CZECH TECHNICAL UNIVERSITY IN PRAGUE
Faculty of Civil Engineering
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HIGH-PERFORMANCE CONCRETE MIXTURES CONTAINING GLASS POWDER

Optimization of mechanical properties, durability, and environmental impacts for use in construction and design applications

DOCTORAL THESIS

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DECLARATION

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Title of the doctoral thesis: High-performance concrete mixtures containing glass powder: Optimization of mechanical properties, durability, and environmental impacts for use in construction and design applications

I hereby declare that this doctoral thesis is my own work and effort written under the guidance of the tutors prof. Ing. Petr Hájek, CSc., FEng., doc. Ing. Tereza Pavlů, Ph.D. and Ing. Kristina Fořtová, Ph. D. All sources and other materials used have been quoted in the list of references.
The doctoral thesis was written in connection with research on the projects:

- SGS17/010/OHK1/1T/11: "Glass Powder Waste Utilization in High Performance Concrete";
- SGS19/093/OHK1/2T/11: "Use of waste materials in HPC in design applications";
- SGS21/096/OHK1/2T/11: "Influence of chemical properties on the use of waste materials in concrete applications";
- SGS22/009/OHK1/1T/11: "Solution of a fire hazardous area in risky places of the building".

In Prague, on 29.6.2023 ....

signature

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Abstract in Czech

Tato práce se zaměřuje na využití skelného prachu z různých zdrojů. Jedná se především o odpadní sklo, které pochází ze střepů z komunálního odpadu a staré sklo z fotovoltaických panelů z důvodu končící životnosti těchto systémů první generace. Dalším zkoumaným typem skla je vedlejší produkt vznikající při výrobě skla. Vedlejší produkty vznikají v mnoha průmyslových odvětvích; sklářský průmysl je v tomto ohledu významným producentem. Byly analyzovány dva druhy skla z různých sklářských závodů. Prvotní studie byla publikována již v roce 2019 a byla mezi prvními v ČR; proto bylo žádoucí navázat dalším výzkumem. Protože možnosti použití skelného prachu v betonu vyvolává mnoho zásadních otázek, tento výzkum analyzuje odpadní a vedlejší materiály zejména z chemického, fyzikálního a toxického hlediska. V práci byly provedeny experimenty v několika opakováních a následně byly testovány vzorky betonu s vybranými materiály. Hlavním bodem zájmu bylo ověření potenciální alkalicko-křemičité reakce (ASR), která byla předpokládána z důvodu použití skla v betonu, které může reakci katalyzovat. Testování ASR probíhalo ve dvou opakováních, byly zvoleny mezinárodní a národní testovací postupy. Podobně významně bylo nahlíženo i na potenciální ekotoxicitu skleněných materiálů. Sklo z fotovoltaických panelů a vedlejší skelný produkt výroby byly při testech toxicity vyhodnoceny jako mírně toxické. Po použití skla jako substitutu v betonu však byly všechny výsledky na bezpečných úrovních pod limitem stanovených vyhláškou. Vzhledem k následnému vývoji aplikací (obkladů a zdiva) bylo nutné tyto potenciálně nežádoucí vlastnosti důkladně otestovat. U většiny směsí se tak potvrdil předpoklad pozitivního vlivu skelného prachu na betonovou směs z hlediska ASR a toxicity. Zároveň byla na závěr navržena metodika hodnocení stavebních materiálů z hlediska ekotoxicity.

Klíčová slova: odpadní skelný prach, vysokohodnotný beton, recyklované materiály, alkalicko-křemičitá reakce

Abstract in English

This thesis focuses on the use of glass powder from various sources. These are mainly waste glass that comes from shards from municipal waste and old glass from photovoltaic panels due to the end of the service life of these systems from the first generation. Another type of glass investigated is a secondary product of glass production. By-products are created in many branches of industry; the glass industry is a significant producer in this respect. Two types of glass from different glass plants were analyzed. The initial study was already published in 2019 and was among the first in the Czech Republic; therefore, it was desirable to follow up with further research. Since the use of glass powder in concrete, in addition to the possibility, raises many fundamental questions, this research analyzes the materials as such, especially from the chemical, physical and toxic points of view. Repeated experiments were carried out in the thesis, and concrete samples with these materials were subsequently tested. The main point of interest was verifying the potential alkali-silica reaction (ASR), which was assumed due to the use of glass, which can catalyze the reaction. ASR testing took place in two iterations, international and national testing procedures were chosen. The potential ecotoxic threat of glass was viewed similarly significantly. Glass from photovoltaic panels and glass as a secondary production product was slightly hazardous in toxicity tests. However, after encapsulation in concrete, all results were at safe levels below the limit. Due to the subsequent development of tiles and masonry applications, it was necessary to test these potentially undesirable properties thoroughly. Thus the assumption of a positive effect of glass powder on the concrete mixture in terms of ASR and toxicity was confirmed for most mixtures. At the same time, a methodology was proposed for the evaluation of building materials from the point of view of ecotoxicity.

Keywords: waste glass powder, high performance concrete, recycled materials, alkali-silica reaction

Table of content

Nomenclature

The following nomenclature is used in the work carried out within this thesis. Nomenclature in other chapters is taken over from the original referred sources and explained within the text.

Abbreviations	**Explanation**
CTU	Czech Technical University in Prague
FCE	Faculty of Civil Engineering
UCEEB	University Centre for Energy Efficient Buildings
UCT	University of Chemistry and Technology, Prague
SDGs	Sustainable Development Goals
SEP	State Environmental Policy
EGD	European Green Deal
HPC	High-Performance Concrete
UHPC	Ultra High-Performance Concrete
GP	Glass Powder
WGP	Waste Glass Powder
SF	Silica Flour
ASR	Alkali-Silica Reaction
LCA	Life Cycle Analysis
DHA	Soil Dehydrogenase Activity
HP	Hazard Properties
HSC	Hazard Statement Codes
SGS	Student Grant Competition
B	Boron

Cr	Chromium
Ni	Nickel
Cu	Cumprum (Copper)
Zn	Zinc
As	Arsenic
Sc	Scandium
Mo	Molybdenum
Cd	Cadmium
Sb	Stibium (Antimony)
Ba	Barium
Hg	Hydrargyrum (Mercury)
Pb	Plumbum (Lead)

1. General Introduction

1.1. Background

The development of industry and the construction evolution of the last century have contributed to a significant increase in the carbon footprint and a reduction in the sources of primary non-renewable raw materials and resources [1], [2]. Despite the great boom, there was an early realization of this situation and an accumulation of organizations that began to deal with the solution and elimination of these problems using long-term strategies and realistic scenarios to achieve the lost balance of ecosystems and the environment [3], [4]. Due to the growing population, these steps are necessary, and materials research (and ideally, the entire construction industry, etc.) must be subordinated to them.

After water, concrete is the second most used material in the world. About 7-8 % of total CO2 production is from cement fabrication. Therefore, in recent years, there has been an effort to reduce this material or to lower environmental impacts by using new types of optimized or recycled concrete [5]–[7]. These efforts are closely connected with important resolutions of the United Nations or the European Commission.

Degradation of the environment and ecosystems, climate change, and, in recent years, the COVID-19 pandemic are topics that The European Green Deal (EGD) works with [8]. The fundamental pillars of protecting the climate, nature, energy, and transport include reducing emissions by up to 55% by 2030 compared to 1990. The document describes challenges aimed directly at the industry. Specifically, it involves technology innovation, product sustainability, and the development of low-emission approaches to production to achieve climate neutrality by 2050. To achieve these goals, it is necessary to mobilize the industry fully, and energy-intensive industries will play a key role. Reducing the carbon footprint and innovative technological solutions should lead to the developing of new business models.

In addition to international documents, the Czech Republic also has a program that deals with environmental issues. State Environmental Policy 2030 (SEP), with a view to 2050, has three main pillars - environment and health, transition to climate neutrality and circular economy, and nature and landscape. In the construction industry, this is mainly about reducing energy-intensive technologies, increasing energy efficiency and utilization of renewable energy sources, reducing greenhouse gas emissions, and preventing waste.

The Sustainable Development Goals (SDGs) appear to be another important pillar for orientation in the industry's requirements in the upcoming years, which at several points shed light on the plan to maintain humanity, ecosystems, nature, and the planet as such [9]. The points relevant to the construction industry are mainly summarized in goal 12 (specifically in 12.1, 12.2, and 12.6). All these points were considered when motivating and setting the goals of this doctoral thesis. The main aims are to use the secondary resources efficiently, reduce waste and prevent and integrate sustainable management in the construction products and industry life cycle.

1.2. The Scope of the Thesis

The thesis is dealing with a wide range of problems summarized in the points below:

1.1.1 Elemental Analysis of Glass Material

(Appendix 1, Appendix 4, Chapter 3.1 and Chapter 3.2)

The chemical properties were a basis for further research, particularly regarding toxicity, environmental impact, and the alkali-silica reaction (ASR).

The waste regulations stipulate the maximum concentration of certain elements in the material. In compliance with Czech legislation, risk metals were tested, including B, Cr, Ni, Cu, Zn, As, Sc, Mo, Cd, Sb, Ba, Hg, and Pb. Both glass powders and concrete specimens underwent analysis before any proposed application. Chemical composition was analyzed using X-ray fluorescence (XRF) spectrometry and atomic absorption spectrometry with flame atomizer 280FS AA.

1.1.2 Potential Threat of Alkali-Silica Reaction

(Appendix 2 and Chapter 3.6)

ASR is a chemical reaction between silica and alkali in concrete, causing cracking and degradation. Two short-term testing methods, ASTM C1260, and Czech Method TP137, were chosen to investigate ASR. ASTM C1260 offers quicker results and a more aggressive environment simulation. These methods were selected based on pilot research performed and published in 2021.

1.1.3 Verification of Mechanical and Durability Resistance with a Focus on Improvement

(Appendix 3, Appendix 5, Appendix 6, Chapter 3.4, and Chapter 3.5)

Mechanical properties of building materials were tested using destructive methods according to Czech standards. Compressive and tensile bending strength were measured on samples of different shapes and sizes. The results showed satisfactory strength values that increased with a longer solidification time. Conclusions from this research have been presented at conferences, with additional results to be published soon.

Durability is crucial in High-Performance Concrete (HPC) testing. Freeze-thaw resistance was tested on samples according to ČSN 73 1322. The samples were subjected to multiple cycles, with satisfactory results even after 200 cycles. Compressive strength and tensile strength were measured after each set of cycles.

1.1.4 Environmental Impact Assessment: LCA and Ecotoxicity

(Appendix 1, Appendix 4, Appendix 5, Chapter 3.3 and Chapter 3.9)

Ecotoxicology, which studies the toxic effects caused by natural sources, is relevant in assessing the potential harm of waste materials, secondary materials from production, and concrete, which may pose to the environment. The thesis focused on four types of ecotoxicity testing: duckweed, freshwater algae, daphnia, and mustard germination. Aqueous leachates were tested, and various parameters such as chlorophyll content, root elongation, and organism viability were evaluated and compared with control organisms. Evaluating the impacts of the materials used in concrete in terms of the life cycle is the key trigger of the entire research.

A summary of provided experiments connected to the published papers is in Table 1.

Table 1 Summary of provided experiments.

Properties tested/Experiments performed	**Described in**
Specific surface area	Chapter 3.2
Chemical composition	Appendix 1, Chapter 3.1
Ecotoxicity tests	Appendix 1, Appendix 4, Chapter 3.3
Compressive strength	Appendix 3, Appendix 4, Chapter 3.4
Flexural strength	Appendix 3, Appendix 4, Chapter 3.4
Freeze thaw resistence	Appendix 1, Chapter 3.5
Carbonation	Appendix 5
Life cycle analysis	Appendix 5, Chapter 3.9
Alkali-silica reaction (ASTM C1260)	Appendix 2, Chapter 3.6
Alkali-silica reaction (TP137)	Appendix 2, Chapter 3.6
Fire resistance	Appendix 6, Chapter 3.7
Water absorption	Chapter 3.10
Thermal properties	Chapter 3.10

The results are partially published in follow-up research and articles summarized in Chapter 4.1.

2. State of The Art

This chapter summarized the information about the problems dealt with in the thesis. The ranges are summarized in the chapters below.

2.1. High-Performance Concrete as Sustainable Approach

Concrete is one of the high energy consumers, creating many emissions, and there is a generally known association with negative environmental impact. Recently, there has been an increasing tendency to use special kinds of concrete with greater strength, resistance, or durability. Such concretes are usually classified of High-Performance concrete (HPC) or Ultra High-Performance Concrete (UHPC). The main focus of this research on HPC was picked because high-quality concrete benefits from better properties, strength, and high durability with relatively small consumption of material (smaller in proportion to classic concrete to achieve the same properties). The highest concentration, therefore, leads to the reduction of energy requirements and the reduction of the carbon footprint caused by the raw materials that are commonly used in concrete utilizing technologies such as recycling, the use of secondary raw materials, and waste materials - based on the analysis of the European Green Deal points and SEP.

HPC or UHPC has a very small fraction of used aggregates compared with ordinary concrete, and they also have a very small water/cement ratio due to the use of superplasticizers. Unfortunately, these concrete have almost always a large amount of cement. One sustainable approach is replacing some parts of the cement (or other component) with more environmentally friendly materials. This work, therefore, began with a very extensive theoretical study of possible substitutes for the individual components of concrete (aggregate, cement, silica flour, microsilica). Subsequently, these possibilities were also tested in the laboratory. Most advanced meaningful results were published at national or international conferences or in journals [10]–[13] .

After evaluating all the results, the main topic to deal with was the replacement of cement (silica flour). Considering the chemical properties, research [14]–[16], and risks associated with ASR (see below), the use of the sub-1mm fraction was an obvious choice.

2.2. Recycling Rates of the Glass Industry

One of the appropriate materials is glass, which is one of the most recyclable materials (almost 100%) [15]–[18], and it is one of the most available solid waste materials. On the one hand, glass is chemically resistant to external influences and has excellent heat-insulation properties. On the other hand, it is non-decomposable material. Therefore, it is necessary to landfill waste glass or unused glass by-products – but impurities may occur due to the transporting and landfilling of waste glass. The utilization of waste glass in the construction industry is convenient because the demand for glass purity is decreasing. However, the use of glass is still high compared to the recycling ratio, and concerning landfill numbers (Table 2), a new recycle or reuse attitude is necessary.

Table 2 Produced, recycled and landfilled glass in thousands of U.S. tons (2000-2018).

	2000	**2005**	**2010**	**2015**	**2017**	**2018**
Produced	12.770	12.540	11.520	11.470	12.300	12.250
Recycled	2.880	2.590	3.130	3.190	3.070	3.060
Landfilled	8.100	8.280	7.030	6.840	7.580	7.550

Glass can be produced by melting a mixture of silica, sodium carbonate, dolomite, and limestone at temperatures up to 1600 °C. The mixture then cools down due to unwanted crystallization – thus, the glass becomes a solid amorphous material [19]. The advantage of recycling glass is, for example, a lower temperature during processing. Specific properties or colors can be achieved with special additives[17].

Almost everyone has this relatively general knowledge. Although the chemical composition of glass and cement or aggregates may seem different, the properties have been confirmed in other studies abroad [17], [20]. The production and use of glass go back to ancient history (before our era), although it has yet to be discovered exactly when and how glass was made for the first time. Studies and scientists are already moving toward recycling and reusing glass [5], processing glass as a secondary raw material from production, and generally preventing glass landfills. A large amount of waste is a global problem [17] and is addressed by many scientific branches. Construction waste is one of the largest items of globally produced waste, and, unfortunately, emissions and the overall negative impact on the environment are also related to this [6]. The general effort is, therefore, to eliminate these impacts to a certain (high) extent. Waste glass utilization is appropriate in HPC (or UHPC) because less water is used there than in regular concrete. This thesis deals with four basic types of glass, but glass from photovoltaic panels can be considered the main topic that was investigated in the most detail.

2.2.1. Growth of Photovoltaic Technologies

In recent years, the utilization of photovoltaic (PV) technologies has been proliferating; a cumulative global installed capacity of 222 GW was already reached at the end of the 2015 [21]. Photovoltaics is used for economically advantageous and ecological electricity production, history of PV dates to 1990. However, it is a technology whose aging is still insufficiently explored because, during the service years, only mechanically damaged panels were disposed of. Currently, the lifespan of the PV panels is defined by the time when the performance drops by 20%, which is usually declared by the manufacturer after 25 years of use. At the same time, most manufacturers declare a maximum decrease of roughly 10% after ten years.

Nevertheless, the end-of-life period of the first era of photovoltaic panels is already coming, and decommissioning, dismantling, and disposal must be figured out. Nevertheless, this direction could be better due to upcoming regulations and stricter requirements for waste management, circular economy, and sustainability [22]. Recycling is the ideal way. Even so, with such a complicated material, a detailed search of options and ways to recycle the panels is required.

The launch of solar energy production in the early 1990s was supported by the launch of the grant programs, initially mainly used by Germany, but over time they reached the whole world, including the Czech Republic. This act was the main beginning of the massive production of photovoltaic panels and their installation and application on all types and sizes of constructions. Despite a few earlier installations, it can be stated that most of the oldest panels in the Czech Republic were installed between 2000 and 2006. However, the total number of installed panels during this period is deficient compared to the following years. 2006 there was a big turnaround thanks to the introduction of support for purchasing electricity from renewable sources according to Act No. 180/2005 Coll. And just as the global PV market is growing, so is the volume of discarded PV panels, with a cumulative global flow of 43,500-250,000 metric tons at the end of 2016, roughly 0.1% to 0.6% of the cumulative weight of all installed panels. With these numbers, a large amount of waste is expected, which will continue to grow until a particular time. This growth will subsequently be slightly reduced thanks to the effort to develop panels with longer service life and less material consumption [23].

Total annual global electrical and electronic waste (e-waste) already reached 41.8 million metric tons in 2014, while the annual amount of waste from PV panels was 1,000 times lower in 2014. However, there is an assumption that by 2050 PV waste will exceed this number by up to 10%. This assumption, therefore, points to the fact that it is necessary and desirable to use the experience of managing e-waste and turn it into opportunities for the management of waste from PV panels in the future.

2.2.2. Current Trends in PV Recycling

Due to the panels' lifetime, a more significant number of elements for recycling can be expected after 2030. After 2040, approximately 20,000 tons of panels are expected to be recycled annually [24]. The largest share of the weight of crystalline panels is glass (60-70 %) and aluminum frame (around 20 %). For thin-film panels, the proportion of glass and aluminum is over 95 % [23]. Both materials are normally almost 100% recycled. Other metal materials are valuable raw materials that are worth recovering from waste. Plastics can be recycled only partially or not at all. A detailed table of materials with possible recycling methods is enclosed below in Table 3.

Table 3 List of the materials used in PV panels and current trends in their recycling.

Material	Recycling Method
Glass	The advantage of glass is that in most cases the material can be recycled into the original product, but often due to unwanted impurities, glass cannot be used in this way
Aluminum	Easily recycled with very low energy consumption.
Plastic Components	Usually degrade due to the climate conditions and it is not possible to reuse them.
Photovoltaic Cells	At the end of their life, crystalline cells are essentially unchanged, and there is already practical experience with recycling whole cells or plates. For thin-film cells, their recovery is more efficient than production from primary raw materials.
Heavy Metals	Due to toxicity, it is necessary to separate heavy metals from the environment, even though they represent minority components (weight, price, power consumption). They will probably be replaced by other material in the future (depletion of economically extractable reserves).

One of the frequently used recycling methods for PV panels is thermal recycling. It is an advanced method of recycling panels generally heated to a temperature above 500 °C (the design and testing took place at the German company Deutsche Solar AG). This temperature guarantees the evaporation of the plastic elements (with subsequent combustion in the next chamber). The rest of the materials are manually divided, and if the panels are undamaged, it is possible to use almost 85% of the panel with roughly 70% less energy consumption. However, this method can only be used for panels made of crystalline cells and therefore does not solve thin-film panels.

The second widely used method is the mechanical-chemical method, which is mostly applicable to thin-film panels. Although the first step is manually dismantling the aluminum frame, followed by crushing and sorting the materials into the specified fractions, this method has a lower proportion of manual labor than the previously mentioned one. Still, the result is only crushed raw materials. Separation methods are used for fluid and wet floats and electrodynamic separation. Important metals such as silver and others are obtained chemically and pyrometallurgical and can subsequently be used as raw materials in the metallurgical industry; plastics are disposed of with the possible use of heat from the combustion [25].

The end of the life of PV panels signals the possibility of a new industrial sector, which is also possible for the emergence of new economic values per the global path to sustainable development. This industry can go into both the public and private sectors. The basic ideas are reduced, reuse, and recycle.

The composition of solar panels is expected to require fewer raw materials as research and development and technological advances continue to mature the industry. Currently, two-thirds of globally manufactured PV panels are crystalline silicon (c-Si), including hazardous materials such as silver, tin, and lead traces. Thin-film panels have a higher percentage of non-hazardous materials like glass, polymer, and aluminum. By 2030, current trends in panel efficiency suggest that the raw material inputs for c-Si and thin-film technologies could be significantly reduced, decreasing the use of hazardous and rare materials in the production process and improving the recyclability and resource recovery potential of end-of-life panels.

Rapid global solar panel industry growth is expected to create a strong demand for used or repaired panels and components. Early failures in the lifetime of a panel can be repaired and resold at a lower cost, providing an opportunity for countries with limited financial resources to access the solar PV market. This secondary market for used panels and components also allows buyers to purchase partly repaired panels or components [26], [27].

As solar panels end their lifespan, recycling and material recovery is becoming preferable option for disposal. The PV recycling industry currently processes end-of-life panels through separate batches within existing recycling plants, allowing for the recovery of significant components such as glass, aluminum, and copper at yields greater than 85% of the total panel mass. In the long term, specialized panel recycling plants can increase treatment capacities, maximize revenues, and recover a greater fraction of the embodied materials. Research on PV-specific recycling technologies has been ongoing for the past decade, and it is important to learn from this research to develop cost-efficient and material-efficient recycling plants [21].

However, technical and regulatory systems must be established to ensure that PV panel waste streams are sufficient for profitable operation. For the preparation of specific plants for the recycling of entire panels, which according to studies, is hugely financially demanding, the Czech Republic is not currently ready. This assumption is based on the number of panels to be processed (recycled), which leads to the efficient production of the required recycling line in the 2040 [23]. Although there are efforts not only in the Czech Republic to reuse most PV panel components, but the most likely scenario is also when parts of the panels will have to be used differently. It is necessary to consider the possibility of impurities on existing parts, especially glass ones. In case of increased contamination of glass parts, it is advisable to look for alternative use. In the Czech Republic, around 2020, leading technical universities and their research teams began to investigate the possibility of using glass waste from PV panels in concrete mixtures, including the possibility of subsequent applications.

2.3. Possibilities of Glass Powder Utilization in HPC

Several studies deal with replacing some of the concrete components with glass. Two main ways to use waste glass in concrete are possible – aggregate replacement or cement replacement. Some researchers combine these attitudes.

2.3.1. Volume and Particle Size of the Substitute

Hongjian Du and col. investigated the influence of replacing cement with glass powder from communal waste in high volumes up to 60% to the mechanical and durability properties of concrete [28]. Topcu and col. investigated the tensile bending strength of concrete with waste glass as a coarse aggregate [29]. Waste glass powder was used as a pozzolanic material in Shayan and Xu's research – they replaced up to 30% of cement in concrete mix [30], [31]. Another research group has investigated the possibility of replacing aggregate with waste glass in concrete [18], [32], [33]. These studies concluded that coarser fractions worsen the properties of concrete. Based on them, it could be said it is more suitable to use waste glass as a fine aggregate in concrete. Schwarz and col. compared the properties of concrete containing waste glass powder with fly ash concrete[34]. There are several studies to investigate the amount of waste glass powder in concrete [35], [36]. The results of the replacement range varied from 10% to 40% - the ideal amount should be around 10% - 20 % to achieve the highest values of mechanical properties and durability. Soliman and Tagnit-Hamou developed ultra-high-performance glass concrete with a compressive strength of up to 220 MPa. However, this is the only study dealing with ultra-high-performance concrete (UHPC) [37]. According to [20], with the utilization of waste glass in concrete as a replacement for cement or fine aggregate, saving up to 19% of greenhouse gases and 17% of primary energy consumption is possible.

