_2 emissions, the preparation of new clinker-free hydraulic binders that could replace Portland cement in the future is becoming a topical issue. A suitable material for the preparation of such clinker-free binders appears to be calcined clays, which are still being deposited in large quantities as waste overburden material after the mining of coal or other mineral resources[1]. For the calcination of these clays, it is important to achieve suitable pozzolanic properties. An advantage over cement is the significantly lower calcination temperatures 500–900 °C, which significantly reduces the carbon footprint and energy requirements of the process compared to cement clinker calcined at 1,450 °C[1,2]. In the future, binders containing calcined clays will have the potential to replace, for example, today's mixed cements, which contain pozzolans or latently hydraulic substances (blast furnace slag, fly ash, silica fume). The problem with mixed cements is that the quantity of these admixtures will gradually have to be reduced in the future due to ecology. Calcined clays are a promising low-emission source of pozzolans, which can contribute to further reducing environmental impacts[2]. Nowadays, many researchers are engaged in the study of binders based on calcined clays. For example, Srcivener et al.[3,4] prepared a mixed binder containing partially cement clinker (50%), calcined clay, gypsum and limestone called Limestone Calcined Clay Cement (LC^3), while more examples of extensive research dedicated to the partial replacement of clinker with calcined clays can be found, for example, in publications[2,5,6]. However, a more ecological option is the complete replacement of cement clinker with another type of hydraulic binder. According to new research ongoing at UCT Prague in recent years, such a clinker-free binder called 3C could only be based on calcined clay (metakaolin), calcium sulfate ($CaSO_4$ anhydrite II) and lime. It has been proven that these three components together can create a promising and stable sulfocalcic hydraulic binder with suitable cement-like mechanical properties[7,8].

Since the use of clinker-free binders prepared from calcined clays in the construction industry is a relatively new trend, only very little is known about their resistance to FT at the moment and specifically for purely sulfocalcic binders based on calcined clays FT tests were never performed. Resistance to FT is particularly important for outdoor construction applications. Concrete is damaged during freezing, mainly due to the volume expansion of the soaked water as it turns to ice, and also due to chemical de-icers, which are often used as road salt. The resistance of concrete against de-icers can be increased, for example, by using a low water to binder ratio (w)[9,10]. FT research to date for composite binders containing calcined clays is insufficient. In 2021 Sharma et al.[11], dealing with the LC^3 binder, pointed out insufficient research on the FT properties of binders based on calcined clays. The aforementioned authors predict a higher FT resistance of the LC^3 binder compared to Portland cement due to the finer microstructure of the hydrated binder consisting of less interconnected pores (similar to other mixed cements). From another paper by Wang et al.[12] published in 2023, the FT properties of LC^3 mixtures with high-strength cement are known, which showed higher FT resistance compared to the reference cement. Regarding the influence of FT results by using different types of clays, FT cements mixed with different calcined clays (kaolinitic 700 °C, illitic 900 °C and bentonite 900 °C) were addressed by Trümer and Ludwig[13], who pointed out the increase in FT resistance only when kaolinitic clay was used and the increase in resistance was attributed to the finer microstructure of the hydrated sample similarly to Sharma[11].

As a follow-up to the previous research on the properties of the sulfocalcic binder called 3C[7,8], a set of slurries and mortars with different ratios of raw materials was prepared, and the FT corrosion behavior was subsequently studied according to the standard ČSN EN 73 1326, Z1 *Resistence of cement concrete surface to water and defrosting chemicals*[14], which deals with monitoring the amount of surface waste after cycling (alternating temperatures below and above freezing point according to the freezing cycles determined by the standard). The results were compared with the values of the reference Portland cement.

Materials and methods

Raw materials

In this work, three raw materials were used for the production of 3C binder:

- Metakaolin Mefisto L05 (České lupkové závody, CZ) – calcined aluminosilicate clay
- Anhydrite AII $CaSO_4$ (Anhydritec GmbH, DE) – power plant gas desulfurization product
- Lime $Ca(OH)_2$ (Čertovy schody, Lhoist, CZ) – calcined limestone

The basic characteristics of these raw materials such as phase composition (XRD), oxide composition (XRF) and particle size distribution (PSD) are shown in the following Tables I-III. Furthermore, Portland cement CEM I 42.5 (Cement plant Mokrá, Heidelberg Materials, CZ) was used as a reference material. XRD was measured on X'Pert3 Powder diffractometer (PANanalytical, NL) and qualitative and quantitative analyses were evaluated by HighScore Plus 4.0 software (PANanalytical, NL) using a Rietveld method. The amorphous content was determined by the internal ZnO standard. XRF was measured on X-ray spectrometer ARL 9400 XP (Thermo Scientific ARL, CH). PSD was measured using Bettersizer ST Laser Particle Size Analyzer (Dandong Bettersize Instruments Ltd., CN).

Table I

Phase composition, XRD [wt.%]

Material	Amorph.	Anhydrite	Portlandite	Quartz	Calcite	Mullite	Muscovite	Anatase
Calcined clay	90	0	0	5	0	2	2	1
AII	0	100	0	0	0	0	0	0
$Ca(OH)_2$	0	0	98	0	2	0	0	0

Table II

Oxide composition, XRF [wt.%]

Material	Al_2O_3	SiO_2	CaO	SO_3	TiO_2	Fe_2O_3	MgO	K_2O	Others
Calcined clay	46.4	49.2	0.2	0.0	1.6	1.4	0.2	0.8	0.2
AII	0.1	0.4	44.5	54.8	0.0	0.1	0.1	0.0	0.0
$Ca(OH)_2$	0.0	0.0	99.1	0.1	0.0	0.0	0.7	0.0	0.1

Table III

Particle size distribution [µm]

Material	D10	D50	D90
Calcined clay	1.24	5.58	19.51
AII	1.60	18.43	68.93
$Ca(OH)_2$	1.50	5.78	47.91

Preparation of samples

Five 3C binder mixtures and one reference cement mixture were prepared, which were in the form of slurries (marked K) and mortars (marked M). The specific ratio of binder raw materials for the preparation of mixtures can be found in Table IV. During mixing, water to binder ratio w = 0.35 and superplasticizer content of 2–2.5 wt.% were used for slurries preparation. Mortars were prepared by adding 3 parts of sand fractions to 1 part of binder 3C or cement prepared according to Table IV., while water to binder ratio was w = 0.36 and superplasticizer content was 2–2.5 wt.%. The amount of superplasticizer was dosed to maintain the same consistency of the mixtures. Mixing time was 2–4 minutes. Immediately after mixing, cylindrical bodies were created from the mixture using polypropylene pipes with a diameter of 100 mm. To achieve optimal aeration, the samples were vibrated using a vibrating table for 2 minutes. The bodies were stored in humid environment (RH > 95%) for 28 days to ensure sufficient strength before FT cycling.

Table IV
Composition of slurries [wt.%]

Mixture	Calcined clay	AII	$Ca(OH)_2$	Cement
H2	50	25	25	0
H9	60	15	25	0
H15	65	20	15	0
H17	65	30	5	0
H40	45	35	20	0
CEM	0	0	0	100

Freeze-thaw method

Automatic FT cycling was carried out according to ČSN 73 1326, Z1, method C[14], in the Memmert CTC256 environmental test chamber. Tap water or 3% NaCl solution was poured on the surface of the samples to a height of about 20 mm, and the samples covered with aluminum foil were placed in the FT chamber. The temperature alternated from -18 ± 2°C to 5 ± 2°C with a residence time of 3 hours at each extreme. At the end of every 25 cycles, the waste was scraped off, filtered, dried to constant weight and weighed. FT cycling was performed up to 200 FT cycles. The evaluation, carried out according to the standard ČSN 73 1326, Z1, method C, is shown in the following Table V.

Table V
Corrosion evaluation of surface according to standard ČSN EN 73 162, Z1, method C[14]

FT corrosion evaluation	[g.m^{-2}]
1. Undisturbed	up to 50
2. Slightly disturbed	50–500
3. Disturbed	500–1000
4. Severely disturbed	1000–3000
5. Crumbled	over 3000

Results and discussion

FT

The following graphs (Figures I–II) show the resulting cumulative waste values after FT in H_2O or 3% NaCl environment for all prepared slurries and mortars. Corrosion evaluation lines from Table V taken from the standard ČSN EN 73 162, Z1 are marked in the Figures I and II.

From both Figures I and II, one can generally see a lower FT resistance in NaCl environment and a decrease in resistance with the number of FT cycles. Figure I with the results of the 3C binder slurries shows that the lowest FT resistance was observed in the H17 slurries (with the lowest lime content) and the reference CEM slurries in both environments. Furthermore, it can be seen that after 200 cycles, the H40 slurry exhibited the best resistance in water, and the H9 slurry exhibited the best resistance in NaCl. The low resistance of H9 in water compared to NaCl is probably due to the fact that after 125 FT cycles, a large compact piece broke off from the surface of the sample, which caused a jump in the weight of the waste. When comparing the resistance of slurries and mortars, it should be noted that according to the ČSN EN 73 162, Z1 standard, the test is optimized only for mortars, which generally have a higher FT resistance due to aggregates and greater material density[9]. The FT measurement on the slurries was carried out for the sake of comparison and the subsequent possibility of measuring the phase composition.

Figure II shows the results of mortars from 3C binder in both environments. As before, lower FT resistance was observed in the NaCl environment and a decrease in resistance with the number of FT cycles. Mortar H17 again had the lowest resistance to FT in both environments, followed by mortars H40 and H2. The long-term result was that the H15 and H9 mortars in this case had minimal or no waste during 200 FT cycles. This makes them even more durable than the reference CEM Portland cement mortar; this corresponds to results from the literature[11,12]. The durability of H15 and H9 mortars was high and corresponded to an undisturbed surface after 200 cycles in the H_2O environment and to a slightly disturbed surface after 200 cycles in the NaCl environment.

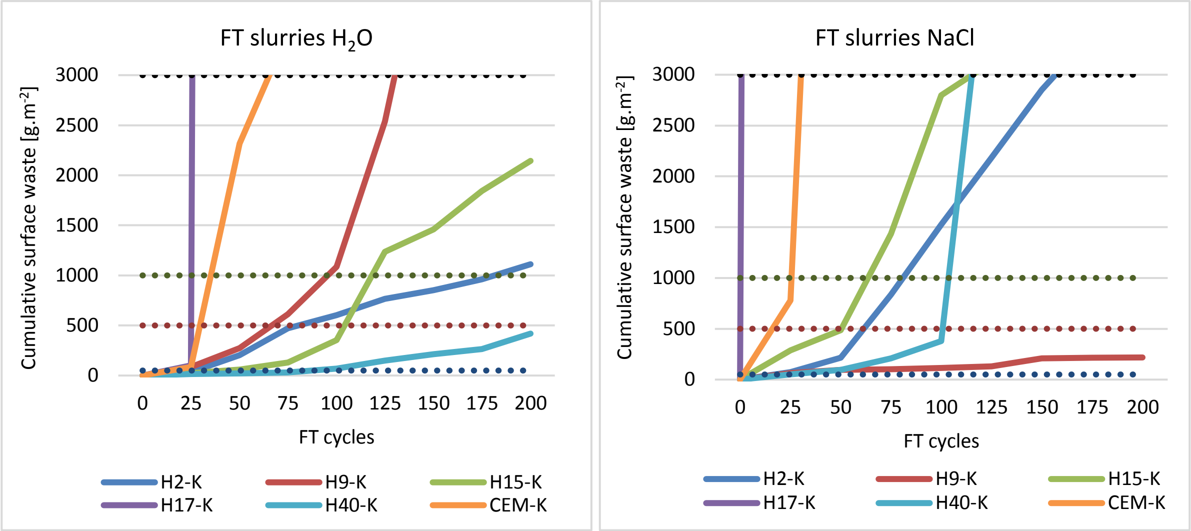

Figure 1. FT resistance of slurries in H_2O (left) and NaCl (right)

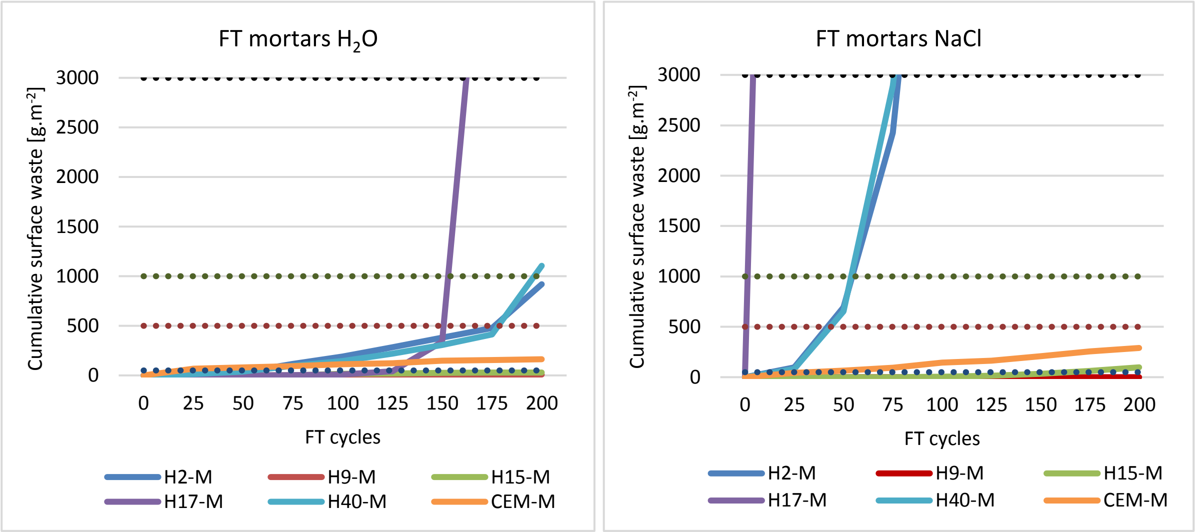

Figure 2. FT resistance of mortars in H_2O (left) and NaCl (right)

Phase composition during FT

During the FT cycling, the phase composition of the selected H15 slurry was monitored using XRD, both in water and in NaCl. After each elapsed 25 cycles, the weighed waste was pulverized and mixed with the ZnO internal standard. The results showed that, in general, the H15 slurry contained a high proportion of the amorphous phase. Ettringite was observed as the main crystalline phase, and residual anhydrite, calcite and quartz were the other detected phases. FT treated H15 slurry in water and 3% NaCl environment showed the decreasing amount of amorphous phase during cycling. At the same time, a corresponding increase in ettringite was observed with FT cycling. The amount of unreacted anhydrite and quartz is within error constant with cycling. In general, it can be concluded that the trend of phase change behavior is similar in both H_2O and NaCl environments and similar trends of phases during FT were observed as for example for the FT treated sulfocalcic binder based on FBC ash[15].

Conclusion

It was found that with increasing number of FT cycles, the resistance decreases for all samples; however, it is important to maintain the same water ratio and slurry/mortar consistency so that the results can be compared with each other. In general, the FT resistance is higher in the H_2O environment and FT resistance is higher for mortar samples. The best results found for H9 and H15 mortars in both H_2O and NaCl. No FT resistance of H17 is probably due to too little lime content (5%) of 3C mixture. From the point of view of the phase composition during FT of selected H15 sample, the proportion of amorphous phase decreased, the proportion of ettringite increased, new phases were not found during FT. With a suitable composition 60-65 wt.% calcined clay + 15–20 wt.% $CaSO_4$ AII + 15-25 wt.% $Ca(OH)_2$, the 3C binder mortars are FT resistant in H_2O and NaCl. Compared to CEM, an even higher FT resistance was observed for the optimal composition of the 3C binder.

Acknowledgement

This project was financially supported from the state budget by the Technology Agency of the Czech Republic within the scope of TREND Program FW01010195.

This work was supported from the grant of Specific university research – grant No.A2_FCHT_2024_033 and Specific university research – grant No.A1_FCHT_2024_008.

References

1. Siddique, R., Cachim, P., Eds. *Waste and Supplementary Cementitious Materials in Concrete*, 1st ed.; Woodhead Publishing: UK, 2018.
2. Bishnoi S., Eds. *Calcined clays for sustainable concrete,* 1 st ed.; Springer: Singapore, 2020.
3. Scrivener, K.; Martirena, F.; Bishnoi, S.; Maity, S. Calcined Clay Limestone Cements (LC^3). *Cem. Concr. Res.* **2018**, *114*, 49–56. doi:10.1016/j.cemconres.2017.08.017.
4. Sharma, M.; Bishnoi, S.; Martirena, F.; Scrivener, K. Limestone calcined clay cement and concrete: A state-of-the-rt review. *Cem. Concr. Res.* **2021**, *149*, 1–13. doi:10.1016/j.cemconres.2021.106564.
5. Ayati, B.; Newport, D.; Wong, H.; Cheeseman, Ch. Acid activated smectite clay as pozzolanic supplementary cementitious material. *Cem. Concr. Res.* **2022**, *162*, 1–8. doi:10.1016/j.cemconres.2022.106969.
6. Krishnan, S.; Bishnoi, S. A numerical approach for designing composite cements with calcined clay and limestone. *Cem. Concr. Res.* **2020**, *138* (8), 1–9. doi:10.1016/j.cemconres.2020.106232.
7. Škvára F., Šídlová M., Polonská A.: Composite hydraulic binder, producing and using it. CZ patent 308850, May 26, 2021.
8. Škvára, F.; Šídlová, M.; Šulc, R.; Pulcová, K. Activation of Metakaolin by CaO and $CaSO_4$ Anhydrite II. *Ceramics-Silikáty* **2023**, *67* (1), 1–9. doi:10.13168/cs.2022.0054.
9. Page, C. L.; Page, M. M. *Durability of concrete and cement composites*, 1st ed.; Woodhead Publishing Limited: Cambridge England, 2007.
10. Harnick, A. B.; Meier, V.; Rosli, A. Combined influence of freezing and deicing salt on concrete: physical aspects, *Durability of building materials and components, Eds. P J Sereda and G G Litvan* 1980, 474–484.
11. Sharma, M.; Bishnoi, S.; Martirena, F.; Scrivener, K. Limestone calcined clay cement and concrete: A state-of-the-art review. *Cem. Concr. Res.* **2021**, *149*, doi:10.1016/j.cemconres.2021.106564.
12. Wang, L.; Zhu, Z.; Ahmed, A. H. Self-healing behavior of high-strength strain-hardening cement-based composites (HS-SHCC) blended with limestone calcined clay cement (LC^3). *Construction and Building Materials* **2023**, *370*, doi:10.1016/j.conbuildmat.2023.130633.
13. Trümer, A.; Ludwig, H. M. Assessment of Calcined Clays According to the Main Criterions of Concrete Durability. In *Calcined Clays for Sustainable Concrete*, 3rd International Conference on Calcined Clays for Sustainable Concrete; Bishnoi, S., Ed.; Springer, 2020; pp 475–481. doi:10.1007/978-94-024-1207-9.
14. ČSN 73 1326, Z1. *Resistance of cement concrete surface to water and defrosting chemicals,* Praha: Czech Standards Institute, 2003. 24 p.
15. Pulcová, K.; Šídlová, M.; Šulc, R.; Kohoutková, M. Degradation of a Sulfocalcic Binder in a Mixture with Cement due to Freezing and Thawing. *Ceramics-Silikáty* **2022**, 66 (4), 453–461. doi:10.13168/cs.2022.0041.

REACTIONS OF SILICON CARBIDE IN WATER-STABILIZED PLASMA

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Abstract

Silicon carbide (SiC) possesses a range of extreme physicochemical properties that make it suitable for applications across various industrial sectors. At normal or slightly elevated temperatures, it is used in engineering as an abrasive or machining material and finds applications in optics, electronics, and electrical engineering. Its high corrosion resistance and particularly its radiation stability are also utilized in the construction of equipment exposed to nuclear fuel or directly within nuclear reactors. However, its behaviour at extremely high temperatures, oxidation phase, or structural transformations and inconsistent thermal decomposition pose challenges. Published data on these properties are highly contradictory due to the experimental difficulty in studying materials at temperatures above 3000 K. This article describes the behaviour of silicon carbide in the plasma generated by a hybrid water-stabilized plasma torch WSP-H 500, capable of achieving temperatures up to 25000 K at its output. The study focuses on the products formed during the deposition of powdered SiC on graphite substrates, aiming to elucidate the differences between passive and active oxidation of SiC, which are attributed in literature to the presence of volatile and unstable Si_2O_2 molecules formed at extreme temperatures.

Introduction

The motivation for this contribution stemmed from findings regarding the causes of the Fukushima Daiichi Nuclear Power Station accident in 2011. Analyses revealed that the accident was caused by inadequate protection of uranium nuclear fuel encapsulated in zirconium alloys with low radiation stability. These alloys reacted with water vapor at temperatures exceedingly approximately 2000 K in the light water reactor, producing hydrogen which led to a catastrophic explosion [1, 2].

$$Zr + 2\ H_2O = ZrO_2 + 2\ H_2 \qquad (1)$$

According to recent information, current considerations focus on protecting fuel rods so that zirconium alloys do not directly contact primary reactor water. One of the proposed solutions involves encapsulating fuel elements in silicon carbide (SiC) composites known for their high radiation stability, mechanical strength at high temperatures, and other properties crucial for nuclear energy. The main drawback in nuclear reactor applications, however, lies in SiC's low oxidation resistance at high temperatures, especially in environments containing hydrogen and oxygen released during nuclear reactions. Therefore, research efforts are dedicated to studying the structural and chemical stability of SiC at extreme temperatures. Research at high temperatures is limited and complicated primarily by technical constraints in equipment and apparatus capable of reaching temperatures above 3000 K [3, 4]. Nonetheless, the water-stabilized plasma generator developed and patented by the Institute of Plasma Physics of the Czech Academy of Sciences [5-7] can create chemical and thermal environments suitable for simulating conditions that may occur in nuclear reactors with uranium fuel rods protected by silicon carbide-based materials. This study aims to gather information on SiC behaviour in water-stabilized plasma at temperatures up to 25000 K.

Experimental

The research utilized a water-stabilized hybrid plasma torch WSP-H-500 with a power output of up to 160 kW. Commercial SiC powder variants SiC F500 and SiC F240 (supplier: TGA s.r.o. Kunštát) were processed, from which commercial products of any shape and size under the brand ROCAR® are prepared by the SiSiC sintering method at a maximum temperature of 1800°C or by the SSiC method at temperatures above 2000°C at CERAMTEC Ltd. [8]. The approximate temperature characteristics of the plasma at the output of the plasma torch nozzle with a carbon cathode WSP 500 are shown in Figure 2 [7].

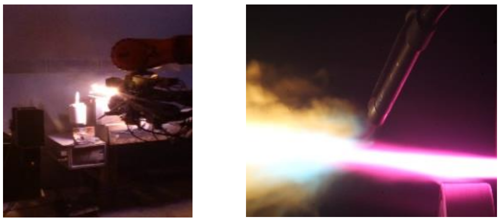


Figure 1 Plasma torch WSP-H-500 and detail of SiC powder injection into the plasma stream

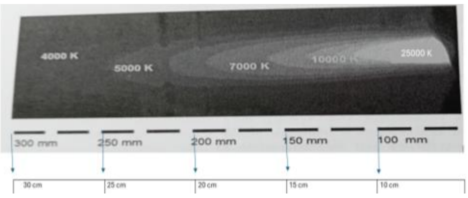
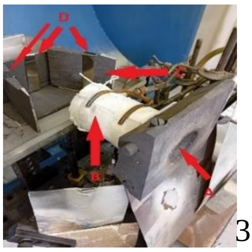


Figure 2 Temperature map of the plasma flame [9]

The first experiment was designed to introduce fine-grained SiC F500 powder with a median grain size of 16 µm into the plasma stream without the need for a protective non-oxidizing atmosphere. The plasma stream containing SiC particles was directed into a graphite tube 10 cm in length, positioned 10 cm from the nozzle of the plasma torch, as shown in Figure 3a and the schematic diagram in Figure 3b.



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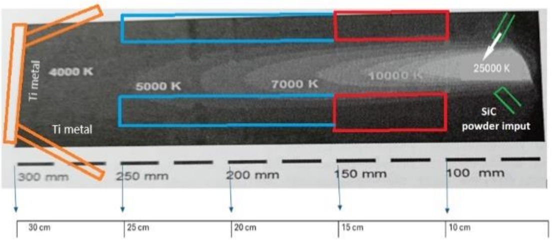

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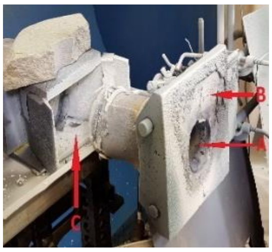


3c

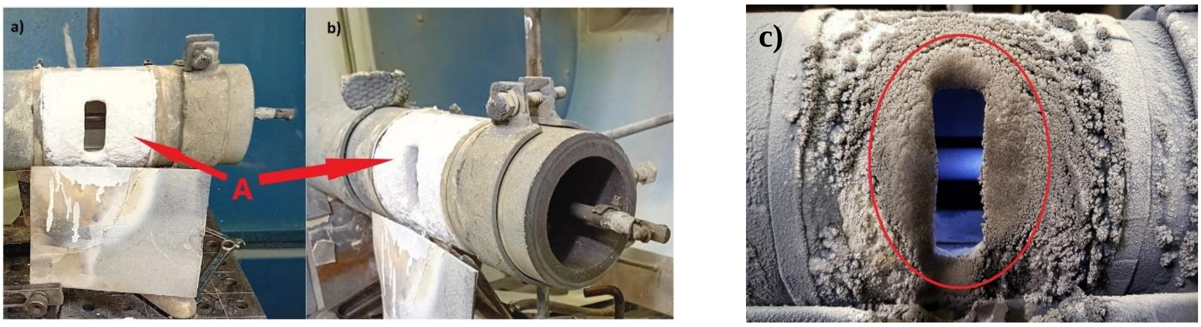
Figure 3a Graphite tube assembly and placement of titanium substrates

Figure 3b Schematic of the geometric arrangement of the assembly (with simulated background temperature distribution from the plasma torch outlet according to [9])

Figure 3c Assembly after plasma spraying of SiC with sample collection points marked A, B, and C

At the end of the graphite tube, a graphite partition was placed to capture the passed-through product that did not adhere to the front and inner walls of the tube. Additionally, titanium sheet substrates were placed in various parts of the assembled apparatus to obtain preliminary information on the oxidation state in remote sections of the apparatus.

The second experiment was conducted in an apparatus consisting of a graphite tube positioned perpendicular to the axis of the plasma flame. A slot for the entry of plasma and the investigated SiC powder was located in the frontal part of the tube. Inside the tube, a graphite rod with a diameter of 13 mm and a length of 90 mm served as a substrate, mounted on a sliding device allowing oscillatory movement towards the inlet opening (Figures 4a, 4b, 4c). For studying the reaction of silicon carbide with plasma at higher temperatures, the powder fraction F240 with an average grain size of 50 µm was selected.



Figures 4a, 4b, 4c Graphite tube with the placement of the carbon substrate and sampling points marked (Position A indicating the primary protective layer of deposited TiO_2)

Results

Analytical results from the first experiment confirmed that at the longest monitored distance from the entry point of SiC powder into the plasma stream (position C, i.e., 30 cm) where a titanium target with a melting point of 1668°C was placed, it melted and subsequently oxidized to TiO_2. At the same distance but at an angle of approximately 60° from the side, titanium substrates were only slightly oxidized; according to literature DTA analyses, oxidation of titanium begins at around 600°C [10]. Large SiC particles (>16 µm) were fixed on their surfaces which even during plasma passage did not completely react to SiO_2. This roughly characterized the thermal and oxidative environment in the lateral part of the plasma flam

A sample taken from the front surface of the graphite wall (Figure 3c - position B) showed good consolidation and allowed for the preparation of a cross-section for microscopic observations. From the microscopic image in Figure 5, it is evident that some thermally undecomposed and unoxidized SiC particles are connected by a molten silica oxide. According to the diffractogram in Figure 6, the presence of both amorphous and crystalline phases of silicon dioxide is apparent.

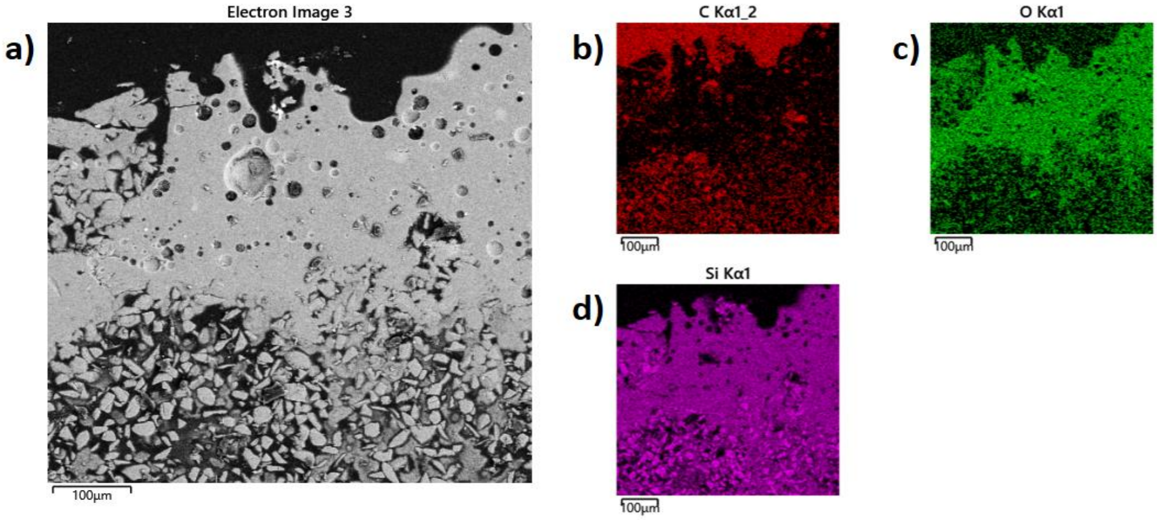
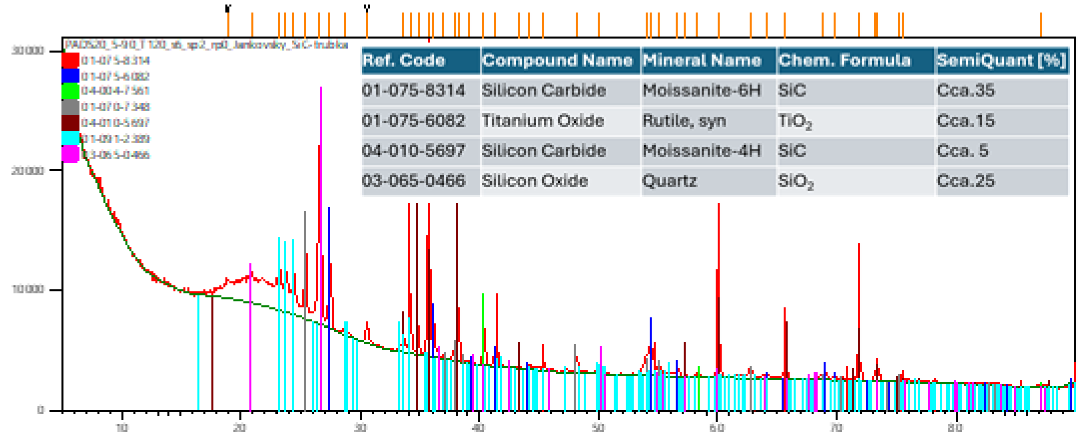


Figure 5 Structure of the sintered sample taken from the highest temperature area on the graphite substrate and the elemental distribution map



Ref. Code	Compound Name	Mineral Name	Chem. Formula	SemiQuant [%]
01-075-8314	Silicon Carbide	Moissanite-6H	SiC	Cca.35
01-075-6082	Titanium Oxide	Rutile, syn	TiO_2	Cca.15
04-010-5697	Silicon Carbide	Moissanite-4H	SiC	Cca. 5
03-065-0466	Silicon Oxide	Quartz	SiO_2	Cca.25

Figure 6 Diffractogram of the sample from position 3c-B. The elevated background between 20 – 30° 2Θ indicates the presence of the amorphous phase of silica.

The consolidated sample used for preparing the microscopy cross-section confirmed information about the formation of cavities in the silica melt [1]. Spherical cavities in a thick oxide layer were formed by the decomposition of SiC with water vapor, which can be expressed by the equation:

$$SiC(s) + 3\ H_2O(g) \xrightarrow{1200\ ^\circ C} SiO_2(s) + 3\ H_2(g) + CO(g) \qquad (1)$$

However, it was not possible to distinguish whether this layer was passive or active. Further analyses and comparison of oxygen content measurements by the LECO method and a new method involving the reaction of silicon oxides with scandium oxide forming the well X-ray-detectable thortveitite $Sc_2Si_2O_7$ contributed to resolving this issue:

$$2\ SiO_2 + Sc_2O_3 \xrightarrow{1200\ ^\circ C} Sc_2Si_2O_7 \qquad (2)$$

Figure 7 illustrates the result of the reaction on the surface of oxidized SiC grains with excess scandium oxide at 1200°C. The shape of SiC crystals is clearly visible, surrounded by a layer of formed thortveitite $Sc_2Si_2O_7$ and excess unreacted Sc_2O_3 as documented in the subsequent diffractogram in Figure 8.

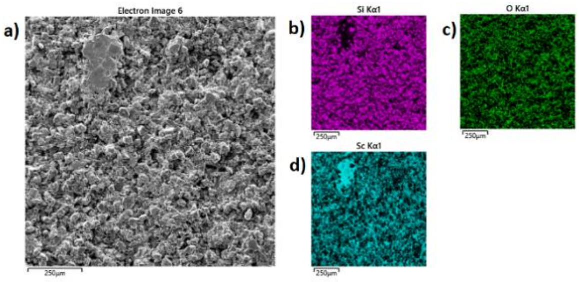
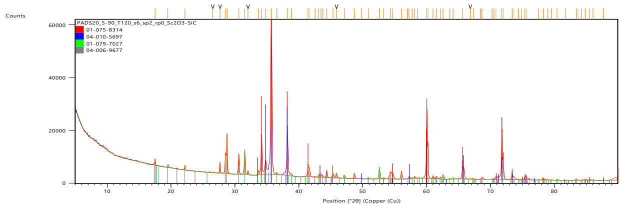


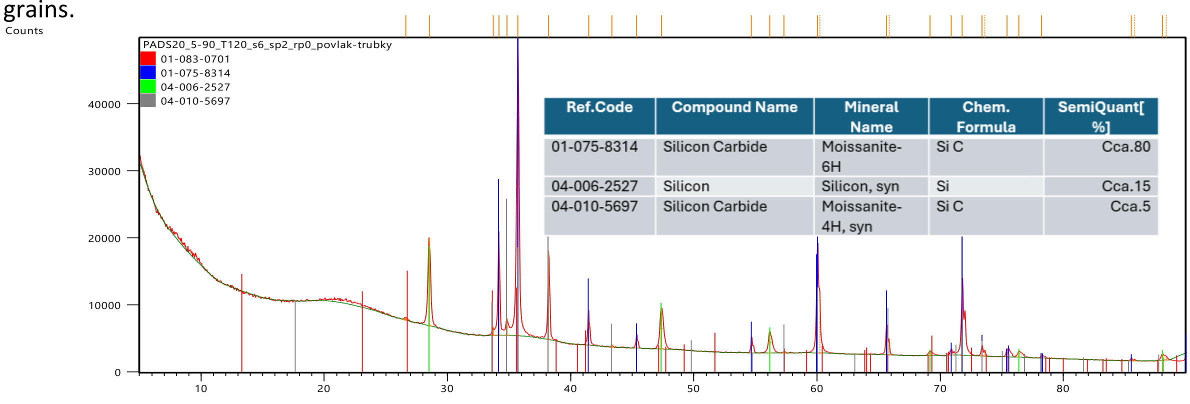
Figure 7 Image of element distribution in the sintered sample after the reaction of Sc_2O_3 + SiO_2 using the SPS method



Ref.Code	Compound Name	Mineral Name	Chem. Formula
01-075-8314	Silicon Carbide	Moissanite-6H	Si C
04-010-5697	Silicon Carbide	Moissanite-4H, syn	Si C
01-079-7027	Scandium Oxide	Kangite, syn	Sc2 O3
04-006-9677	Scandium Silicate	Thortveitite, syn	Sc2 (Si2 O7)

Figure 8 Diffractogram of the reaction product SiC + SiO_2 + Sc_2O_3

A crucial result was obtained after analyzing a sample taken from the inner wall of the graphite tube (position A). Evaluation of the diffractogram (Figure 9) revealed partial thermal decomposition of SiC resulting in elemental silicon. The diffractogram lacks lines of crystalline SiO_2; however, the presence of an amorphous band around 20 θ suggests the possibility of an amorphous passivation layer likely formed after the sample cooled on the SiC grains.



Ref.Code	Compound Name	Mineral Name	Chem. Formula	SemiQuant[%]
01-075-8314	Silicon Carbide	Moissanite-6H	Si C	Cca.80
04-006-2527	Silicon	Silicon, syn	Si	Cca.15
04-010-5697	Silicon Carbide	Moissanite-4H, syn	Si C	Cca.5

Figure 9 Diffractogram of a sample taken from the inner wall of the graphite tube (position A))

In the second series of experiments, it was possible to observe the reaction of SiC at the highest achievable temperature under the given geometric conditions of the setup ranging from approximately 10000 K to 5000 K. On a cylindrical graphite substrate (Figure 10) a homogeneous ceramic crystalline layer was formed (Figure 11), where diffractometric analysis confirmed the presence of elemental silicon. Infrared spectra did not show any presence of SiO_2. Similarly, the formation of a silicon surface layer was confirmed in a microscopic cross-section of the graphite substrate rod (Figure 12).

Figure 10 Cylindrical graphite substrate before and after deposition

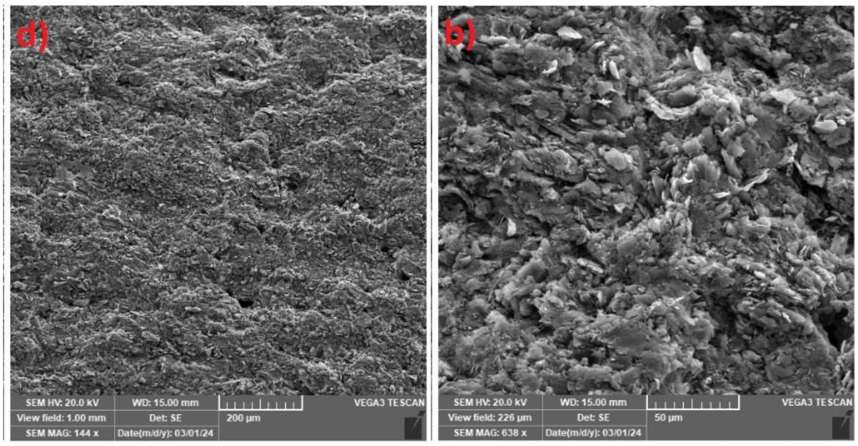


Figure 11 Homogeneous crystalline ceramic surface layer on the graphite substrate

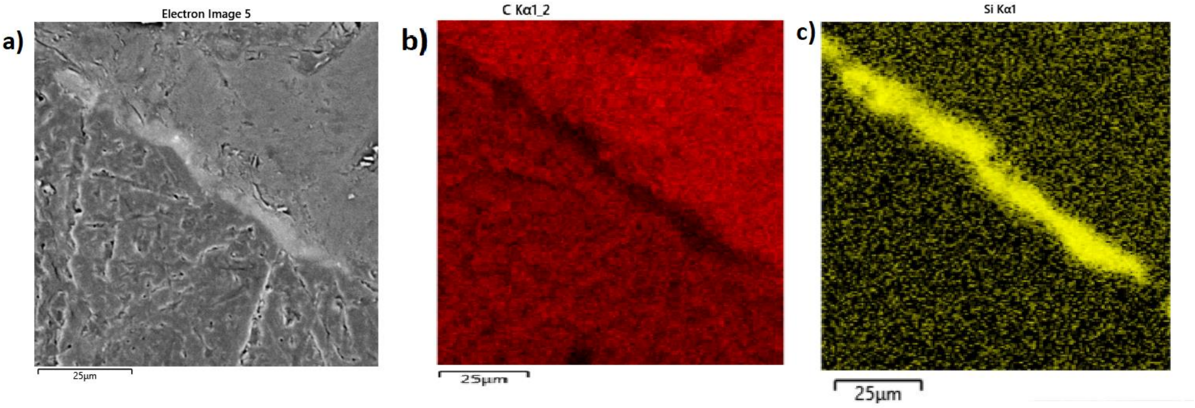


Figure 12   Image of the perpendicular cut through the graphite substrate with the silicon layer

However, the thickness and weight of the resulting silicon layer did not correspond to the quantitative parameters of the introduced SiC into the reaction chamber. The surface layer formed on the substrate during the SiC spray at temperatures above approximately 5000 K and its weight loss were likely caused by the progression of reactions leading to SiO_x suboxides. A typical reaction involves the formation of volatile Si_2O_2 with a boiling point of 1880°C [12] according to the equation: $2\ SiO_2 + 2\ CO = Si_2O_2(g) + 2\ CO_2$. This reaction occurs intensively especially in environments with low partial pressure of oxygen achieved in our case by introducing nitrogen into the apparatus originally intended to function as a non-oxidizing atmosphere. Further losses of silicon could be related to its boiling point of 3264 °C.

Conclusions

When introducing powdered SiC into the stream of water-stabilized plasma, several reaction pathways occur simultaneously. The presence of oxygen or oxygen ions from the plasma induces primary passivation oxidation: $SiC + 3/2\ O_2 = SiO_2 + CO$ resulting in the formation of crystalline SiO_2 for coarser SiC fractions, which transforms into an amorphous state during brief exposure to temperatures above 3000 K. Concurrent oxidation from the carbon environment of the graphite apparatus construction producing CO and CO formation during SiC combustion enables a reverse reaction type where Si_2O_2 is formed: $2\ SiO_2 + CO = Si_2O_2(g) + 2\ CO_2$. The resulting Si_2O_2 with a boiling point of 1880°C is volatile, leading to the loss of the passive layer and subsequent oxidation, including mass loss and reduction in size of oxidized SiC grains. Above 3000 K, simultaneous decomposition into elemental silicon occurs, which upon cooling cannot react back with carbon due to thermodynamic preferences favoring the formation of gaseous CO or CO_2 under these conditions. An additional finding is that under water plasma conditions, elemental silicon does not react with nitrogen from the protective atmosphere.

References

1. Pham H.V., Kurata M., Steinbrueck K., Thermo 2021, 1(2), 151-167 Doi.org/10.3390
2. Chen S., Zeng Y., Xiong X., Lun H., Journal of the European Ceramic Society Vol. 41, Issue 11 (2021), 5445
3. Joyce M., Nuclear Safety and Regulation. Nuclear Engineering, Ed. Butterworth-Heinemann, 2018; pp 323-5
4. Yoon D-H., J. Korean Ceramic Society, Vol.57, 246-270 (2020)
5. Janata M., Chráska P., Mušálek R.: Průmyslové spektrum. [1-2] 6-7 (2014)
6. Hrabovský M., Kopecký V., Sember V., Kavka T., et al. Transactions on Plasma Science 34, 1566-1575 (2006)
7. Mašláni A., Sember V., Hrabovský M., Plasma Physics and Technology 2, 159-165 (2015)
8. CeramTec ROCAR. www.ceramtec-industrial.com/en/materials/silicon-carbide/rocar (June 20, 2024).
9. Leitner J., Voleník K., Neufuss K., Czech Journal of Physics 56, 1991-1400 (2006)
10. Khosravi M., Toroghinejad M. et al. J. Mater. Science 31, 7150-7163 (2020)
11. Park D.J., Jung Y.I., et al. Corrosion Science 88, 416-422 (2014)
12. Ming T.,Turishchev S., Schleusener A., et al. Small 2021, 17, 2007 650 (1-6) © 2021 Wiley-VCH GmbH

CORROSION PROPERTIES AND BOND STRENGTH IN CONCRETE OF CONVENTIONAL PRESTRESSING STEEL REINFORCEMENT WITH PLASMA SPRAYED Si-SiC-SiO$_2$ COATINGS

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Abstract

In this study is verified the possibility of corrosion protection of conventional concrete prestressing reinforcement (Y1860 S7 15.7) by application of a protective ceramic coating based on decomposition products after plasma deposition of silicon carbide. The composition of the coating was investigated by cross-sectional scanning electron microscopy (SEM). The barrier protection properties of the silicon carbide coating (Si-SiC-SiO$_2$) partially incongruently decomposed into elemental silicon and amorphous SiO$_2$ were comparatively verified in NaCl solution by measuring the time dependence of the polarization resistance (R_p). Furthermore, the bond strength of coated prestressing reinforcement in normal strength concrete was comparatively tested using pull-out test arrangement. The coating provides enhanced barrier corrosion protection in an electrolyte with chloride anions. The presence of a top significantly porous coating layer reduces the bond strength in normal strength concrete by approximately 30 % for 2.0 mm slip.

Introduction

Corrosion damage to conventional prestressing reinforcement placed in the grouting channel by chloride anions can lead to unpredictable collapse of reinforced concrete structures, preferably bridges and footbridges. The most significant corrosion damage is in the area of inadequate filling of the grouting channel [1-3]. A typical example is the destruction of the Morandi Polcevera in Genoa Italy in 2018 [4] or the Troja footbridge in Prague in 2017 [5, 6]. The results of expert work on this topic confirm that the collapse of the Troja footbridge was due to corrosion of the prestressing reinforcement stimulated by chloride anions [5, 6]. In this paper is studied the possibility of applying corrosion protection in the form of a protective coating formed after the decomposition reaction of silicon carbide in water-stabilized plasma. The barrier protective properties of the silicon carbide coating [7] partially incongruently decomposed into elemental silicon and amorphous SiO2 were comparatively verified by measuring the time dependence of the polarization resistance (R_p) in sodium chloride solution. Furthermore, the bond strength the coated prestressing reinforcement in normal strength concrete was comparatively tested using pull-out test arrangement. Bond strength testing was carried out normatively on cubic concrete specimens [8]. The assumed mechanism of displacement of the bond strength reinforcement in concrete at high values of bond stress was also discussed.

Experimental

For the coating process was chosen a high carbon steel prestressing reinforcement with a significant manganese content of Y1860 S7 15.7, i.e. strand with 7 wires. The steel composition of the prestressing reinforcement is shown in Table I (content of Ni, S, N are completely minor).

Table I. Composition of prestressing steel strand reinforcement (Y1860 S7 15.7)

Alloying element	C	Mn	Si	Cr	P	Fe
wt.%	0.82	0.70	0.26	0.07	0.04	balance

The separated wires of this steel were coated for the used corrosion tests (time dependence of polarization resistance) and the steel strand for the bond strength in normal strength concrete by the pull-out test arrangement. The coating of the steel was carried out in a form referred to as plasma spraying using a 160 kW WSP-H-500 water-stabilised plasma torch. The starting material for the preparation of the ceramic coating was powdered SiC, the chemical and granulometric analysis of this powder is given in Table II and Figure 1. The coatings were prepared on 300 mm long rotating steel bars (or wires) without prior surface roughening by conventional corundum abrasive blasting. The feed distance of SiC powder into the water-stabilized plasma stream was 45 mm, the distance of the steel rods from the mouth of the plasma torch was 200 mm, and the SiC dosage was 150 g/min.

Table II. Chemical analysis of SiC powder F240 (T.G.A. s.r.o. Kunštát)

element	SiC	Al	S	Cl	Ca	Ti	V	Fe	Ni
mass %	99.571	0.097	0.007	0.042	0.021	0.011	0.023	0.190	0.014
error	0.1	0.009	0.003	0.006	0.004	0.003	0.005	0.01	0.004

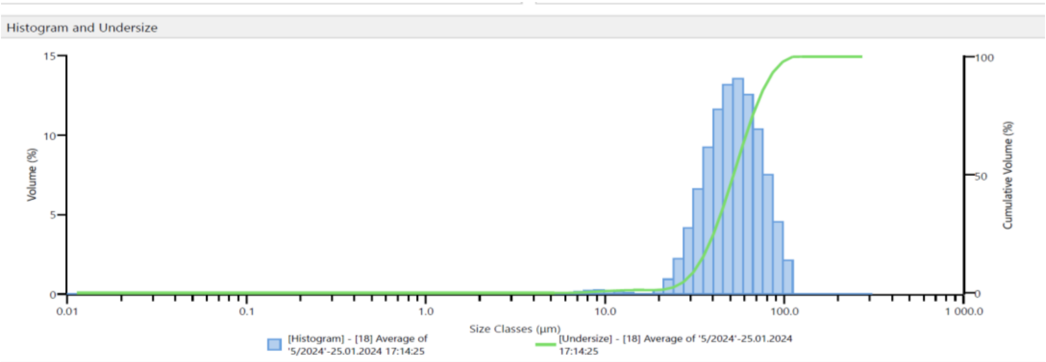

Figure 1. Granulometric analysis od powder SiC F240

Silicon carbide reacts at high temperatures in the plasma stream in several opposite ways [9], depending on the partial pressure of oxygen. It starts to oxidize in the air atmosphere from about 800°C to form crystalline SiO_2, which at further temperature increase above 1700°C goes into an amorphous form. SiC decomposes to elemental silicon above 2830°C [10]. In all these reactions are always formed carbon dioxide and carbon monoxide simultaneously from the carbide carbon, which can then react secondarily to form the gaseous suboxide Si_2O_2, which can lead to the loss of the coating material. In the presence of water vapour, either in the molecular state or as a plasma, bubbles of amorphous SiO_2 then form in the molten surface oxide layer.