2.3.2. Basic Strength Properties of Concrete Containing GP

My previous research describes a study investigating the potential of using waste glass from photovoltaic panels in high-performance concrete. It was found that the waste glass can be an excellent pozzolanic material and improve the mechanical and durability properties of the concrete. This thesis highlights the potential of using the waste glass from photovoltaic panels in other industries [38].

Another research presents the conclusions of a study on replacing natural aggregate in cement composites with recycled glass from PV panels. The research came to similar findings as was done in my research. Replacement of natural aggregate with recycled glass fraction 0/10 mm is possible, and the densities of recycled glass fractions are similar and reach approximately 2.5 mg/m^3. The consistency of the fresh cement mixture based on recycled glass was within an acceptable range. The flexural and compressive strengths of the cement composites are almost identical and within an acceptable range. With 100 % replacement of natural aggregate with recycled glass, there is a decrease in flexural and compressive strength by 20-30 %. The image analysis results confirm the non-disruption of the contact zone between the grains of the recycled glass and the cementing compound. The permeability of cement composites with recycled glass from PV panels shows similar values to conventional cement composites. Future research will focus on increasing the flexural strength to a minimum of 6 MPa and testing the alkali-silica reaction of recycled glass grains from solar panels, as well as the surface treatment of the designed cement composites for potential use in interior paving or tiling material [39], [40].

Other major problems include, for example, corrosion. Another experimental study [40] dealt with the biocorrosion of cement composites in beams and crumbling, using photovoltaic glass as a replacement for natural aggregate in four different grain fractions. Three species of microscopic algae were used in the experiment as they were found to be part of the biofilm involved in biocorrosion. The results show that the growth of the microscopic algae was small and low in abundance due to the lack of supporting microbiotas and the high pH value of the samples. The high level of recycled glass in the samples also affected the growth of the algae as it affected the availability of nutrients for their nutrition [40].

Another important factor that significantly affects the properties of high-quality concrete is the water/cement ratio, which must be significantly reduced when using glass. Although we mainly deal with the fine fraction below 1 mm, the risk of alkali-silica reaction (ASR) increases with the growing amount of water. Many cases may cause concrete degradation; when considering replacing silica powder with waste glass powder, ASR is one of the most important causes. It is crucial to notice that based on alkali-silica reactions are significant only in aggregates with amorphous silica [41]. Besides the amount of waste glass powder in concrete, there is a question about the size of the particles. Little research was made on [42]–[44]. Research by Z. Bažant found that particles smaller than 0,25mm caused no expansion. On the other hand, a particle size of around 1,5mm caused excessive expansion [42].

Based on this research, the waste glass powder is suitable for utilization in high-performance concrete as a partial replacement for fine aggregate in concrete. The potential risk is lower compared to coarse aggregate - it is known that particles smaller than 1mm are reactive too, but the pressure is so slight that there are no cracks at the surface. According to Carsana and col. research that investigated the comparison between waste glass and other supplementary cementitious materials, mortars with waste glass showed long-term durability – the samples did not show any degradation after seven years' immersion in water, and compressive strength was higher [45].

2.3.3. ASR Threat

The latest review, which summarizes knowledge about the use of glass in concrete, points to problems associated with ASR, the size of the particles used, the chemical composition of the material, etc. [15]. As part of this research, the effect of ASR is continuously tested according to the American standard ASTM C 1260. However, there are many obstacles to the continuous improvement of the mixture. Based on reviews and research carried out in previous years, the results agree on the suitability of using finer fractions in concrete, where some risks are partially eliminated by the appropriate particle size [6], [15], [17], [46], [47]. For comparison, in addition to the international standard, the Czech technical condition TP137 from the Ministry of Transport was used, and the tests were carried out according to it. The use of national regulations is important in terms of comparing local raw materials. The Czech technical condition TP137, which deals with ASR, modifies the American ASTM standard in part, but the testing frequency is stricter - it is tested more often.

2.3.4. Environmental Danger - Ecotoxicity

Due to suspicions about the tendency of materials towards reactivity and unwanted chemical processes, possible toxicity is closely connected with glass powder and its use in concrete. Considering the aforementioned goals (EDG, SDGs, etc.), the focus on ecotoxicity appeared to be an indispensable component for developing material suitable for use in an ecologically favorable environment, which worldwide is trying to maintain/build.

The concept of ecotoxicity can be summarized as properties of waste that pose a danger to some of the components of the environment are summarized under ecotoxicity - according to Ministry of Health Decree No. 376/2001 Coll. Ecotoxicity can be detected by specific ecotoxicological tests, which are specific by exposing test organisms to different concentrations of test substances. By the reaction of this organism, it is possible to assess the ecotoxicity of the tested material - the reaction is considered to be the inhibition or death of the organism, and it is also possible to examine, for example, the specific movement or growth of the organism [48].

However, it should be mentioned that the decree deals with waste. Despite the scope of the research, it was found that the evaluation of ecotoxicity for building materials of secondary origin is not established. Evaluating these materials as waste in the long term is not appropriate. Therefore, as part of the doctoral thesis, a methodology was developed for evaluating the ecotoxicity of building materials - products intended for supplementation or the resulting building mixtures and samples [47].

This work dealt mainly with four types of ecotoxicity testing, watercress, freshwater algae, daphnia, and mustard germination were tested. The experiments are based on testing aqueous extracts. All ecotoxicological data (chlorophyll content of duckweed and algae, mustard root elongation, and daphnia viability) were subsequently evaluated and compared with the test organisms in leachates with control organisms. The analysis and the results were the basis for drafting the methodology. One of the aims of this thesis was to help adapt the legislation to the current modernizing technology and rapid development of materials, which is a typical feature of the construction industry.

The entire hazard property assessment was analyzed based on research that dealt with waste data from four states and suggested their classification [49]. Hazard Properties (HP) and Hazard Statement Codes (HSC) must be examined, and based on this, it is possible to classify whether it is hazardous or non-hazardous waste. Basic indicators also include the amount and proportion of heavy metals. Further analyzes are only necessary if specific requirements are met.

3. Motivation and Methodology

To fulfill such extensive and long-term goals, despite the narrow focus of this doctoral thesis, it is necessary to create solid foundations secured by several tests confirming all the assumptions. The research should verify the results and the effect of changing local resources. This chapter will summarize the motivation and justification of the objectives.

The tendency to use secondary raw materials has appeared in recent years in all sectors, and the construction sector is no exception. The most used building materials are usually completely dependent on primary raw materials and non-renewable resources. Therefore, these sources of materials are decreasing, and due to their non-renewability, the use of secondary raw materials is a logical step forward. Furthermore, those efforts appear not only on the part of scientists but also nations and politicians trying to design documentation that should lead precisely to lower emissions, less waste, and regulation of non-renewable resources and energy consumption.

The main motivation and aim of this work is, among other things, the fulfillment of these expectations, which will become an obligation in a few years. Therefore, it is appropriate to prepare and know the possibilities of the future of construction.

Nevertheless, when replacing primary raw materials, it is always necessary to consider the required properties of the resulting material or even the final application. However, summarizing the resulting materials and application properties is only the second step.

Firstly, it is necessary to consider the secondary raw materials' properties. Consequently, another motivation was to learn about glass, which in many ways, is generally known for its properties. Still, due to the use of different types, it was found that each glass has different properties in some respect. In the construction industry, it is a big challenge to process a material with such specific properties as glass, and it would only be possible to use this material after verifying its chemical composition, analysis of elements and heavy metals, or toxicity.

Two glass types were chosen, created by producing glass jewelry and other glass design applications. Many more types are analyzed in further research, but two basic and characteristic types from different companies have been selected for this thesis. The other two types of glass were waste destined for landfill due to the end-of-life application (photovoltaic panels) or significant contamination of the material (glass bottles from municipal waste). In total, this research processes four types of glass which were analyzed and examined:

- Glass powder from communal waste – used as silica flour substitute as 50% and 100% replacement (waste glass - WG)

- Two types of glass powder acquired as a by-product during production - used as silica flour substitute as 50% and 100% replacement (glass from production – GP)
- Glass powder and fine sand from discarded photovoltaic panels (PP) – are used as 100% silica flour replacement and 100% fine sand substitute.

Two types of waste materials were used because of the possibility of recycling, which is a better option than landfilling. Recycling in its original meaning is returning to the process in which the waste originated (original purpose or same system). In a broader sense, recycling can be considered as any reuse of material – it doesn't have to be necessary to utilize the same system as before. However, any waste return to the process is considered a success – at least for the environment.

Based on verifying glass powders from different sources and previous research, nine mixtures were designed for this thesis. One was used as a reference mixture containing only NA, and eight glass powder or sand mixtures were designed and optimized. The composition of these mixtures is in Table 4.

Table 4 Composition of designed mixtures for research connected with a thesis in 2019.

Component/Mixture (kg)	**REF HPC**	**HPC 50% GP1**	**HPC 100% GP1**	**HPC 50% CW**	**HPC 100% CW**	**HPC 50% GP2**	**HPC 100% GP2**	**100% PP sand**	**100% PP SF**
Cement I 42.5R	650	650	650	650	650	650	650	650	650
Aggregates	1200	1200	1200	1200	1200	1200	1200	600	1200
Fine aggregate from photovoltaic panel glass	-	-	-	-	-	-	-	600	-
Silica flour (SF)	240	120	-	120	-	120	-	240	-
GP from production	-	120	240	-	-	-	-	-	-
GP from jewelry production	-	-	-	-	-	120	240	-	-
Communal waste GP	-	-	-	120	240	-	-	-	-
Photovoltaic panels GP	-	-	-	-	-	-	-	-	240
Microsilica	175	175	175	175	175	175	175	175	175
Superplasticizer	30	30	30	30	30	30	30	30	30
Water	180	180	180	180	180	180	180	180	180

After the first concreting, the mixes were tested and analyzed for basic properties, including mixtures testing (concrete spill test). After curing, mixtures with waste glass powder from photovoltaic panels were found unsuitable due to the expected reaction between the microsilica and the PP glass (Figure 1). However, due to the large amount of this glass that will appear more and more due to the end of life of many photovoltaic panels, the motivation to use and recycle this material remains one of the main aims of this research. Therefore, these mixtures were analyzed again, the problem was identified, and the PP concrete mixtures were optimized and designed as one final mixture one year later, see Table 4. Microsilica was omitted from the mixture due to the objectionable reaction.

Figure 1 First version of concrete mixture designed in 2019 with waste glass powder from photovoltaic panels.

Although this doctoral thesis is focused on a very specific material and subsequent narrow use, the key points have been widely explored. Cooperation with UCT and FCE CTU was necessary to achieve the set aims. The UCEEB laboratories were used for accurate laboratory results, which generally direct and help the sustainability and efficiency of buildings. It is necessary to start locally to achieve such global goals as reducing the carbon footprint and eliminating the waste of non-renewable raw materials and resources. Each tool needs to be defined individually; it does not apply to all countries and environments. This work aimed to develop a methodology for assessing the toxicity of building materials that can be recycled or used as secondary materials from production by-products. All these categories have so far been evaluated only according to the waste decree. Therefore, a draft methodology was made (Appendix 4), according to which mixtures and elements were further evaluated (Appendix 2). The entire research process for this doctoral thesis is shown in Figure 2 below.

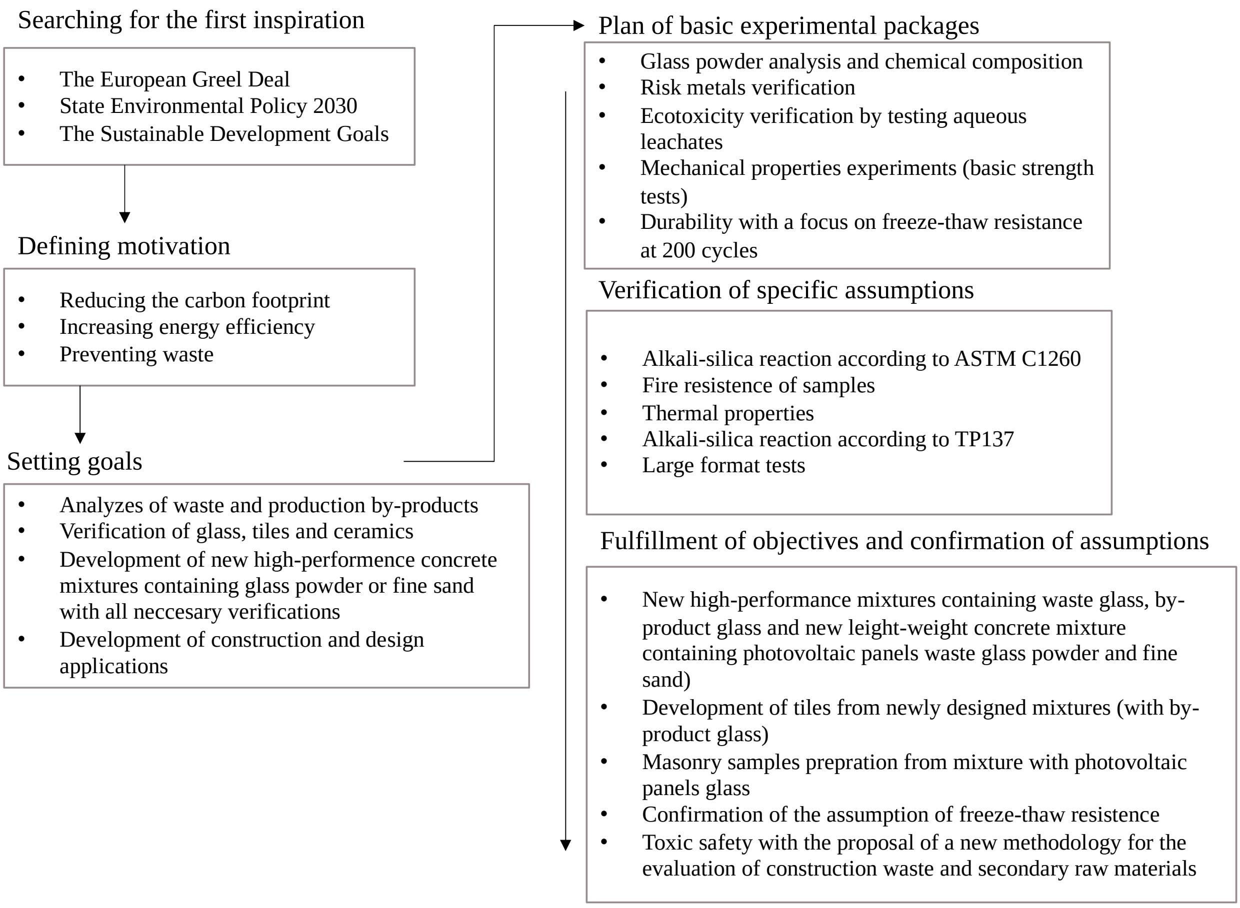


Figure 2 Diagram of the preparation, progress and final aims of the doctoral thesis

For the comparison, other waste materials determined to land-fill were also recycled. The properties of vitrified tiles and ceramic tiles were examined and tested. However, these tests were only marginal, and the results were indicative entirely to compare the properties and possibilities of waste materials. The decision to use these tile materials was made mainly because of the large amount of material available from ongoing renovations. Thanks to the analysis and experiments carried out, the material has been used to a large extent to obtain data and create design applications, such as new tiles and wall coverings. The work thus gained practical experience and the form of recycling - not just the theoretical part. The transition of motivation into practice perfectly fulfills the set goals, although, for now, it is not industrial production.

During the development process of materials and applications, it is essential to eliminate as many risks as possible, which may arise from many different sectors connected to the given material or application. As part of this doctoral thesis, not only the mechanical properties of materials and the development of applications were discussed, but various risk possibilities were also marginally addressed, and mainly durability, chemical, and toxic properties were tested, but secondary points of interest were also fire resistance, water absorbency or thermal conductivity.

The framework content and rationale are described below, and the detailed description, methodologies, testing, results, discussion, and conclusions are summarized in the publications (Appendix 1-6). Other publications supplementing the compactness of the entire work are described in Chapter 4.1. Follow-up projects and publications.

3.1.Chemical Composition

When starting work with concrete and waste or secondary production materials, it was considered a priority to analyze the chemical properties before testing the general mechanical properties. The physical properties were solved mainly within the diploma thesis and needed to be further developed. The chemical properties are the basis for follow-up research on toxicity, environment, and other chemical reactions, especially ASR.

The decree 273/2021 Sb. on waste determines the maximum possible concentration of certain elements in the material. According to the Czech legislation, the risk metals were tested (aligned by proton number - B, Cr, Ni, Cu, Zn, As, Sc, Mo, Cd, Sb, Ba, Hg, and Pb). All glass powders and, subsequently, concrete specimens were analyzed before any application was proposed. The chemical composition was analyzed by X-ray fluorescence using XRF spectrometer, and selected elements were analyzed by atomic absorption spectrometry with flame atomizer 280FS AA. All details and specifications regarding chemical analyses are in particular in Appendix 2 and Appendix 4.

3.2.Specific Surface Area

As part of the dissertation, the specific surface of the glass samples was tested. The measurement of the specific surface of the samples was carried out on a COULTER SA 3100 device. During the actual testing, the sample was heated in a special container to 150 °C under high pressure for 240 minutes. After degassing, the sample in the container was weighed, and the container was plugged into the measuring port of the instrument and immersed in liquid nitrogen. The sample would then be evacuated again into a high vacuum, and precisely measured volumes of nitrogen gas would be added to the container from the dosing device in steps. After each step, the equilibrium pressure was measured, and the adsorbed amount of nitrogen was calculated. The nitrogen adsorption isotherm at its boiling temperature (i.e. - 196 °C) was measured using the given procedure.

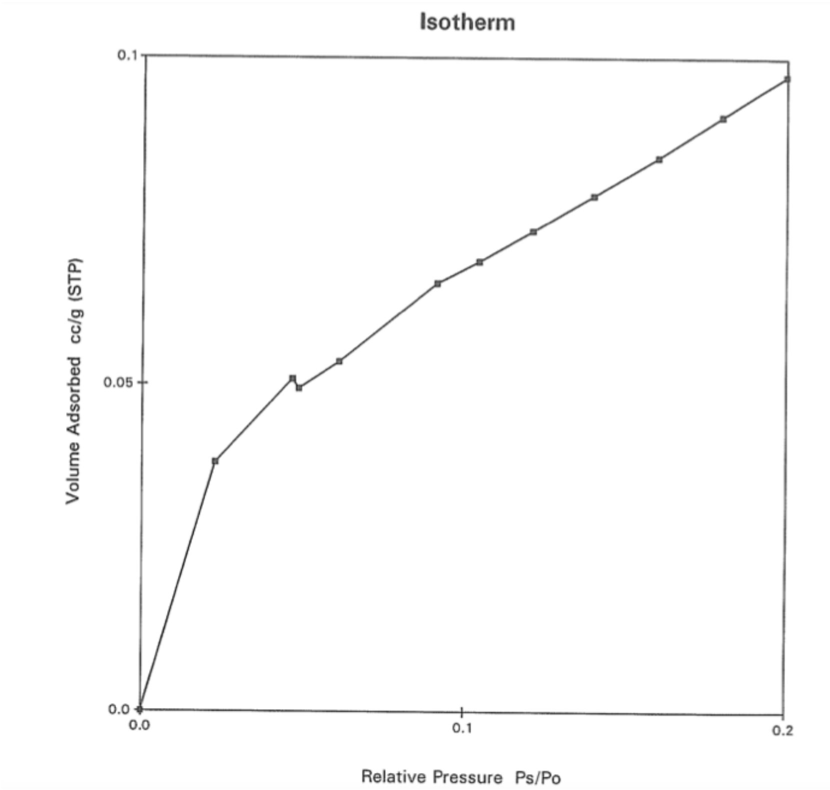
The specific surface area was subsequently calculated from the course of the nitrogen adsorption isotherm in the area of relative pressures 0 - 0.2; the values of the amount of adsorbed nitrogen were evaluated using the BET equation, and the specific surface of the sample were subsequently determined from the obtained coefficients. The testing results of the supplied samples show the expected dispersion of specific surfaces in the range of 0.09 to 0.42 m^2/g. Detailed results are summarized in Table 5 below.

Table 5 Results of specific surface area test.

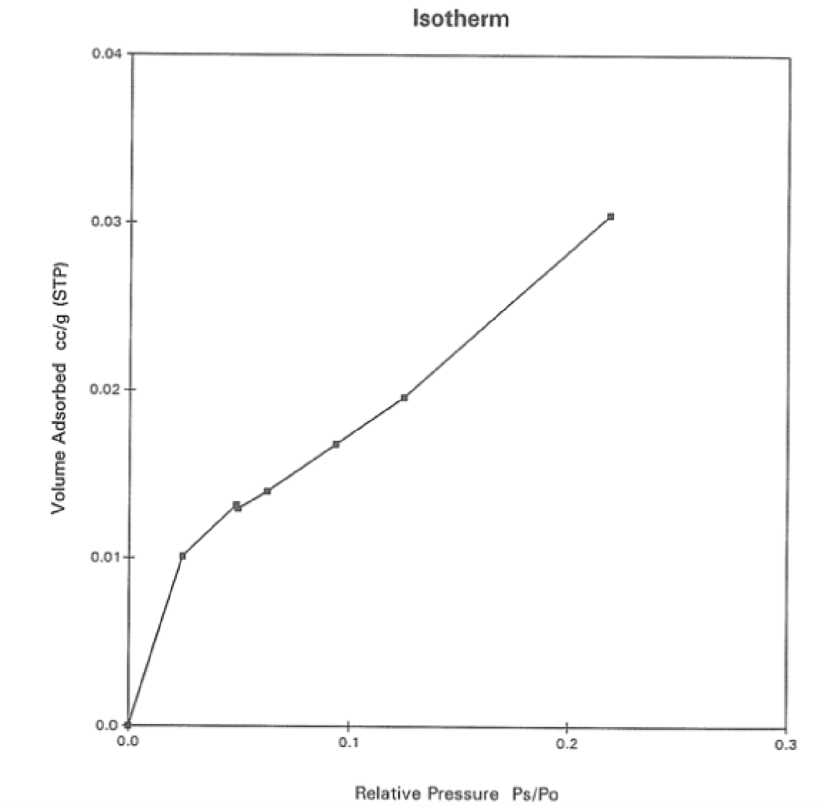
Sample identification	**Specific surface area [m^2/g]**
PP	0,094
GP1	0,405
WG	0,423

From the point of view of testing the porous structure of building materials, the dispersion of specific surfaces does not significantly affect the resulting structure of the concrete mixture. The specific surfaces of all analyzed samples have very low values and are, therefore, negligible.

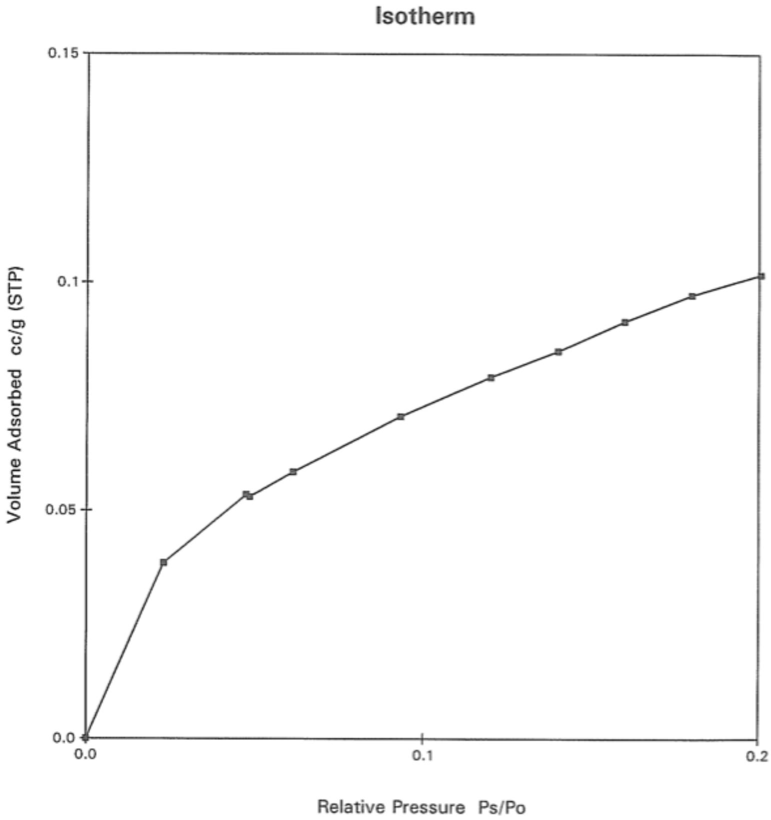
The resulting graphs are inserted below (Figure 2).



a)


Isotherm
Volume Adsorbed cc/g (STP)
0.04
0.03
0.02
0.01
0.0
0.0
0.1
0.2
0.3
Relative Pressure Ps/Po

b)



c)

Figure 3 Surface area report – isotherm: a) GP1, b) PP, c) WG

3.3. Ecotoxicity Analysis

Due to work with waste materials, secondary materials from production, and concrete, a burning question about the toxicity of these materials arises. Ecotoxicology is a study that deals with toxic effects caused by natural sources. Properties of waste that pose a danger to some of the components of the environment are summarized under the name ecotoxicity, according to Ministry of Health Decree No. 376/2001 Coll. Ecotoxicity can be detected by specific ecotoxicological tests, which are specific by exposing test organisms to different concentrations of test substances. By the reaction of this organism, it is possible to assess the ecotoxicity of the tested material - the reaction is considered to be the inhibition or death of the organism, and it is also possible to examine, for example, the specific movement or growth of the organism.