The metallographic cross-section view (Figure 2) of the coated steel reinforcement shows the distribution of the individual Si and SiO_2 phases, Figure 3 shows the results od X-ray analysis of the powder taken from top layer of the coating surface.

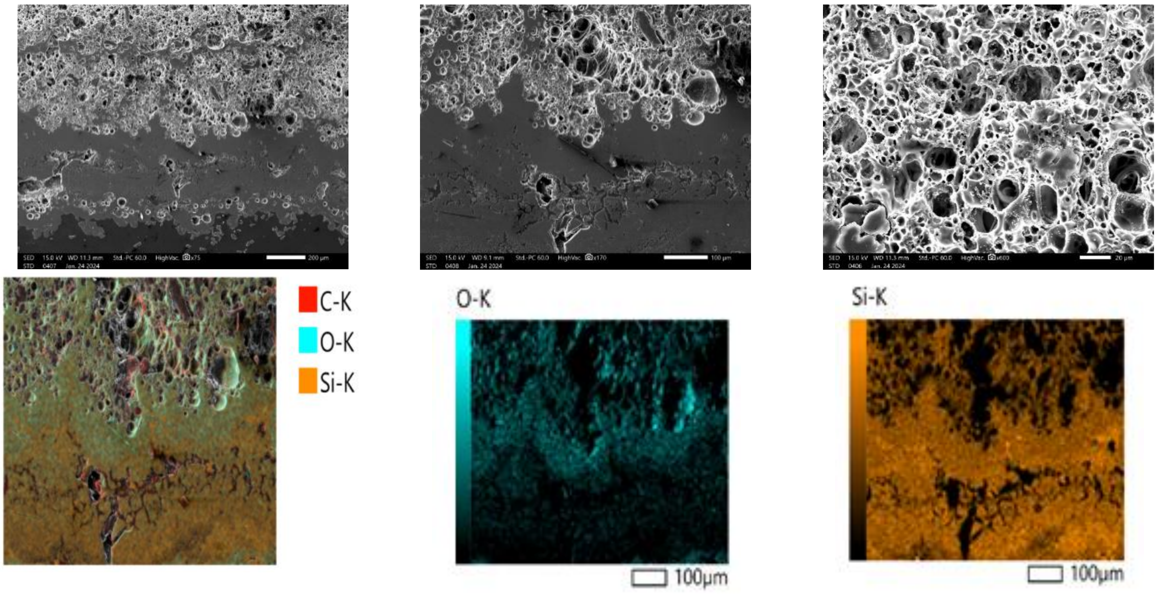

Figure 2. Detail of cross section of coated steel strand prestressing reinforcement showing element maps (content of oxygen and silicon)

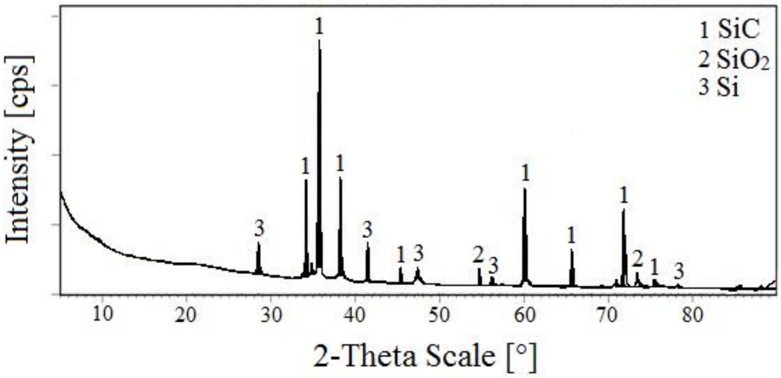

Figure 3. Results of X-ray diffraction analysis of powder taken from the top layer of the coating

For the electrochemical corrosion tests, a total of 5 parallel wire samples (bottom surface insulation) were made. The exposure was carried out in 3.5 wt.% NaCl solution. Polarization resistance values (R_p) was evaluated as the linear coefficient of wire current density and potential in the vicinity of E_{corr} (-20 to +20 mV). Rate of polarization was 0.1 $mV \cdot s^{-1}$. The measurements were carried out for 5 hours and run discontinuously for 30 minutes. For the mechanical bond strength test was chosen (pull-out test arrangement) cubic samples (a = 150 mm). A total of 14 normal strength concrete cubes with embedded reinforcement were produced (7 parallel specimens). Portland cement CEM I (42.5 R) was used to prepare the concrete cubes - the cement composition is described in Table III. The mixing recipe for the formation of the individual concrete samples is described in Table IV. The placement of the individual steel strand in the centre of the moulds was ensured by an internal wooden liner and an external polymer liner created through 3D printing. The samples were aged in a closed atmosphere for 28 days (90% RH, 21.0 ± 1°C). The total cubic strength of the concrete (compressive strength) corresponds to normal strength concrete C30/37.

Table III.
Cement composition guaranteed by producer (CEM I 42.5 R)

compound	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
content (wt. %)	64.2	19.5	4.7	3.2	1.3	3.2	0.78	0.09

Table IV.
Content by m^3 of concrete cubic samples for compressive strength measuring

admixture	content (kg/m^3)	note
cement (CEM I - 42.5 R)	365	pure Portland cement
aggregate	900	fraction 0/4 - fine sand
	585	fraction 4/8
	285	fraction 8/16
mixture w/c	0.55	-

Bond strength in concrete testing was carried out on an MTS 500 kN loading machine. The test was controlled by the displacement of the unloaded end of the strand reinforcement (stable load 0.005 $mm \cdot s^{-1}$) - see experimental arrangement of the pull-out test in Figure 4.

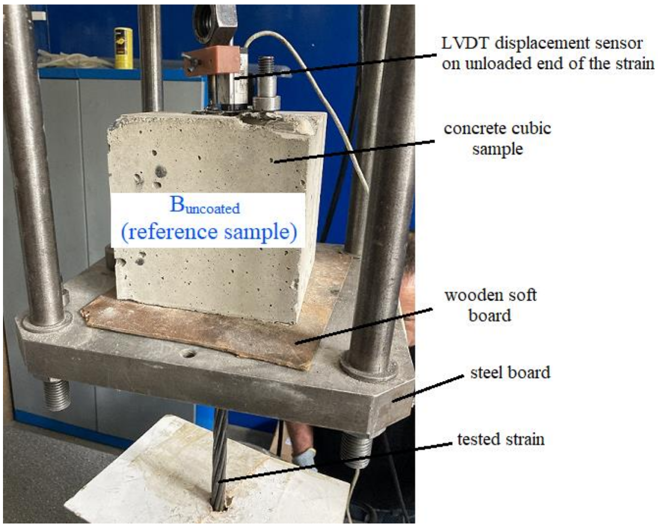

Figure 4. Experimental arragement of bond strength pull-out test of prestressing strand reinforcement in normal strength concrete

Results

The results of the average values of the time dependence of R_p for both samples are shown in Figure 5. The average value of the polarization resistance for the uncoated wire is about 400 Ω·cm^2. There is a gradual increase of the polarization resistance values in the case of uncoated steel over the exposure time (gradual precipitation of iron corrosion products). R_p values were detected at the beginning oft he exposure more then double high in the case of coated wires. R_p decreases and stabilizes to values about 50% higher than in the case of uncoated steel after 1 hour of exposure. The results of the electrochemical corrosion tests indicate barrier protective properties of the coating, but also the coating shows obvious open porosity which limits the protective properties. These pores will be filled with corrosion products and consequently the resistance to corrosion will continue to increase. With regard to corrosion engineering, it would be appropriate to measure the corrosion behaviour of such coated steel by EIS (electrochemical impedance spectroscopy) for a better understanding oft he corrosion mechanism.

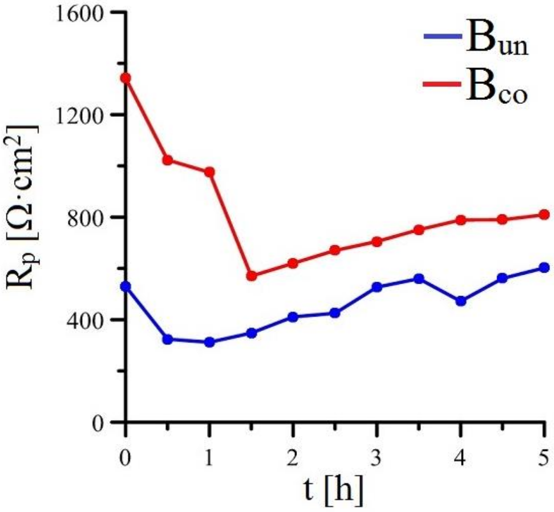

Figure 5. Time dependence of the measurement of R_p (Ω·cm^2) for both sample wire types

The results of the bond strength tests are summarized in Figure 6 and Figure 7, with Figure 6 showing continuous curves of bond stress versus slip and the bar chart in Figure 7 comparing ultimate bond stress (bond strength) and slip for coated prestressing steel reinforcement and uncoated steel. In general, it can be summarized that the presence of amorphous coating with closed spherical pores reduces the bond strength of prestressing reinforcement in concrete. At the beginning of the loading (0.04 mm slip), the bond stress of the coated prestressing reinforcement is approximately 15% lower, but subsequently the difference in bond stress between the two groups of specimens increases to a final value (slip: 2.0 mm) of approximately 30% (see Figure 6). The curves are identical for both types of specimens only at the beginning of the loading. For larger values of slip (> 0.5 mm), the increase in bond strength for the coated reinforcement is only gradual, whereas for the reference group of specimens the increase in bond stress values is faster. It is evident that during bond strength tests, damage to the coating (cracking and spalling) is associated with a reduction in the bond strength of the reinforcement in the normal strength concrete. This finding corresponds to the fact that the surface of the coating is amorphous thin-walled SiO_2 with a large number of spherical pores, which have minimal mechanical strength and can be disturbed and opened by crystallisation pressures due to the hydration of the cement.

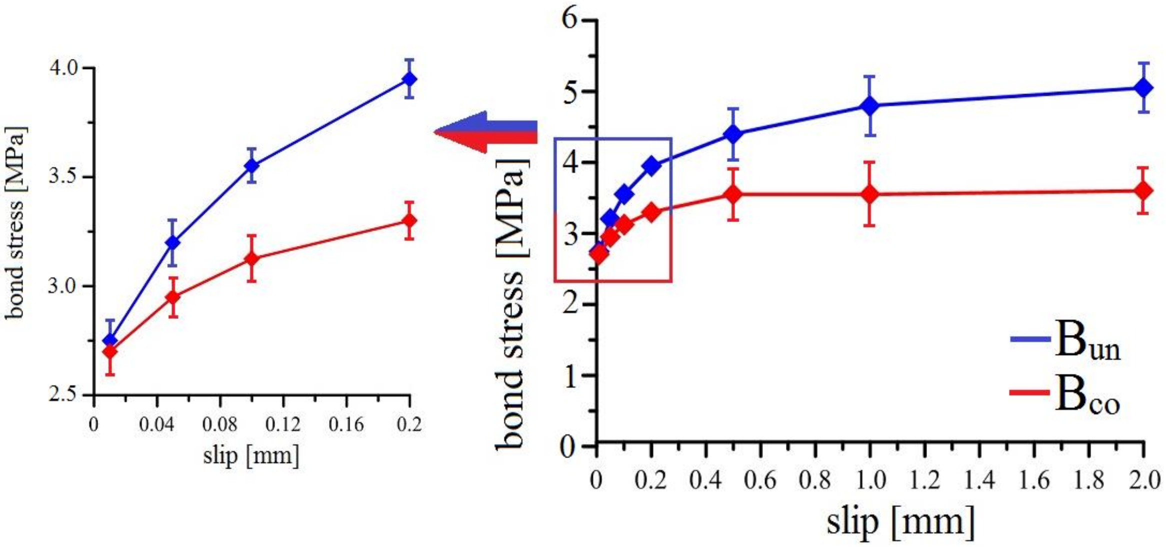

Figure 6. Comparative bond stress vs slip diagram of bond strength of uncoated and coated prestressing strand reinforcement in normal strength concrete

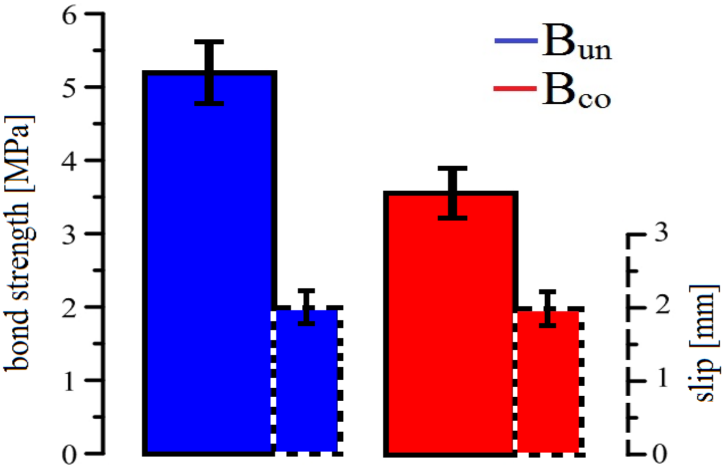

Figure 7. Comparative results of bond strength and ultimate slip for both variants of prestressing reinforcement samples

Conclusion

Based on the first informative experiments described above, the following conclusions can be drawn. In the first stage before the actual application of prestressing reinforcement in normal strength concrete, the barrier protection properties are very significant (verified in NaCl solution), due to the significant stability of both SiC and SiO_2 [7,11]. At longer time intervals, the corrosion resistance decreases due to the porosity, but the barrier protective effect of the coating is still significant. The open pores gradually start to fill with iron corrosion products and thus corrosion damage is reduced. The electrochemical corrosion damage is controlled by the rate of oxygen diffusion to the steel surface in this case. For a more accurate assessment of the barrier protective effects of the formed mixed coating, it is necessary to perform an electrochemical impedance spectroscopy EIS analysis. However, when the coated steel reinforcement is applied to normal strength concrete, the mechanical loading and crystallization pressures of the hydrating cement result in the failure of the mechanically low-strength SiO_2 coating with a large number of closed thin-walled spherical pores. The coated prestressing reinforcement thus damaged exhibits a reduced bond strength in normal strength concrete compared to the uncoated reinforcement of approximately 30 % (at a slip of 2.0 mm). The barrier corrosion protection properties of the coating are sufficient against atmospheric form of corrosion damage and no form of corrosion damage (compared to uncoated reinforcement) was observed on the individual steel reinforcements throughout the experimental period. However, in the case of prestressing strain reinforcement, the coating is discontinuous and porous at the points of tangential contact of the individual wires. Improvement could probably be achieved with a thicker coating. It is clear that plasma-sprayed Si-SiC-SiO_2 coating may be a promising form of barrier corrosion protection for any concrete reinforcement. Further testing of various parameters of coating application to the reinforcement steel surface is necessary.

Acknowledgement

This work has been supported by the Czech Science Foundation (project No. 24-12783S "Study of mechanisms and kinetics of hydrogen corrosion damage of conventional prestressing reinforcement in concrete bridge structures").

References

1. Hart W. H., Lee S. K., Modelling and projecting the onset and subsequent failure rate of corroding bridge post-tension tendons arising from deficient grout, Corrosion 74 (2), 241-248 (2018).
2. Messina D., Proverbio E., Effect of prestressing corrosion on failure in bridges, Structural Concrete 24 (1), 227-238 (2023).
3. Pepé, T. M., Melchers R. E., The effects of corrosion on 45-year-old prestressed concrete bridge beams, Structure and Infrastructure Engineering 7(1-2), 101-108 (2010).
4. Morgese, M., Ansari, F., Domaneschi, M., Cimellaro G. P., Post-collapse analysis of Morandi's Polcevera viaduct in Genoa Italy, Journal of Civil Structural Health Monitoring 10, 69-85 (2020).
5. Čížek P., Kuboň Z., Kander L., Material Analyses of prestressed concrete bridge failure, Conference Metal, Tanger, 26. – 28. 5. Brno, Czech Republic (2021).
6. Kálalová P., Polák M., Stančík V., Experimental analysis of the railway truss bridge using modern methods, Acta Polytechnica CTU Proceedings 40, 39-47 (2023).
7. Brožek V., Živný O., Mastný L., Matušek M., Pokorný P. Corrosion of ceramic silicon carbide in hydrofluoric acid, Ceramics-Silikáty 65, 158-169 (2021).
8. RILEM RC6: Bond test for reinforcement steel. 2: Pull-Out test, E & FN SPON: Paris, France 1983.
9. Özorak Ch., Islak S., Microstructure, wear and corrosion properties of Cu-SiC/WCCo composite coatings on the Cu substrate surface by plasma spray method, Materials Chemistry and Physics 314, 128903 (2024).
10. Kang, H-K., Kang S-B. Thermal decomposition of silicon carbide in a plasma-sprayed Cu/SiC composite deposit, Materials Science and Engineering 428, 336-345 (2006).
11. Herrmann M., Sempf K., Schneider M., Sydow U., Kremmer K., Michaelis A., Electrochemical corrosion of silicon carbide ceramics in H_2SO_4, Journal of the European Ceramic Society 34, 229-235 (2014).

CORROSION EFFECT OF ORGANIC BUFFERS ON BIOACTIVE GLASS

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Abstract

This work aimed to study the corrosion behaviour of the TRIS and HEPES buffers and compare the rates of bioactive glass dissolution, as well as their effect on the HAp formation. Bulk bioactive glass samples were tested under the static-dynamic conditions in three different solutions: i) SBF without TRIS buffer (**SBFnoTRIS**), ii) **SBF+TRIS** (ISO 23317:2014 standard) and iii) **SBF+HEPES**. The concentrations of the elements (Ca, P, and Si) in eluates were analysed using ICP-OES. The pH was measured at physiological temperature (36.5 °C). The surface of glass samples and newly formed layers were observed by SEM/EDS and analysed by XRD methods. This work confirmed that TRIS and HEPES buffers used in SBF produced false positive results of *in vitro* tests. Moreover, the chemical composition, morphology, and crystallinity of the newly created apatite layer formed in buffered SBF are distinct.

Introduction

Bioactive glasses are non-crystalline materials that can induce a specific biological response between an implant and the surrounding tissue. They are widely used as synthetic bone grafts. In treating jawbone defects, they provide a suitable environment for securing a titanium post. After implantation, there is an ion exchange between the glass and the surrounding area, leading to the formation of a bone-like apatite layer. This process leads to a strong connection with the bone without forming an unwanted capsule around the implant. [1,2,3].

The first step in testing bioactive glass is to place the material in a water-based solution without cells. This allows the study of ion release and apatite precipitation. Currently, the most commonly used method for *in vitro* bioactivity testing, involves simulated body fluid (SBF), as described by ISO standard 23317:2014. SBF solution mimics the inorganic composition of human plasma [4]. However, this standard has not changed for years and does not meet current clinical requirements because it only deals with solid samples, not powders or granules, which are more frequently used in practice. In 1991, Kokubo et al. showed that bioactive materials must form apatite in SBF. Since then, bioactivity has been assessed only based on the formation of hydroxyapatite (HAp) on the surface of the biomaterial.

Maintaining a neutral pH during *in vitro* tests is necessary because it affects the dissolution of glass/ glass-ceramic material. The standardized SBF solution is very saturated with hydroxyapatite and has a much higher concentration of Cl^- ions. Another difference is the buffering system. In human plasma, bicarbonates act as buffers, but they are unstable under laboratory conditions [5,6]. Therefore, TRIS buffer is added to the SBF solution. Rohanová et al. have shown that TRIS buffer does not maintain a stable pH and interacts with the glass-ceramic *scaffolds*. The TRIS/HCl buffering system accelerates the dissolution of *scaffolds* and promotes the formation of crystalline apatite (HAp) on the surface [7]. Other buffers, including HEPES, BES, and TES, were investigated to replace TRIS buffer. Testing on glass-ceramic *scaffolds* indicated that these buffers are not inert in SBF either [8,9].

In summary, using buffers in *in vitro* tests can give false positive results. The interaction of TRIS buffer with glass-ceramic *scaffolds* shows that evaluating material reactivity based only on HAp formation (ISO 23317:2014) provides only partial information about the material's surface reactivity. Therefore, relying solely on HAp formation should not be the only indicator to assess material bioactivity. Understanding biomaterial behaviour in SBF solution requires monitoring pH changes, Ca and P concentrations, and the release of dissolution markers like silicon (Si) in the case of glasses and glass-ceramics [10].

In the previously mentioned studies, TRIS and HEPES buffers were tested on glass-ceramic *scaffolds*. In this work, we returned to the basic glass material 45S5, where changes caused by the presence of organic buffers can be observed much more easily. This work deals with the corrosion behaviour of TRIS and HEPES buffers in simulated body fluid (SBF) compared to SBF solution without a buffer. Bulk samples of 45S5 bioactive glass were the tested material.

Experiment

Material preparation

The tested material was 45S5 bioactive glass. The glass was melted in a PtRh alloy crucible at 1300°C for 4 hours in an electric lab furnace. To ensure homogeneity, the mixture was stirred twice during melting. After melting, the glass was poured onto a smooth steel mould and tempered at 560°C for 1 hour, followed by gradual cooling. Table I shows the composition of 45S5 bioactive glass. Impurities such as Al_2O_3 and Fe_2O_3 were found in the glass, originating from the SiO_2. Glass samples were ground into rectangular blocks (8 x 6 x 2.5 mm) with a mass of 0.400 ± 0.100 g (Figure 1).

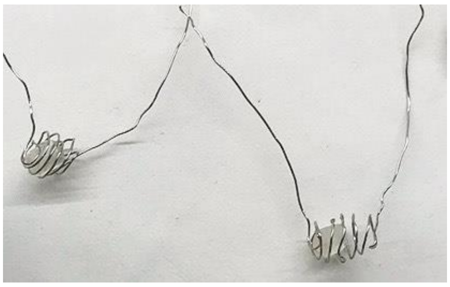

Figure 1. Prepared bulk 45S5 bioglass samples in platinum spirals

Table I
Composition of 45S5 bioactive glass, XRF (wt. %).

oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	SrO
wt.%	25.6	<0.1	0.3	42.8	5.4	<0.1	25.6	<0.1	<0.1	<0.1

Solutions

The bioactive glass samples were exposed to three types of solutions: **SBF+TRIS** prepared according to ISO 23317:2014 standard, **SBFnoTRIS** without the TRIS buffer, and **SBF+HEPES** using HEPES (acid) as the buffer with 1M NaOH to maintain neutral pH. The added Na^+ ions were accounted for by adjusting the initial NaCl amount to match the Na^+ concentration specified by ISO standard. The ionic composition of the solutions is shown in Table II.

Table II
Ion composition of SBF+TRIS, SBF+HEPES, SBFnoTRIS and human blood plasma (BP) in mmol·dm^{-3} [4].

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	$(HCO_3)^-$	$(HPO_4)^{2-}$	$(SO_4)^{2-}$	buffer
SBF+TRIS	142	5	1.5	2.5	**185.0**	4.2	1	0.5	50
SBF+HEPES	142	5	1.5	2.5	**124.2**	4.2	1	0.5	50
SBFnoTRIS	142	5	1.5	2.5	**149.3**	4.2	1	0.5	-
BP	142	5	1.5	2.5	103.0	27	1	0.5	-

* The bold chloride ion values were calculated and correspond to the actual concentration (considering the addition of HCl).

Static-dynamic conditions of *in vitro* tests

Bioglass bulk samples were placed in a platinum spiral in plastic bottles, with each bottle containing 50 ml of only one of three types of solutions (SBF+TRIS, SBFnoTRIS, SBF+HEPES). Every 24 hours, the bulk samples were immersed in fresh solution and placed in a thermostat set to 36.5 °C. The advantage of the static-dynamic test over the static setup is that it prevents the depletion of essential elements (Ca and P) from SBF solutions. This type of test can partially simulate conditions similar to those in the human body.

Eluates and material analysis

- pH was measured using an inoLab pH meter with a combined glass electrode at a temperature of 35°C.
- Concentrations of Ca, P, and Si were determined using inductively coupled plasma emission spectrometry with a 5900 ICP-OES instrument (Agilent, USA).
- Scanning electron microscopy (SEM) was used to observe the glass morphology and to identify chemical composition of the glasses (EDS). Analyses were performed using a Jeol JSM 6510 electron microscope equipped with an Inca EDS SSD detector (Oxford Instruments).
- Phase composition of the layers formed on the bioactive glass was analysed using XRD (PANalytical X´Pert PRO diffractometer, Netherlands).

Results and discussion

The initial interaction between bioactive glasses and solutions involved **pH** monitoring (Figure 2a). On the first day, pH increased in all solutions: reaching 7.5 in buffered SBF+TRIS and SBF+HEPES, and 8.2 in unbuffered SBF. Changes in silicon (**Si^{IV}**) concentration indicate the dissolution of bioactive glass (Figure 2b). In SBFnoTRIS, the silica network did not dissolve. In buffered solutions, 12-19 mg.dm^{-3} of Si^{IV} were released. Dissolution slowed in SBF+HEPES after the first day and stopped by the sixth day. In SBF+TRIS solution, dissolution continued until the eighth day, then also stopped.

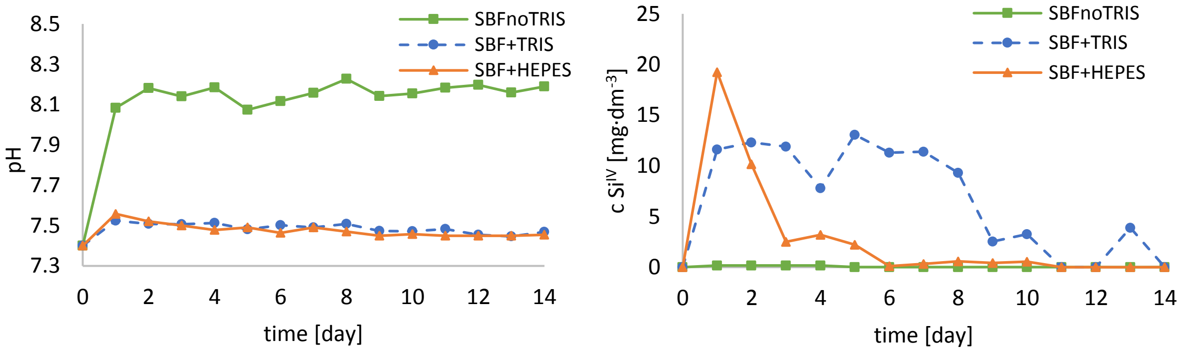

Figure 2. (a) pH values in SBFnoTRIS, SBF+TRIS, SBF+HEPES with 45S5 bioglass, (b) concentration of Si^{IV} in SBFnoTRIS, SBF+TRIS, SBF+HEPES with 45S5 bioglass

The increase in **Ca^{2+}** ion concentration (Figure 3a) on the first day in buffered solutions indicates the dissolution of bioactive glass. In the following days a decrease in Ca^{2+} ion concentration, indicating the formation of a calcium layer. This trend matches the changes in **(PO$_4$)$^{3-}$** ion concentrations (Figure 3b). The decrease in (PO$_4$)$^{3-}$ concentration in SBF+TRIS and SBF+HEPES solutions indicates the formation of a Ca-P layer on the surface of the bioactive glass samples.

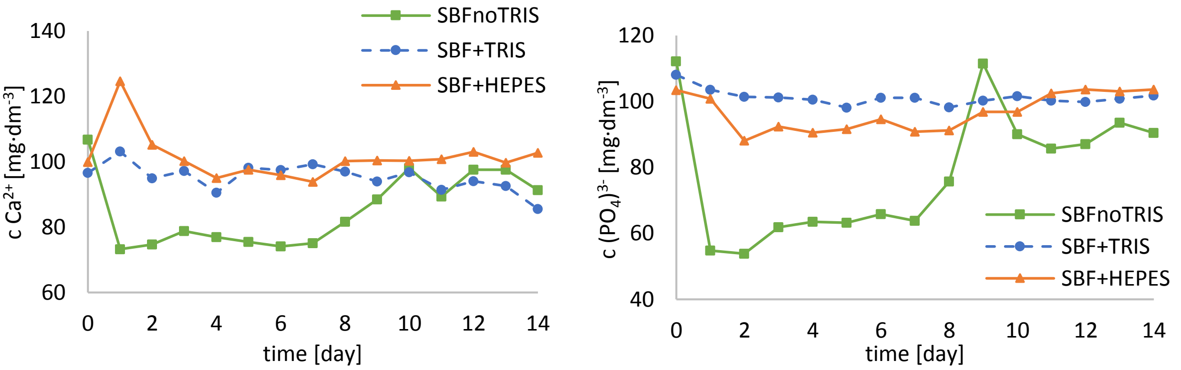

Figure 3. (a) concentration of Ca^{2+} ions in SBFnoTRIS, SBF+TRIS, SBF+HEPES with 45S5 glass, (b) concentration of (PO$_4$)$^{3-}$ ions in SBFnoTRIS, SBF+TRIS and SBF+HEPES with 45S5 glass

Monitoring the weight changes of 45S5 bioglass after interaction with the solutions showed that the greatest dissolution occurred in the buffered solutions SBF+TRIS and SBF+HEPES (Figure 4a). These results correspond with cumulative dissolution of SiO_2 (Figure 4b). It is clear that minimal SiO_2 was released into the SBFnoTRIS solution, indicating that the bioglass barely dissolves in it. In the buffered solutions, very intense dissolution of the bioactive glass was observed during the first four days. In SBF+HEPES solution, dissolution slowed after the fourth day due to the precipitation of a new, dense apatite layer (up to about 2.5 wt% of bioglass dissolved). In contrast, in the SBF+TRIS solution, bioglass continued to dissolve until the end of the test (up to about 5 wt% of bioglass dissolved).

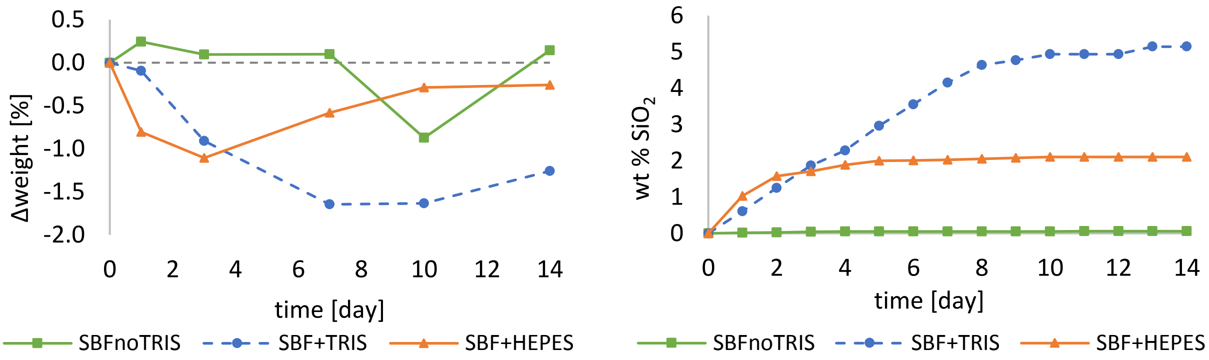

Figure 4. (a) 45S5 bioglass weight changes in SBFnoTRIS,SBF+TRIS, SBF+HEPES, (b) cumulative dissolution released SiO_2 from 45S5 glass in SBFnoTRIS, SBF+TRIS, SBF+HEPES solutions

Monitoring the thickness and composition of layers (using SEM/EDS) after *in vitro* testing in buffered solutions showed a clear difference between a corroded SiO_2 layer and a newly formed Ca-P layer (Figure 5a and 5b). Between these layers, there is an interlayer containing SiO_2, calcium, and phosphorus. Chemical analysis (EDS) revealed that in SBF+TRIS solution, chlorine incorporated into layers, while $(SO_4)^{2-}$ ions were found near the intact glass in SBF+HEPES. In SBFnoTRIS solution, the glass surface did not corrode even after a fourteen-day of exposition, but a very thin layer of amorphous calcium-phosphate formed on the surface (Figure 5c). XRD analysis confirmed that hydroxyapatite (HAp) formed in buffered solutions (Figure 5d and 5e), along with NaCl on the surface. In SBFnoTRIS solution, only crystalline NaCl was detected (Figure 5f).

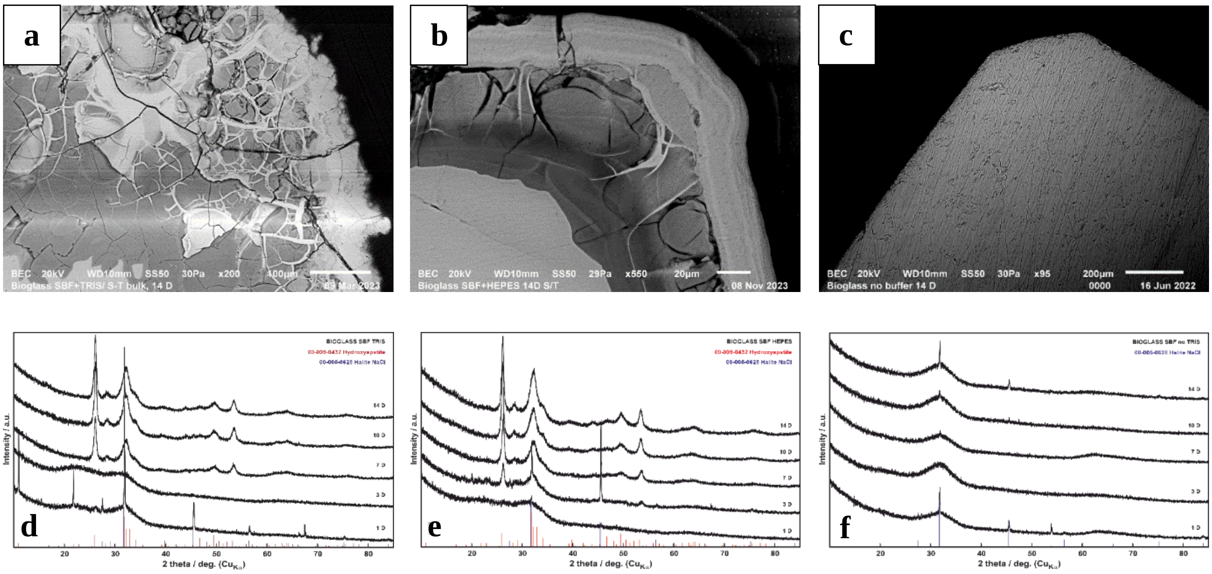

Figure 5. (a) SEM image (vertical cut of the 45S5 glass sample) after 14 days of interaction with SBF+TRIS, (b) SEM image (vertical cut of the 45S5 glass sample) after 14 days of interaction with SBF+HEPES, (c) SEM image (vertical cut of the 45S5 glass sample) after 14 days of interaction with SBFnoTRIS, (d) XRD patterns of 45S5 glass with SBF+TRIS after 14 days, (e) XRD patterns of 45S5 glass with SBF+HEPS after 14 days, (f) XRD patterns of 45S5 glass with SBFnoHEPES after 14 days.

Also, the composition of corroded layers and thickness of newly formed layers in buffered solutions were examined (Figure 6a and 6b). The layer reached about 150 µm thick after 14 days in SBF+TRIS, with the apatite layer around 40 µm. In SBF+HEPES solution, the thickness of the corroded SiO_2 layer stayed around 20 µm throughout the exposure. This matches the stop of bioglass dissolution in SBF+HEPES after five days. The hydroxyapatite layer in SBF+HEPES was about 25 µm thick, half the thickness of the layer in SBF+TRIS.

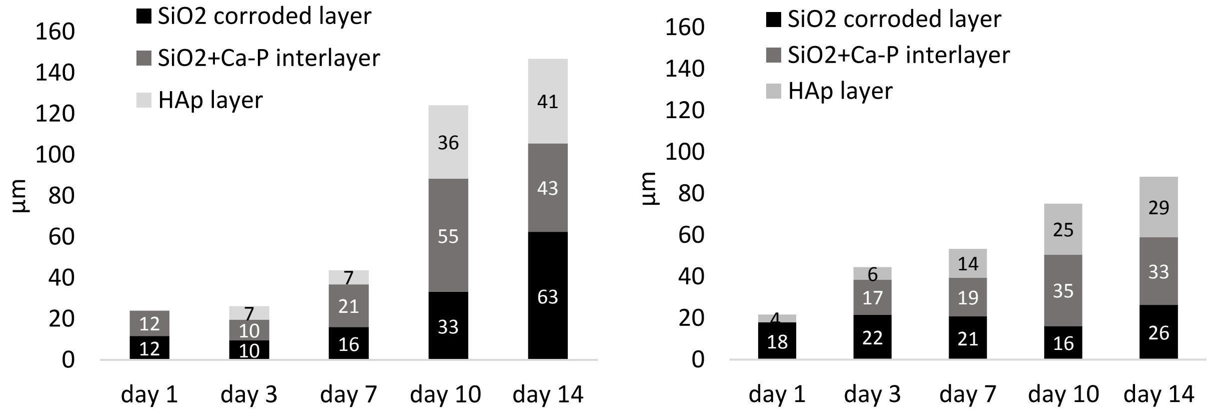

Figure 6. Thicknesses of the corroded and apatite layers formatted in SBF+TRIS (a) and SBF+HEPES (b)

Observing the surface of the sample after exposition in buffered solutions reveals significant differences (Figure 7a and 7b). The layers formed on 45S5 bioglass in the SBF+TRIS solution were heavily cracked, revealing individual layers. These layers allow the solution to pass through, leading to their growth and the sample dissolution during the entire experiment. In contrast, the Hap layer formed in SBF+HEPES solution was very dense and covers the entire sample surface.

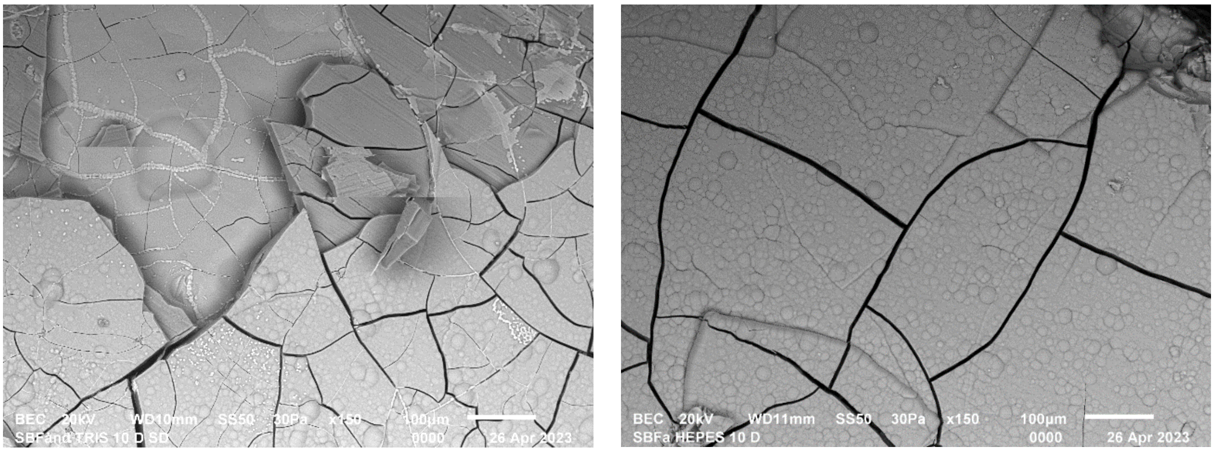

Figure 7. Morphology of the 45S5 bioglass surface exposed to SBF+TRIS (a) and SEBF+HEPES (b)

Conclusion

In the SBF without buffer, bioactive glass did not dissolve and formed only a thin layer of amorphous calcium phosphate and crystalline NaCl. TRIS and HEPES buffers significantly help dissolve the bioglass, leading to the formation of crystalline apatite layers only in SBF+TRIS and SBF+HEPES solutions. The newly created apatite layer in buffered SBF has a different chemical composition, morphology, and crystallinity. As a result, TRIS and HEPES buffers produced false positive results in *in vitro* tests.

Acknowledgement

This work was supported from the grant of Specific university research – grant No A1_FCHT_2023_005.

References

1. Cao W., Hench L. L.: Ceram. Int., *22*, 493 (1996).
2. Tilocca, A.: J. Mater. Chem., *20*, 6848 (2010).
3. Shearer A., Montazerian M., Sly J. J., Hill R. G., Mauro J. C.: Acta Biomater., *160*, 14 (2023).
4. Kokubo T., Takadama H.: Biomaterials, 27, 2907 (2006).
5. Jones J. R.: Acta Biomater.: *23*, S53 (2015).
6. Hench L. L.: An introduction to Bioceramics, second edition (2013).
7. Rohanová D., Boccaccini A. R. Yunos D., Horkavcová D., Březovská I., Helebrant A.: Acta Biomater., *7*, 2623 (2011).
8. Rohanová D., Horkavcová D., Paidere L., Boccaccini A. R., Bozděchová P., Bezdička P.: J. Biomed. Mater. Res. B: Appl. Biomater., *106*, 143 (2018).
9. Horkavcová D., Stříbny A., Schuhladen K., Bezdička P., Boccaccini A. R., Rohanová D.: Mater. Today Chem., *21*, 2468 (2021).
10. Rohanová D., Horkavcová D., Helebrant A., Boccaccini A. R.: J. Non-Cryst. Solids, *432*, 53 (2016).

SEPARATION OF SCANDIUM AND THORIUM FROM RARE EARTH MINERALS

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Abstract

In addition to a significant amount of thorium, uranium ores and the phosphorus mineral monazite also contain industrially usable amounts of rare earth elements - lanthanides, including scandium and yttrium. Similar variations have been identified following the recent announcement of the discovery of new lanthanide deposits in the Kiruna region of Sweden. The processing of such raw materials for the extraction of rare earth elements and scandium primarily requires the removal or isolation of radioactive thorium. This can be achieved by carbide of the raw material followed by the conversion of hydrolyzable carbides into soluble compounds, suitable for ion exchange separation. The possibility of thorium carbide formation by reaction with carbon at a temperature of 2200°C using Spark plasma sintering was verified on a raw material from the Czech uranium deposit Jáchymov. The temperature was sufficient only for the formation of Sc_2OC and Sc_4C_3 carbides. The reaction of thorium dioxide present in the raw material to carbide occurred only when heated above 2500°C in an Acheson-type microfurnace. After hydrolysis with the release of allylene, scandium was transferred to a solution whose radioactivity did not exceed the values for further safe processing permitted by the Office for Nuclear Safety SÚJB.

Introduction

The Swedish city of Kiruna, in the Arctic Circle, is not only home to the world's largest underground iron ore mine, but also the LKAB's Konsauln ore mine, where the digitalised, autonomous and electrified mine of the future is being developed. The area is also home to Europe's largest known rare earth deposit, named after the prominent Swedish geologist Per Gaijer, who explored the deposit in 1949-1950 [1]. It is therefore surprising that the number of publications and information about the discovery of the supposedly richest European deposit of rare earths has recently been increasing, but it is no longer emphasized that their content is tied to the presence of other elements, especially uranium and thorium. In Sweden, 35% of electricity is generated from nuclear power, but nuclear fuel is supplied from Namibia, Canada and Russia. This is due to amendments to the Minerals Act of 1991 and 2018, which prohibit the prospection, mining and processing of uranium in Sweden. It suggests the use of a proverb about the irony of fate when comparing the conditions of an equally important deposit of uranium ores containing rare earths, or scandium, in our Czech region of Jáchymov. From 1945 to 1992, all uranium mining, after certain chemical modifications on our territory, was supplied to the Soviet Union, and a number of rare earth elements can be found in waste products and tailings ponds that have never been used in our country. Quantitative data on uranium mining began to be published only after 1992 [e.g.2]. So if Sweden primarily mines rare earths- lanthanides, uranium will formally be a waste product.

Experimental

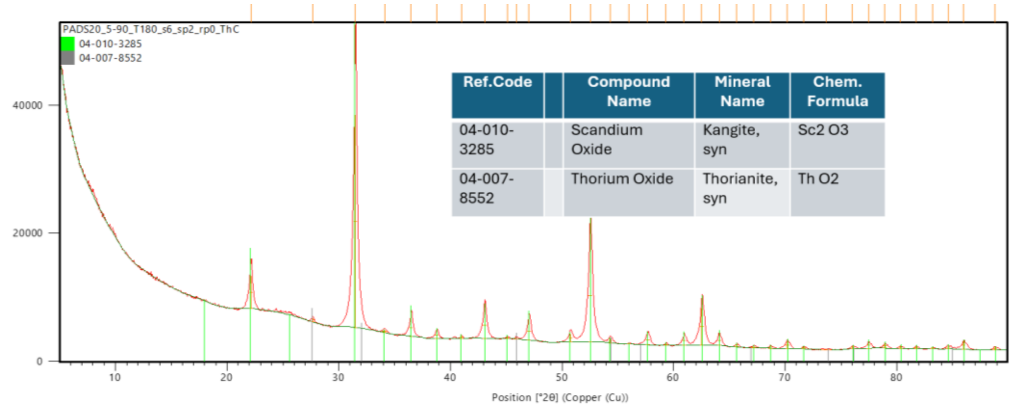
When processing raw materials to obtain rare earth elements and scandium, it is primarily necessary to remove/isolate radioactive thorium. Removal or isolation of Th can be achieved, among other things, by carbide of the raw material, with subsequent conversion of hydrolyzable rare earth carbides of the MC, MC_2 and M_3C_4 types to hydroxides, which are easily soluble in compounds, suitable for separation on ion exchangers. Several variants of waste wolframite raw material remained in the tailings ponds of Czech uranium industry companies after the primary removal of uranium compounds. Their characteristics are given in Table I and Figures 1 and 2. The raw material with the highest content of thorium compounds was selected for processing in this paper.