This thesis dealt with four basic types of ecotoxicity testing - duckweed, freshwater algae, daphnia, and mustard germination were tested. The experiments are based on testing aqueous leachates. All ecotoxicological data (chlorophyll content of duckweed and algae, mustard root elongation, and daphnia viability) were subsequently evaluated and compared with the test organisms in leachates with control organisms.

Ecotoxicity tests have been running since 2019 in collaboration with UCT. Over the years, we came up with a solution to answer all of the questions connected with the secondary raw materials, waste materials, and HPC containing these materials. The experiments started with powders and ended up with concrete. The most exciting results were picked and put into the articles (Appendix 1, Appendix 4, Appendix 5). Due to the comprehensiveness of the field, other student works (internships, conference contributions, or bachelor's theses) were also partially connected. Subsequently, photosynthetic pigments and soil enzymatic tests were determined and evaluated. Soil dehydrogenase activity (DHA) was determined.

For the experimental procedures, EN 12457-4, ISO 8692, ISO 6341, and ISO 20079 were followed to perform the correct procedure.

The results are summarized in Appendix 1; further discussion and analysis related to recycled aggregates are included in Appendix 4 and Appendix 5.

3.4. Mechanical Properties

Mechanical properties are considered one of the fundamental pillars of building materials. The process occurs according to Czech standards [50]–[57]. Tests of mechanical properties were made using destructive methods. The tests were made on samples after 28, 60, and 90 days. Prepared samples were examined to determine the compressive strength and tensile bending strength.

In this thesis, compressive strength was tested on fragments of samples 40 mm × 40 mm × 160 mm and cubes 100 mm × 100 mm × 100 mm and 150 mm × 150 mm × 150 mm. Standard conditions were followed (EN 12350-1, EN 12390-1, EN 12390-2 or EN 12504- 1, EN 12390-4).

Tensile bending strength is described in ČSN EN 12390-5 [58]. The test is realized on block specimens with dimensions 40 mm × 40 mm × 160 mm. Tensile bending strength is defined by a three-point press according to ČSN EN.

The results met expectations in satisfactory compressive and tensile strength values, which increased with longer solidification time (Appendix 3). Most of the conclusions were published at national or international conferences [10], [59]–[62], and the last results will be published at the end of this year.

3.5. Durability Verification

Durability is an essential factor to be met during the development of HPC. This was assumed mainly from the point of view of the freeze-thaw resistance of the materials. Samples for testing had dimensions 40 mm × 40 mm × 160 mm, and the test was performed according to ČSN 73 1322 [63]. The detailed procedure is described in Appendix 3.

The samples were tested after 25, 50, 75, and 100 freeze-thaw cycles during the first phase of this work (Appendix 3). After basic testing, the experiment was expanded (due to the HPC utilization) to more cycles – in the second phase; samples were tested after 50, 100, 150, and 200 cycles. After testing, the freeze-thaw resistance of all mixtures was confirmed even after 200 cycles with 50% and 100% substitutions with waste glass or glass from production. After the planned number of cycles, the samples were constantly tested for compressive and tensile strength. The summary of unpublished results is clear in Figure 3 and Figure 4. The results of mixtures with 50% replacement of silica flour are shown there.

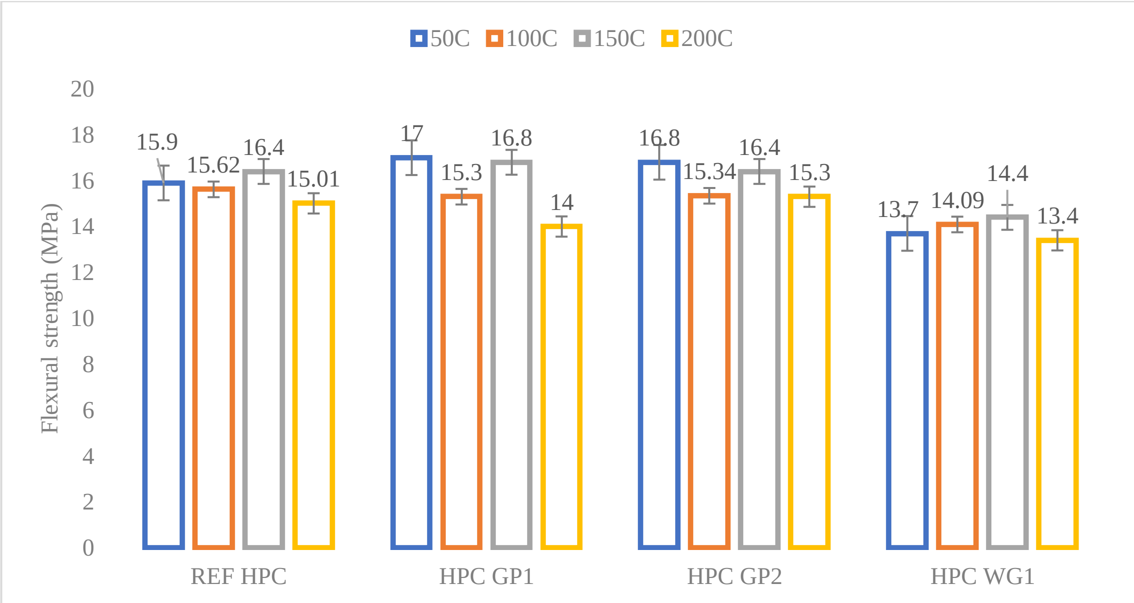


Figure 4 Unpublished results of flexural strength after freeze-thaw cycles

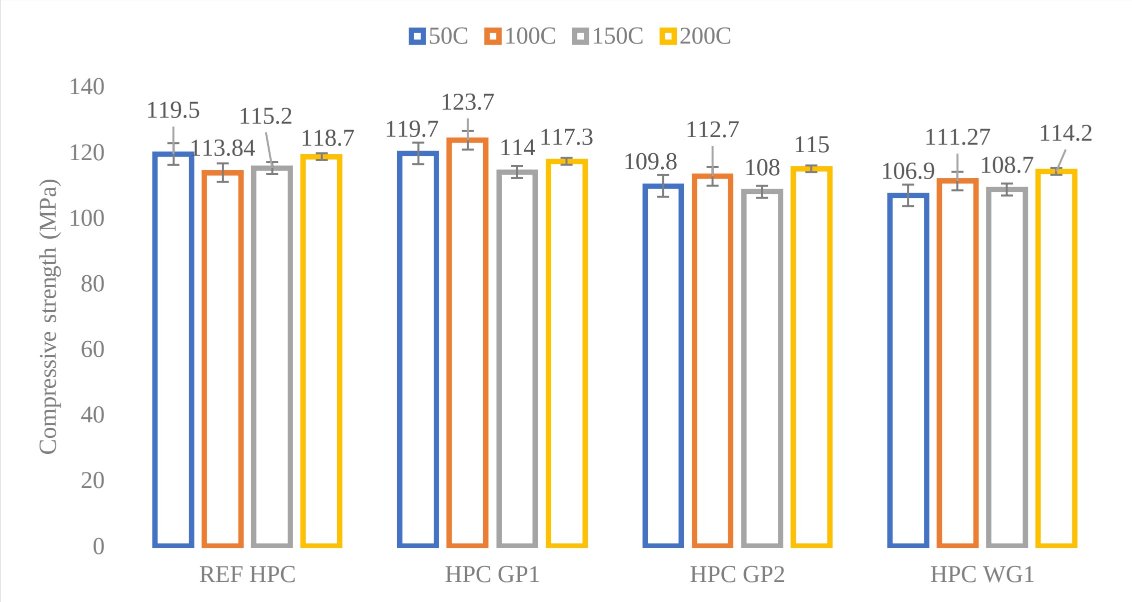


Figure 5 Unpublished results of compressive strength after freeze-thaw cycles

The highest decrease in bending tensile strength was found for HPC GP1, which is almost 10% after 200 cycles. At the same time, HPC GP2 experienced an increase in strength compared to HPC REF by 1%, and HPC GP1 had a decrease of 6.7%.

The compressive strength was much more consistent; the highest fluctuation was for HPC WG1 (3.7%) and the smallest for HPC GP1 (1.1%). All alternative proposed mixes declined from the HPC REF, but the decline was insignificant compared to previous research.

This thesis, therefore, confirms the correlation between the amount of material and the size of its particles. Although a minor replacement partially shows better results, more detailed research is desirable before the causality of the phenomenon is confirmed.

3.6. Alkali-Silica Reaction

Alkali-silica reaction is a chemical reaction of amorphous or poorly crystalline silica (SiO2) with hydroxide of alkali (KOH, NaOH). The hydroxyl ions (OH-) in the pore solution and reactive silica in the aggregate react in the first step [64]. The final product is a dense gel, which occurs in cracks in concrete – the specific surface cracks are destroyable for concrete, even after a decade of use and normal construction function.

Many reasons cause the degradation of concrete, but ASR is one of the most common ones. The alkali in Portland cement reacts with the silica in aggregate [65]. The potential alkali-silica reaction is necessary to investigate because it is a long-term process [41]. There is a premise that glass could eliminate the process of ASR. However, the question is whether a high concentration of NaOH does not only mask the released alkali from the glass [66]. A few main factors affecting ASR are known – time, external influences, and certain materials.

For this work, two main methods were chosen for ASR testing. Compared to the others (Czech Standard ČSN 72 1179 or British Standard BS 812-123), the picked methods are the short-term ones. ASTM Method C1260 is the standard test method for potential alkali reactivity of aggregate, where the values are prepared for evaluation within 16 days. ASTM C1260 is based on the NBRI accelerated test method. The method is extremely rapid since the conditions are higher than in long-term methods (ČSN 72 1179, BS 812-123). The full description is available in Appendix 2. Czech Method TP137 is based on short-term testing as well. The conditions are similar to the ASTM Method. However, reading conditions are stricter and more frequent. There are detailly described in Appendix 2 as well.

The methods were chosen based on pilot research; results are below in Figure 5. The American standard ASTM C1260 was chosen – advantageous is the shorter testing time and the more aggressive environment that can occur at any time. For the comparison, the Czech method TP137 was chosen as well.

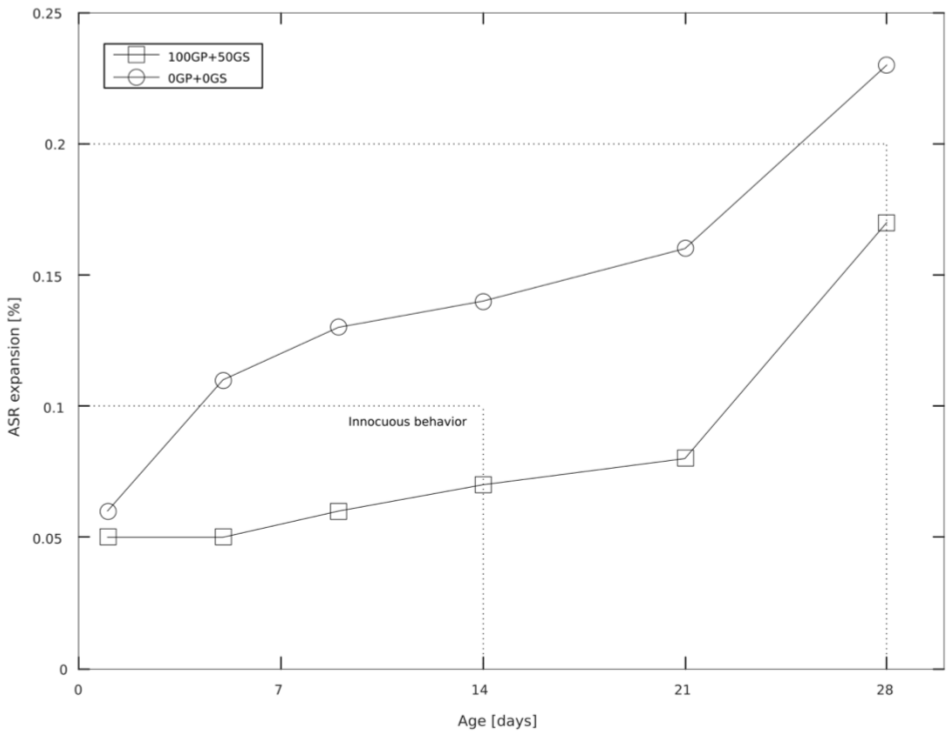


Figure 6 The results of the pilot ASR research from 2019 according to ASTM C1260

After the initial tests, various types of glass were tested. In 2021, I was approached by a large Czech company that processes glass and currently focuses on the ecological disposal of excess assortment and waste, which amounts to thousands of tons per year. That is why the last tests were designed to focus on the glass of the company Precios Ornela (PO). The possibility of the influence of color on concrete was solved - this is how concrete samples containing red glass (RG), green glass (GG), blue glass (BG) and yellow glass (YG) were created. The results are summarized in the chart below (Figure 7).

Mixtures, where 100 % silica flour and cement were replaced were compared. Specially treated glass was used, created as a secondary production product by the company PO. Among other things, the color of the glass impacts the results; due to the different chemical compositions (primarily different amounts of silicon and calcium), we can also have slightly different results. According to previous studies, the partial or complete replacement of cement with waste glass has considerable potential, which, when combined with the replacement of microsilica, can revolutionize the development of concrete mixtures. However, it will be necessary to carry out long-term durability tests concerning the alkali-silica reaction because the results of the test according to ASTM C1260 only preliminarily confirm the possibility of a positive effect of glass dust on the course and eventual elimination of ASR.

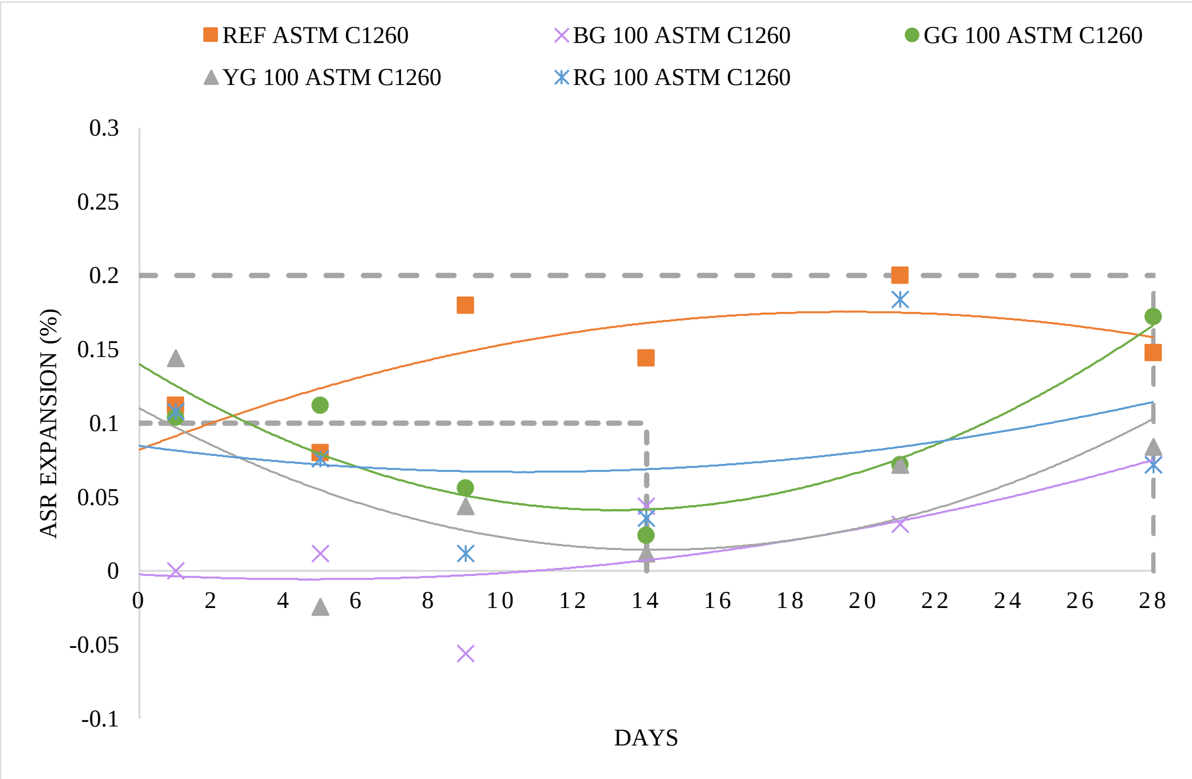


Figure 7 The results of the latest ASR research from 2022 according to ASTM C1260 with a focus on Preciosa Ornela glass

3.7. Fire Resistance

The test was performed based on a test regulation based on large-scale tests conditions for testing fire resistance ČSN EN 1363-1 and ČSN 1365-2 [5,6]. The test aimed to describe the different behavior of test specimens from HPC with an admixture of glass powder from photovoltaic panels exposed to high temperatures compared to a reference specimen from HPC. ISO 9705 Reaction to fire tests - Room corner test for wall and ceiling lining products - Part 1: Test method for a small room configuration can be considered as a related test [9]. A detailed description of the methodology and the results are summarized in Appendix 6.

During the experiment, the concrete layers of Reference HPC were gradually split. The beginning of the splitting of the concrete layers was about 5 minutes. HPC with glass powder did not show any non-standard behavior caused by high temperature; there was no splitting of the concrete layers or its destruction. The conclusion of the experiment is shown in Figure 6.

The fire resistance of the sample was an important element on the way to the concept of creating tiles and, subsequently a masonry structure – concrete blocks.

Figure 8 Tested samples after the experiment (left - HPC with glass powder, right – Reference HPC).

3.8. Applications

During the development of the mixtures, it was directly aimed at certain applications, which should serve as recycled building components or design elements.

The first application dealt with mainly within the framework of the first SGS (student grant) was tiles. The idea arose precisely from the collection of tiles and tiles from the reconstruction of the house and the design studio Archtiles, which had a large amount of waste. After analyzing and applying these waste elements in the mixtures, similar tiles containing glass powder are created with the design by Zuzana Jirkalova (Figure 9).

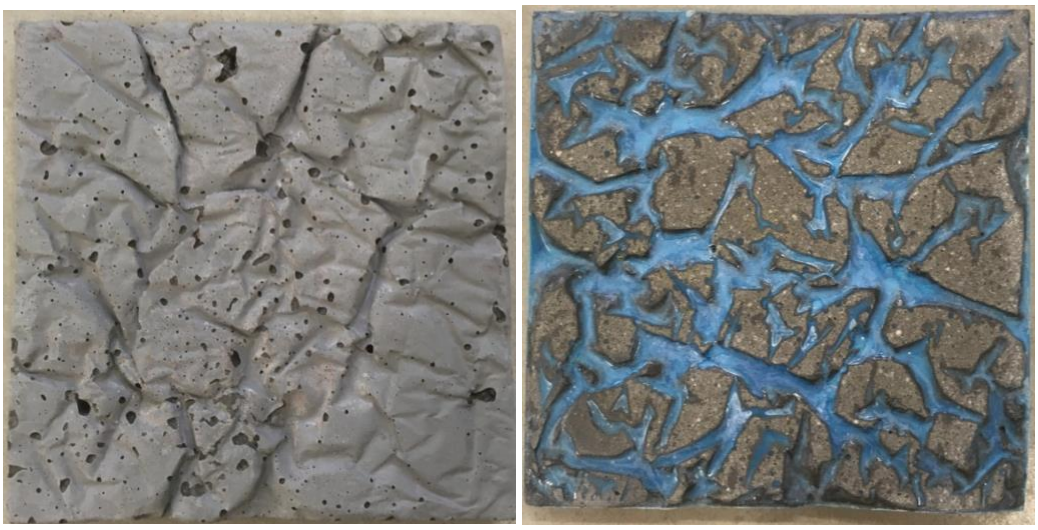


Figure 9 Development of the application - tiles (2020)

Another application still under development is the masonry structure – concrete blocks (the mould is shown in Figure 10). The mixture for this application contains waste glass from photovoltaic panels in two fractions and is a lightweight concrete block with thermal insulation properties and fire resistance. The dimensions of the blocks will be adjusted according to the current requirements; for now, the laboratory dimension, which the current form has, is assumed to be 500 mm × 100 mm × 250 mm and 500 mm × 300 mm × 250 mm. The development of these concrete blocks will be completed during the following years.

Figure 10 Mould constructed in UCEEB, CTU Prague as preparation for concrete blocks from PPG 100% mixture.

3.9. Life Cycle Assessment

The technique used to assess the environmental benefits or impacts of a product or process is called the Life Cycle Assessment (LCA) [67]–[69]. Evaluating the LCA of materials is essential to understanding and reducing their environmental impact. The life cycle assessment (LCA) method was used to evaluate the environmental performance of the mixtures described in the thesis, considering the entire life cycle. This method is primarily used to assess the environmental impacts caused by processes throughout the life cycle of a product or service. The LCA method involves four steps: definition of goals and scope, inventory analysis, impact assessment, and interpretation. Following the scope and other conditions specified in EN 15 804 + A2 for construction products, the LCA method was used to assess all elementary flows, including the inputs and outputs of materials and energy to the environment in various phases, such as raw resource production, transport of resources to the facility, production of ready-mix concrete, and disassembly of concrete and its disposal in a landfill.

Therefore, the LCA of cement or concrete comprises four steps:

- Goal and scope definition
- Life Cycle Inventory (LCI)
- Life Cycle Impact Assessment (LCIA)
- Interpretation of the results

The goal and scope of the LCA study primarily involve describing the study's aim and the system boundary considered. The second phase, LCI, involves summarizing all elementary flows between the environment and the product system, which covers the consumption of raw materials, generation of waste and emissions, and energy flow like heat. LCIA determines the extent of environmental impact in different impact categories [70]. In the last phase of LCA, the obtained results are interpreted.

A thesis was conducted to evaluate the environmental impact of waste glass in the LCA of concrete mix. This study's system boundary includes extracting, processing, and transporting raw materials to the plant, processing the materials, and producing concrete.

3.9.1. Description of system boundaries, functional unit and life cycle inventory

The declared unit for assessing the environmental impacts of the mixtures was defined as 1 m3 of the concrete mixture. The system boundaries for comparing the concrete mixtures included various stages such as raw material supply (including cement production, water production, and production of primary or recycled aggregate), transport of resources to a facility, mixing of materials, and their transport to the site. However, the use phase of concrete mixtures was not considered per EN 15 804 + A2. The system boundaries also encompassed the end-of-life phase (EoL), which involved the excavation of concrete during the deconstruction process, transportation and demolition of concrete waste in the landfill, and disposal of waste in the landfill.

GaBi software was utilized to create the environmental model of the life cycle of the mixtures. To model upstream processes, generic data from the GaBi database were used to assess the environmental impacts of resource production. Moreover, the end-of-life processes of concrete were also modeled using the same generic data. Data from the reference year 2016 and the Czech energy mix were used to model the energy supply. Transport processes were modeled based on a truck trailer (EURO 3, up to 28 t gross weight) traveling for 50 km.