Table I

Analysis of Sc/Th raw material

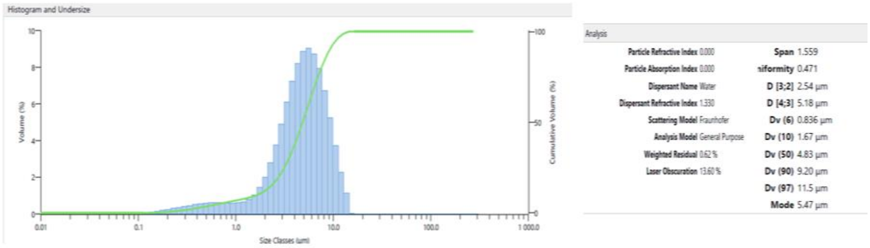
element		Zinnwaldite - wolframite after tungsten separation (mass %)	Fluoride concentrate after tungsten separation, processed in Spolchemie Ústí n/L. (mass %)	Waste concentrate of Spolchemie Ústí n/L **used in this study** (mass %)
8	F	--	16.57 - 18.57	--
10	Na	--	0.23 - 0.35	--
12	Mg	0.13	--	--
13	Al	0.14	0.21 – 0.24	0.16
14	Si	3.99	40.12 – 40.17	0.11
15	P	0.03	0.99 - 1.06	0.04
16	S	0.62	0.39 - 0.44	0.008
17	Cl	0.06	0.46 – 0.51	0.44
19	K	0.04	0.07 – 0.07	--
20	Ca	0.27	0.35 – 0.39	0.08
21	Sc	0.15	32.43 – 34.71	83.84
25	Mn	--	0.04 – 0.06	--
26	Fe	0.56	0,18 – 0.19	0.07
29	Cu	--	0.28 – 0.29	--
33	As	--	0.01 – 0.03	--
39	Y	1.04	0.08 – 0.09	0.26
41	Nb	--	0.05 – 0.06	--
50	Sn	--	0.40 – 0.45	--
56	Ba	--	---	1.78
58	Ce	39.49	0.01 – 0.02	0.08
59	Pr	5.06	0.01 – 0.03	0.03
60	Nd	21.78	0.01 -0.04	0.01
70	Yb	--	0.04 – 0.05	0.13
73	Ta	--	0.04 – 0.05	--
74	W	--	0.78 – 0.86	0.05
82	Pb	0.26	0.04 - 0.05	--
83	Bi	--	0.04 – 0.05	0.01
90	Th	0.89	3.59 – 3.81	7.52
92	U	0.03	--	--

PANalytical Quantification of samples R.M.S.: 0.025 Result status: Sum before normalization: 60.8 %
Normalised to: 100.0 % Sample type: Loose powder



Ref.Code		Compound Name	Mineral Name	Chem. Formula
04-010-3285		Scandium Oxide	Kangite, syn	Sc2 O3
04-007-8552		Thorium Oxide	Thorianite, syn	Th O2

Figure 1 Diffractogram of wolframite waste concentrate Spolchemie



Particle Refractive Index 0.000
Particle Absorption Index 0.000
Dispersant Name Water
Dispersant Refractive Index 1.330
Scattering Model Fraunhofer
Analysis Model General Purpose
Weighted Residual 0.62 %
Laser Obscuration 13.60 %

Span 1.559
niformity 0.471
D [3;2] 2.54 µm
D [4;3] 5.18 µm
Dv (6) 0.836 µm
Dv (10) 1.67 µm
Dv (50) 4.83 µm
Dv (90) 9.20 µm
Dv (97) 11.5 µm
Mode 5.47 µm

Figure 2 Granulometry of Sc-Th raw material from Table 1

In this work, the results of processing of input raw material number 3 from Table 1 are presented. Samples of input materials were mixed with 10 % excess carbon (Carbon Black Unipetrol > 21 m^2/g, 99.45 C, 0.55 S) and compacted using sintering plasma equipment (SPS, FCT Systeme HP D 10, Franckenblicke, Germany). In addition, the graphite matrix, its walls and both pistons were covered with graphite paper. The sample was compressed with a pressure of 48 MPa and heated at a heating rate of 100 °C/min up to a compaction temperature of 2000°C and 2200 °C and a dwell time of 10 min. After this segment, the maximum cooling rate of the SPS machine was used until the samples reached room temperature. The prepared compact specimens had a circular shape with a diameter of 20 mm. A record of the reaction in the SPS apparatus is shown in Figure 3. According to the diffraction pattern Figure 4, hydrolyzable carbides Sc_2OC and Sc_4C_3 were formed, but carbide of the present ThO_2 did not occur, even when using the more reactive carbon form of graphene.

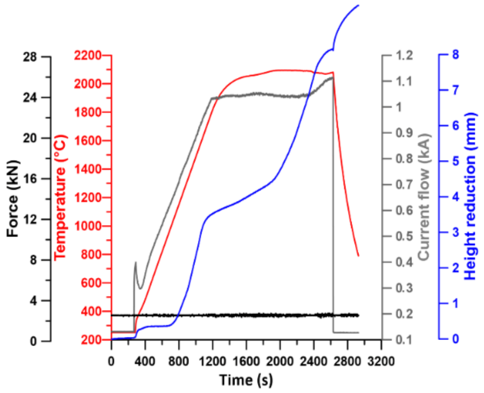
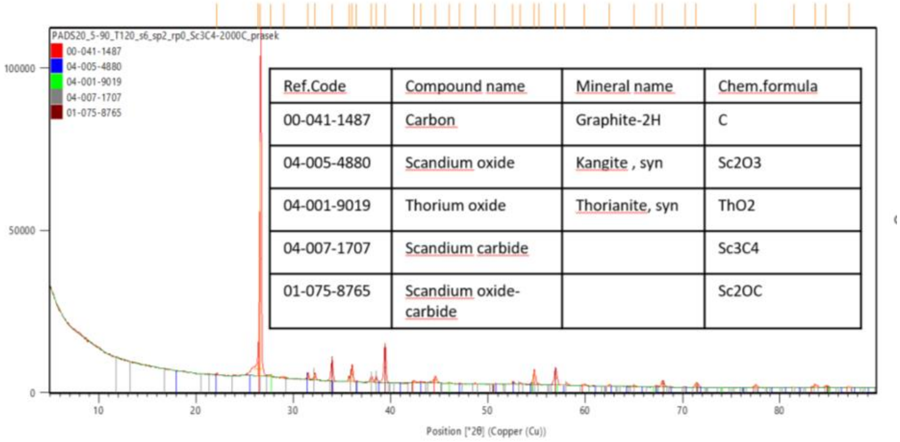


Figure 3 Recording the progress of the SPS reaction



Ref.Code	Compound name	Mineral name	Chem.formula
00-041-1487	Carbon	Graphite-2H	C
04-005-4880	Scandium oxide	Kangite , syn	Sc2O3
04-001-9019	Thorium oxide	Thorianite, syn	ThO2
04-007-1707	Scandium carbide		Sc3C4
01-075-8765	Scandium oxide-carbide		Sc2OC

Figure 4 Diffractogram of the SPS reaction product at 2000°C

Thermodynamic calculation of the reaction

$$ThO_2 + x\,C \rightarrow ThC, ThC_2 + y\,CO \quad (1)$$

was problematic because the FactStage database doesn't need validated data for these reactions. Combining calculations from known data for reaction

$$ThO_2 + 3\,C \rightarrow ThC_2 + CO_2 \text{ or } ThO_2 + 3\,C \rightarrow ThC + 2\,CO \quad (2)$$

indicated that the reaction can take place to form CO above 2480 K, which is the temperature in the SPS apparatus at the limit of achievability (see Table I).

Table II

Thermodynamic calculation of the reaction ThO_2 with carbon

Reaction $ThO_2 + 3C \rightarrow ThC + 2\,CO$ p = 0.1 MPa						
T (K)	Delta H°(J)	Delta G° (J)	Delta Vol (l)	Delta S°(J/K)	DeltaCp (J/K)	Keq T
300	879033.2	767751.9	$4.98 \times e^{+01}$	370.9	15.617	$2.44 \times e^{-134}$
1000	869386.1	510114.5	$1.66 \times e^{+02}$	359.2	-26.334	$2.26 \times e^{-27}$
2000	840071.8	161788.8	$3.32 \times e^{+02}$	339.1	-31.327	$5.95 \times e^{-05}$
3000	805088.2	-170115.7	$4.98 \times {}^{e+02}$	325.0	.38.171	$9.16 \times e^{+02}$
Reaction $ThO_2 + 2C \rightarrow ThC + CO_2$ p = 48 MPa						
T (K)	Delta H°(J)	Delta G° (J)	Delta Vol (l)	Delta S°(J/K)	DeltaCp (J/K)	Keq T
300	706542.0	647981.7	$2.49 \times e^{+01}$	195.2	3.139	$1.51 \times e^{-113}$
1000	698737.2	514668.8	$8.31 \times e^{+01}$	184.0	-16.778	$1.30 \times e^{-27}$
0,2000	691087.9	337298.0	$1.66 \times e^{+02}$	171.8	-18.439	$1.55 \times e^{-06}$
3000	659776.3	169738.1	$2.46 \times e^{+02}$	163.3	-23.749	$1.10 \times e^{-03}$

The reaction at higher temperatures was verified in an Acheson-type furnace with a graphite or tungsten heating core with the possibility of reaching temperatures up to 3400°C. An Acheson-type miniature furnace with a graphite sample case (Figure 5) was constructed. The second furnace with a heating tungsten core was assembled from hexagonal boron nitride (Figure 6). The reason for the miniaturization of the furnaces was mainly the fact that, according to the regulations of the Institute for Nuclear Safety (SONS), it is possible to work with a maximum amount of 256 mg of thorium in a sample [6]. The setting of this limit concentration was achieved by "diluting" the weight with excess carbon. In the case of the thorium-rich input raw material from the uranium sludge ponds in Jáchymov (Table I - up to 8 % Th), the total permitted amount of sample weight for thermal treatment was 3.2 g, which was achieved in the SPS apparatus (the volume of the moulding max. 3 cm^3). The construction of the miniature Acheson furnace has a working volume of about 1 cm^3.

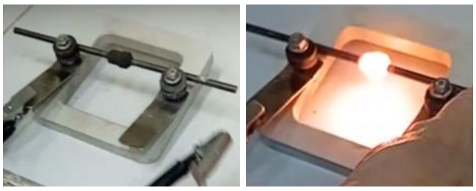


Figure 5 Miniature furnace with graphite heating core

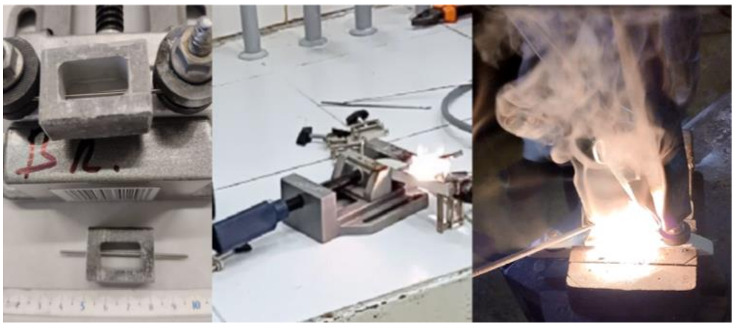


Figure 6 Construction of a miniature Acheson-type furnace with a tungsten heating core

The maximum temperature reached in these experiments was estimated from the fact that the heating tungsten element (with a melting point of 3422 °C) melted (not burned out) after the power supply was interrupted.

After hydrolysis of the products prepared in this way, the gas phase was used to identify allylene, a typical product of the hydrolysis of scandium carbides [7], by measuring IR spectra (Figure 7).

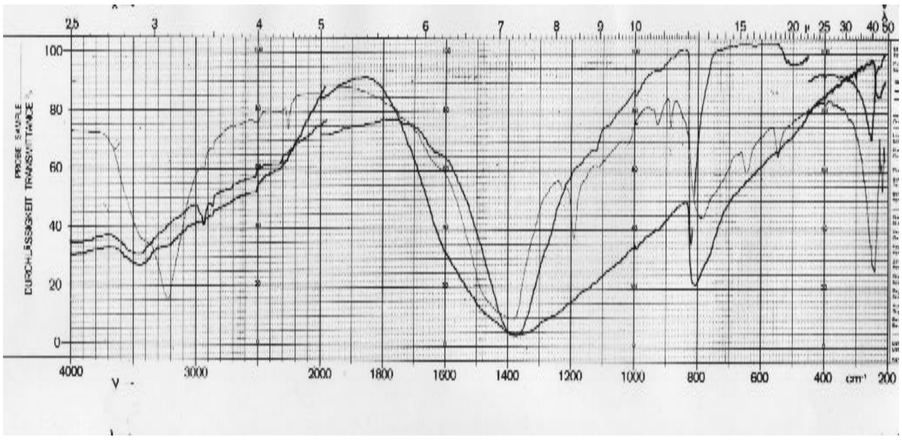


Figure 7 IR spectra of the gas phase after hydrolysis of samples prepared at 2200°C

The samples were dissolved in dilute hydrochloric acid(0.1 M HCl), filtered and the filtrate dried in a graphite crucible. Only radioactive monocarbide ThC (type Fm3m) [8] was identified in the undissolved residue. The value of radioactivity of the leachate after the removal of thorium, suitable for further safe processing, was on the border of the release level according to the SÚJB standard, i.e. 68 Bq CoMo-70 was informatively measured.

Conclusion

The possibility of thorium carbide formation by reaction with carbon at a temperature of 2200°C using the Spark plasma sintering method was tested on a raw material from the Czech uranium deposit Jáchymov, containing rare earths and scandium. The temperature was sufficient only for the formation of Sc_2OC and Sc_4C_3 carbides. The reaction of thorium dioxide present in the raw material to carbide occurred only when heated above 2500°C in an Acheson-type microfurnace. After hydrolysis with the release of allylene, scandium was transferred to a chloride solution, the radioactivity of which did not exceed the values for further safe processing permitted by the Office for Nuclear Safety of the State Office for Nuclear Safety (SÚJB) according to Act No. 263/2016 Coll.

References

1. Geijer P., The rector ore body Kiruna, Sveriges Geologiska UndersÖkning , Ser.C-514, Ärsbok 43 (1949) No.12
2. Menard D.S., Project at the Department of Earth Sciences, ISSN 1650-6553 Nr 581, Uppsala University 2022
3. Kališová O., Energetika.tzb-info.cz (2017)
4. Hájek B., Karen P., Brožek V., Journal of the Less Common Metals, Vol. 98, 245-252 (1984)
5. Brožek V., Dušek B., Novák M., Trantina V., APROCHEM 2012, Vol.1. 109-123, ISBN 978-80-02-02376-0
6. Zákon č.263/2016 Sb. Atomový zákon se změnami 284/2021 a 465/2023 Sb.
7. Brožek V., Dušek, B., Novák M., Chemické listy, 105(4), 287–291 (2011).
8. Bradley M.J., Ferris L.M., Journal of Anorganic and Nuclear Chemistry 27, 1021-1036 (1965)

OIL PETROCHEMICALS BIOFUELS

EXPERIENCE WITH THE OPERATION OF NEW GENERATIONS OF PYROLYSIS HEATERS

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Abstract

The pyrolysis section of ORLEN Unipetrol's steam cracker consists of eleven pyrolysis heaters. The type of the operated heaters changed significantly after an incident in 2015, when four of ten heaters were heavily damaged by fire. This part of the pyrolysis section was totally rebuilt in 2016 by T.EN. Due to the very positive experience with new heaters the last eleven one – identical to units built in 2016 was commissioned last year. The recently operated pyrolysis section therefore offers a unique opportunity to compare the operation of three different designs of pyrolysis heaters – the original heaters equipped with SRT III reactors from the 70's, the revamped heaters from the beginning of the new millennium and up-to-date design represented by newly built heaters fitted with GK6 and SMK reactors arranged in three parallel rows. Since the rebuilt of the pyrolysis section followed by the re-commissioning of the steam cracker in 2016, no comparison of the individual heater designs has been made, both in terms of the economics of operation and the achieved yield vectors. Such a comparison presented in this paper was made possible by a detailed analysis of operational data and also by the utilization of a hot cracked gas sampling method developed at ORLEN Unipetrol. The results obtained by the detailed analysis of the operational data and a comparison of the yield vectors are discussed focusing on the innovative technical solutions distinguishing the new pyrolysis heaters from the original ones. The current increase of energy costs, emission fees as well as other operating costs make a constant pressure on the identification of ways how to reduce energy consumption and optimize assets operation. Thus the pyrolysis section consumes on average 60 percent of the total steam cracker energy consumption, any system improvement or better technical solution has a significant impact on the overall economy of plant operation. The results presented in this paper prove this goal was successfully achieved.

Introduction

On 13 August 2015, an incident occurred at the ethylene unit. It was about an explosion of propylene vapour cloud and fire of 4 pyrolysis heaters. The cause of the event was interruption of cooling water into propylene splitters condensers, chattering of propylene splitter PSV caused an outburst of propylene vapour cloud followed by an explosion. Pyrolysis heater BA-109 caught fire when quench oil leaked through the pyrolysis coil rupture inside radiant box – reverse flow caused by forced isolation of the heater from primary tower. Fire finally spread out to other three heaters – all four heaters were very seriously damaged/destroyed (BA-107-110).

Four new pyrolysis heaters from T.EN were delivered and commissioned in 2016 a the last heater BA-111 built in 2021-22, commissioned this year – increase of plant capacity. New heaters represent up-to date equipment fitted with BAT solutions (TLE, radiant coils, burners). Comparison of the technical specifications is given in Table I and figure 1, 2.

Table I
Technical specifications between original and new pyrolysis heaters

Original pyrolysis heaters	Comparison	New pyrolysis heaters
SRT III, $GK6_{old}$	Reactor type	SMK, $GK6_{new}$
6	Number of reactors	16
3	Transfer line exchangers (TLE)	2
6 pass configuration	Feed distribution	2 pass configuration
Bottom burners – 12 Side burners - 126	Burners	Bottom burners – 16 Side burners - 16
3	Quench oil fittings	1
No ABC test	ESDS functions	ABC test
No individual feed shut valves		Individual feed shut off valves
Decoking air manual isolation		Decoking air shut off valves

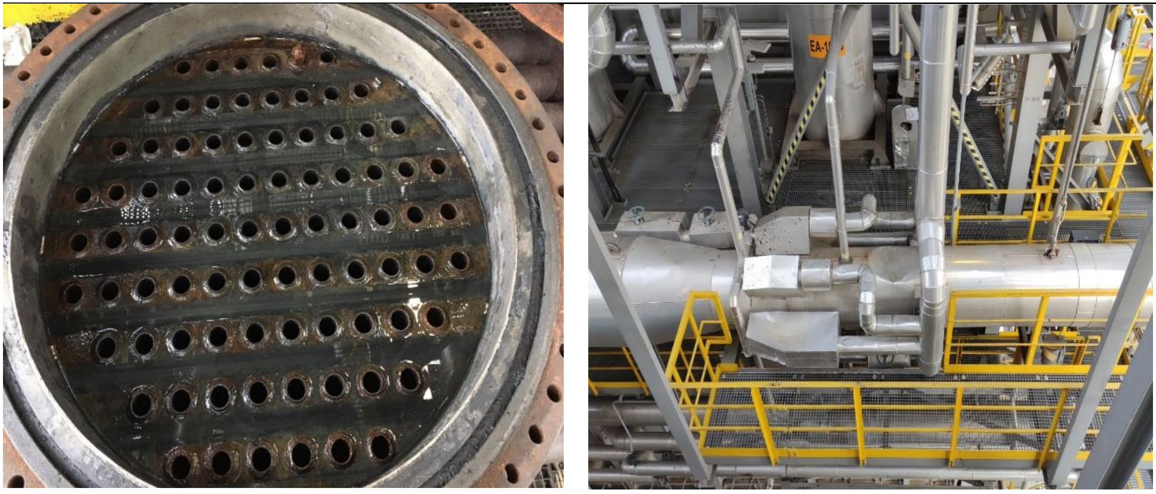
Figure 1. TLE tubes layout


Figure 2. Quench oil fittings

Figure 3. New pyrolysis heaters

Discussion and result analysis

Experience with duration of the operation cycle and decoking

Duration of operation cycle depends on the feedstock, process parameters and coking rate and decoking on the new pyrolysis heaters takes 32–36 hours (original heaters 24–48 hours). The least number of days have original heaters on the naphtha, on the contrary, most days have new heaters on the naphtha. LPG and ethane – new heaters have a similar number of days and original heater on ethane around 30 days, average days these are shown in figure 4.

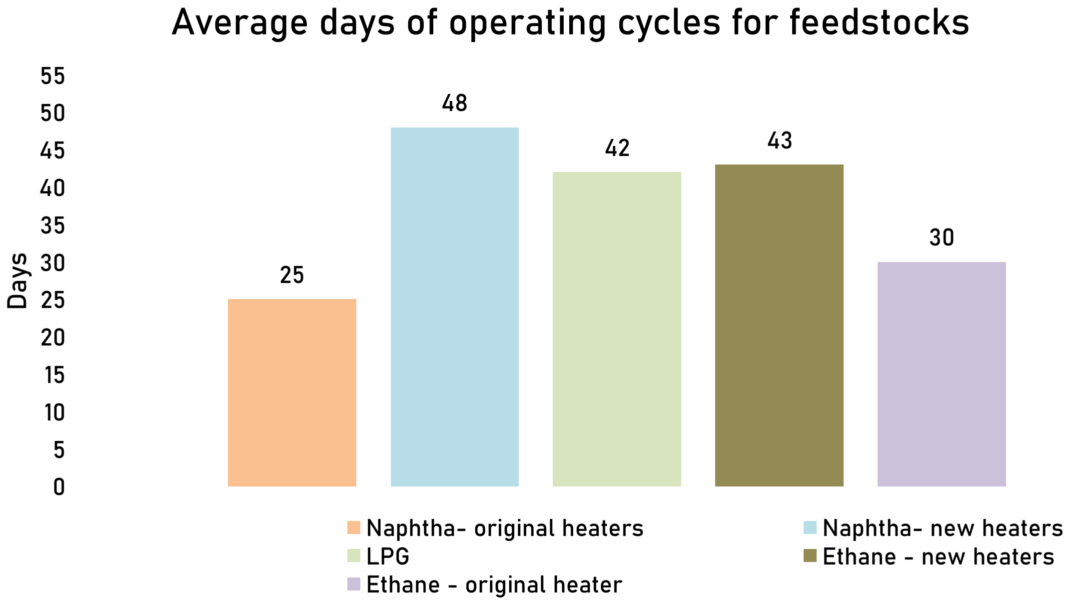

Figure 4. Average days of operating cycles for feedstocks

Lifetime of the pyrolysis coils and other advantages

Pyrolysis coils lifetime 55–60 thousand hours (in practice no deformations reported), the earlier replacement was necessary due to the accumulation of maintenance activities (all heaters were started up almost at one moment in 2016). The operating hours of the original and new pyrolysis heaters are there in Tables II and III.

Table II
Operating hours of the original pyrolysis heaters

Original heaters	Operating hours
BA-110 (SRT I)	24 000
BA-101, 103, 105 (GK6)	32 000
BA-102, 104, 106, 107, 108, 109 (SRT III)	45 000

Table III
Operating hours of the new pyrolysis heaters

New pyrolysis heaters	Operating hours
BA-107 (SMK)	49 635
BA-108 (SMK)	54 408
BA-109 (GK6)	47 218
BA-110 (GK6)	46 613

The main advantages of the new pyrolysis heaters from the original are the energy savings, maintenance costs savings and coils of lifetime.
The yields of individual products from each pyrolysis heater were compared at: different ratios S/O (hydrocarbons/vapours), COT (coil outlet temperature) and with different of feedstocks of feed which there are in table IV.

Table IV
Comparison of naphtha feedstock heaters

Heaters	Reactors	Feed (t/h)	S/O ratio	COT (coil outlet temperature °C)	Yield (wt%)				
					Methane	Ethylene	Propylene	C4	Benzene
BA-101 BA-103 BA-105	$GK6_{original}$ 2 lanes	18.0-28.5	0.45-0.50	830-845	15.28	25.85	13.83	8.24	8.56
BA-102 BA-104 BA-106	SRT III 1 lane	18.0-28.0	0.45-0.50	825-840	13.27	24.59	13.57	8.29	10.75
BA-107 BA-108 BA-111	SMK 3 lanes	20.0-27.0	0.45-0.50	830-845	15.33	24.92	13.43	8.46	9.58
BA-109 BA-110	$GK6_{new}$ 3 lanes	20.0-27.0	0.45-0.50	830-845	14.36	25.16	14.20	9.80	8.65

Measurements were also made on the LPG feedstock. The original pyrolysis heaters were compared with the new heaters. Pyrolysis with LPG only or copyrolysis with naphtha or ethane at: different ratios S/O (hydrocarbons/vapours), COT (coil outlet temperature) and feed, which there are in table V.

Table V

Comparison of SMK heaters with old heaters with LPG feedstock

	Heaters	Reactors	Feed (t/h)	S/O ratio	COT (coil outlet temperature °C)	Yield (wt%)				
						Methane	Ethylene	Propylene	C4	Benzene
From 2016	BA-101 BA-103 BA-105	SMK 3 lanes	18.0-27.0	0.45-0.55	830-850	22.40	28.02	17.20	11.47	4.90
	BA-107*	GK6 2 lanes	18.0-28.5	0.45-0.50	830-845	18.53	25.86	17.22	13.86	6.16
Before 2015	BA-108 BA-109	SRT III 1 lane	20.0-22.0	0.45	845-850	22.73	27.08	16.16	9.11	5.09
	BA-110**	SRT I 1 lane	18.0-22.0	0.35-0.50	835-845	x	x	x	x	x

*Mixed feedstock (naphtha/LPG) 1:2 **Mixed feedstock (ethane/LPG) 9:1

Finally, the yields were compared on SMK heaters with ethane feedstock, which which there are in figure 5 a 6.

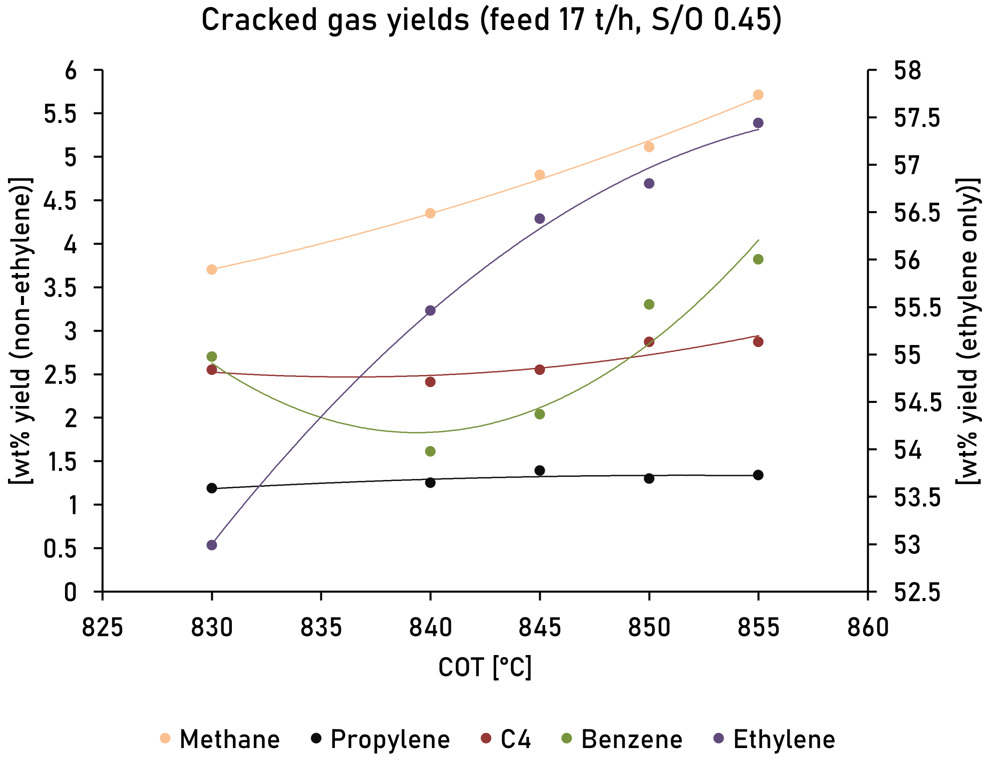

Figure 5. Cracked gas yields (feed 17 t/h, S/O 0.45)

The pyrolysis of ethane is specific compared to the pyrolysis of other feedstocks in that the vast majority of the products are gaseous simple hydrocarbons and hydrogen. The amount of pyrolysis gasoline is minimal and pyrolysis oil is practically absent from the products. In accordance with theoretical assumptions, ethane conversion increases with increasing reactor outlet temperature, as do the product yields of methane, ethylene and propylene. The yields of the C4 fraction and benzene show anomalies at both ends of the observed range of exit temperatures, contrary to the assumptions. The significantly higher yield of benzene at 830 °C can be explained as a consequence of the ongoing polycyclic reaction (Diels-Alder reaction of buta-1,3-diene and ethylene to form benzene), while the increased yield of the C4 fraction is due to the lower reaction temperature – very soft pyrolysis taking place outside the optimum pyrolysis reaction region.

The high yield of benzene at 855 °C can again be explained as a result of the Diels-Alder reaction mentioned above. In this case the reaction conditions are already so extreme that a large proportion of the buta-1,3-diene formed reacts with ethylene to form benzene. This reaction results in a significant increase in the yield of benzene, while the yield of buta-1,3-diene increases only to a limited extent.
From the point of view of determining the optimum temperature for the pyrolysis of ethane at an injection rate of 17 t/h and a dilution ratio of 0.45 kg.kg, a temperature of 845 °C, at which the ratio between the main products appears to be ideal (high ethylene yield, maximum propylene yield, yields of the C4 fraction and especially benzene do not increase significantly), appears to be suitable.

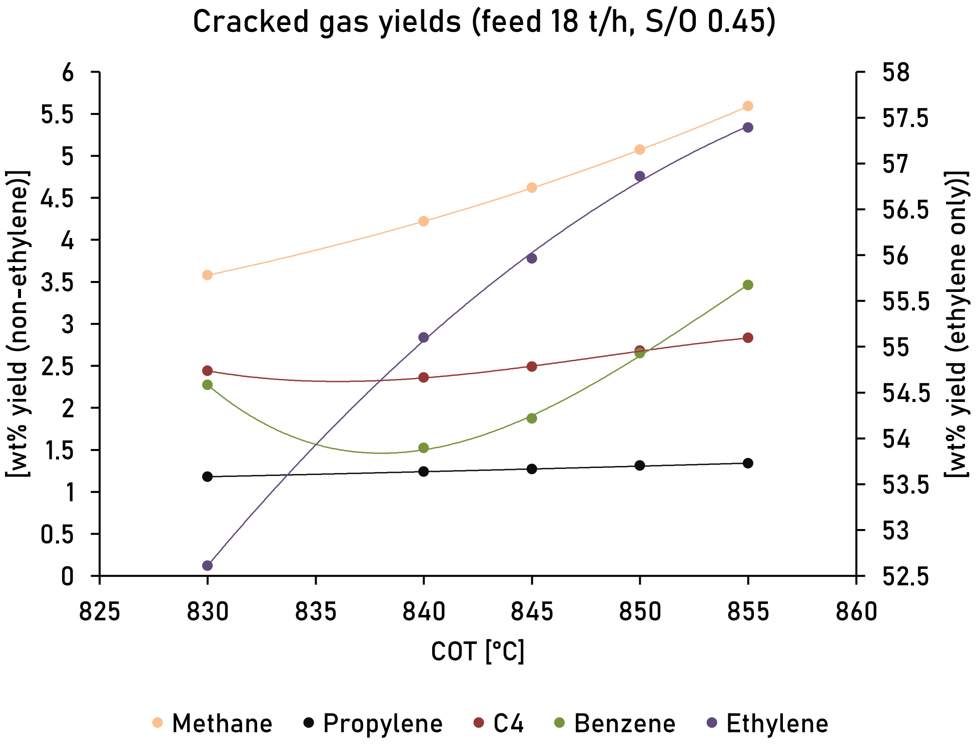

Figure 6. Cracked gas yields (feed 18 t/h, S/O 0.45)

The results of a series of experiments carried out at a load of 18 t/h and a dilution ratio of 0.45 kg.kg are shown in figure 6. The results of the second series of baseline sampling show similar changes in yield vectors as the first series, which can be explained in the same way. By simply comparing the values of the individual products at the same outlet temperatures, it is clear that an increase of 1 t/h in the injection rate results in a decrease in the yields of the same products by a few tenths of a weight percent. Therefore, to achieve the same yields at higher injection rates it is necessary to increase the outlet temperature – for this reason the optimum outlet temperature should be 848 °C.

Conclusion

The design of new heaters has shown a significant improvements in:

- Energy savings (new low emission burners, heat distribution).
- Maintenance costs (longer coils lifetime, suppressed coils deformation, lower frequency of TLE cleaning), operation routines (longer time on stream, shorter decoking, better control).
- Safety (improved ESDS logic and operators interface).
- Both used type of reactors are the best commercially available ones regarding the ethylene selectivity being tailored to pyrolysed feedstock (GK6 – naphtha, SMK – ethane).
- Utilization of BAT in burners technology and TLE technology secures the very low emissions and higher high pressure steam production making new heaters more environment friendly (suppressed NOx and CO_2 emissions).

Acknowledgement

The author would like to thank ORLEN Unipetrol RPA for their support of this research.

References

1. Herink, T. Využití průmyslových dat k modelování pyrolýzy uhlovodíků Doktorská disertační práce, Vysoká škola chemicko-technologická v Praze, Praha, 2002.
2. Doskočil, J.; Hroch, M.; Coman, R.; Bláha, R.; Bernard, L.; Merhout, M. Technologický reglement pro výrobnu Etylénové jednotky. 2021.

POLYMERS COMPOSITES

USE OF WASTE LIGNIN FOR MODIFICATION OF CONIFEROUS WOOD TO INCREASE FIRE RESISTANCE

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Abstract

In current ecological and circular economy trends, emphasis is placed on recycling and innovative use of industrial waste materials. Waste black liquor from pulp production, rich in lignin, represents a significant material with ecological potential. This paper examines using of acidic and alkaline waste black liquors for wood impregnation to enhance its fire protection and optimize its properties. The analysis of total heat release showed that the impregnation of spruce wood with black sulphite liquor reduced the heat release to 19.14 MJ/kg and with kraft black liquor to 18.39 MJ/kg, representing a 6% decrease compared to the reference spruce (19.58 MJ/kg). Similar trends were observed for pine wood. Other parameters studied included wood surface properties, smoke production during combustion, and the ability of the wood to bind the liquor. The goal is to demonstrate that waste black liquors can be used without additional treatment, benefiting the wood processing industry, ecology, and supporting the principles of the circular economy.

Introduction

Lignin is a widely occurring polyphenolic biopolymer material, which is also a waste product from industrial pulp production and is available worldwide. The global trend of moving away from fossil resources due to fears of their depletion is forcing scientists worldwide to turn their attention to biomass and green materials. Lignin, as a biopolymer, is one of the leading materials with the greatest potential. Its chemical modification offers several uses[1]. Recently, lignin has been increasingly used as an alternative to traditional antioxidants. For example, in the industry, lignin can be used as a natural antioxidant to extend the stability of polypropylene[2]. It is also used as a surfactant[3]. Additionally, lignin can be used in the production of biopolymers and other chemicals for various industrial applications, including adhesives and coatings[4]. Despite these innovative uses, lignin has yet to find broader commercial application. The challenge remains to optimize extraction and modification processes to make it competitive with traditional raw materials on the market. Other research teams are working on applications such as: Wei Hu and his team synthesized flame-retardant polyurethane based on lignin[5]. They replaced conventional non-renewable petroleum-based polyol with renewable aromatic polyol, using lignin as a raw material for polyurethane film synthesis. The high char yield of lignin slowed the combustion of the polymer. Gianmarco Griffini and his team synthesized a thermoset polyurethane coating with a high lignin content[6]. They first extracted lignin using the bio-solvent 2-methyltetrahydrofuran. Then, lignin was cross-linked with aromatic polyisocyanate based on toluene diisocyanate, and the resulting derivative was spin-coated onto a glass substrate. This coating exhibited improved thermal stability, adhesive properties, and hydrophobic character. Thermoset polyurethane based on lignin has high potential for use in coatings and adhesives. Klein and his team synthesized bioactive polyurethane coatings based on lignin (LPU)[7]. They used demethylation to improve the selectivity of the reaction towards polyurethane synthesis. Many research teams are exploring lignin's use as an effective flame retardant and as a replacement for fossil resources. The largest sources of lignin are kraft liquor and sulfite liquor, by-products of pulp production. There are several methods for extracting pure lignin, such as precipitating it from black liquor using sulfuric acid, followed by filtration and washing. These methods are effective but time-consuming and involve the use of additional chemicals, increasing the carbon footprint. This paper explores the use of untreated kraft and sulfite black liquors for wood impregnation to enhance its fire-resistant properties. This supports the circular economy by utilizing waste materials and minimizing the need for new chemicals, thereby reducing the overall carbon footprint.

Experiment

Experimental materials

For the experiments, two types of wood were used: Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). These woods are most commonly utilized for structural purposes in timber constructions. Norway spruce has an average density of 430 to 480 kg/m³ and is a non-heartwood species, which means it has a relatively high effective yield. The calorific value of Norway spruce wood is approximately 13.1 kJ/kg. Scots pine is a heartwood species, and its physical and mechanical properties differ between the heartwood and sapwood. The density of Scots pine ranges from 480 to 520 kg/m³, and its average calorific value is 13.6 kJ/kg.

Preparation of test specimens

The preparation of test specimens for measuring the optical density of smoke was conducted as follows: Test specimens were machined to dimensions of 75 × 75 × 20 mm and oriented so that the larger surface area was in the tangential direction. Test specimens for determining the calorific value were prepared with dimensions of 10 × 15 × 10 mm, and the orientation of the surfaces was not critical for these specimens. Each batch of samples was assigned a unique code and divided into corresponding groups based on their further use, ensuring proper tracking and evaluation of individual experiments.

Kraft black liquor

Kraft black liquor, is a chemical solution used in the kraft process for paper and pulp production. This solution primarily contains sodium hydroxide ($NaOH$) and sodium sulphide (Na_2S), making it suitable for processing various types of wood, including conifers, deciduous trees, and annual plants. Kraft liquor is a crucial component in the breakdown of lignin, which allows for the separation of cellulose fibers. Specific properties of kraft liquor according to Mondi Štětí include alkaline lignin concentration: 29.6 g/l. Specific heat capacity (c): 12.74 MJ/kg dry solid matter. These values indicate the high efficiency of kraft liquor in breaking down lignin and its suitability for different types of wood due to its chemical composition. The alkaline lignin concentration demonstrates the ability of kraft liquor to effectively dissolve lignin and separate cellulose, which is critical for producing high-quality pulp. The specific heat capacity provides essential information for energy balance and optimization of thermal processing during production. Additionally, it suggests the potential use as a natural flame retardant. Kraft black liquor for this experiment was supplied by Mondi (Štětí, Czech Republic).

Sulphite black liquor

Sulphite black liquor is a chemical solution used in the sulphite process for paper and pulp production. This process utilizes various forms of bisulfite in combination with sulphur dioxide (SO_2) and water (H_2O) to effectively break down lignin and separate cellulose fibers. Sulphite liquor is particularly suitable for processing Norway spruce and deciduous woods. Variants of Sulphite Liquor: Calcium sulphite liquor ($Ca(HSO_3)_2 + SO_2 + H_2O$): This type is used at the Lenzing Paskov and is suitable for processing Norway spruce and deciduous trees. Sulphite liquor with soluble base: Various variants of this liquor exist, all suitable for Norway spruce and deciduous trees: Sodium sulphite liquor ($NaHSO_3 + SO_2 + H_2O$), Magnesium sulphite liquor ($Mg(HSO_3)_2 + SO_2 + H_2O$), Ammonium sulphite liquor ($NH_4HSO_3 + SO_2 + H_2O$). Alkaline sulphite liquor: This type is used for processing straw and other annual plants: Sodium alkaline sulphite liquor ($Na_2SO_3 + NaOH$). Sulphite liquor is a versatile chemical solution that, due to its various variants and chemical combinations, adapts to different types of raw materials, whether wood or annual plants. Each variant offers specific advantages for certain types of raw materials, enabling efficient and high-quality pulp production for the paper industry. Sulphite black liquor for this experiment was supplied by Lenzing (Paskov, Czech Republic).

Modification

Before the modification with individual waste liquors, the test specimens designated for pressure impregnation were dried in a Memmert UF 160 mplus oven (Memmert Ltd., Germany) at 103°C to achieve 0% moisture content. This condition corresponds to a stable weight. The samples were then transferred to a desiccator, where the temperature was gradually reduced to the laboratory environment level of 20 °C, without absorbing atmospheric moisture. Subsequently, the individual wood specimens were placed into beakers and weighted down. They were then immersed in the respective waste liquors and placed into a pressure impregnation chamber. The impregnation was conducted in the VTIZ 0.5 × 2 chamber (VYVOS s. r. o., the Czech Republic). The impregnation regime was kept very simple. First, a vacuum of –0.8 bar was applied for 15 minutes, followed by pressure equalization to ambient level. Then, the pressure was increased to 7 bar for 60 minutes. This short and single-cycle regime was intentionally chosen to determine whether it is possible to introduce a sufficient amount of impregnation agent into the material within a very short impregnation cycle. After impregnation, the samples were removed from the impregnation solution and left in the laboratory environment at 20 °C and 65% relative humidity to drain for 30 minutes. During this period, any excess impregnation material on the surface of the test specimens was removed. The samples were then transferred to an oven and dried at 105 °C to reach zero moisture content. Subsequently, the samples were weighed. The difference in weight indicates the amount of material that was impregnated into the sample.


Figure 1. Pressure impregnation chamber VYVOS and storage of impregnated bodies in the dryer.

Calorific value test

The calorific value was measured using a 6,400 Calorimeter model A1435DDEE (Parr Instrument Company Inc., USA). When determining the total calorific value, the moisture content of the test sample is crucial. For greater objectivity, the samples were tested at zero moisture content to eliminate the influence of moisture and isolate the effect of the impregnation medium. The test is performed in a closed pressure vessel in an atmosphere of pure oxygen. The ignition of the sample is initiated by a resistance wire, which ignites a cotton thread that transfers the flame to the sample. The calorimeter calculates the calorific value based on the change in temperature of the inner and outer containers. This value is corrected by the weight of the sample placed in the device and is reported in MJ/kg.

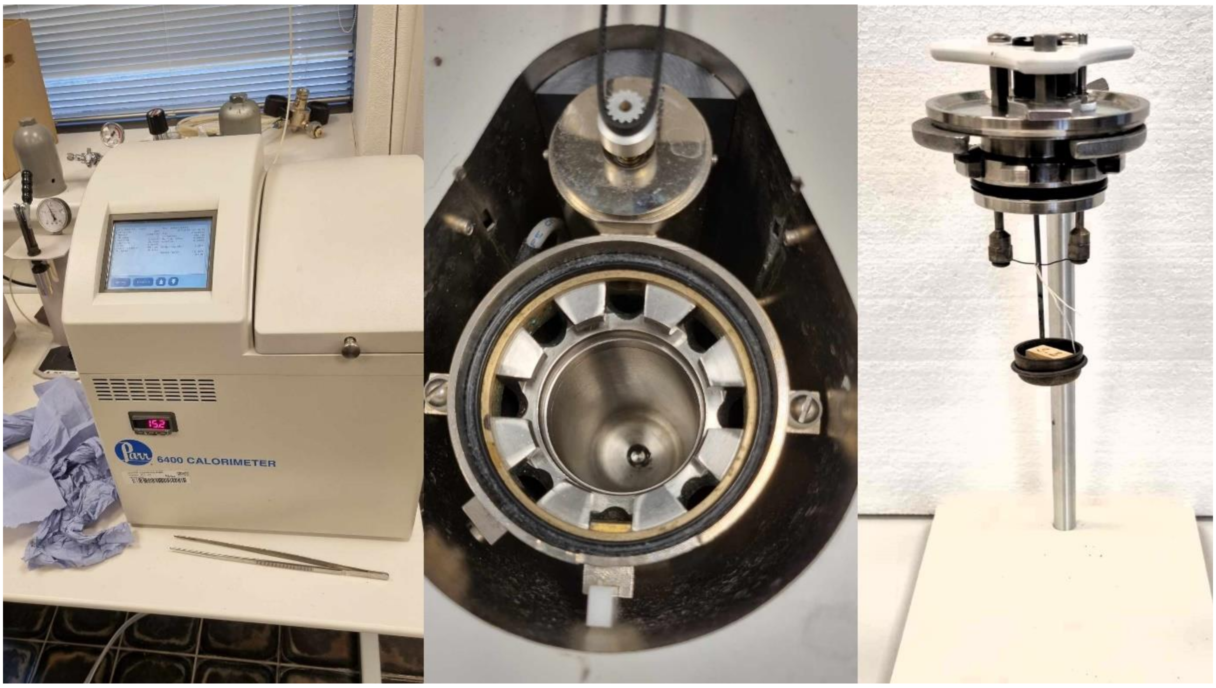

Figure 2. Calorimeter 6,400 Parr Instrument Company. Principle of establishing the sample to be measured.

Smoke density test

The smoke development test was conducted in a testing device according to the EN 5659-2 standard[8]. The test specimen was placed in a special holder with a defined opening of 70 × 70 mm. Radiant heat at an intensity of 25 kW/m² was applied to this surface for 15 minutes. Smoke development in the closed chamber was monitored using a light beam, calibrated before each test. The reduction in light transmission through the smoke in the chamber was used to determine the specific optical density of the smoke. This experiment is essential for evaluating the behaviour of materials when exposed to high temperatures, which is crucial for safety standards and fire regulations. Measuring the specific optical density of smoke provides valuable data on how the material contributes to smoke development during combustion, which is essential for assessing the risks associated with fires in buildings and other structures.


Figure 3. Chamber for measuring the specific density of smoke according to the EN 5659-2 standard.

Results

The evaluation of the impregnation cycle can be assessed in two ways. The first method is by comparing the density at 0% moisture content of the sample. The density of the impregnated specimen significantly increased compared to the reference specimens, as shown in Table I. It is important to note that density depends on dimensions, and after exposure to waste liquors, the dimensions of the specimens may not return to their original state. The most significant increase in density was observed with the application of black kraft liquor on spruce wood, with an increase of nearly 64 kg/m³.

Table I
Basic data on the effectiveness of impregnation

Wood	Weight gain in % (w 0 %)		Density (kg/m^3)		
	Sulphite liquor	Kraft liquor	Before impregnation	Sulphite liquor	Kraft liquor
Spruce	15.2	17.2	456.9	499.8	521.3
Pine	12.3	15.2	421.1	491.0	503.2

Another method for determining the amount of impregnation substance is gravimetric measurement, which involves observing the increase in weight in an absolutely dry state. It is evident that with the use of black kraft liquor, the total weight of the impregnated specimen increased by 17.2% for spruce and 15.2% for pine. With black sulphite liquor, this increase was approximately 2.5% lower.

The calorific value for dry organic matter, such as wood or biomass, ranges from 15 to 20 MJ/kg. Our measured results indicate that impregnation with black kraft liquor reduces the calorific value by 6% to 18.4 MJ/kg. This trend was not confirmed for black sulphite liquor, and the calorific value reduction was only 2.2% for spruce wood. This effect was nearly negligible for pine wood, at only 0.7%.

Table II
Values of heat of combustion depending on the modified substance ingested

Wood	Percentage decrease in specific heat capacity		Specific heat capacity (MJ/kg)		
	Sulphite liquor	Kraft liquor	Reference	Sulphite liquor	Kraft liquor
Spruce	2.2	6.0	19.58	19.15	18.40
Pine	0.7	5.0	19.66	19.52	18.67

When monitoring the optical density of smoke, only impregnation with black kraft liquor showed significant effects, markedly reducing smoke development and density. After completing this test, the samples exhibited less damage and degradation from radiant heat compared to samples modified with black sulphite liquor or reference samples. This result indicates that black kraft liquor not only effectively reduces smoke production but also enhances the material's resistance to thermal damage. In contrast, impregnation with sulphite liquor did not significantly impact smoke reduction or improve resistance to radiant heat, suggesting its limited efficacy under these specific conditions. This difference in effectiveness between the two types of impregnation agents is essential for further research and applications in fire safety and material protection.

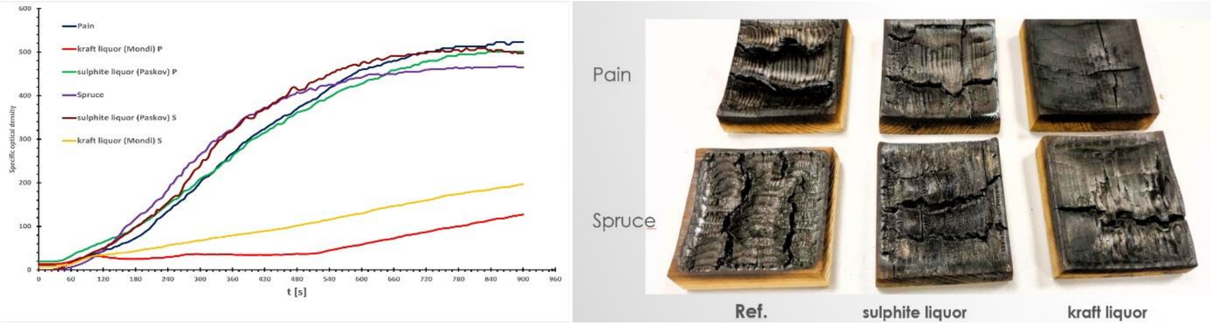

Figure 4. Smoke Density Development and Illustration of Degradation After Tests.

Discussion

Based on our research, it is evident that using black kraft liquor is one of the potential methods to enhance the fire resistance of biomaterials for use in timber constructions. The increasing societal pressure to construct new residential units from renewable resources is noticeable in all European Union countries. The demonstrated benefits, such as the reduction of smoke production during a fire, are among the essential parameters for the safe evacuation of people from buildings during a fire. This opens up wider applications for wood-based building materials in construction or for external and internal cladding.

Another significant advantage is the increased overall integrity of the material, which suggests the potential future use of such modified wood in load-bearing structures to enhance evacuation times, particularly in the case of multi-story buildings. The overall reduction in calorific value indicates a lower energy output from the resulting fire, thus reducing the rate of fire spread and increasing the effective response time for rescue teams.