Table 6 Composition designed for testing prototypes from by-product glass in concrete mixtures.

Component	Density (kg/m^3)	Proportion (kg/m^3)		
		Silica Powder	Blue Glass	Green Glass
CEM I 42.5R	3100	650	650	650
Silica fume 940 U-S	2200	175	175	175
Silica powder	2500	240	–	–
Glass powder	2500	–	240	240
Sand I	2500	600	600	600
Sand II	2650	600	600	600
Superplasticizer	1084	30	30	30
Water	1000	180	180	180

As part of the thesis, LCA was carried out for the investigated basic materials used in concrete mixtures, focusing on the environmental impact. Impact categories such as human toxicity (cancer), freshwater ecotoxicity, and climate change were monitored. The normalized and weighted results per kg of cement, glass powder, and silica powder show that cement has a very high impact (up to 9x more than silica powder). Glass powder has a lower environmental impact - about 29.4% lower compared to silica flour, which points to the possibility of 100% substitution of silica powder with glass powder.

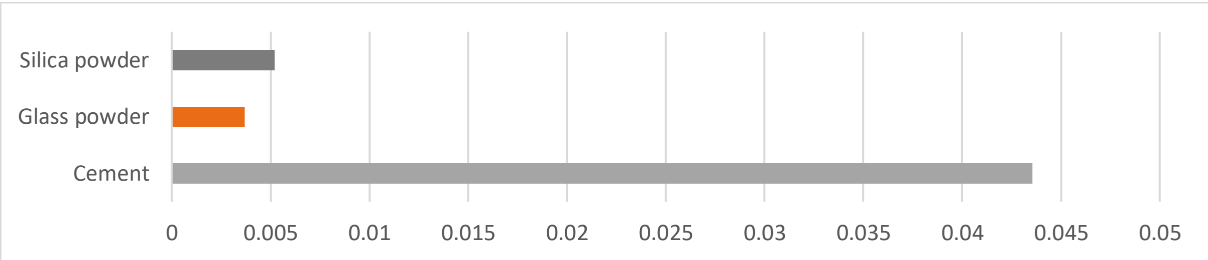


Figure 11 LCA results of primary used materials in designed concrete mixtures.

3.10. Other Properties

Besides the primary verifications, other properties that could impact the results and were crucial to the development of the applications – tiles - and the subsequent development of the concrete blocks were also marginally tested.

In Table 7, there are the results of water absorption. Some of the results were used in conference papers.

Table 7 Water absorption values of designed mixtures (2019-2022)

Concrete mixtures	Water absorption (%)
REF	2.78
HPC 50 % GP1	2.87
HPC 100 % GP1	2.85
HPC 50 % CW	3.50
HPC 100 % CW	3.43
HPC 50 % GP2	3.30
HPC 100 % GP2	3.24
PPG 100 %	8.55

Thermal properties were verified due to the planned utilization as concrete blocks in structural masonry. The mixture selected for use as a concrete block was 100% replacement of fine sand with waste glass from photovoltaic panels (Table 8).

Table 8 Composition of concrete mixture with fine sand and silica flour replacement with waste glass from photovoltaic panels PPG 100 % (optimized in 2020)

Mix content	kg
Cement I 42.5 R	650
Coarse aggregate Waste glass fine aggregate from photovoltaic panels	600 600
Glass powder from photovoltaic panels	240
Superplasticizer	30
Water	180

The silica flour in the mixture was also replaced 100% with waste glass powder from photovoltaic panels. The mixture was verified for all the basic parameters mentioned above and the thermal insulation properties. The comparison was made theoretically with YTONG (based on technical sheets and subsequently with HPC REF in the laboratory (by conducting experiments). The measurement was performed on 28-day-old samples, and the value measured on the HPC REF 2.684 W/mK. Meanwhile, the value measured on HPC containing PP waste glass was 0.676 W/mK.

During the last year, research development towards other authoritative properties was addressed. Carbonation was tested in the laboratory and analyzed, especially during curing in stable laboratory conditions. It is eliminated during solidification in water, but a theoretical study - LCA - was also created, which considered the advantage of CO2 binding to concrete (Appendix 5). In this direction, it is planned to develop the research further so that there is a detailed verification of the proposed mixtures, especially when it comes to using in HPC, but also in the case of tiles and concrete blocks.

Soil enzymatic activity and photosynthetic pigments were also investigated because of their safe use in foundations (Appendix 5). However, further development of these properties is planned outside of follow-up work or study. Nevertheless, this doctoral thesis opens up other possible research directions.

4. Summary and Conclusion

The dissertation thesis summarizes existing information on the utilization of waste glass in concrete and, due to the extensive research of these secondary raw materials, brings new knowledge, including the design of new concrete mixtures containing waste or secondary glass products. The conclusions and benefits of the work to the research field can be summarized in several highlights, which are described below:

- A fundamental building block for assessing the possibilities of adequate use of selected materials is chemical analysis. A critical feature is the content of selected heavy metals in the glass materials used in this work.
- To understand the structure of the newly used material, the specific surface area was also measured, where it was found that glass from photovoltaic panels has a specific surface area of more than two times more significant compared to glass from municipal waste or glass created as a by-product. However, from the point of view of the effect of the porosity of the structure, the results are still below the significant limit, and even such a significant difference does not have a fundamental effect on the subsequent design of the mixtures.
- Extensive ecotoxicity tests were performed to confirm environmental innocuousness. According to the assumption, it was confirmed that the glass samples themselves could be hazardous (glass from photovoltaic panels). Inhibition was also detected in glass products. The only harmless type evaluated was glass from municipal waste. Nevertheless, after the incorporation of the materials into concrete mixes, all samples were classified as non-toxic.
- In-depth studies of the impact of materials on the environment also resulted in a new methodology for evaluating the degree of impact of building materials and constructions.
- Due to the design of the new mixtures, complex experiments testing the mechanical properties of the concrete mixes were carried out to verify the potential of glass replacement in concrete. The results met expectations in satisfactory compressive and tensile strength values, which increased with longer solidification time.
- The freeze-thaw resistance test is considered the main durability indicator in this work, which was repeatedly performed on all proposed mixtures. The samples were tested at 25, 50, 75, and 100 cycles during the first phase of this work. After the basic testing, the experiment (due to the use of HPC) was extended to more cycles - in the second phase; the samples were tested in 50, 100, 150, and 200 cycles. After testing, frost resistance was

confirmed for all mixtures even after 200 cycles with 50% and 100% substitution with waste glass or glass from production.

- Many causes cause the degradation of concrete, but ASR is one of the most common, and therefore this reaction has been tested over several years of my work. One international and one national standard was selected, according to which the testing was subsequently carried out in two repetitions. Except for one mixture (100% glass replacement by product type 1), all mixtures were evaluated as safe from the point of view of ASR, and thus the initial assumption of this work was confirmed.
- As part of the work, other properties key to the planned use of mixtures in structural elements and design applications were also tested. The fire resistance was verified, which was higher, especially for mixtures with photovoltaic glass, than for the standard tested HPC mixture.
- The life cycle analysis of the materials used was also verified, which is lower than cement and quartz flour.
- One of the last severe tests carried out as part of the work was the absorbency of the proposed mixtures, except for a mixture containing 100 % glass replacement from photovoltaic panels, which was around values similar to the reference HPC.
- The conclusion of the work was also the design of applications for use in the construction and design industry (design of lightweight fittings and cladding or paving), which is now undergoing further testing and verification.

4.1. Follow-up to Projects and Publications

Based on the topic of the doctoral thesis and the interest of the doctoral student, several school projects were solved as part of Student Grant Competitions (SGS) of Czech Technical University (CTU). Involvement in international projects was a matter of course during the studies. At the same time, under the auspices of the Faculty of Civil Engineering (FCE), CTU Prague, there was collaboration within the department with other students, which led to the connection and linking of the topics of doctoral theses and research. Thanks to the broad scope and focus, the existing cooperation with UCT was established and subsequently expanded, which made it possible to work on grant topics in a high-quality manner. A solid background for experiments and eventual testing of edge properties was made possible thanks to UCEEB. A detailed list of grants with the participation of a doctoral student is listed below, divided according to the involvement:

Main researcher:

- SGS19/093/OHK1/2T/11: “Use of waste materials in HPC in design applications”;

- SGS21/096/OHK1/2T/11: “Influence of chemical properties on the use of waste materials in concrete applications”;

Collaboration on projects:

- SGS22/009/OHK1/1T/11: “Solution of a fire hazardous area in risky places of the building”.

Based on projects:

- SGS17/010/OHK1/1T/11: “Glass Powder Waste Utilization in High Performance Concrete”;

Researcher in projects:

- TH02030649 EESDOK: “Environmentally Efficient Construction and Demolition Waste for Structures” – Ing. Tereza Pavlů, Ph.D.;
- TN01000056/03: “Recyklace vody a odpadů v rámci zelené infrastruktury měst” – doc. Ing. Michal Sněhota Ph.D.;
- 36211/202/2021602V000 MPO TRIO RENCO FV10397: “Recyklovaný enviromentální beton pro stavební konstrukce” – Ing. Tereza Pavlů, Ph.D.;
- CZ.07.1.02/0.0/16_040/0000377 Koncepty Fakulty stavební pro Prahu 2017 – dílčí concept 03: “Stavby pro bydlení a poskytování sociálních služeb seniorům s využitém lehkého železobetonového skeletu a doplňkových konstrukcí na bázi dřeva” – doc. Ing. Arch. Karel Hájek Ph.D.;
- LTAIN19205: “Návrh a ověření vlastnosti betonů s recyklovaným pískem ze stavebních a demoličních odpadů” – prof. Ing. Petr Háek, CSc., Feng.;
- TJ02000119: “Development of concrete lightweight columns with carbon reinforcement as an element for load-bearing structures with loading and fire test” – Ing. Tomáš Vlach;
- SS03010302: “Vývoj efektivních nástrojů pro minimalizaci vzniku stavebního a demoličního odpadu, jeho monitoring a opětovné využití”.

For the completeness of the doctoral thesis, other experiments were performed, and other theories were analysed. The main results that complement this work are listed below:

- Mariaková, D.; Pavlů, T. ; “Možnosti využití odpadního skla a keramiky do betonu”; In: RECYCLING 2019 - Recyklace a využití stavebních odpadů jako druhotných surovin. Brno: Vysoké učení technické Brno, 2019. p. 68-74. ISBN 978-80-214-5728-7.
- Mariaková, D.; Jirkalová, Z.; Řepka, J.; Vlach, T.; Hájek, P.; “Využití odpadního skla z fotovoltaických panelů ve vysokohodnotném betonu; In: Sborník příspěvků 16.

KONFERENCE SPECIÁLNÍ BETONY. Ostrava - Zábřeh: SEKURKON, 2019. p. 25-30. ISBN 978-80-86604-81-7.

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- Mariaková, D.; Jirkalová, Z.; Řepka, J.; Vlach, T.; Hájek, P.; "Utilization of photovoltaic panels waste glass in high-performance concrete"; In: SPECIAL CONCRETE AND COMPOSITES 2020: 17th International Conference. Melville, NY: AIP Publishing, 2021. AIP Conference Proceedings. vol. 2322. ISSN 0094-243X. ISBN 978-0-7354-4066-1.
- Roztočilová, H.; Mocová, K.A.; Mariaková, D.; "Stavební odpad jako náhrada jemné frakce v betonech – hodnocení fytotoxicity vůči okřehku"; ENTECHO. 2021, ISSN 2571-1040.
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4.2.Suggestions and Plans for Further Research

Nowadays, it is desirable to come up with technological improvements, innovations in the formulation of mixtures, or the use of more environmentally friendly materials due to the need to reduce emissions and the overall impact on the environment. When trying to replace primary raw materials, it is important to focus on the properties of the substitute, see above. The principle of HPC production was initially similar to that of conventional concrete. Still, the process was more controlled; the raw materials were selected more carefully, and, over time, superplasticizers replaced plasticizers. This step contributed to a significant reduction of the water coefficient, which was manifested as a significant factor in the achieved strengths - with a reduced water coefficient, not only the strength but also the modulus of elasticity were affected, the permeability also decreased, and the durability improved. All the experiments and steps performed in this work are the beginning of extensive research toward an ideal material that eliminates the use of primary raw materials as much as possible.

First, it is necessary to adequately optimize the entire technology of grinding glass and preparing this raw material for use in concrete. Current technologies need to be more adequate and create unnecessarily high demands on energy consumption, negating the ecological nature of the proposed solution. A project proposal to develop optimized glass grinding technology was submitted in 2022 as part of the TAČR TREND program in cooperation with one of the leading Czech glass factories.

The second partial aim of the follow-up research is to reduce the need for cement. It is a cement composite that generally has the potential to reduce the need for the amount of concrete, leading to partial elimination of the negative impact on the environment due to the saving of other primary raw materials, such as aggregate. At the same time, however, a higher amount of cement and other raw materials are appearing, which were initially used as a by-product of production - microsilica - the use of which was previously considered environmentally effective and economically advantageous, but nowadays there are fewer producers of microsilica (e.g. the closure of the Slovak branches) and at the same time the economic side is no longer advantageous, on the contrary, microsilica is becoming the most expensive commodity in the composition of high-value concrete mixtures. Therefore, the next direction of research is the search for the possibility of replacing not only cement, but also microsilica.

Long-term ASR testing is also necessary, which forms the basic building block of further research when verifying new mixtures.

The partial conclusion of the research should then be the complete elimination of cement and the creation of new alkali-activated mixtures.

All research conclusions need to be adequately verified from an environmental point of view in the form of laboratory toxicity tests at the same time as theoretical testing and life cycle analyse

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Appendix 1

Waste Glass Powder Reusability in High-Performance Concrete: Leaching Behavior and Ecotoxicity

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Abstract: This paper deals with the possibility of using different types of waste glass powder in high-performance concrete (HPC) mixtures as a fine fraction replacement. Subsequently, both fractions are used in this research in concrete as a substitute for fine sand and silica flour. To use waste glass in a basic building material such as concrete, it is necessary to verify the basic chemical properties of the selected waste materials. Apart from the basic chemical properties, its environmental impact also appears to be an essential property of waste materials in general. Therefore, the research is mainly focused on the leaching and ecotoxicity experiments on high-performance concrete. HPC mixtures are designed based on the results of the analyzed chemical properties and previous research performed by our research team. Ecotoxicity of these concretes is then verified using Czech standards. The results showed a positive impact on the ecotoxic properties of waste glass when used in concrete. A new ecotoxicity classification of waste materials and concrete mixes containing waste materials is proposed as a result of this research and summarized in the conclusion of this paper.

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Waste Glass Powder Reusability in High-Performance Concrete: Leaching Behavior and Ecotoxicity

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Abstract: This paper deals with the possibility of using different types of waste glass powder in high-performance concrete (HPC) mixtures as a fine fraction replacement. Subsequently, both fractions are used in this research in concrete as a substitute for fine sand and silica flour. To use waste glass in a basic building material such as concrete, it is necessary to verify the basic chemical properties of the selected waste materials. Apart from the basic chemical properties, its environmental impact also appears to be an essential property of waste materials in general. Therefore, the research is mainly focused on the leaching and ecotoxicity experiments on high-performance concrete. HPC mixtures are designed based on the results of the analyzed chemical properties and previous research performed by our research team. Ecotoxicity of these concretes is then verified using Czech standards to evaluate. The results showed a positive impact on the ecotoxic properties of waste glass when used in concrete. A new ecotoxicity classification of waste materials and concrete mixes containing waste materials is proposed as a result of this research and summarized in the conclusion of this paper.

Keywords: high-performance concrete; waste glass powder; leachate; ecotoxicity

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1. Introduction

In the last few years, one of the main problems has been the declining number of non-renewable resources and raw materials. However, these materials are closely linked to negative environmental impacts, including high primary energy consumption and CO_2 emissions. This issue is related to the global increase in waste [1]. According to the latest data from the Czech Statistical Office (from 2019), up to 41% of this waste is generated by construction activities (construction, demolition, reconstruction, etc.). In recent years, there has been an effort to reduce the amount of concrete, which represents the larger volume of building materials used, or improve its impact on the environment.

About 10.9 thousand tons of this waste is glass, and about 39.7 tons of waste glass is from municipal waste [1]. Recycling is a term generally connected to glass and already has very wide importance. Glass from municipal waste is reusable in the form of glass bottles. As a standard, up to 60% of every new glass bottle is made of recycled glass. This process is repeatable for a limited period, and, after that, due to impurities, the glass is usually landfilled [2]. However, glass recycling does not necessarily mean only the reuse of, e.g., glass bottles for the same purpose repeatedly. Utilization in concrete is suitable because the purity demands are lower and the properties of glass are suitable for concrete composition. Czech Republic has a long tradition in jewelry, decoration, and accessory glass production. Accordingly, another used glass comes from brushing the jewelry, where impurities occur as well, and the landfill problem appears again. Due to the tested chemical properties, landfilling has been shown to be unsuitable due to the negative impacts on soil. There is an effort on so-called reuse of waste in other directions. Therefore, it is possible to use glass in a different way from how it was used before [3]. This research deals with the glass component of the photovoltaic panels, which is the last investigated material. Photovoltaic panels are creating an established system for renewable energy utilization. The average lifetime of crystalline silicon photovoltaic module is 25–30 years [4]. This means that the first generation of photovoltaic panel system is coming to the end of its lifetime. Due to the special chemical composition (i.e., high level of aluminum) and higher melting point, landfilling is an inappropriate approach; thus, it is necessary to develop the right way to recycle this technology [5].

Within these intentions, it is appropriate to consider regular and high-quality concretes, which, with lower material consumption, may have the same (or better) properties than regular concrete. This study seeks to provide the possibility that the use of waste glass would bring. It is necessary to be aware of the risks associated with the use of waste materials and to verify, in particular, the impact on the environment and toxicity, given that efforts are being made to reduce the use of primary raw materials not only because their resources are depleted but also due to environmental threats.

Focused on the ingredients of concrete, and especially its effect on the environment, the attention of researchers is preferentially directed towards cement. Its properties when used in concrete are indispensable; however, the energy expended in its processing, in relation to carbon dioxide that is produced, is significant. In terms of CO_2 emissions, cement has the largest footprint and energy consumption. Therefore, the reduction in size of the cement industry is one of the global sustainability concerns of the 21st century [6]. As a partial replacement for cement, various materials began to be used in our country it—primarily silica flour and microsilica. This paper deals with the mixtures in which silica flour is fully replaced by waste glass powder, and in which microsilica is completely omitted.

Silica flour is formed after the crushing and subsequent grinding of quartz sand to the required roughness. Quality and especially volume uniformity is ensured by modern equipment in production. The properties of silica flour have been investigated in several studies, usually compared with cement and limestone powder as well [7,8]. It has been verified that silica flour produces paste with different rheological properties when substituted at the same volume level [9].

Microsilica (also silica fume) is known as a by-product of the smelting process of silicon metal and ferrosilicon manufacturing. After some research [10–12], microsilica was verified as a possible partial replacement for cement in concrete. The knowledge gained about microsilica is partly summarized in a review by Siddique [13]. The paper presents a summary of the physical and chemical properties of microsilica and the reaction mechanism and hardening properties of concrete.

While the use of microsilica in concrete was based on research [10,13–15] moving in the right direction, with the increasing consumption of this material, the amount produced as a by-product is not sufficient for use in concrete and microsilica began to be produced on purpose. However, this knowledge returns to the inequality and unecology of this solution and goes back to the core of the problem; it is necessary to look for a material that is purely waste material and has properties that are in some way unsuitable for landfilling and at the same time have similar properties to silica flour, silica fume, or cement, which are originally replaced. The chemical composition is one of the main problems when replacing cement in concrete. There are several types of fume whose chemical composition varies according to the type of produced metal. For example, the fume from a ferrosilicon furnace generally contains more iron and magnesium oxides than from a furnace producing silicon metal [15].

After summarizing all these factors, a convenient raw material for the partial replacement of cement, silica flour, or fine sand in concrete, another perfect pozzolan—glass—was chosen. This choice was based mainly on chemical characterization, which was partly solved in previous research [16]. Regarding the strict limitations and increasing demands of these materials, this research is focused on the problem, which was founded in the idea of replacing cement with silica powder.

The question is whether it is necessary to replace raw materials in concrete. Three types of waste glass powder are used as a full silica flour replacement in concrete. Although the chemical properties vary while using different types of waste glass powder, the properties verified for proper concrete utilization are tested, optimized, and verified [16,17]. Based on the chemical properties, microsilica was fully omitted from one of the mixtures.

To verify the suitability of the use of waste glass and concrete that contains waste glass, specific procedures were chosen according to the decrees of the Czech Republic. One of the main points of this work (apart from the high priority of chemical composition) is ecotoxicity. Ecotoxicology is a multidisciplinary field of modern attitude to deal with the verification of environmental and anthropogenic impacts on ecosystems (aquatic and terrestrial) [18]. The experiments are provided under certain conditions, which are usually given by international organizations such as OECD, ISO, and ASTM in our research [19–22]. Most of the experiments are included in the European law system.

The ecological risk assessment is mostly expressed in EC50 (effective concentration causing 50% effect in comparison with control). The other possibilities are LC50 (lethal concentration causing 50% effect, in comparison with the control) or LOEC (lowest observed effect concentration) [18]. The values indicate whether the tested samples are hazardous for the environment, and, based on the results, it is possible to evaluate the general ecological danger. The ecological point of view is becoming one of the main factors these days. In the near future, the quality of the environment is gradually becoming the most important thing that will need to be maintained.

The novelty of this study is in the performed ecotoxicology tests, with the focus on building materials such as concrete. It is common that concrete is tested to verify mechanical or physical properties (tensile bending strength, compressive strength, freeze–thaw resistance). However, equally important are the environmental issues and the caused impacts.

The aim of our research was to investigate whether a hazardous glass waste leaching and ecotoxic potential could significantly decrease after incorporation into concrete mix.

2. Methodology and Material Characterization

2.1. Methodology

The work procedure is graphically explained below in Figure 1.

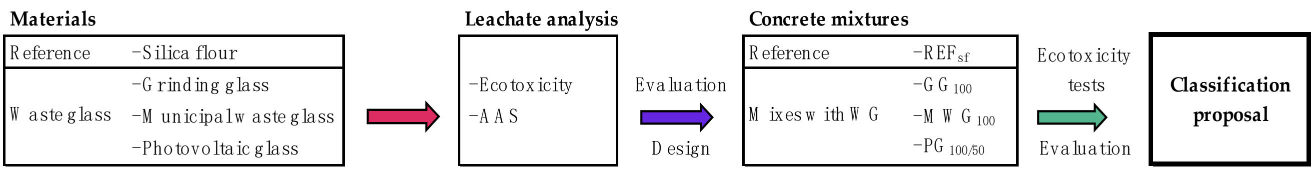


Figure 1. Methodology of experimental work.

Three samples of waste glass powders from different sources were chosen. Grinding glass, municipal waste glass, and photovoltaic glass in the form of powder were measured and analyzed to evaluate their impact on the environment. Silica flour (used as the reference sample) was exposed to the same experiments for comparison. AAS was made to collect the basic properties and evaluate the potential risks.

Given the results, the design of concrete mixtures was made. One reference mix as the sample (REF_{SF}) and three concrete mixtures containing waste glass (GG_{100}, MWG_{100}, and $PG_{100/50}$) and ecotoxicity experiments were made to verify the prediction of eliminating the ecotoxicity of waste glass when used in concrete.

After the evaluation of all collected results, our research team came with a methodology. Due to the lack of methodology in this field, the ecotoxicity classification proposal of waste materials and concrete was made.

2.2. Material Characterization

Glass is an amorphous pozzolanic material. The properties of different types of waste glass have been examined and tested in previous research [3,23]. Due to the examined properties, such as particle size distribution, chemical analyses, durability, and ecotoxicity experiments, the suitability of waste glass as an aggregate in concrete is explored. This statement is supported by numerous studies [24–27].

Three types of waste glass were used in this research and were selected based on the need to recycle them. All samples were tested in the form of powder. A summary of the tested samples is in Table 1 and shown in Figure 2a–d.

Table 1. Summary of tested samples.