In the future, it is necessary to continue addressing this issue and work on technological processes for implementation into serial production. The entire process must be environmentally friendly and carbon neutral.

Acknowledgments

The authors are grateful for the support of project CZ.111/1.1.11/11.1111 Ministry of Education, Youth and Sports and private company Wotan Forest, a.s.

The attendance to this conference was supported by the European Liaison Committee for Pulp and Paper through a EUCEPA Student Grant.

References

1. Laurichesse, S., Avérous, L.: Prog. Polym. Sci. *39(7)*, 1266–1290 (2014).
2. Pouteau, C., Dole, P., Cathala, B., Averous, L., Boquillon, N.: Polym. Degrad. Stab. *81(1)*, 9–18 (2003).
3. Amen-Chen, C., Pakdel, H., Roy, Ch.: Bioresour. Technol. *79(3)*, 277–299 (2001).
4. Prieur, B., Meub, M., Wittemann, M., Klein, R., Bellayer, S., Fontaine, G., Bourbigot, S.: Polym. Degrad. Stab. *127*, 32–43 (2016).
5. Wang, Y., Zhang, Y., Liu, B., Zhao, Q., Qi, Y., Wang, Y., W., Sun, Z., Liu, B., Zhang, N., Hu, W., Xie, H.: Compos. Commun. *21*, 100–382 (2020).
6. Griffini, G., Passoni, V., Suriano, R., Levi, M., Turri, S.: ACS Sustain. Chem. Eng. *3(6)*, 1145–1154 (2015).
7. Klein, S.E., Alzagameem, A., Rumpf, J., Korte, I., Kreyenschmidt, J., Schulze, M.: Coat. *9(8)*, 489–494 (2019).
8. ISO 5659-2:2017 Plastics — Smoke generation. Part 2: Determination of optical density by a single-chamber test. International Organization for Standardization, Geneve 2017.

POSSIBILITIES OF 6PPD REPLACEMENT IN THE RUBBER COMPOUNDS

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Abstract

6PPD (N-[1,3-dimethylbutyl]-N'-phenyl-p-phenylenediamine) is important constituent of the rubber compounds. It is distinguished by its excellent efficiency, because it acts as the antioxidant and antiozonant simultaneously. This advantage motivates its worldwide application.

However, there are serious signals indicating the toxicity of this substance and mainly the quinone formed by its oxidation. The proven toxic effect on the Coho salmon gave the first alert. Following extensive research have shown adverse effects on the nerves, heart, lungs or intestines of the fishes and mammals. The tire abrasion is considered for the main source in the environment.

The negative effects motivated the search for the alternative antioxidant/antiozonant.

Following strategies are applied:

1. Design of structures preventing to the formation of the toxic quinones
2. Modification of rubber compounds by the reinforcement with carbon nanofillers, which enables to apply less efficient but ecologically safe antioxidants
3. Application of antioxidants of the native origin.

DUSLO is important producer of 6PPD and the issues related to the potential toxicity of this substance motivate the company to join the effort in the looking for the alternative. VUCHT, the daughter company of Duslo, has potential to design the structure replacing 6PPD and develop the technology of its production. The cooperation with the rubber compounders is necessary to achieve successful transition from the 6PPD to the less harmful alternative.

Introduction

N-[1,3-dimethylbutyl]-N'-phenyl-p-phenylenediamine abbreviated as **6PPD** is the important antidegradant for the rubber compounds.

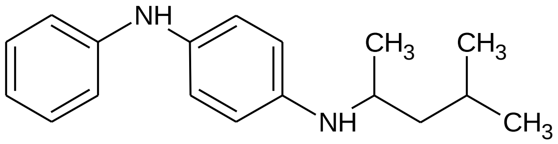


Figure 1. Structure of 6PPD

This antidegradant is the derivative of p-phenylene diamine (PPD). Its structure (Figure 1) enables to fulfill several functions in the rubber matrix:

- Protection against ozone.
  6PPD is readily reactive with ozone to prevent crack formation on the surface of the rubber, but not too reactive in order to prevent premature depletion.
- Protection against oxygen.
  The compound is reactive with oxygen to prevent hardening of the rubber, loss of strength, improve tire wear, and maintain long-term durability, while not reacting so aggressively with oxygen as to cause premature depletion.
- Protection against fatigue.
  The antidegradants is reactive with the free radicals generated by breaks in rubber polymer during flexing. These free radicals can break the polymer chains and crosslinks in the rubber compound that would lead to a loss of strength for body plies, sidewall and tread.
- Optimal migration rate/ diffusion.

6PPD has the adequate solubility and diffusivity in rubber compounds, also referred to as migration and mobility, which allows the chemical to move to the tire surface where it is needed to react with oxygen and ozone to ensure long term protection of the tire from oxygen and ozone damage over its life.

- Compatibility with manufacturing processes.
  The additive has no adverse effects on the rubber cure rate, tack, viscosity, etc.

The optimum combination of properties mentioned above is the reason of the widespread application of 6PPD in the rubber products and mainly in tires. However, the excellent technical performance of 6PPD becomes overshadowed by the news about its adverse health and environmental effects. This report provides a brief survey of the known impact of 6PPD on the animal species and describes different concepts of dealing with the problem.

Discussion

Environmental and health effects of 6PPD

Significant decline in the population of Coho salmon (Oncorhynchus kisutch) has been attributed to the oxidation product of 6PPD in the article published by the group of 27 authors in the year 2021[1]. The oxidation product is identified to be 6PPD-quinone:

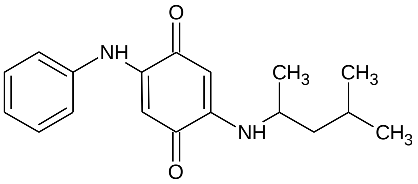


Figure 2. Structure of 6PPD quinone

The negative effects of 6PPD and 6PPD quinone were further observed in the liver of mice[2]. The repeated exposition of mice to 6PPD quinone in another study has confirmed the damage of liver and also the lungs, kidney and testes of males[3]. The neurotoxicity of 6PPD – quinone was studied with *Caenorhabditis elegans*[4]. The tests performed with this organism have also shown that 6PPD-quinone causes the accumulation of lipides in its body[5]. The study of 6PPD effect on zebrafish (*Danio Rerio)* has proven its cardiotoxicity.

Formation of 6PPD-Q

6PPD quinone is formed by the oxidation of 6PPD with ozone. The team working on Berkeley University elucidated the details of the oxidation process and established, that the process starts with the O_3 interaction with the carbon atoms of the 6PPD molecule and not with the nitrogen atoms as assumed before [6, 7].

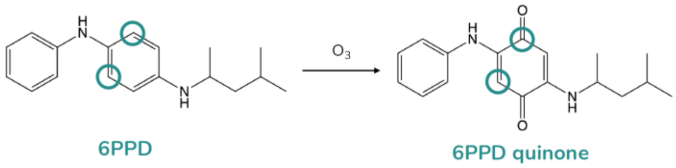


Figure 3. Locci of O_3 attack on the 6PPD molecule and resulting quinone formation according to authors of 6 and 7

Transfer to the environment

The tire wear particles are formed by the tire abrasion on the routes. The rainwater flow is the main driving force which transfers these particles into the soil, extracts 6PPD and 6PPD-Q and further distributes these materials into the ground water, rivers and food cycle[8].

The brief survey shows that the information about the adverse effect of 6PPD and mainly 6PPD-quinone accumulates. These compounds are going to be considered as a problem and the pressure of their replacement strengthens. This pressure is also projected into the legal issues: The Institute for Fisheries Resources (IFR) and the Pacific Coast Federation of Fishermen’s Associations (PCFFA) filed suit against U.S. tire manufacturers over the use of the chemical 6PPD in rubber tires[9]. The U.S. Environmental Protection Agency (EPA) is granting a petition from the Yurok Tribe, the Port Gamble S’Klallam Tribe, and the Puyallup Tribe of Indians to address the use of the 6PPD in tires[10]. On the other hand, the US tire industry association warns against “premature” restrictions on 6PPD in tires and emphasized that protection materials such as 6PPD are essential for tire performance and safety[11].

This pressure motivates the effort to find the suitable alternatives for 6PPD in the rubber industry. Several approaches to this challenge are described in the following paragraphs.

Application of alternative PPD derivatives

The toxicities of seven PPD derivatives and their corresponding quinones were tested with salmon coho and rainbow trout[12]. The toxicity of antidegradants depended on the side chain of the substituted PPD derivative. The toxicity of 6PPD and its quinone was high, but PPD derivatives with different side chains were considerably less toxic. Authors relate this difference to the hydroxylation of the side chain proceeding in the tissue. Dependence of this process on the side chain structure opens the possibility to find the less harmful antidegradant based on alkylated/arylated PPD.

These results are supported by the work of the research team, which developed the method of multigram synthesis of the 77PD quinone[13]. Juvenile coho salmon was exposed to 5 concentrations of 77PD and 77PD-quinone in water. 77PD was found to be toxic to coho salmon with a 96 hour LC50 value of 24 µg/L active ingredient. No lethal effect of 77PD quinone was observed at 226 µg/L. Comparing with LC50 determined for 6PPD quinone (0.095 µg/L), 77PD quinone is practically nontoxic.

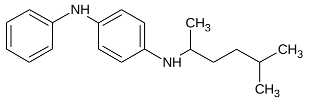
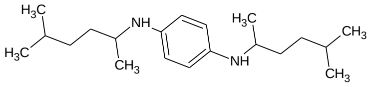
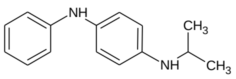
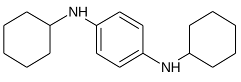
These studies suggest that there may be lower acute toxicity of quinones derived from 77PD, CPPD, DPPD, DTPD, and IPPD relative to 6PPD quinone. However, these results will require validation by other laboratories and further studies.

Approach of USTMA – evaluation of known alternative antidegradants

The approach of US Tire Manufacturers Association (USTMA) utilizes the available information about 40 alternative antidegradants known in 2023. The data were evaluated, and the promising candidates were selected using two screens:

- **First screen** is based on the evaluation of **hazard score**. The data of human health and environmental hazard parameters are used to calculate the hazard score. However, only 19 of 40 alternatives were possible to evaluate because of the insufficient data of health and environmental effects.
- **Second screen** is based on the **performance evaluation.** Most of alternatives were eliminated due to the lack of performance data.

The screening of possible alternatives provided following 5 candidates[14] for the final evaluation in the 2nd stage of the tests:

No.	Label	Structure	Chemical name
1	7PPD		N-(1,4-dimethylpentyl)-N'-phenyl-p-phenylendiamine
2	77PD		N,N'-Bis(1,4-dimethylpentyl)-p-phenylenediamine
3	IPPD		N-isopropyl-N'-phenyl-p-phenylenediamine
4	CCPD		Dicyclohexyl-4-Phenylenediamine
5	Grafene	Macromolecular	

The performance of the selected candidates will be verified in the laboratory and pilot scale and finally in the manufacturing scale.

Alternative structures

Prevention of quinone formation

The research related to the 6PPD toxicity revealed that the formation of the quinone is the critical step affecting its adverse effects. Better knowledge of the oxidation mechanism of 6PPD to the toxic 6PPD quinone gave idea how to prevent this undesirable process by the modification of the 6PPD structure[6,7]. The modification is based on the alkylation of phenyl groups to change the course of the O_3 attack. The ketone is formed instead of the quinone after the O_3 oxidation (Figure 4).

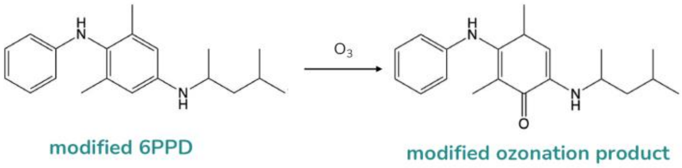


Figure 4. Modification of 6PPD structure preventing the quinone formation according to authors of 6, 7.

Similar approach is chosen by the authors of patent CN113072741B[15]. They propose the structure of antidegradant possessing substituted phenylene ring, which does not enable the quinone formation.

Novel structures of antiozonants

The structure of the most utilized antioxidants resembles the derivatives of p-phenylene diamine (PPD). The effort to eliminate the negative features of 6PPD is reflected in the growing number of other structures with antidegradation effect, such as acridine, indole, carbazole, phenoxazine, diazepine, phenazine or quinoline. The boom of new structures can be illustrated by the number of patent applications in this field: Fifteen applications have been filed in the period 2020–2022, but 26 applications in the single year 2023. The detailed description of the new structures exceeds the scope of this report.

Natural materials

Lignine contained in the black liquor was modified by the reaction with formaldehyde and diethylenetriamine to prepare aminated lignine[16]. This material can be incorporated into the rubber matrix and shows excellent anti-aging properties. It provides the combination of thermal stability and ozone/fatigue resistances through radical scavenging effect.

The free radical scavenging activity and protective mechanism of **melanin** on natural rubber's oxidative resistance was explored using molecular dynamics and quantum mechanical calculations[17]. The results revealed that the intermolecular interactions at the rubber/antioxidant interface benefited the antioxidant melanine to bind tightly to the rubber thus exhibiting improved dispersion, O_2 barrier properties, and thermo-oxidative stability.

Rubber nanocomposites

Carbon nanotubes developed by Molecular Rebar Design are incorporated into the elastomer matrix. They impart significant abrasion, tear, and crack propagation resistance properties to elastomers. Ozonation related microcrack propagation is lessened, preventing coalescence of microcracks, and thus reducing larger crack occurrence. With this additional reinforcement in a tire compound, the quantity of 6PPD used can be reduced, or 6PPD can be replaced with a less effective, but environmentally safer antiozonant- like 77PD[18]. Molecular Rebar Design has been awarded a Small Business Innovation Research Phase I Award from the U.S. Environmental Protection Agency.

Addition of **graphene flakes** into the rubber compound creates the tortuous path for the oxygen or ozone molecules entering the rubber matrix, retards the oxidation and also the crack propagation. It comprises to the suppression of the rubber degradation and enables to decrease or eliminate the 6PPD addition. Patent US11753529[19] protects the preparation and application of graphene flakes, that are used in the role of the additive in the tire sidewalls and replace 6PPD in this application.

Conclusions

The toxicity of 6PPD and especially 6PPD quinone is proven by many tests and observations, new information confirming its adverse effects accumulates. The pressure to replace 6PPD increases simultaneously. The proposed solutions can be classified in two groups:

1. Replacement of 6PPD with alternatives, that are available "here and now". US Association of Tire Manufacturers (USTMA) is the main representative of this approach. Five alternatives selected for the pilot and production tests are well known antidegradants produced by many companies. Their performance and health hazards are familiar to their users. This group of antidegradants can be incorporated relatively quickly.

2. Application of new structures including natural materials or nanofillers. This approach provides promising original solutions. They have potential to bring environmentally friendly elastomers with longer lifetime on the marked. However, their incorporation into rubber technology will require longer optimization and more extensive investment. The positive effect of these solutions can be expected after a longer timespan.

Consequences for Duslo j. s. c.

DUSLO j. s. c. is the important producer of 6PPD. The issues related to this antidegradant have a vital importance for the company. The alternative antiozonant IPPD is also in its production portfolio. VUCHT, the daughter company of Duslo has also developed the technology of 7PPD production. Both compounds are present in the group of alternative antidegradants selected by USTMA for the pilot and production tests as the 6PPD replacements.

Another alternative antidegradant N-(1-phenylethyl)-N'-phenyl-1,4-phenylenediamine (SPPD) has been also developed by VUCHT[20]. The application tests confirmed the performance of this stabilizer in rubber compounds. Additional tests of health hazard, mainly the toxicity evaluation of the corresponding quinone are necessary for its classification among the favourable alternatives of 6PPD. VUCHT is also active in the development of new antidegradant structures and cooperates with the tire producers in their evaluation. However, present situation enhanced the importance of the simultaneous cooperation with the laboratories evaluating the toxicity of the potential rubber stabilizers. Duslo and VUCHT are open to the partnership in this area.

References

1. Tian, Z; Zhao, H; Peter, KT; et al. Science Vol *371*, (Issue 6525) p.185 (2021).
2. Fang, L., et al., Science of The Total Environment, *2023*, p. 161836.
3. Wenmiao He, Aihua Gu, Dayong Wang, Science of The Total Environment, Volume *894*, (2023), p. 164842.
4. Xin Hua, Xiao Feng, Geyu Liang, Jie Chao, and Dayong Wang, Environ. Sci. Technol., *57*, 12, p. 4940 (2023).
5. Yuxing Wang, Xin Hua, Dayong Wang, Environ. Poll. Volume *333*, 15. September 2023, p. 121937, DOI:10.1016/j.envpol.2023.121937.
6. Boxer, E, Heras, E, Hollenbeck, K., Rigutto, G., Rossomme, E, Wilson, J.: Greener Solutions course at UC Berkeley, December, 2021, https://bcgc.berkeley.edu/greener-solutions-2021-alternatives-6ppd-tire-manufacturing.
7. Rossomme E., Hart-Cooper W., Orts W., McMahan C., Head-Gordon M., ChemRxiv. Cambridge: Cambridge Open Engage; 2022-11-21, DOI:10.26434/chemrxiv-2022-xxpqc.
8. Ricci Nicomel, N., Li L. Y,: Ecocycles Vol. *9,* No. 3 p. 33 (2023).
9. Rubber World, 10. November 2023, https://rubberworld.com/u-s-fishing-groups-sue-thirteen-of-the-largest-tire-manufacturers-over-6ppd/.
10. Rubber World, 27. November 2023, https:// the-u-s-epa-grants-tribal-petition-to-protect-salmon-from-6ppd/.
11. European Rubber Journal, 13. November 2023.
12. Nair P., Sun Jianxian, Xie Linna, Kennedy L. et al.: ChemRxiv 20. June 2023; https://chemrxiv.org/engage/chemrxiv/article-details/648ccfec4f8b1884b7669239.
13. Chapelet j., Malik Al-Afyouni, Tyhurst J., et al: ChemRxiv. Cambridge, 25 October 2023, Version 1, https://chemrxiv.org/engage/chemrxiv/article-details/65315e0d87198ede07cb645a.
14. Schunk A.: Rubber News April 01, 2024.
15. Jia Weijie; Wang Bin; Zhang Hao; Zheng Dongju; Xu Yi; Zhang Dan: Patent CN113072741B, Eve Rubber Res Institute, 2022.
16. June-Young Chung, Uiseok Hwang, Junyoung Kim et al.: ACS Sustainable Chemistry & Engineering *11* (6), p. 2303 (2023).
17. Sattar M. A., Patnaik A.: J. Phys. Chem. B *127*, 38, p. 8242, (2023).
18. Schunk A., Rubber News, December 11, 2023.
19. Aschall D., Halasa A. F, Rodgers M. B.: US11753529(B2), 15.7.2021, Akron Polymer Solutions Inc.
20. Macak I, Uhlar J., Lehocky P. et al.: SK286712 (B6), 5.3.2009, Duslo, a.s.

TECHNOLOGY FOR ENVIRONMENTAL PROTECTION

GUANIDINE POLYMERS AS NITRIFICATION INHIBITORS FOR GRANULAR NITROGEN FERTILIZERS

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Abstract

One of the most important elements in plant nutrition is nitrogen (N). Its content in the soil can change in a short time, which can significantly affect the harvest of farming products. Losses of nitrogen through leaching or gaseous emissions reduce the efficiency of fertilization. The N content depends on several factors, such as type of soil, climatic conditions or the sort of used nitrogen fertilizer. One of the alternatives to reduce and limit N losses is using nitrification inhibitors, which slow down or delay the oxidation of ammonia N (NH_4^+) to nitrate N (NO_3^-) [1]. The application of guanidine polymers as inhibitors of the nitrification process was not known until now. These polymers are used exclusively as biocides[2]. In the laboratories of VUCHT a.s. the properties of guanidine polymers as nitrification inhibitors of nitrogen fertilizers were studied and tested. Polymers of guanidine hydrochloride with diamine compounds were prepared, which were applied in the form of an aqueous solution on the surface of granules of nitrogenous fertilizer, or added directly to the slurry of the fertilizer before the formation of granules. A copolymer of guanidine hydrochloride polymer with 1,2 diaminopropane and ε-caprolactone as a nitrification inhibitor was also prepared and applied to granular nitrogen fertilizers[3,4]. The nitrification inhibitory effects of granular fertilizers with the addition of guanidine polymers or copolymers were determined in soil pot tests as well as in small-plot field experiments on the agricultural crops such winter wheat, winter rapeseed and seed corn. By using the mentioned nitrification inhibitors, a significant reduction of nitrogen losses in granular nitrogen fertilizers has been achieved.

Introduction

Nitrifocation inhibitors

Nitrification is a process in which bacteria convert the ammonium form of nitrogen NH_4^+) into the nitrate form NO_3^-) Nitrification inhibitors are chemicals designed to slow down this process, thereby reducing the risk of nitrogen loss through leaching or denitrification (the process of reducing NO_3^-) to nitrogen oxides and molecular nitrogen).

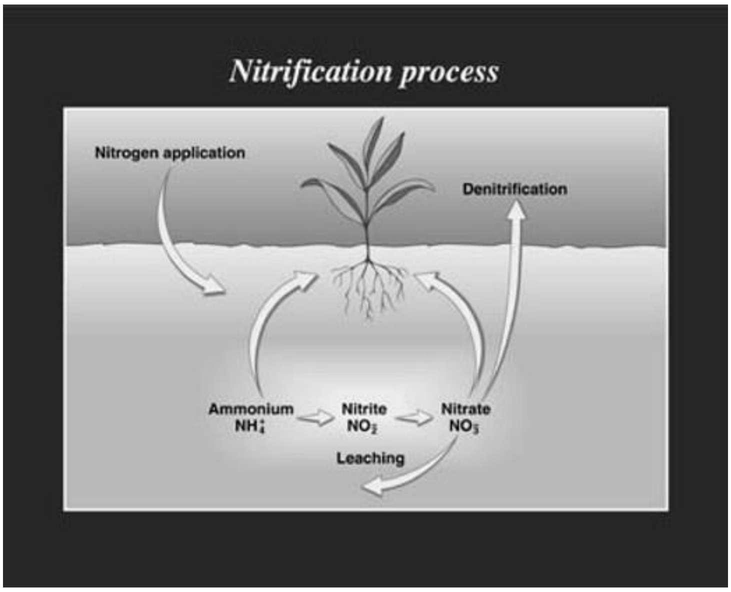


Figure 1. Nitrification process

The use of guanidine polymers as inhibitors of the nitrification process was not known until now. These polymers are used exclusively as biocides. In the laboratories of VUCHT a.s. properties of guanidine polymers and copolymers as nitrification inhibitors of nitrogen fertilizers were investigated and tested.