Material	Abbreviation	Figure
Silica flour (reference sample)	SF	Figure 1a
Grinding glass	GG	Figure 1b
Municipal waste glass	MWG	Figure 1c
Photovoltaic glass	PG	Figure 1d

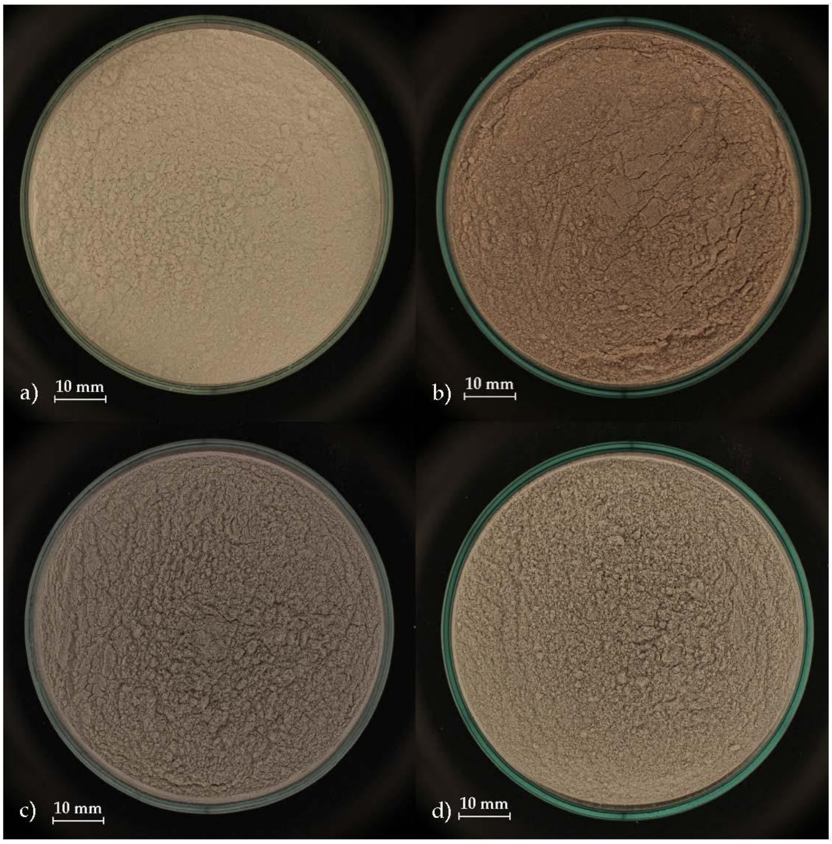


Figure 2. Tested samples: (**a**) SF; (**b**) GG; (**c**) MWG; (**d**) PG.

Glass from municipal waste is reusable in glass bottles, as mentioned before. This process can be repeated many times until the glass is filled with impurities, and another method of reuse is required. The utilization of glass in concrete is suitable because the purity demands are lower and the properties of glass are suitable for concrete composition.

Another source of used glass is in brushing jewelry. This type of glass powder also contains impurities, but there is a potential for use in concrete due to the pozzolanic properties. The finest fraction is used as a silica flour replacement to create high-performance concrete and verify the chemical properties and microscopic structures.

The last type of glass we explore in this research is glass from photovoltaic panels. Photovoltaic panels are a modern source of energy in the Czech Republic, and their use on a massive scale began approximately 15–20 years ago, which subsequently contributed to the reduction in panel prices in 2009–2010 [28,29]. As the aim of using energy from photovoltaic panels was to reduce CO_2 emissions, it is appropriate to consider their recycling so that their landfilling does not endanger the soil, for example. In the case of photovoltaic panels, recycling is ideal by disassembling the panels and using them individually. Glass from the photovoltaic panels was crushed into two fractions—fine sand and glass powder (flour). Subsequently, both fractions are used in this research in concrete as a substitute for fine sand and silica flour. The main aims are to save the number of primary resources and eliminate carbon dioxide production [6].

2.3. Concrete Mixes

Based on the results of the chemical properties, the concrete mixes were designed. With regard to the results, one reference concrete mix and three concrete mixes containing different types of waste glass were tested.

The reference concrete mixture was made according to the recipe verified by the Department of Architectural Engineering at the Faculty at Civil Engineering, CTU Prague.

The mixture containing waste glass from grinding jewelry (grinding glass, GG) and crushing municipal waste glass (MWG) was added, as a full replacement for silica flour, to the concrete mixture. The replacement, in both cases, was realized in full weight ratio. The replacement ratio is 100% in both mixes (GG_{100} and MWG_{100}).

Based on the chemical results and previous research [3,16,23,30], the concrete mixture containing photovoltaic glass was modified. Due to the specific chemical composition of the photovoltaic glass, which was verified in the recent experiments, the adaptation of the mixture was necessary to allow further testing of this mixture. The specification of the composition of this mixture omits microsilica from this type of concrete. This component caused premature cracking of the specimens during concrete hardening.

Full replacement of silica flour was provided by waste glass powder from photovoltaic panels. In addition, 50% of the natural sand (fraction 01/06) was replaced by photovoltaic glass with the requisite fraction (fine sand 01/06). The replacement ratio was 100% with silica flour and 50% with sand ($PG_{100/50}$).

A more detailed description of the composition of the designed concrete mixes is given below in Table 2.

Table 2. Concrete mixes composition.

Material (kg)	REF_{SF}	GG_{100}	MWG_{100}	$PG_{100/50}$
Portland cement	650	650	650	650
Silica flour	240	-	-	-
Grinding glass	-	240	-	-
Municipal waste glass	-	-	240	-
Photovoltaic glass	-	-	-	240
Sand	1200	1200	1200	600
Photovoltaic sand	-	-	-	600
Microsilica	175	175	175	-
Water	180	180	180	180
Superplasticizer	30	30	30	30

The summary of basic information about the tested concrete mixes is in Table 3, and the final samples are shown in Figure 2a–d. All tested samples were cubes with dimensions $50 \times 50 \times 50$ mm^3.

The concrete samples used for testing ecotoxicology properties are shown in Figure 3. The testing methods of the experiments are described in detail below in Section 2.6 and subsections. The surfaces of the concrete samples differ slightly; this is especially evident when comparing REF_{SF} with $PG_{100/50}$. A more porous structure is a sign of material with lower density, which predetermines different mechanical properties.

Table 3. Summary of tested concrete mixes.

Concrete Mix	Abbreviation	Figure
Reference concrete mix	REF_{SF}	Figure 2a
Concrete with grinding glass	GG_{100}	Figure 2b
Municipal waste glass concrete	MWG_{100}	Figure 2c
Concrete with photovoltaic glass	$PG_{100/50}$	Figure 2d

Figure 3. Tested concrete samples: (**a**) REF_{SF}; (**b**) GG_{100}; (**c**) MWG_{100}; (**d**) $PG_{100/50}$.

2.4. Testing Methods

All experiments were made following international standards. The used testing methods are summarized in Table 4. The methodology is described in Sections 2.5 and 2.6.

Table 4. Used testing methods.

Method	Experiment	Sample
EN 12457-4	Leachate	REF, GG, MWG, PG
ISO 8692	Algal toxicity test	REF, GG, MWG, PG + concrete mixes
ISO 6341	Daphnia toxicity test	REF, GG, MWG, PG + concrete mixes
ISO 20079	Duckweed toxicity test	REF, GG, MWG, PG + concrete mixes

2.5. Leaching Experiments

For silica flour and glass, air-dried samples of 100 g were mixed with 1000 mL of H_2O and homogenized on an overhead shaker (7 rpm) for 24 h [19]. Consequently, the solid particles in the leachates were settled for 10 min, and the liquid phase was centrifuged (2360× *g*, 10 min, 25 °C) and filtered through a membrane paper with pores of 5 µm. For the concrete samples, the leachate procedure was adjusted: concrete cubes (aged 28 days) were placed in 3.6 L bottles and covered with H_2O in the ratio 100 g/1000 mL. The bottles were covered, and the samples were left, without shaking, at room temperature. After 24 h, the concrete cubes were removed, and the leachates were filtrated without centrifugation step. pH and electrical conductivity were determined in the filtrated leachates at room temperature. All leachates were prepared in two replicates. Selected elements (B, Na, Mg, Al, Si, K, Ca, Cr, Fe, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Hg, and Pb) were determined using atomic absorption spectrometry with flame atomizer 280FS AA, developed by Agilent Technologies, Inc. (Santa Clara, CA, USA), in leachates after acidification by HCl to a pH of 2.0.

2.6. Ecotoxicity Experiments

Ecotoxicological bioassays were performed with original untreated leachates, leachates diluted with nutrient media in a concentration range between 330–800 mL/L, and leachates diluted 10 times and amended with relevant inorganic nutrients according to the control media of the given test species (sample concentration 100 + n $mL \cdot L^{-1}$). pH adjustment was not included in the leachate's treatment.

2.6.1. Daphnia Acute Toxicity Test

An acute toxicity assay was performed with *Daphnia magna* juveniles aged up to 24 h, which were hatched from ephippia obtained from Microbiotests Inc. (Mariakerke (Gent), Belgium). The experiment was designed following ISO guideline 6341 [21], with some adjustments. Freshly modified ADaM medium (pH ~ 7.3–7.6) prepared according to [31] was used as the control sample.

Five juvenile individuals were transferred into 25 mL beakers with 20 mL of leachate or control sample, covered with transparent film, and put under stable temperature (20 ± 1 °C) and light cycle (fluorescent light, 1000–2000 lx; 16 h light/8 h dark). Each sample was represented by four replicates, whereas the control was represented by six replicates. The inhibition of daphnia mobility (viability) was observed after the 48 h exposition.

2.6.2. Freshwater Algae Toxicity Test

Algae growth inhibition test was performed with the freshwater green algae *Desmodesmus subspicatus*, strain Brinkmann 1953/SAG 86.81, which was obtained from CCALA IBOT, AS CR (Trebon, Czech Republic) partly following the ISO guideline 8692 [22]. Bold Basal Medium (BBM; pH 6.6 ± 0.2) according to [32] was used as the control medium. For the test, 25 mL Erlenmeyer flasks were filled with 15 mL of leachate/control sample and inoculated with precultivated algae (80,000 cells per 1 mL). Samples and controls were represented by triplicates or quadruplicates, respectively. Flasks were covered with sterile cellulose caps and placed under a stable temperature (23 ± 1 °C) and light cycle (16 h of light period) with continuous shaking (130 rpm) for 72 h. An LED light with selected wavelengths (450–455 nm and 660–665 nm) and an illuminance of 3000–3500 lx was used as the light source. Algal cell density was determined via cell counting using a microscope and Bürker chamber (Hecht, Sondheim, Germany). Biomass was determined indirectly as optical density at 684 nm using spectrophotometer Shimadzu UV-1900 (Kyoto, Japan).

2.6.3. Duckweed Growth Inhibition Test

A duckweed assay was proposed by ISO guideline 20079 [20] using *Lemna minor*, strain Steinberg originated from Federal Environmental Agency (Berlin, Germany). Steinberg medium modified by Altenburg (pH 5.5 ± 0.2) [20] served as the control. The test was carried out in 150 mL beakers, filled with 100 mL of sample/control medium. Samples and controls were represented by three and five replicates, respectively. Each vessel was inoculated with 10 fronds of duckweed of a similar total frond area and covered with transparent film. Test vessels were kept in a stable temperature (24 ± 2 °C) and exposed to a light cycle (fluorescent light, 5000–6000 lx; 16 h light/8 h dark).

The total frond area was determined by image analysis using NIS Elements (Version 5.20, Laboratory Imaging, Prague, Czech Republic). Growth rate (GR) was calculated from the values based on repeated measurements during the test exposure, i.e., 0th, 3rd, and 7th day. After the 7-day exposition, fronds were extracted by pure methanol (48 h; 4 °C, dark) and the total chlorophyll content was determined spectrophotometrically (Shimadzu UV-1900) according to [33].

2.6.4. Evaluation of Ecotoxicity Data

In algae and duckweed, the growth rate (GR), based on cell number and frond area, respectively, was calculated using Equation (1):

$$r = \frac{\ln X_{t1} - \ln X_{t0}}{t_1 - t_0} \tag{1}$$

where r is the growth rate per day, X_{t0} is the value of the parameter in t_0 (d), and Xt_1 is the value of the parameter in t_1 (d). [20].

All ecotoxicological data (daphnia viability, algal and frond GR, algal biomass, and chlorophyll content) were consequently expressed as the values of inhibition/stimulation in percentage, where tested organisms in leachate were compared to control organisms using the following equation:

$$I = \frac{X_{c0-} X_{ci}}{X_{c0}} \times 100 \tag{2}$$

where I is the inhibition/stimulation of growth (%), X_{c0} is the average value of control, and X_{ci} is the average value of sample *i*. [20].

EC50 values were calculated from the inhibition data for all ecotoxicity tests using non-linear regression. A one-way ANOVA and Dunnett's post-hoc test was performed to compare samples with controls at the α level of 0.05. Based on the Dunnett test, the highest sample concentration, which was statistically not different from the control sample and had no stimulation effect at the same time, was chosen as the NOEC value. The statistical analyses were performed using GraphPad Prism software (Version 9.1, GraphPad Software, San Diego, CA, USA). The level of ecotoxicity was finally classified according to Table 5.

Table 5. Ecotoxicity classification.

Toxicity Class	Abbreviation	NOEC ($mL \cdot L^{-1}$)	EC50 ($mL \cdot L^{-1}$)
Non-toxic (NT)	NT-0	1000	>1000
	NT-1	800	>800
	NT-2	<800	>500
Inhibitory	I	<500	100–500
Hazardous waste	HW	100 + n leachates cause ≥ 50% inhibition	
Mild toxic	MT	<100	10–100
Toxic	T	<10	1–10
Strong toxic	ST	<<1	<1

3. Results and Discussion

3.1. Physico-Chemical Properties of the Leachates

The ecotoxicity testing of wastes is required by the Czech legislation. Provided that the material is miscible with water, chemical analysis and aquatic toxicity of the leachate are performed [34]. According to this decree, the concentration of 13 risk metals (B, Cr, Ni, Cu, Zn, As, Sc, Mo, Cd, Sb, Ba, Hg, and Pb) has to be determined. In the present study, all these metals were below the limit given by the decree and, in vast cases, even below the detection limit. The highest content of Cu (0.11 $mg \cdot L^{-1}$) and Zn (0.11 $mg \cdot L^{-1}$) was found in MWG leachate. These metals can be problematic in natural freshwaters. However, *Desmodesmus subspicatus* (previously named *Scenedesmus subspicatus*) was found tolerant to similar contents of these metals [35]. Therefore, it was more interesting to determine the selected elements that represent the major components in the solid materials, i.e., Na, Al, Si, K, Ca, and trace elements that are important microelements not only for photosynthetic activity (Mg, Fe). The results are showed in Table 6.

Table 6. Selected elements determined in leachates (mg·L^{-1}).

Type	Sample	Ca	K	Na	Si	Al	Fe	Mg
Reference	SF	3.44	1.89	0.71	24.04	<0.8	~0.03	0.29
Waste glass powder	GG	3.00	110.48	194.67	8.22	7.86	~0.08	0.47
	MWG	5.74	4.47	128.30	14.81	3.02	0.21	0.59
	PG	6.14	0.69	87.05	14.74	27.90	~0.11	0.95
Concrete samples	REF_{SF}	20.36	18.64	2.21	~3.0	< 0.8	~0.07	0.20
	GG_{100}	20.41	20.77	6.20	~2.3	< 0.8	< 0.03	0.17
	MWG_{100}	26.47	15.62	3.57	~2.5	< 0.8	~0.04	0.17
	$PG_{100/50}$	54.22	8.83	6.34	5.215	< 0.8	~0.05	0.39

In leachates prepared from concrete mixes, the majority of 13 risk metals were also below the detection limit, Ca increased while Na and Si decreased, Al decreased below the detection limit, and Mg and Fe decreased or stayed at a similar level when compared to leachates from glass materials. Higher leaching of the selected elements (Si, Na, Al) in glass powder, compared to concrete cubes, was expected due to the higher surface area of the powders. Moreover, concrete mixes are formed of only approximately 10% of glass powders (GG_{100} and MWG_{100}) and around 36.5% of photovoltaic glass and photovoltaic sand ($PG_{100/50}$). Elements which are common components of Portland cement, i.e., Ca and K, were leached more intensively from the concrete mixes, with one exception (GG_{100}).

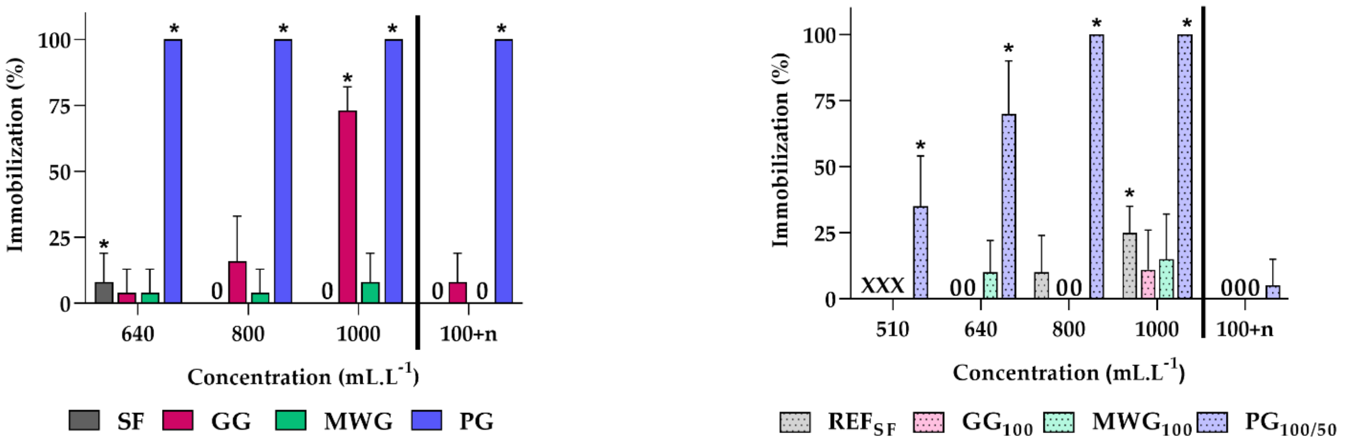
The pH of the leachate also often contributes to the toxicity. Duckweed and algae are relatively tolerant to wider changes; duckweed was reported to survive in the pH up to 9.0 [20], and algae are also tolerant to pH fluctuations [36]. On the contrary, daphnia is not so tolerant to pH changes. Silica flour had a neutral pH, while all glass samples ranged between 10.3 and 10.9, and the concrete mixes had even more alkaline pH values (Table 7). The highest pH value (11.4) was found in $PG_{100/50}$ leachate, and, even after dilution, the pH value remained at a similar level. This might be caused by the highest content of calcium (54.22 mg.L^{-1}) in this leachate. The concrete mix with photovoltaic glass had different features from the other concrete mixes, as expected. Due to a high porosity of $PG_{100/50}$ (Figure 3d), the leaching potential was also higher than the rest of the concretes (Table 7). The alkaline pH of concrete leachates decreases after dilution with neutral or acidic water, and the decrease is easier when electrical conductivity is relatively low [37], which was observed for all concrete mixes in this study. The lower conductivity of the leachates, indicating decreased leachability, was most possibly caused by the relatively low surface area of the concrete cubes, in comparison with the homogenized samples [30,37], as well as with the glass materials GG and MWG.

Table 7. Conductivity and pH of tested samples (measured in the laboratory temperature 25°C).

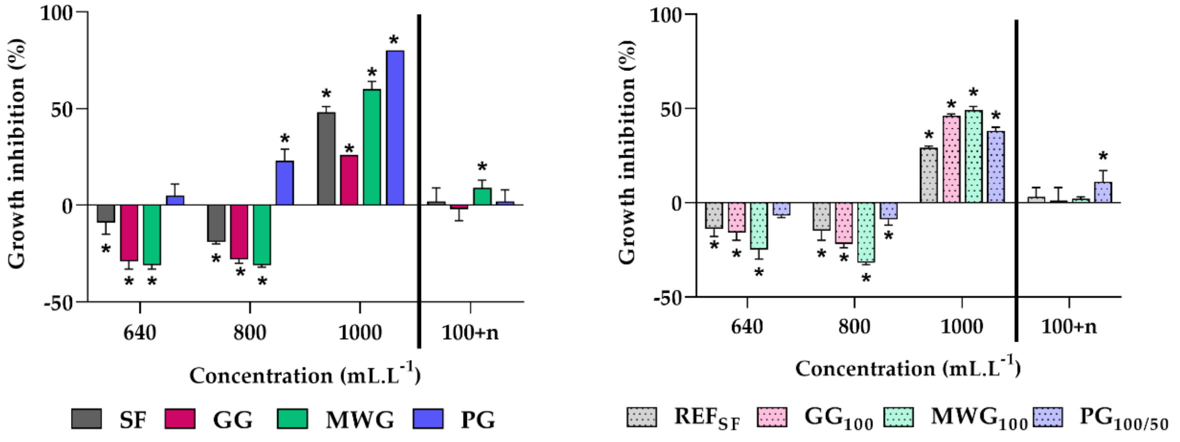
Type	Sample	pH	El. Conductivity (µS·cm^{-1})	Weight of Sample (g)
Reference	SF	6.8 ± 0.1	29 ± 1	-
Waste glass powder	GG	10.9 ± 0	606 ± 1	-
	MWG	10.5 ± 0	1291 ± 13	-
	PG	10.3 ± 0	384 ± 7	-
Concrete samples	REF_{SF}	11.0 ± 0	245 ± 5	293.55
	GG_{100}	11.0 ± 0.1	317 ± 25	273.84
	MWG_{100}	11.1 ± 0	317 ± 4	280.6
	$PG_{100/50}$	11.4 ± 0.1	534 ± 3	162.12

3.2. Ecotoxicity Characterization

The concentrations of the leachates exposed to test organisms were selected in our previous work [30]. The original leachates of both glass materials and concrete mixes usually caused lethality or a high degree of growth inhibition (Figure 4), most likely due to a lack of nutrients. However, the addition of nutrients to concentrated samples was found to be relatively problematic. When nutrients were added to leachates rich in various chemicals, salt precipitation often occurred. Precipitation can cause cluster formation in algae and interfere the precise observation of small organisms such as daphnia, interfere with the algal biomass when optical density is measured, and, in the end, may decrease the nutrient bioavailability. In addition, under natural conditions, the dilution of waste leachate by natural water is a common process, as opposed to enrichment with other nutrients. Therefore, in this study, only original and diluted leachates were taken into account. Furthermore, leachates diluted 10 times followed by nutrient addition, according to the current Czech legislation [34], were included. These samples (100 + n) contained the same amount of nutrients as the control media but only 10% of the original leachate, which led to precipitation of the salts only in leachates with higher content of metals and generally higher values of conductivity, i.e., GG and MWG (Tables 6 and 7, and Figure 5d,h).

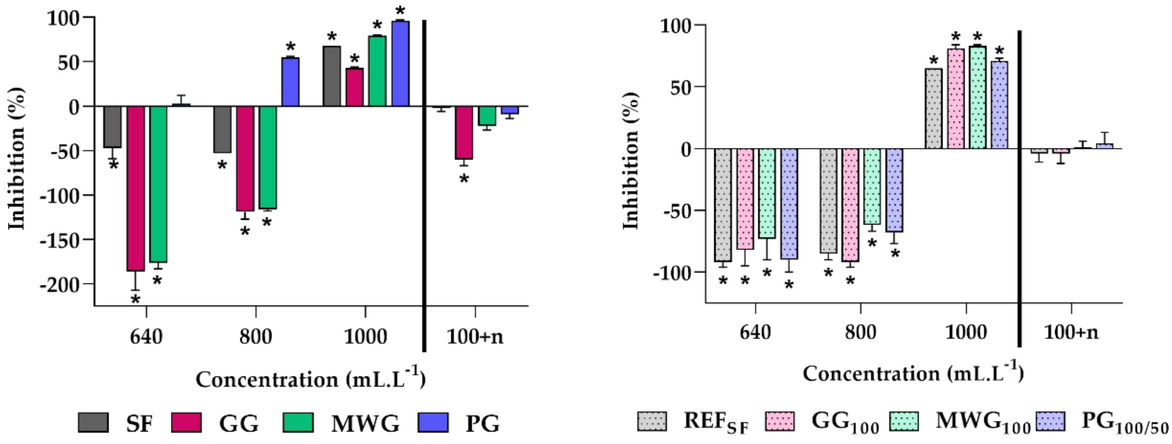


(**a**)

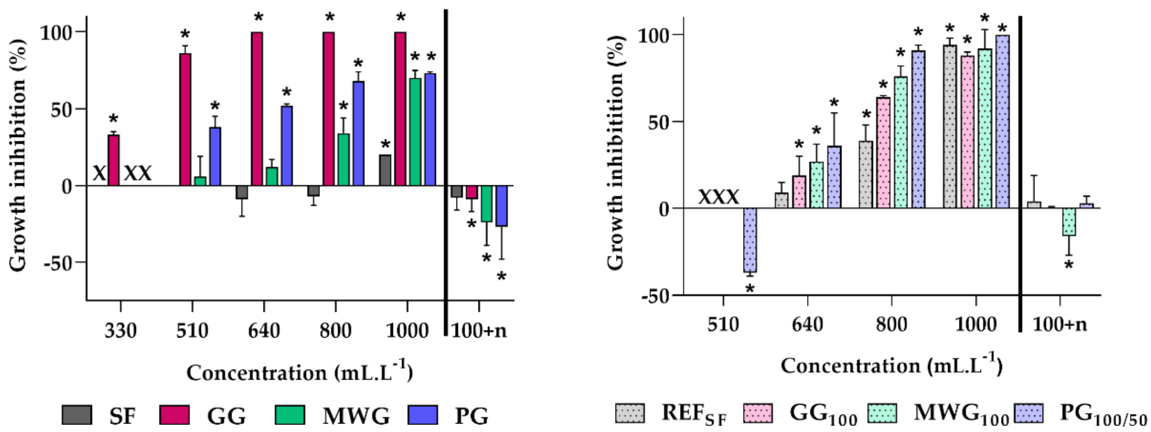


(**b**)

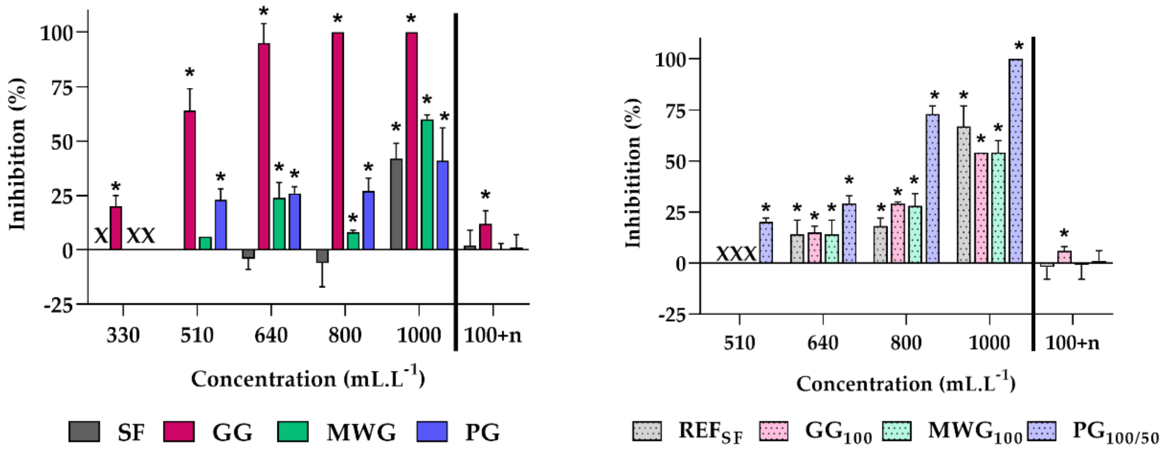
Figure 4. *Cont.*



(**c**)



(**d**)



(**e**)

Figure 4. The results of ecotoxicity experiments: (**a**) Daphnia immobilization, (**b**) algal growth rate, (**c**) algal biomass, (**d**) duckweed growth rate, (**e**) duckweed chlorophyll content. X—not determined, 0—zero values, 100 + n—leachates (100 mL.L^{-1}) amended with nutrients, *—statistically significant difference from zero values (Dunnett test; α = 0.05).

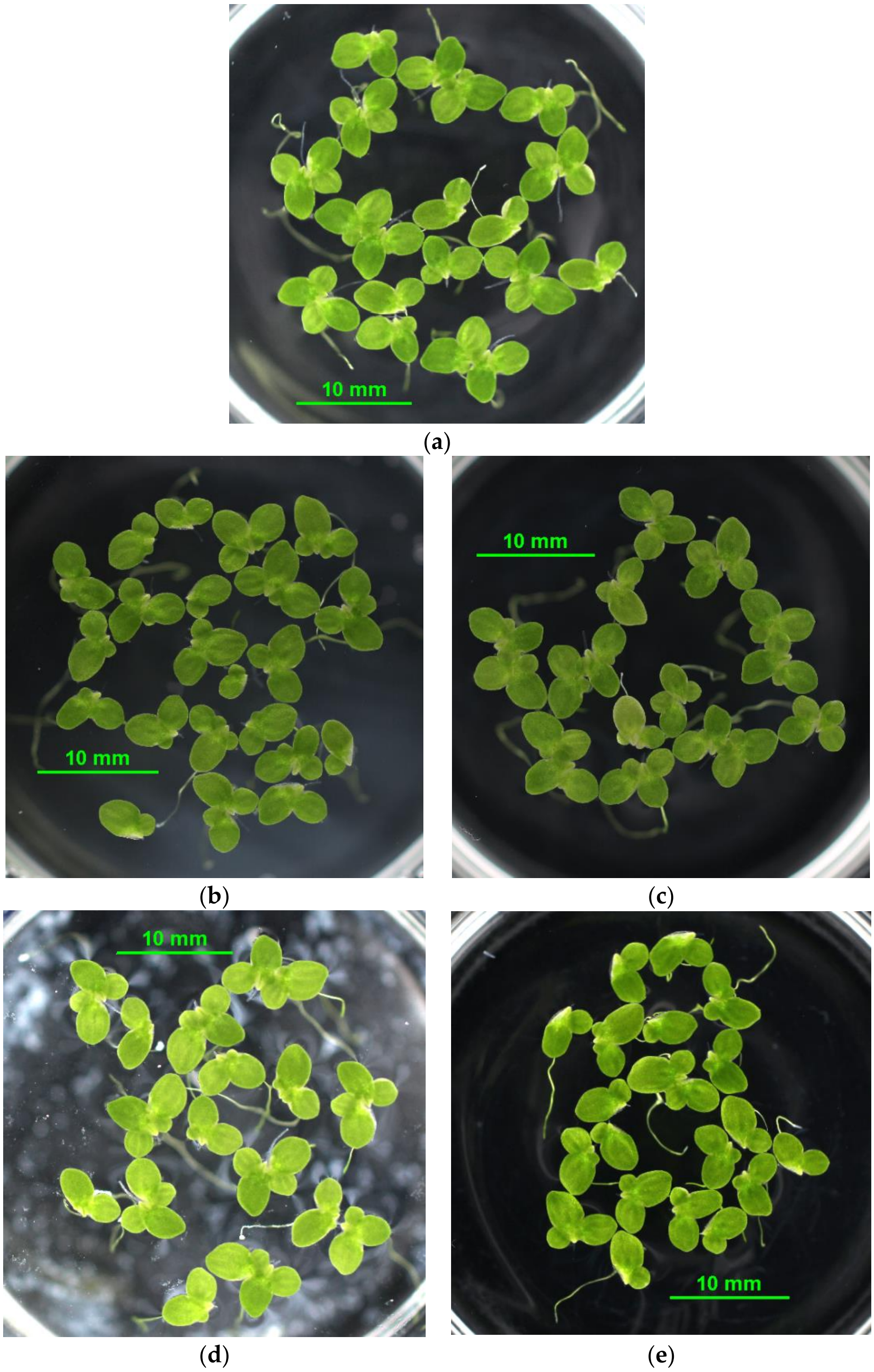


Figure 5. *Cont*.

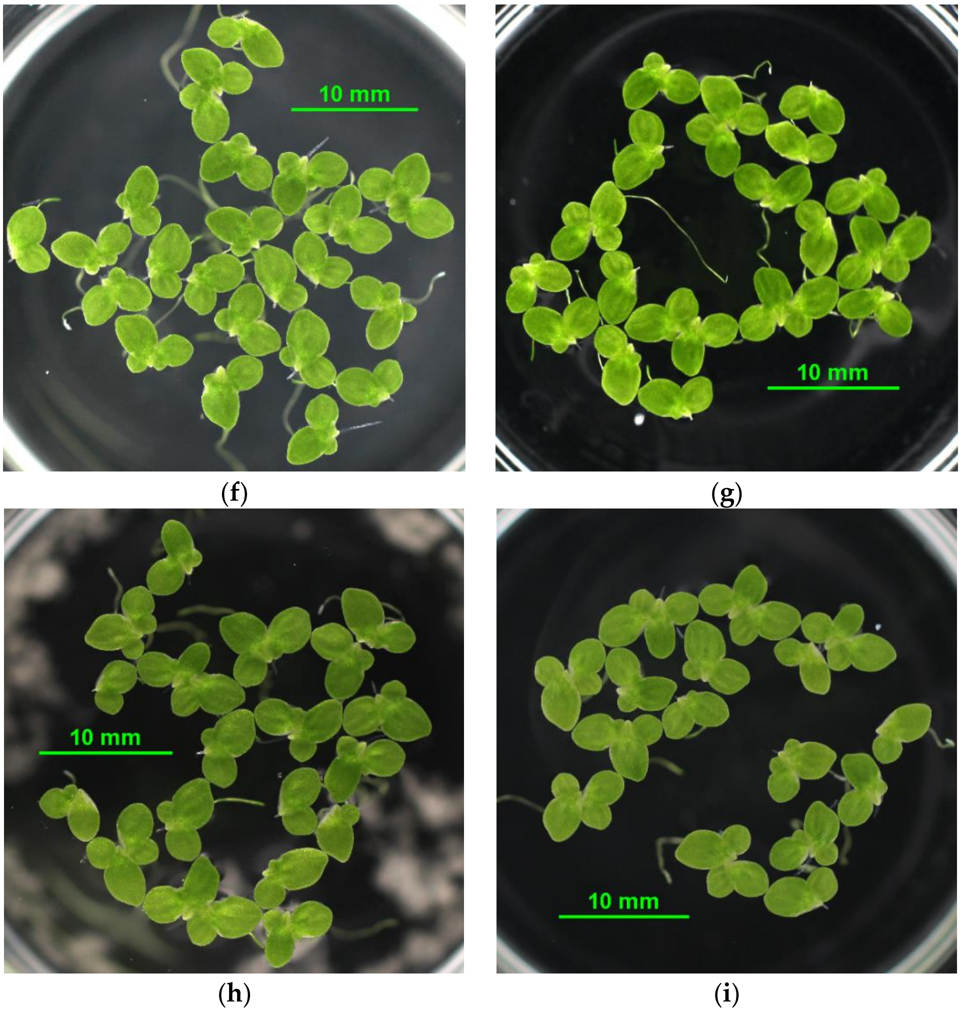


Figure 5. Duckweed test plants photo-documentation: (**a**) control, (**b**) SF, (**c**) REF_{SF}, (**d**) GG, (**e**) GG_{100}, (**f**) MWG, (**g**) MWG_{100}, (**h**) PG, (**i**) $PG_{100/50}$. All samples represent treatment 100 + n (100 $mL \cdot L^{-1}$ with nutrients addition).

When dilution of the leachate decreased the lethality/high inhibition thoroughly, a sample was considered non-toxic. For this purpose, the original toxicity scale was proposed, as presented in Table 5. The scale based on two sources concerning the characterization of solid wastes was suggested [34,38]. According to current Czech legislation [34], waste leachates diluted with control media to 100 $mL \cdot L^{-1}$ and amended with control nutrients (represented as 100 + n in this study), which cause ≥50% inhibition effect in any test species, are considered ecotoxic, i.e., the original solid waste is classified as hazardous. This category, i.e., hazardous waste, was retained in the proposed scale for waste characterization, mainly for the needs of applied research in the use of wastes as secondary raw materials in the construction sector.

The reference material, silica flour (SF), was found to be non-toxic since only the lack of nutrients in the original leachate inhibited the growth of organisms. This result was expected, because this material is considered inert [39]. Glass is generally also considered an inert material and, so far, has not behaved as ecotoxic. However, there are various types of glass in terms of chemical composition. Glass waste can contain potentially toxic elements, such as As, Cd, Pb, and Zn, in hazardous amounts [40]. Cathode ray tube funnel glass contains high amounts of Pb, due to which the waste glass is classified as hazardous [41]. Another problematic element is aluminum, which was found to be potentially eluted from glass used in the pharmaceutical sector. The elution of aluminum depends on the pH of the eluate and temperature [42,43]. Moreover, glass powder has an increased surface area, and the leaching of potentially toxic elements should be, therefore, examined. The amount of Cu detected in MWG leachate was more than eight times higher than the EC50 reported for daphnia (0.013 mg·L^{-1}) [44]; nevertheless, the untreated leachate was only slightly inhibitory to this test species (Figure 3a). This might result from the different chemical composition of the sample. MWG sample was also classified as non-toxic. The GG sample was found inhibitory due to a significant negative effect on duckweed growth and chlorophyll formation (Figure 3d,e). The inhibition could result from the high content of sodium (195 mg·L^{-1}), which was approximately 1000 times higher than that of the Steinberg medium, and lack of magnesium (0.47 mg·L^{-1} in GG vs. 9.87 mg·L^{-1} in Steinberg) at the same time. In addition, GG also contained increased levels of aluminium (7.84 mg·L^{-1}). Finally, the PG sample was classified as hazardous waste because it was found to be lethal to daphnia at every concentration tested, including the 100 + n sample treatment. The lethality of PG leachate was caused, most likely, by the high content of Al (27.9 mg·L^{-1}). Aluminum poses a high environmental risk for the water flea (*Daphnia magna*) and other species of crustaceans. [44] found that 3.9 mg·L^{-1} represented EC50 in the daphnia acute test. Our results were close to this finding, since the nominal concentration of Al in PG (100 + n) mg·L^{-1} was 2.79 mg·L^{-1}. The lethality (100% immobilization) of this PG dilution was possibly caused by the presence of other chemicals and the overall different chemical composition of the leachate, in comparison to pure aluminium chemical ($AlCl_3$) dissolved in the control medium [44]. One interesting note is that PG leachate did not have such a drastic effect on plant test species.

Aluminium is known to be toxic under highly acidic and highly alkaline conditions, while, under neutral pH, it tends to form insoluble complexes, which are not bioavailable for organisms [45]. The lower toxicity of PG leachate to algae and duckweed could, therefore, result from the lower pH of BBM and Steinberg media, which might neutralize the leachate and lead to the formation of insoluble and, thus, biounavailable particles (Figure 5h). Moreover, as [46] reported, Al can be biosorbed by the extracellular glycoprotein of algae, which decreases the bioaccumulation and consequently the toxicity for algae. Silica was found to be an efficient Al-binding ligand, which decreases the absorption and bioaccumulation of Al in algae [46]. The different ratio of Al:Si in silica flour and waste glass leachates could be, therefore, another reason for the different toxicity of the original materials. The ratio of Al:Si in leachates of the materials decreased in the following order: PG (1.89) > GG (0.96) > MWG (0.20) > SF (0.03), which was in accordance with the decrease in toxicity of the leachates (Table 8).

Table 8. EC50, NOEC values, and ecotoxicity assessment of leachates of materials. GR—growth rate; Chl—chlorophyll content; TC—toxicity class. EC50 and NOEC values expressed in mL·L^{-1}.

Material	Daphnia	Algae GR	Algae Biomass	Duckweed GR	Duckweed Chl	Toxicity Level
SF						
EC50	>1000	>1000	>800	>1000	>1000	
NOEC	1000	1000	800	800	800	
TC	NT-0	NT-0	NT-1	NT-1	NT-1	non-toxic
GG						
EC50	939	>1000	>1000	488	500	
NOEC	800	800	800	<330	<330	
TC	NT-1	NT-1	NT-1	I	I	inhibitory
MWG						
EC50	>1000	>800	>800	882	1000	
NOEC	1000	800	800	640	510	
TC	NT-0	NT-1	NT-1	NT-2	NT-2	non-toxic
PG						
EC50	<100 + n	905	779	654	>1000	
NOEC	<100 + n	640	640	<510	<510	
TC	HW	NT-2	NT-2	NT-2	NT-2	hazardous waste

In the concrete mixes, generally, both EC50 and NOEC values were relatively high (above 500 mL.L^{-1}). $PG_{100/50}$ leachate had the lowest EC50 value in daphnia and duckweed, which indicated the highest inhibition effect among the concrete mixes (Table 9). Nevertheless, the differences among samples were not significant, and all concrete leachates were classified as non-toxic. The growth and/or survival of all test organisms at dilutions 100 + n was, in the majority of cases, statistically not different from the control samples (Figures 3 and 4) and all concrete mixes were classified as safe to the environment.

Table 9. EC50, NOEC values, and ecotoxicity assessment of leachates of concrete mixes. GR—growth rate; Chl—chlorophyll content; TC—toxicity class. EC50 and NOEC values expressed in mL·L^{-1}.

Concrete Mix	Daphnia	Algae GR	Algae Biomass	Duckweed GR	Duckweed Chl	Toxicity Level
REF_{SF}						
EC50	>1000	>1000	800-1000	855	989	
NOEC	800	800	800	640	<640	
TC	NT-1	NT-1	NT-1	NT-2	NT-2	non-toxic
GG_{100}						
EC50	>1000	>1000	800-1000	746	853	
NOEC	1000	800	800	<640	<640	
TC	NT-0	NT-1	NT-1	NT-2	NT-2	non-toxic
MWG_{100}						
EC50	>1000	>1000	800-1000	709	857	
NOEC	1000	800	800	<640	<640	
TC	NT-0	NT-1	NT-1	NT-2	NT-2	non-toxic
$PG_{100/50}$						
EC50	639	>1000	800-1000	620	762	
NOEC	<640	800	800	<510	<510	
TC	NT-2	NT-1	NT-1	NT-2	NT-2	non-toxic

3.3. Utilization of Glass Waste in HPC

The solidification of potentially toxic wastes containing heavy metals in concrete mixes, and their further use as construction materials, appears an efficient and sustainable approach [47], which brings several benefits at once. This process stabilizes the toxic substances within the material. The leachability of such stabilized chemicals from the solid material decreases significantly; therefore, they are not bioavailable for organisms. Solidification is often mentioned in connection with the use of fly ash and bottom ash in concrete mixes as a partial substitute for cement [48,49]. Recently, new options of waste utilization have emerged. Hazardous glass waste from cathode ray tube funnels was found recyclable by utilization in ultra high-performance concrete where Pb in concrete leachate was below the limit values [41]. Our research shows the potential use of various types of glass powder in HPC, including photovoltaic waste glass where toxic aluminum is stabilized, making the material safe for the environment.

Using waste of various sources in terms of secondary raw materials reduces the extraction of primary raw materials and reduces the amount of waste disposed in landfills at the same time. All these aspects contribute to a sustainable and environmentally friendly concept in the construction and development sector.

4. Conclusions

The toxicity of materials increased in the following order from hazardous to non-toxic:

$$PG > GG > MWG \sim SF$$

After incorporation of the materials into concrete mixes, all samples were classified as non-toxic.

This study serves as preliminary research, which will be followed by more extensive testing. The safe usage of waste glass in high-performance concrete needs to be verified by the prolonged leaching period of the concrete mixes. Since this study deals only with acute and semi-chronic ecotoxicity tests, long-term (chronic) toxicity tests will be also performed.

In general, it can be said that the view to building structures in terms of ecotoxicology is an innovation that is not common in the Czech Republic. A new ecotoxicity classification is suggested, which is designed for building materials. Consideration of ecological impacts should be one of the first tendencies in determining the suitability of the use of concrete in the natural environment. The effort to solve this question, such as testing or developing a new methodology, is becoming essential not only in the Czech Republic. This specific point of view is considered a very new approach.

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Appendix 2

Alkali-silica Reaction Elimination Potential of High-Performance Concrete Containing Glass Powder

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Abstract: This study is mainly concerned with the assumption that glass powder can eliminate the potential alkali-silica reaction in high performance concrete. Glass is often land filled, produced as a secondary raw material or as a by-product of production. Chemical analyses were carried out, and the ecotoxicity of the material was investigated, serving as a basis for testing a potential alkali-silica reaction. High performance concrete (HPC) containing different types of waste powder (secondary raw material from production (SGP), jewelry production (SGJ), container waste glass (CWG), and glass from used photovoltaic panels (GPP)) are tested according to the international standard ASTM C1260 and the Czech technical condition TP 137. Newly designed mixtures are innocuous from the ASR point of view in the most cases, except SGP HPC.

materials

Article

Alkali-silica Reaction Elimination Potential of High-Performance Concrete Containing Glass Powder

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Abstract: This study is mainly concerned with the assumption that glass powder can eliminate the potential alkali-silica reaction in high performance concrete. Glass is often land filled, produced as a secondary raw material or as a by-product of production. Chemical analyses were carried out, and the ecotoxicity of the material was investigated, serving as a basis for testing a potential alkali-silica reaction. High performance concrete (HPC) containing different types of waste powder (secondary raw material from production (SGP), jewelry production (SGJ), container waste glass (CWG), and glass from used photovoltaic panels (GPP)) are tested according to the international standard ASTM C1260 and the Czech technical condition TP 137. Newly designed mixtures are innocuous from the ASR point of view in the most cases, except SGP HPC.

Keywords: alkali-silica reaction; high-performance concrete; glass powder; recycling

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1. Introduction

Terms such as environment, sustainability, and circular economy appear frequently in scientific works due to the trend towards reducing air pollution, reducing the impact of industry and production on nature, and towards recycling and the reuse of raw materials.

This research deals with the threat of the alkali-silica reaction (ASR) in high-performance concrete (HPC) containing glass powder (GP) and directly follows on from the previous pilot research by the authors about the ASR [1] and a detailed study of the properties of HPC containing GP [2–5]. The authors are actively dealing with recycled aggregates, secondary raw materials, and waste materials during this extensive research in order to acquire sufficient knowledge in all interdisciplinary contexts [6,7]. Since the beginning of the research in 2017, the attention and volume of data that are available on this issue has increased considerably and it is suitable to compare data among individual countries. Due to the effort to use local raw materials, the results may differ slightly between individual countries.

Concrete is still the number one used in the construction industry and is closely linked to negative environmental impacts [8]. It is mainly caused by the production of cement-based materials. However, modern procedures and approaches are implemented to reduce high energy production and CO_2 emissions which are closely linked with concrete production [9–11]. The popularity of concrete is still increasing and the ways to eliminate its negative environmental impact are examined—among the widely tested methods on the way to green concrete is the replacement of different contents of the concrete composition (for example, cement or fine/coarse aggregate) with other materials with similar properties (mechanical, chemical, and physical), resulting in the design of completely new mixtures.

Glass is tested as one of the highly significant materials in the Czech Republic with a very rich history and is widely used in industry and the construction sector. Glass powder is produced as a waste material (WM) and as a secondary raw material (SRM) during production. These materials often have no further use because of insufficient cleanliness, undesirable color, or other. However, glass is natural pozzolan and does not decompose because it is non-degradable in nature [12]. The use of glass powder in concrete can thus hypothetically contribute to reducing the need for landfill sites, saving money and energy resources. Nevertheless, glass ranks among alternative additives to cement, such as supplementary cementitious materials [13]. WM or SRM utilization in concrete increases the need for thorough chemical analysis and overall toxic safety, especially in relation to nature. Ecotoxicological analysis elucidates interactions in biological systems and shows whether alternative concrete mixtures with glass substitutes can reduce the potential toxic effects of glass itself, as both glass and concrete are associated with toxicity that is related to heavy metal leaching or higher pH [2]. These facts often lead to problems with corrosion, dermatitis, or other reactions such as ASR [14].