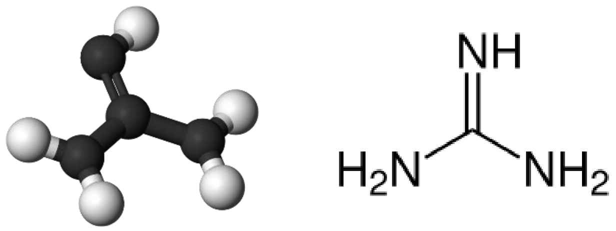
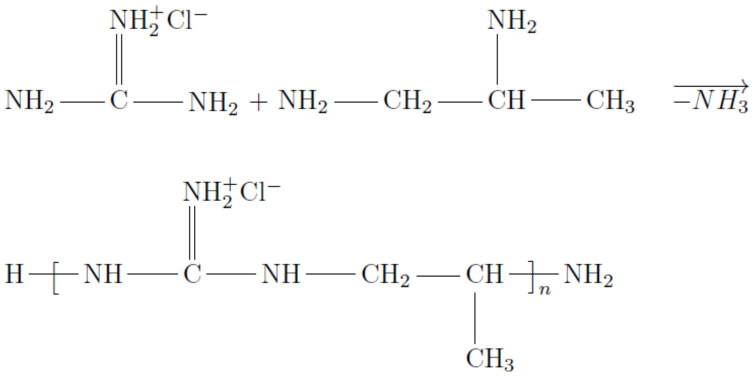


Figure 2. Guanidine (Aminoethanamidine)

Experimental

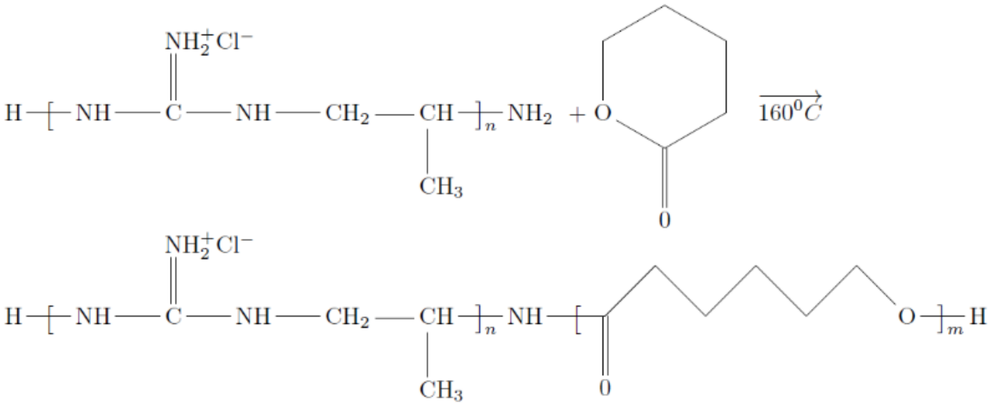
The preparation of the guanidine copolymer consists of two steps:

1st step: Polymerization of guanidine hydrochloride with 1,2-diaminopropane, where the released ammonia is absorbed into water



$$NH_2-\overset{NH_2^+Cl^-}{\overset{\|}{C}}-NH_2 + NH_2-CH_2-\overset{NH_2}{\overset{|}{CH}}-CH_3 \xrightarrow{-NH_3} H-[NH-\overset{NH_2^+Cl^-}{\overset{\|}{C}}-NH-CH_2-\underset{CH_3}{\underset{|}{CH}}]_n-NH_2$$

2nd steps: Copolymerization of the polymer (guanidine hydrochloride with 1,2-diaminopropane) with gradual addition of ε-caprolactone



Preparation of a surface treatment agent with an inhibitory effect is described by the following block scheme (Figure 1):

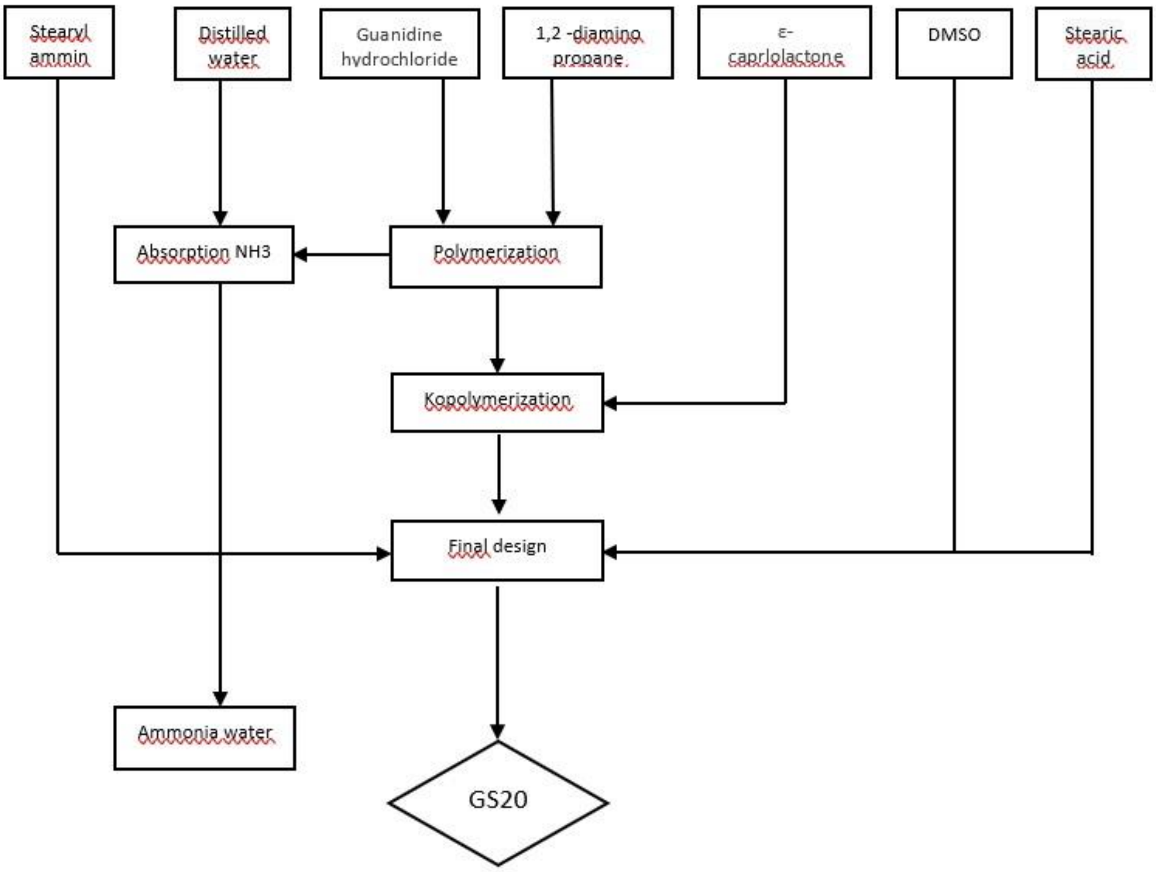
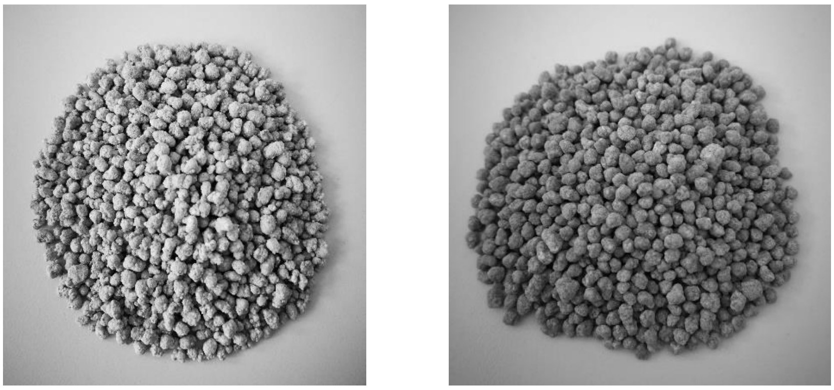


Figure 1: Block scheme of preparation guanidine copolymer

Discussion of results

Granular fertilizers GSA (granular ammonium sulfate) and ASN (ammonium nitrate) with guanidine nitrification inhibitor were prepared, which were tested in field and pot experiments.



GSA with NI inside the pellets ASN with NI on the surface of the pellets

Figure 2. Granular ammonium sulfate with NI and ammonium nitrate with NI

Testing of the inhibitory efficiency of nitrification inhibitors according to the STN ISO 15685 standard has been introduced in the VUCHT a.s. laboratories: „Soil quality. Determination of potential nitrification and inhibition of nitrification. Rapid test by oxidation of ammonium oxidation“.

Table I
Determination of inhibitory efficiency of guanidine polymer inhibitor

Concentration [ppm]	Potential nitrification [ng NO_2-N / g dry matter / h]	Inhibition of activity [%]
0	251	-
30	155	43.9
60	136	59.7
180	120	97.0

In field experiments, In cooperation with the Department of Agrochemistry, Soil Science, Microbiology and Plant Nutrition, Faculty of AgriSciences, Mendel University in Brno, the effect of the application of granular ammonium sulfate (GSA) with the addition of a polymeric guanidine nitrification inhibitor (GSA-NI) has been monitored in comparison with the same fertilizer without NI as well as the classic calcium ammonium nitrate fertilizer (CAN) on the yield and quality of corn, winter rape and winter wheat.

Table II
Testing of fertilizers with the addition of guanidine polymer (effect of tested fertilizers, average value over 3 years)

Crop	Variant	Applied dose N [kg/hectare]	Yield [t/hectare]
Corn	CAN	160	9.9
	GSA	160	10.0
	GSA-NI	120	10.2

In pot experiments, samples of ASN fertilizer containing polymeric guanidine as well as a surface treatment agent with copolymer guanidine were tested in comparison with the ASN fertilizer without NI. The aim of the pot experiments was to evaluate the influence of guanidine nitrification inhibitors on the content of mineral nitrogen in the soil and the microbial activity of the soil (nitrifying and denitrifying bacteria).

Figure 3. Pot experiments at MU

The use of both inhibitors led to a demonstrable reduction in the amount of ammonia-oxidizing soil bacteria and denitrifying bacteria.The population of denitrifying bacteria was significantly reduced by the guanidine copolymer.

Table III
Pot experiments, average value from all sampling t1 until t3, i.e. from 7 to 21 day

Variant	Average content $N\_NH_4^+$ in the soil [mg/kg]	Average content $N\_NO_3^-$ in the soil [mg/kg]
ASN	68.14	81.16
ASN + copolymer	66.59	72.75
ASN + polymer	63.68	75.40

In the test of granular fertilizers with IN under controlled conditions, we wanted to use granular ammonium sulfate as fertilizer, containing a low amount of nitrate nitrogen, instead of ASN fertilizer, for the supposed easier monitoring of the transformation of ammonia nitrogen in the soil. The aim of the pot experiments was to evaluate the impact of selected nitrification inhibitors applied in combination with granular ammonium sulfate on the soil environment.

GSA fertilizer samples containing the guanidine polymer as well as the guanidine copolymer surface treatment agent were tested in comparison to GSA fertilizer without NI. Based on the evaluation of the dynamics of changes of different forms of nitrogen in the soil, GSA with the copolymer has the faster onset of inhibition, however both forms of guanidine show inhibitory effects.

Table IV
Testing granulated fertilizers with NI under controlled conditions, average value from all sampling t1 until t3, i.e. from 7 to 21 day

Variant	Average content $N\_NH_4^+$ in the soil [mg/kg]	Average content $N\_NO_3^-$ in the soil [mg/kg]
GSA	75.45	82.57
GSA + copolymer	90.76	65.42
GSA + polymer	78.44	61.7

Conclusions

Increasing the added value of manufactured fertilizers is one of the long-term goals of research. The plant will really use only about 50 to 70% of the applied N. Thus, the uncontrolled release of N into the soil has negative economic (inefficient use of fertilizer) and ecological consequences – water and air pollution. One of the possibilities is to influence the nitrification process by using nitrification inhibitors, which can reduce application doses of fertilizers, and contribute to more efficient use of nutrients by plants as well as to the reduction of emissions of nitrogen gases into the atmosphere.

In the laboratories of VUCHT a.s. research and development of several types of nitrification inhibitors is ongoing, including inhibitors based on guanidine polymers and original agents for the surface treatment of granular fertilizers with an inhibitory effect based on guanidine copolymers.

In VUCHT a.s. there are several alternative solutions for ecological nitrification inhibitors, or substances with more favorable toxicological and ecotoxicological properties, as a possible replacement of currently used commercial nitrification inhibitors.

References

1. Ducsay L & Varényiová M (2020) Aplikácie hnojív s inhibíciou nitrifikácie, Naše pole, https://nasepole.sk/aplikacia-hnojiv-s-inhibiciou-nitrifikacie.
2. Grigorieva MN, Stelmakh SA, Astakhova SA, Tsenter IM, Bazaron LU & Batoev VB (2014) Biocidal action of copolymers based on aliphatic diamines and guanidine hydrochloride, Journal of Applied Polymer Science, 131, 40319. https://doi.org/10.1002/app.40319.
3. Grigorieva MN, Stelmakh SA, Astakhova SA, Tsenter IM, Bazaron LU, Batoev VB & Mognonov DM (2015) Synthesis of polyalkyguanidine hydrochloride copolymers and their antibacterial activity against

conditionally pathogenic microorganisms Bacillus cereus and Escheria coli, Pharmaceutical Chemistry Journal, 49 (2): 29-33. https://link.springer.com/article/10.1007/s11094-015-1230-z.

4. A kind of compound disease-resistant biological base manure of grape (2018) Patent CN108083902. https://patents.google.com/patent/CN108083902A/en?oq=CN108083902.

EXPLORING SUSTAINABLE FUEL SOLUTIONS AND FUEL QUALITY MEASUREMENT OPTIONS

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Abstract

From the point of view of environmental quality, the pressure to reduce the pollution caused by car traffic is increasing. Furthermore, due to dwindling oil reserves and the closure of oil refineries, the EU has also announced an exemption from the ban on the sale of new gasoline and diesel vehicles until 2035, which will allow internal combustion engine vehicles to run exclusively on synthetic fuels – eFuels. It appears that electric cars are not a complete alternative either, as the European Commission has found that the balance of pure electric cars (referred to as BEVs) must cover the entire life cycle of the car, including battery production and operating losses. It is also worth noting that in most European countries, coal and gas dominate electricity generation. Synthetic fuels are another option to consider. Some car manufacturers are already beginning to address this situation, such as Porsche, which has built a plant in Chile to produce synthetic fuels from water, wind, and CO_2. Fuel quality assessments include a number of methods and techniques to ensure optimal performance and environmental sustainability. One of the prevalent methods involves measuring key parameters such as octane, cetane number, and viscosity, providing insight into combustion efficiency and engine compatibility. In addition, chemical analysis techniques, including chromatography and spectroscopy, allow the identification and quantification of fuel components, which aids in the detection of contaminants. In addition, various biofuels are being added to fuels, increasing sustainability efforts. Direct monitoring of the quality of fuels in vehicles appears to be a promising approach to pollution control, facilitating early interventions to maintain quality. Furthermore, this paper presents the possibilities to measure the quality of fuels by changing the electrical properties of fuels in internal combustion engines and offers an innovative view of quality assessment methodologies.

Introduction

In the context of environmental quality, there is an increasing emphasis on reducing pollution from car traffic. This is coupled with concerns about the dwindling oil reserves and the shutdown of oil refineries. The European Union has responded by allowing the sale of new gasoline and diesel vehicles to continue until 2035, provided that they run exclusively on synthetic fuels, known as eFuels[1]. The effectiveness of electric vehicles (EVs) as an alternative is also being scrutinized. The European Commission emphasizes the need to evaluate the entire lifecycle of battery electric vehicles (BEVs), including the environmental impact of battery production and operational losses. Furthermore, electricity generation in most European countries is still heavily dependent on coal and gas, raising questions about the overall sustainability of EVs. Hence, synthetic fuels are being considered as a viable alternative.

Several optimization scenarios for the future of transportation have been considered[1]. In the "Free" scenario, the only constraint is achieving the planned decarbonization goals. The "E-fuels" scenario mandates that all new light-duty vehicles without battery electric propulsion allowed after 2035 must be powered by e-fuels. The "Purely electric" scenario requires all new light-duty vehicles permitted after 2035 to be battery-electric vehicles. Current European policies for 2035 favor the cost effectiveness of electric vehicles over battery electric vehicles, with the most likely cost scenario projecting a 30% cost gap in favor of electric vehicles. The primary disadvantage of battery electric vehicles lies in their energy supply method.

A similar trend is observed in the Formula 1 industry. Beginning with the 2022 season, Formula 1 cars have switched from E5 to E10 fuel to reduce carbon emissions[2]. By 2026, the regulations will mandate the use of 100% sustainable fuels. However, this transition presents challenges, particularly with formaldehyde emissions. To maintain high performance with ethanol under the new 2026 regulations, the mass flow rate of the fuel will remain high, resulting in persistently high formaldehyde emissions. Consequently, to meet air quality targets at F1 events, advanced exhaust treatment methods will be necessary. This underscores the need for innovative solutions in fuel technology and emission control to balance performance and environmental impact.

Several companies are leading the way in the production of synthetic gasoline, including Royal Dutch Shell, Air Liquide, Linde plc, Maire Tecnimont SpA, Technip Energies NV[3], and Porsche. Porsche, in particular, has made significant strides with its POSYN (Porsche Synthetic) project[4].

Figure 1. Production of synthetic gasoline in Chile for Porsche[3].

As depicted in Figure 1, Porsche uses electricity from a 3.4 GW Siemens Gamesa wind turbine on site to power a Siemens Energy PEM electrolyzer, which splits water molecules. The resulting hydrogen is combined with carbon dioxide, captured directly from the air using Global Thermostat equipment, to form syngas. Syngas undergoes a chemical reaction with a catalyst within a reactor to produce green methanol (CH_3OH). This innovative process showcases how synthetic fuels can be produced sustainably, potentially revolutionizing the automotive industry and contributing to global decarbonization efforts.

Direct monitoring of fuel quality in vehicles emerges as a promising strategy for pollution control. This approach facilitates early interventions to uphold fuel quality standards and mitigate environmental impact. It offers innovative perspectives on methodologies for assessing fuel quality beyond conventional approaches and proposes novel techniques for evaluating fuel quality, potentially revolutionizing the field of pollution control and fuel quality assurance. This paper introduces the concept of assessing fuel quality by altering the electrical properties of fuels within internal combustion engines, specifically through impedance spectroscopy. This technique provides a new dimension to fuel quality monitoring, ensuring that the fuels used are not only sustainable, but also meet the required performance and emission standards.

Materials and methods

Commercial fuels originating from the following fuels were investigated: Orlen EFECTA 95, Orlen VERVA 100, Shell Natural FuelSave 95, Shell V-P Racing 100, OMV Natural 95, OMV MaxxMotion 100, MOL EVO 95, and MOL EVO 100 PLUS. A mixture of E10 biofuels was used in all samples.

Experiment

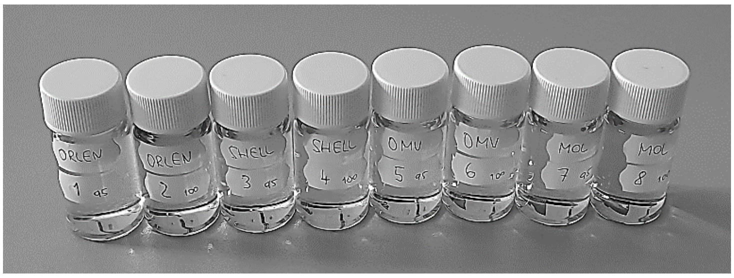

Figure 2. Gasoline samples: 1. Orlen EFECTA 95, 2. Orlen VERVA 100, 3. Shell Natural FuelSave 95, 4. Shell V-P Racing 100, 5. OMV Natural 95, 6. OMV MaxxMotion 100, 7. MOL EVO 95, 8. MOL EVO 100 PLUS.

The eight samples of 95 and 100 octane gasolines from four major suppliers in the Czech Republic were measured. Each sample was placed within a cylindrical copper cell with a capacity of 20 ml. The impedance was measured using a Vector Network Analyzer – Bode 100 (OMICRON-LAB) over a frequency range of 20 MHz to 40 MHz. Before the measurements, the network analyzer was calibrated to zero, infinity, and a specific resistance of 50.4 Ohms. All measurements were made at a constant temperature of 24.0 °C.

Discussion and analysis of results

The impact of octane number on impedance has been confirmed. The impedance response is characteristic of a capacitor, with a phase around -90 degrees. Furthermore, as can be seen from Figure 2, it is possible to distinguish between samples with 95 and 100 octane content, as shown in the figure.

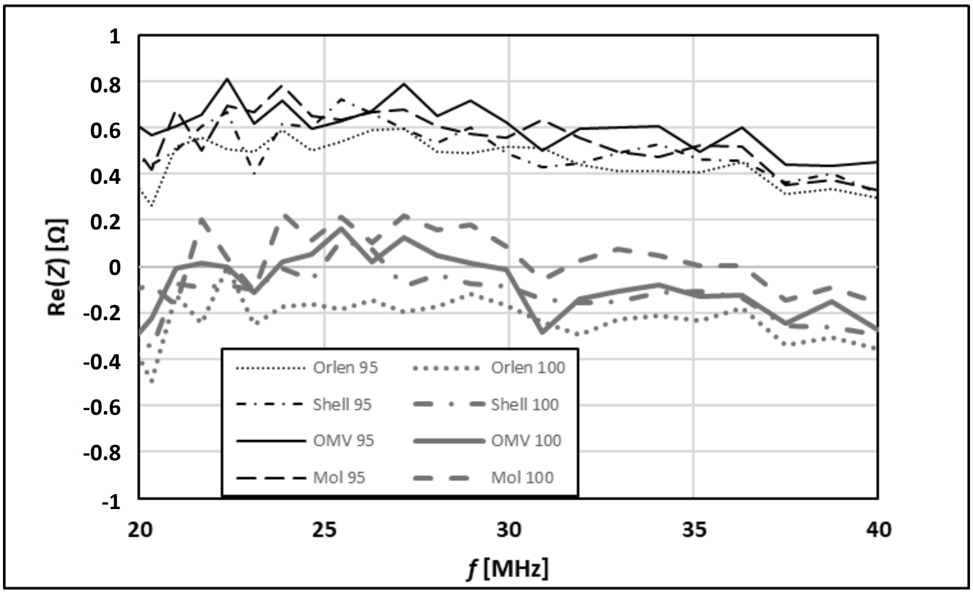

Figure 2. Real part of impedance vs frequency.

However, there is an error in the measurements because the impedance values are negative. This indicates the presence of measurement errors. As seen in Figure 3, it is also possible to distinguish the octane number based on the imaginary part of the impedance. On the basis of experience, it can be anticipated that there is greater sensitivity at higher frequencies, more than 50 MHz.

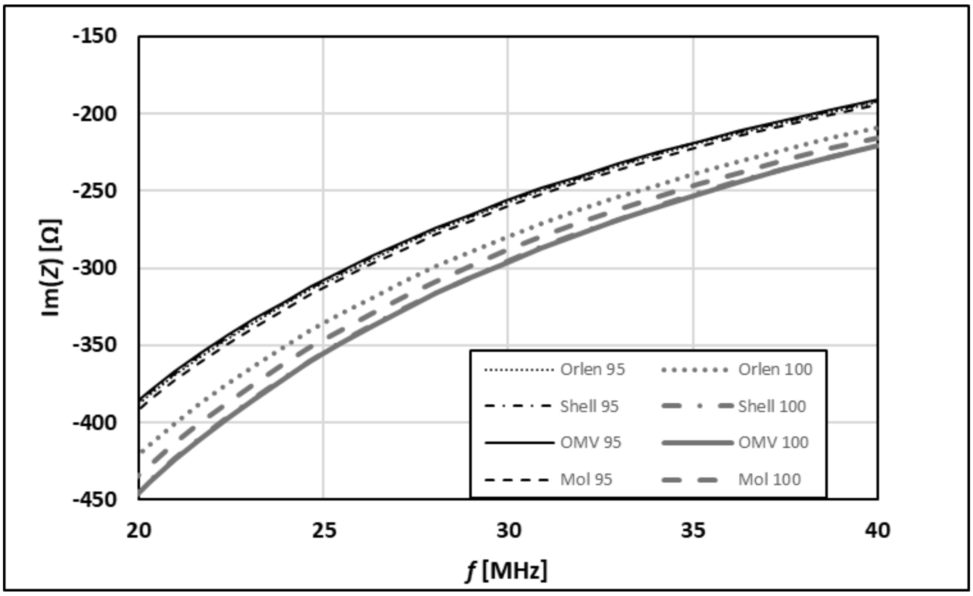

Figure 3. Imaginary part of impedance vs frequency.

Conclusions

With an increasing emphasis on reducing car traffic pollution and switching to synthetic fuels (eFuels), measuring the quality of these fuels is becoming crucial. Synthetic fuels are considered to be a viable alternative to traditional fuels, and direct monitoring of their quality may be necessary to ensure optimal performance and environmental sustainability. As such, impedance spectroscopy could play a vital role in the future of fuel quality assessment, especially as the automotive industry moves to more sustainable fuel options. As has been shown, this technique makes it possible to distinguish between different octane numbers, both in the real and imaginary parts of the impedance. At higher frequencies, there was greater sensitivity. This method can provide a new dimension of fuel quality monitoring, ensuring that not only are the fuels used sustainable but also meet the required performance and emission standards.

References

1. Danieli, P., Masi, M., Lazzaretto, A., Carraro, G., Dal Cin, E., Volpato, G: Energies, *16*(15), 5690 (2023).
2. Reeves, N. and Samuel, S.: SAE Technical Paper, *2023-01-0739* (2023).
3. Ram, V., Salkuti, S. R.: Energies, *16*(6), 2834 (2023).
4. Porsche: *eFuels pilot plant in Chile officially opened*, Porsche Newsroom, 2022.