Ongoing research deals with the ASR mechanism, the conditions affecting this reaction, and the methods that are used for testing. As one of the main degradation processes, ASR damages harden concrete and occurs in concrete under certain conditions. The first identification and initial description of this process was done by Stanton in 1930–1940 [15]. Long-term observations brought new attainment—the alkaline environment and the presence of the reactive aggregate in concrete are the initiators of an alkali-silica reaction. By using Portland cement, an alkaline environment is created due to the presence of $Ca(OH)_2$ and although $Ca(OH)_2$ represents about a quarter of all hydration products, it can be said that the alkali content (specifically Na_2O and K_2O) is much more important in the ASR issue [16]. The problem arises when the reactive aggregate in the resulting strongly alkaline environment begins to form a gel, which creates tension in the concrete and often leads to the formation of cracks.

The chemistry of ASR is a complicated process and was clearly summarized in 2005 by Chatterji et al. [16]. The effort was to understand the mechanism through simple chemistry and to focus on a simple chemical test method to verify ASR. Factors affecting ASR were extended from humidity, temperature, time, and material to the factors such as diffusivity, source, and concentration of the relevant ions.

The measurement and evaluation of the alkali-silica reaction are usually performed according to standards. The American standard [17], the British standard [18], or the Czech standard [19] sets the conditions for laboratory testing—various boundary conditions are given and the main point of interest is the change in the length of the samples, from which the expansion rate is then numerically evaluated. There are, therefore, studies that deal with ASR within these standards and thus evaluate the impact according to the given regulations. These available studies deal mainly with bottles' waste glass (container waste glass) as a concrete content, and researches are describing the role of container glass in controlling ASR in concrete [20–23]. A representative of these type of studies is Dhir et al. [20], who investigated the alkali-silica reaction using the British Standard BS 812-123 [18] with the aim to outcome with specifications for container waste glass (CWG) in concrete. CWG was used as a fine aggregate or filler replacement in concrete. When green and amber glass was used as a fine aggregate replacement, significant expansion occurred.

The potential alkali-silica reaction is necessary to investigate because it is a long-term process—the damages appear years after the construction [24]. There is an assumption that glass could eliminate the process of ASR. However, the question is whether a high concentration of NaOH masks the released alkali from glass [20]. Another assumption is that particles that are smaller than 1 mm have lower reactivity; the pressure is so low that no cracks appear on the surface [24].

The effort of this research is to summarize the findings of short-term tests according to the American standard ASTM C1260 [17] compared to the Czech technical condition TP 137 [25].

2. Materials and Methods

2.1. Materials

The tested samples were GP and reference silica flour (SF), which were prepared in the laboratory (each 100 g). A total of four types of glass powder are used in this project and were selected based on the need to recycle, reuse, or use them up:

- container waste glass = CWG,
- secondary raw material from glass jewelry production = SGJ,
- secondary raw material from glass production = SGP,
- glass from used photovoltaic panels = GPP.

The finest fraction of glass is used as a SF replacement to create high-performance concrete and verify the chemical properties, ASR expansion, and structures regarding the mechanical and durability properties from previous research. The replacement ratio was 50% and 100%. Therefore, 9 mixtures were made and tested:

- reference high-performance concrete mixture = REF HPC,
- high-performance concrete containing 50% replacement of silica flour with container waste glass = CWG HPC 50,
- high-performance concrete containing 100% replacement of silica flour with container waste glass = CWG HPC 100,
- high-performance concrete containing 50% replacement of silica flour with secondary raw material from glass jewelry production = SGJ HPC 50,
- high-performance concrete containing 100% replacement of silica flour with secondary raw material from glass jewelry production = SGJ HPC 100,
- high-performance concrete containing 50% replacement of silica flour with secondary raw material from glass production = SGP HPC 50,
- high-performance concrete containing 100% replacement of silica flour with secondary raw material from glass production = SGP HPC 100,
- high-performance concrete containing 50% replacement of silica flour with glass from used photovoltaic panels = GPP HPC 50,
- high-performance concrete containing 100% replacement of silica flour with glass from used photovoltaic panels = GPP HPC 100,

The concrete mixes were designed on the basis of previous research on the basic properties, particle size distribution, and evaluated results. The mixes that were used in this research are summarized in Table 1. Samples of size 25 mm × 25 mm × 285 mm were made according to the standards, always in a set of three pieces. For testing the chemical and ecotoxicological properties, 27 cubes (3 cubes of each mixture with the dimensions 50 mm × 50 mm × 50 mm) were prepared. Accompanying samples were made to verify the constancy of mechanical properties compared to early research [26].

Table 1. Composition of concrete mixtures.

Content [kg]	REF HPC	CWG HPC 50	CWG HPC 100	SGJ HPC 50	SGJ HPC 100	SGP HPC 50	SGP HPC 100	GPP HPC 50	GPP HPC 100
Cement I 42.5 R	680	680	680	680	680	680	680	650	650
Fine sand 1/6	576	576	576	576	576	576	576	600	600
Coarse sand 6/12	384	384	384	384	384	384	384	600	600
Microsilica	175	175	175	175	175	175	175	-	-
SF	325	162.5	-	162.5	-	162.5	-	120	-
CWG	-	162.5	325	-	-	-	-	-	-
SGJ	-	-	-	162.5	325	-	-	-	-
SGP	-	-	-	-	-	162.5	325	-	-
GPP	-	-	-	-	-	-	-	120	240
Plastificators	29	29	29	29	29	29	29	30	30
Water	171	171	171	171	171	171	171	180	180

2.2. Methodology

The chemical composition of GP was performed by the X-ray fluorescence method using XRF spectrometer ARL 9400 (ThermoFisher Scientific, Waltham, MA, USA). Leachates of both GP and HPC were prepared according to [27]. The chemical and ecotoxicological characterization procedure of leachates is described in [2].

There were two experimental methods that were chosen in order to objectively compare the process and the results of the alkali-silica reaction. One of them is the international American standard [17] and the second is the Czech technical condition by the Ministry of Transport [25]. Both are described below.

2.2.1. ASTM Method C1260

This internationally used method is based on the NBRI accelerated method [17]. The evaluation is possible after 16 days; nevertheless, after this time, it is advisable to continue the measurements for a few more days to improve the reliability of the results. The dimensions of the samples are 25 mm × 25 mm × 285 mm, which is a very subtle element that is under a lot of loads in the extreme environment of this test. The samples are removed from the molds after 24 h and the initial reading is taken. After the initial reading, the samples are placed in the water for 24 h. The samples have to be fully immersed, not touching each other, and be completely surrounded by 80 °C water. After 24 h, the samples are taken out of the bath and the surface is dried. A zero reading is done and the specimens are placed in 1N NaOH (PENTA s.r.o., Prague, Czech Republic) solution. The conditions are similar to those before—the samples have to be fully immersed, completely surrounded by 80 °C NaOH. After 24 h the first measurement is made and another three intermediate measurements are taken between the first and the last, which is after 14 days. If the value is not stable after 14 days, it is advisable to continue with the measurements once a week until the stabilization or disintegration that is caused by massive cracks.

2.2.2. TP 137

This Czech technical condition, published in 2016 by the Ministry of Transport, describes the ASR testing [25], which is processed according to ASTM C1260-14 and Alkali-Richtlinie (Deutscher Ausshucss fur Stahlbeton-Richtlinie Vorbeugende Massnahmen gegen schadigende Alkalireaktion im Beton, April 2010) [28]. This method is similar to ASTM C1260 that is mentioned above and also is used in our laboratory. The experiment conditions are the same. The specimens of specific dimension (25 mm × 25 mm × 285 mm) are removed from the molds after 24 h. The samples are placed in water (totally immersed, for 24 h, temperature 80 °C). After 24 h, the zero reading is taken and recorded. After the zero reading, the samples are relocated from water into 1N NaOH solution (totally immersed, temperature 80 °C). Subsequent measurements of the test specimens shall be performed periodically at least every 2 days for 14 days after the zero reading at approximately the same time. More often, measurements should provide more accurate results compared to the ASTM C1260 [17].

2.2.3. The Evaluation of the ASR Process

The evaluation that is used in this research was based on TP137 [25] and consists of a simple equation; the calculation of which will determine the length change. The length change value of each test specimen is calculated separately and rounded to the nearest 0.001% of the length. The L value is given as the average of three bodies rounded to the nearest 0.001% of the length.

Stumbling-block in this case is a human factor. Measurements must meet strict conditions, such as a perfect temperature environment or accurate measurement and treatment. All the measurements were run for 28 days (almost two weeks longer than demanded in both standards) to ensure the most accurate and informative results.

3. Results

3.1. Chemical Composition and Ecotoxicity

For testing the chemical and ecotoxicological properties, 27 cubes (three cubes of each mixture with the dimensions 50 mm × 50 mm × 50 mm) were made. The tested samples were also GP and reference SF, which were prepared in the laboratory (each 100 g). Leachates were prepared as follows. Table 2 shows the concentration of the selected elements that were released in leachates from the GP and HPC samples. The composition of GP leachates varied significantly. The SGP leachate showed the highest content of silicon. The GPP leachate, which contained an increased concentration of aluminum, was classified as an ecotoxic material. On the contrary, the chemical composition of HPC leachates was more consistent for most samples. In the GPP HPC 100 leachate, the highest concentration of calcium and silicon was found while the lowest amount of potassium was found. This sample also had the highest pH value (11.4). All the HPC leachates were considered environmentally safe.

Table 2. Chemical and ecotoxicological properties of GP and HPC leachates. S—safe, E—ecotoxic (10% leachate caused $\geq$ 50% effect in at least one ecotoxicity test—water flea, algae, duckweed).

Element [mg/L]	SF	CWG	SGJ	SGP	GPP	REF HPC	CWG HPC 100	SGJ HPC 100	SGP HPC 100	GPP HPC 100
Si	24.0	14.8	8.2	48.7	14.7	3.0	2.5	2.3	3.6	5.2
Na	0.7	128.3	194.7	50.6	87.1	2.2	3.0	6.2	1.2	3.6
K	1.9	4.5	110.5	32.7	0.7	18.6	15.6	10.8	18.7	8.8
Ca	3.4	5.7	3.0	1.5	6.1	20.6	26.5	20.4	20.3	54.2
Al	<0.8	3.0	7.9	<0.8	27.9	<0.8	<0.8	<0.8	<0.8	<0.8
pH	6.8	10.5	10.9	11.1	10.3	11.0	11.1	11.0	10.9	11.4
Ecotoxicity	S	S	S	S	E	S	S	S	S	S

3.2. Alkali-silica Reaction Process

The specimens for ASR testing were prepared according to ASTM C1260 and T137 standards. A total of nine concrete mixtures were prepared for testing, of which eight were alternative with the use of different types of powdered glass and one was used as a reference mixture. Samples of size 25 mm × 25 mm × 285 mm were subjected to tests according to two standards, always in a set of three pieces. All the samples passed the experimental process in one piece, which is evident in Figure 1. Small cracks (up to 1 cm) appeared on one reference sample (mixture REF HPC), mainly coming from the edges of the sample. No changes in the surface structure were visible in the other samples.

The measurements were recorded in three decimal places. All the results were graphed and divided according to the standards that were used. A summary of all the results is clearly shown in Figure 2a–d. Due to the large amount of measured data, for clarity, the figures were divided according to the glass replacement that was used, that is the individual glass substitutes were compared with each other according to the tests that were performed. The 50% and 100% replacements are combined into one figure (CWG, GPP, SGP, and SGJ), and each figure also contains a reference sample for comparison (REF).

The ASTM C1260 standard specifies certain values according to which it is possible to assess whether the tested mixture is safe from the point of view of ASR, whether it is necessary to test it further, or whether it is dangerous from the point of view of ASR. In case the mixture is below the expansion value of 0.1% after 14 days, the standard indicates the harmless behavior of the concrete. After this basic period, which both standards indicate for testing, it is advisable to continue testing for at least another 14 days. If the expansion values do not exceed 0.1% after 28 days, it is still possible to declare the mixture as harmless. If the values are in the range of 0.1–0.2%, it is advisable to subject the mixture to further testing. However, if the expansion value at the age of 28 days is greater than 0.2%, the mixture may be at risk of a potential alkali-silica reaction. In this case, it would be advisable to switch to long-term precise testing of the mixture.

The results of this research vary from harmless mixtures to those with potential risk of ASR. The reference sample exceeded the safe value of 0.1% after 14 days but was still within the 0.2% zone after 28 days. From this it can be concluded that further testing is necessary, which is planned in the next phase of this research. Although the reference mixture that was used in this work has been developed for several years, the risk of an alkali-silica reaction has never been verified, and therefore, this research is also being tested as a basis for improving the reference mixture.

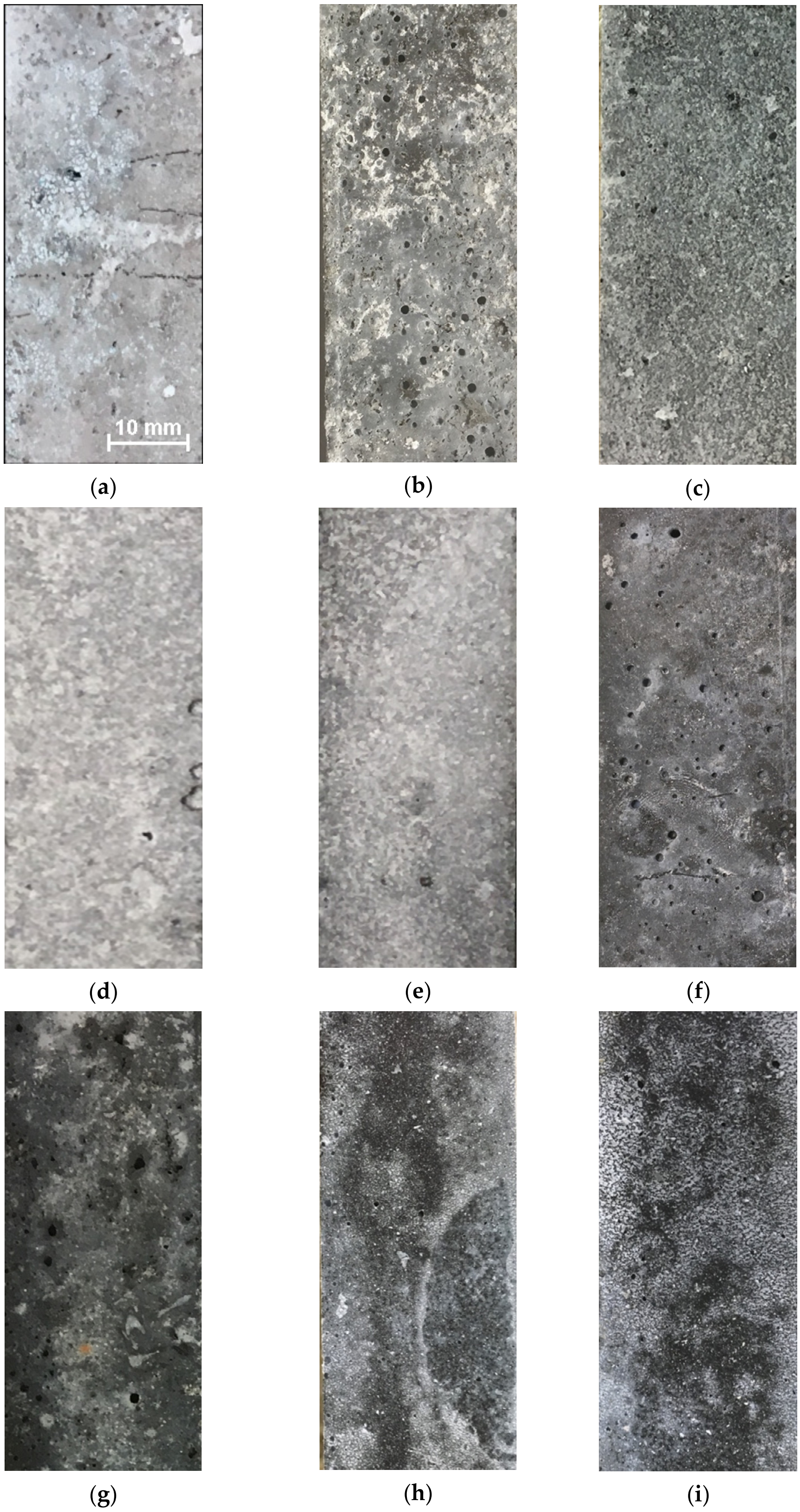
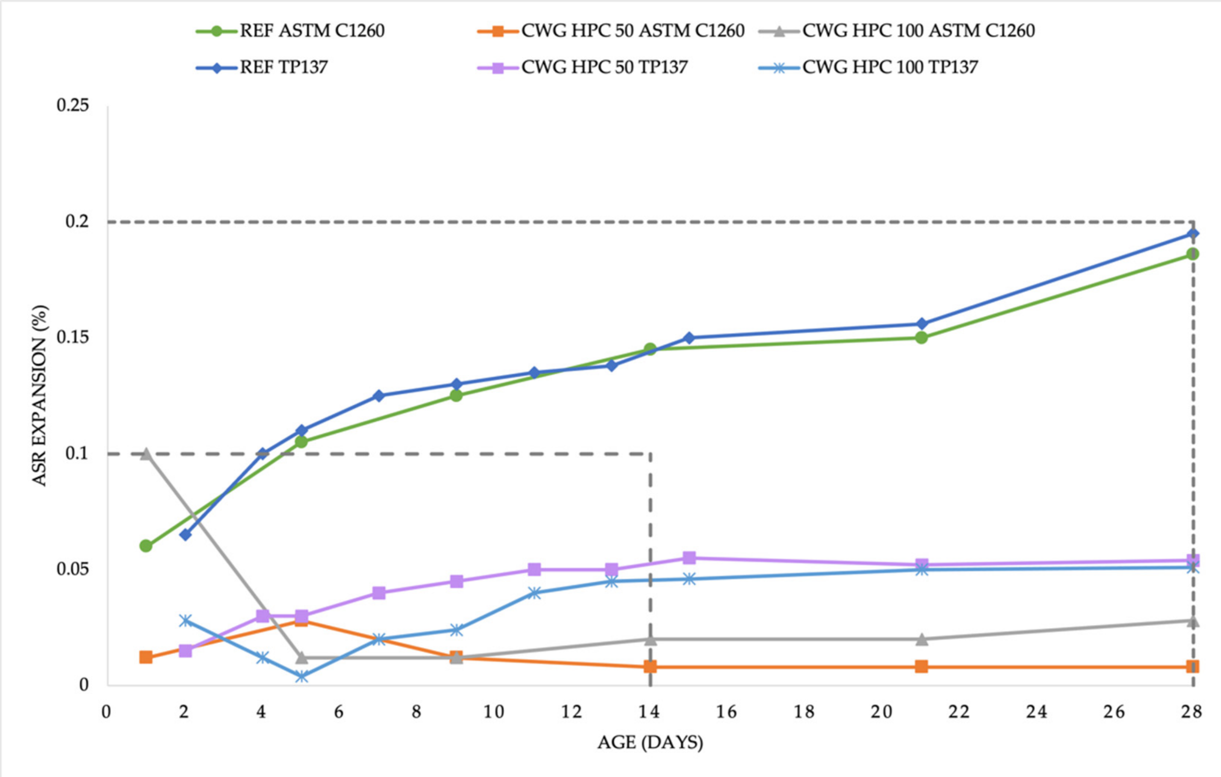
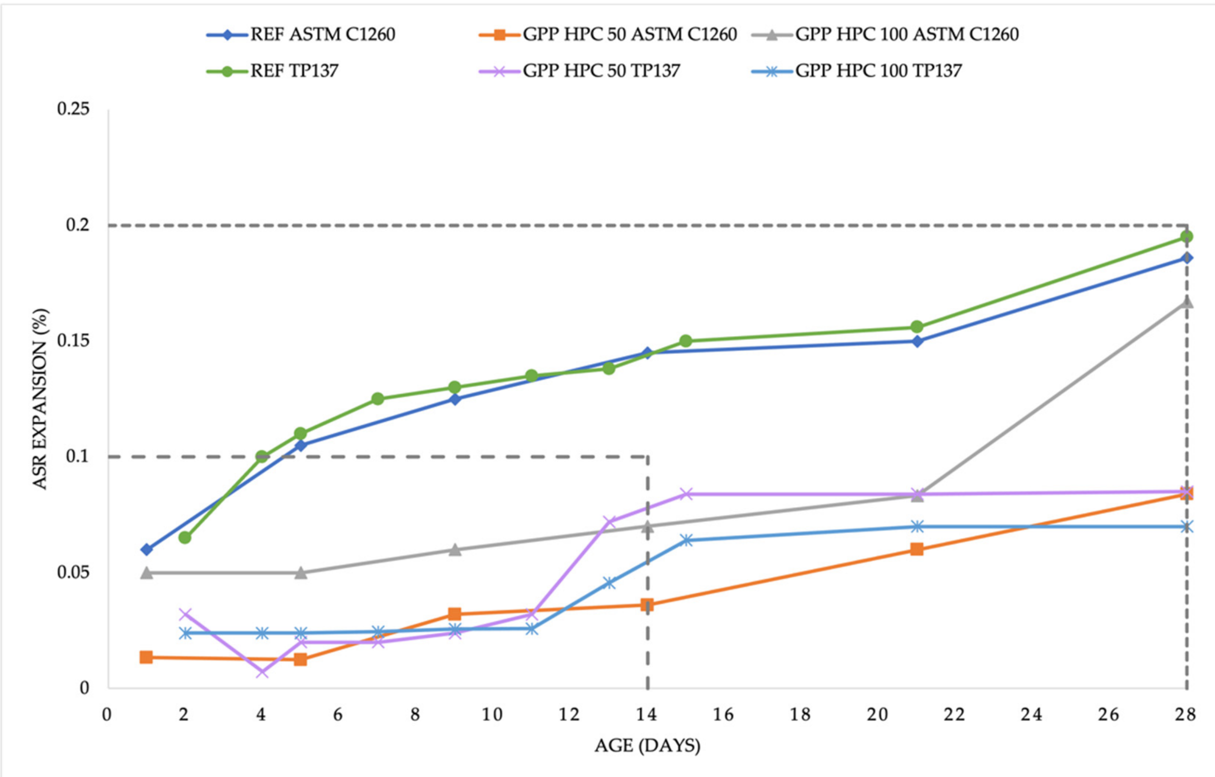


Figure 1. Samples surfaces after ASR testing process according to ASTM C1260 (2020/2021): (**a**) REF HPC; (**b**) GPP HPC 50%; (**c**) GPP HPC 100%; (**d**) CWG HPC 50%; (**e**) CWG HPC 100%; (**f**) SGP HPC 50%; (**g**) SGP HPC 100%; (**h**) SGJ HPC 50%; (**i**) SGJ HPC 100%.

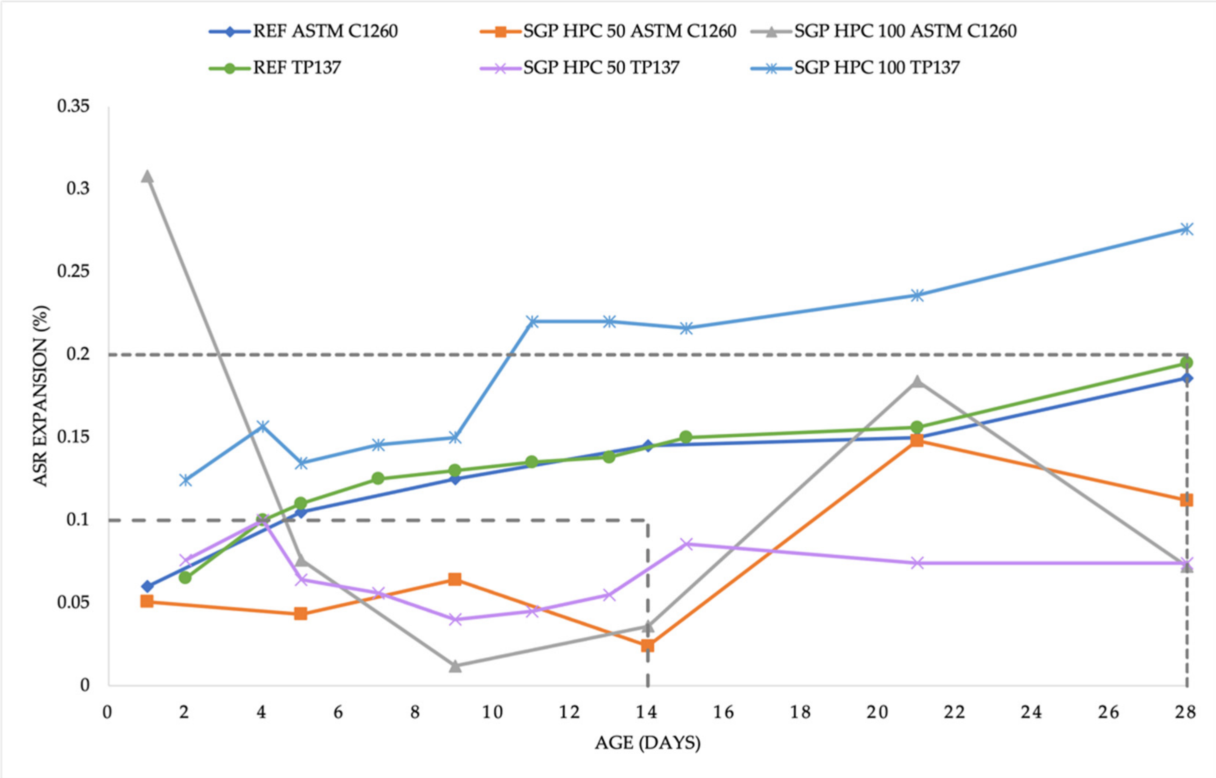


(**a**)

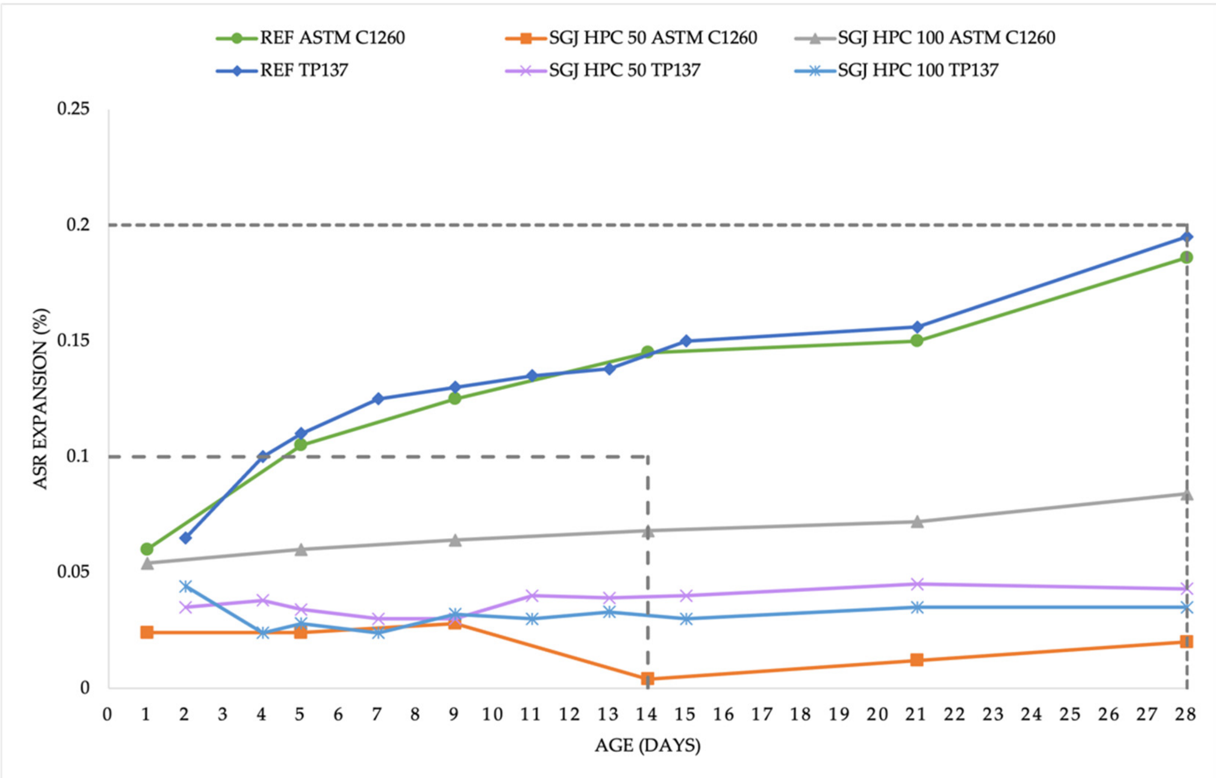


(**b**)

Figure 2. *Cont*.



(**c**)



(**d**)

Figure 2. Dependence of the alkali-silica reaction process on time according to ASTMC1260 and TP137: (**a**) CWG HPC; (**b**) GPP HPC; (**c**) SGP HPC; (**d**) SGJ HPC.

The CWG HPC mixtures had similar results according to both standards. All the outputs met the condition to be considered ASR innocuous materials. After 14 days, according to ASTMC1260, samples that were made from the mixture CWG HPC 50 were below 0.01%, while the values of the CWG HPC 100 mixture were around 0.02%. The results according to TP137 were measured similarly on all samples of both mixtures, around 0.05%. In all cases, after this obligation, the expansion process was stabilized, and the samples no longer showed signs of expansion.

The results with the replacement of silica flour with photovoltaic glass powder differed slightly and did not confirm 100% agreement in the results. Although both mixtures were tested according to TP137 and GPP HPC 50 was tested according to ASTM C1260 showed fairly similar results, GPP HPC 100 tested according to ASTMC1260 differed and after 21 days there was a sharp increase in the expansion instead of the expected stabilization. The increased value ended up at 0.168% and pointed out the requirement of further testing. The other outputs varied from 0.068% to 0.082% and were almost stable after 14 days. The highest increasing tendency was almost identical until the 14th day.

The most diverse course was recorded in the testing of SGP HPC-type mixtures. The expansion took place in a nonstandard and diverse manner in the three measured data. Although the samples were measured according to ASTM C1260, both recorded an unusual fluctuation at 21 days and a subsequent comparison at 28 days and TP137 recorded an almost continuous increase but in diametrically different values. While SGP HPC 50 according to TP137 stabilized after only 14 days and remained almost unchanged at 0.08% until the 28th day, SGP HPC 100 experienced a sharp increase already between the 9th and 11th day and increased dramatically above the safe zone. There was a stabilization at the value of 0.22%; however, after the 21st day, growth began to appear again and continued exponentially up to the value of 0.278%. However, no cracks were still visually evident. The mixture with a 50% replacement of quartz flour according to both standards showed that the limit of 0.1% was met after 14 days; however, due to the following outputs (between 14 and 28 days), it is advisable to consider long-term tests at the same time as repeating the ones that were already carried out.

In all respects, the SGJ HPC samples had very balanced and stable results (especially compared to those of the aforementioned SGP HPC). According to TP137, there was no noticeable fluctuation during the entire test period; both tested mixtures (50% and 100% replacement) remained around the value of 0.04% until the 28th day, when the test was completed. The results were very similar for all samples of both mixtures. The test according to ASTM C1260 had a slightly more varied result but was correlated with the results according to TP137. During the testing, SGJ HPC 50 was around 0.005–0.028% with stabilization at around 0.02%, while SGJ HPC 100 was around 0.054–0.083% and due to continued moderate growth, we cannot talk about a specific stabilization value.

4. Discussion

4.1. Chemical Analysis

From a chemical point of view, there are certain types of compounds that can affect ASR, its formation, and its overall process. In this study, it is mainly SiO_2, however, due to the lower amount in all the GP samples (SGP, SGJ, CWG, and GPP) compared to the reference sample SF, no negative impact is expected. High proportions also appear for CaO and Na_2O. In the case of CaO, no risk is assumed because the test takes place in an alkaline environment, and the same can be considered for Na_2O, where the occurrence of an undesirable chemical reaction is not expected. The results are based on previous research [29] and are summarized in Table 3.

Table 3. Chemical analysis of glass powder on the basis of X-ray fluorescence. All values are expressed as %.

Type	Material	SiO_2	Al_2O_3	Na_2O	CaO	Fe_2O_3	K_2O	Sum
Reference	SF	99.68	0.17	<0.005	0.03	0.03	<0.005	99.9
Glass	CWG	68.94	2.06	14.50	10.50	0.37	0.75	97.1
	SGJ	65.68	1.38	12.27	5.83	0.15	8.60	93.9
	SGP	63.58	0.51	16.61	2.64	0.08	7.02	90.4
	GPP	60.35	19.89	10.36	5.47	0.77	<0.005	96.8

On the other hand, the composition of a pure solid material does not necessarily indicate the resulting leachability and the internal chemical processes in HPC. Although the highest Si content was found in the reference samples (SF; REF), as Table 2 shows, the highest Si content in GP leachates was found in SGP. In HPC leachates, the Si content in SGP HPC 100 and GPP HPC 100 was higher than in the reference, REF HPC. These observations are not unexpected when the HPC samples are considered as various chemical mixtures with various porosities (Figure 1).

4.2. Alkali-silica Expansion

There are many different methods worldwide for testing and then evaluating the alkali-silica reaction. In the Czech Republic, the standard is valid since 1967 [19]. The tested specimens are 40 mm × 40 mm × 160 mm, and the experiment is long-term—the intermediate readings are usually done every month (for 3 months) and then every 3 months. If necessary, the experiment is continuously observed up to 18 months. The conditions are mild (humid air at 40 °C). The British standard BS 812-123 [18], which has a similar character, can be compared with the Czech standard. The British experimental design is used in research [30] and requires milder conditions (38 °C) and a longer testing period—the minimum is 52 weeks. However, measurements are taken until the values stabilize. Due to the high number of mixtures that were tested and the high time and space requirements, the short-term experiments were selected into this work.

Nevertheless, measurement of expansion that is caused by the alkali-silica reaction is a lengthy process that does not require one result and does not end with one result. It is necessary to monitor the course of the measurements, monitor the points at which sudden changes occur, and ideally, wait until the end of the process of stabilization of the measured values. Given the unusual deflections, it is convenient to fit a curve through the resulting points to visualize the testing process; in this case, a second-degree polynomial curve was used. In Figure 3, there is a summary of the results that were established after the ASTM C1260 test. According to the standard definition of the potential risk of ASR, most of the mixtures passed the test successfully and were found to be harmless from the point of view of ASR. A similar result was obtained from the TP137 standard (Figure 4). Except for one mixture with a glass subsitute (SGP HPC 100), all the mixtures were below the critical value of 0.1% after 14 days.

Relative humidity (RH) expresses the water content in structures that are affected by ASR; nevertheless, it is known that the measurement of RH in the field is often inaccurate and uncertain, and therefore, the degree of capillary saturation (DCS) is often a more appropriately used method. The relationship between these quantities is influenced by several factors, the most important of which is the water-cement ratio [22,31]. With a lower w/c concrete, the desorption isotherm is not as steep as with a higher w/c concrete, which means that the RH decreases less with higher porosity than with lower porosity [32]. During the investigation, the cross sections of the two samples were compared after the test according to ASTM C1260 (Figure 5). GPP HPC 100 is highly porous in comparison with REF HPC. It has been found that at $w/c \geq 0.45$, internal moisture develops, and thus the potential development of ASR occurs. Another study is on the lower number—$w/c < 0.4$ [32]. The mixtures that were proposed in this work were, therefore, designed with a w/c of

0.25–0.27 according to the specification of the given mixture and the glass dust that was used. The low rate of diffusion and the lack of moisture can reduce the possible expansion of ASR with a lower w/c [22]. This premise has been confirmed in this research.

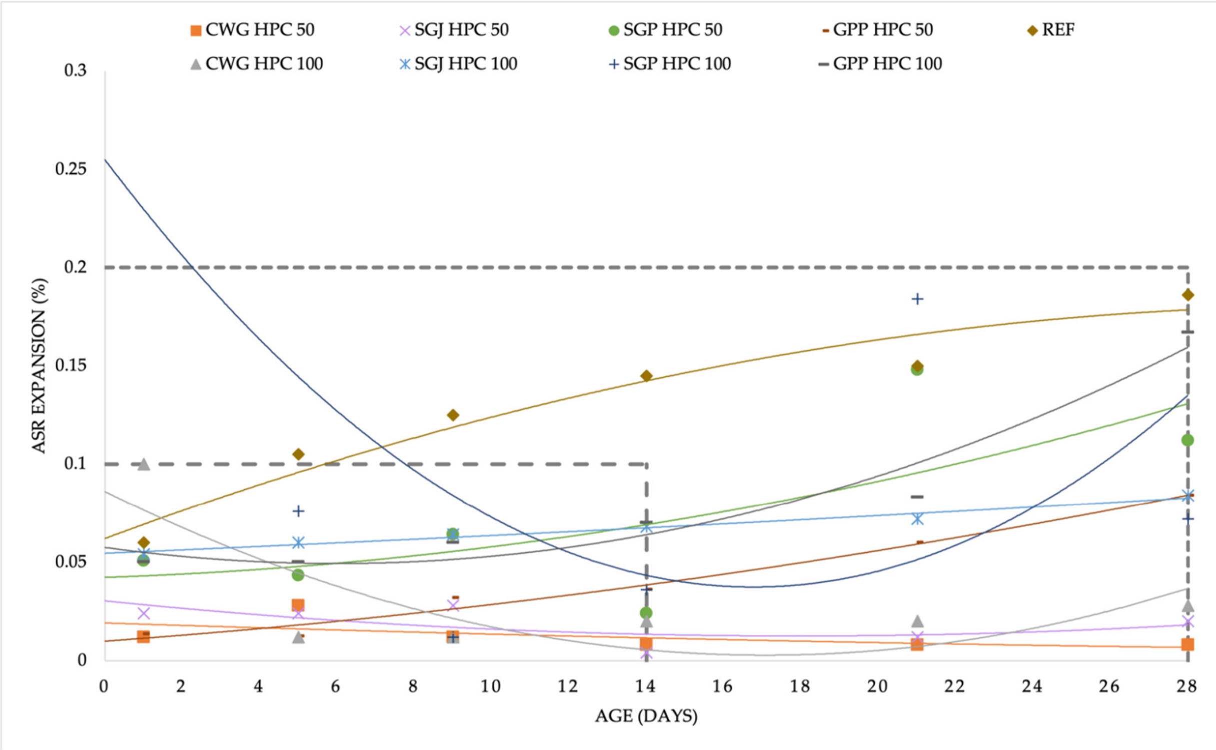


Figure 3. Summarized results of the dependence of the ASR expansion on time according to the ASTM C1260 standard.

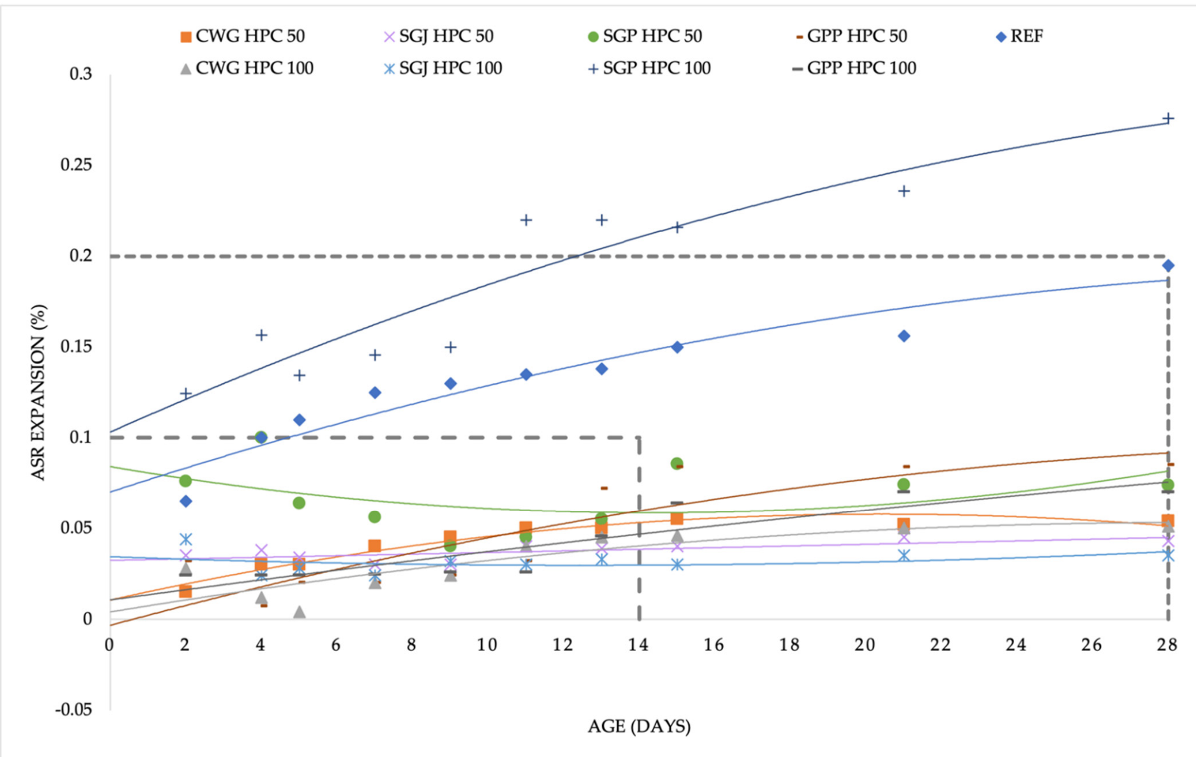
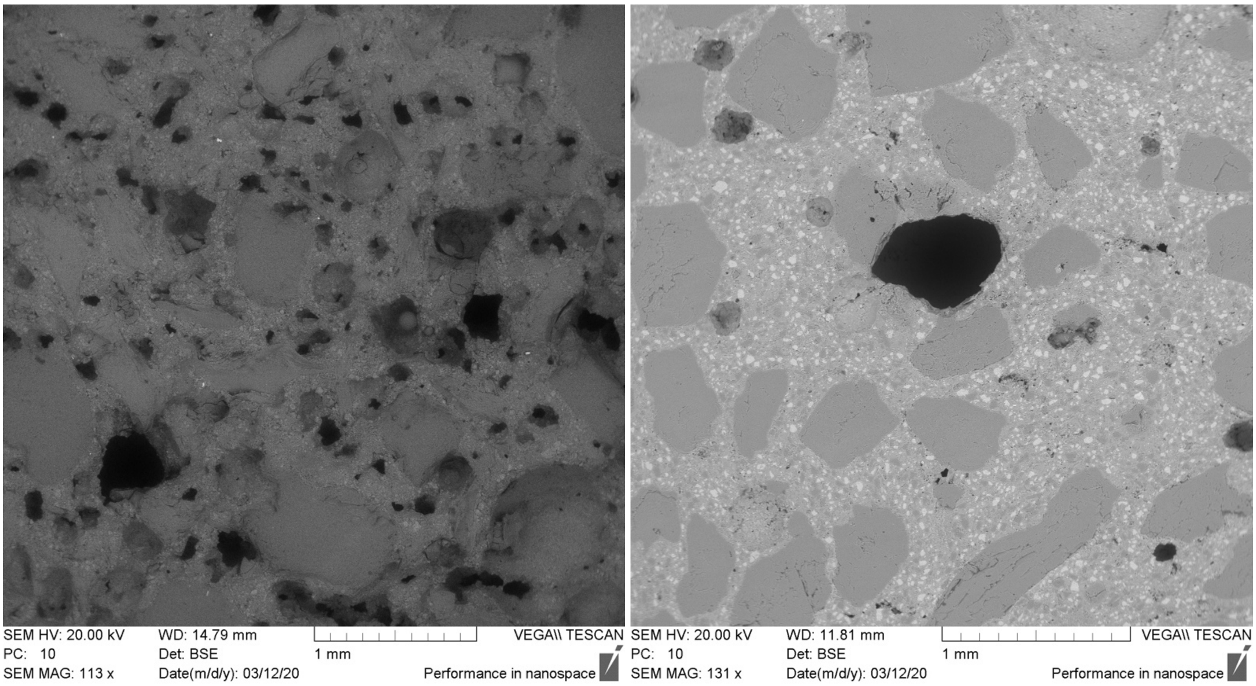


Figure 4. Summarized results of dependence of ASR expansion on time according to the TP137.



(**a**) (**b**)

Figure 5. Microstructure after ASR testing. (**a**) GGP HPC 100, (**b**) REF HPC.

According to Dhir et al. [20], there is no relationship between the amount of glass that is used and the expansion that is caused by ASR. At the same time, he claims that metakaolin, fly ash, or silica fume can also affect the ASR expansion. In this work, in the proposed mixtures of the type GPP HPC 50 and GPP HPC 100, microsilica was removed from the composition of the mixture. In the first pilot test, cracks formed during the setting of the concrete. The mixture was subsequently optimized, and one of the steps in the new mix was the omitting of silica fume. Therefore, this work confirms the assumption of a possible negative effect of silica fume on ASR. But, of course, it depends on the chemical properties of the material [33].

In an alkaline environment, the surface of Si-OH groups of siliceous materials ionizes, thereby acquiring a multiple negative charge. Among the most important aspects of the environment are pH values and the content of NaCl, $BaCl_2$, or other neutral salts. As the concentration of these salts and pH increase, the intensity of the negative charge increases. In an alkaline environment with such a high ionic charge, hydroxyl ions OH^- are also released, entering deeper into the material, and penetrate the center of the material. When OH^- penetration slows down, the ASR rate also slows down. However, the source of ions does not have to be the only solution that is used [16]. If there are enough calcium ions in the solution, the so-called C-S-H gel is formed, which causes cracks in concrete. Changes in the pH occur when the calcium ions Ca^{2+} or SiO_2 in the solution come into contact [34]. This advanced form of ASR was recognized for one reference sample, although the values that were measured during the experiment indicated higher length changes for the SGP HPC 100 mixture (values measured according to TP137). The reason may be precisely the higher content of Si in SF and SGP.

Based on the testing of GP samples, it is not possible to estimate in advance how they will behave as a replacement component in the HPC mixture. Therefore, it is advisable to experimentally verify this behavior repeatedly of both GP and HPC and analyze the possibility of dependence and its possible nature.

In the aggressive conditions that are specific for both experiments that were performed (ASTM C1260 and TP137), it is possible that sudden fluctuations after the standard test period are caused by the extended expansion horizon. These were the SGP HPC 50 and SGP

HPC 100 mixtures according to ASTM C1260 that experienced expansion between 14 and 28 days (Figure 3). However, according to TP137 (Figure 4), a very continuous increase was observed throughout the experiment with SGP HPC 100, and it may be an inappropriate material to be used as a substitute for SF, leading to dangerous expansion that is caused by ASR. However, the directions for further research may vary—apart from the standard option of long-term research (which was carried out by Dhir et al. [20]). In recent years, other directions have appeared, namely numerical calculations of the expansion that is caused by ASR that were presented mainly by Zhuang et al. [35,36].

5. Conclusions

This work compared newly designed mixes and compares international and national testing standards. In contrast to the other research works, this work deals with newly designed mixes that are based on specific types of glass. Therefore, great emphasis is placed on the chemistry and toxicity of the given materials, as it is considered one of the key factors to decipher the chemical processes that are associated with ASR.

The novelty of this research lies mainly in the innovative approach from the point of view of testing, where the testing takes place according to the latest standards, comparison between them, and at the same time, in the importance that is hidden in the use of glass materials in the Czech Republic as a local raw material.

The main contributions and findings of this work include the following points:

- The SGP leachate showed the highest content of silicon.
- The GPP leachate was classified as an ecotoxic material.
- All HPC leachates were considered environmentally safe.
- After ASTM C1260 testing, cracks appeared on one reference sample (up to 1 cm).
- No changes on the surface were observed after TP137 testing.
- GPP HPC 100 and REF HPC expansion after an extended experiment period (28 days) was between 0.1 and 0.2%. Further testing is necessary.
- SGP HPC 100 expansion after standard 14 days period was above 0.2%. Mixture may be at risk of a potential alkali-silica reaction.
- According to the standards, the conditions to exclude the occurrence of an ASR in the mixtures CWG HPC 50, CWH HPC 100, SGJ HPC 50, SGJ HPC 100, SGP HPC 50, and GPP HPC 50 were fulfilled.

In general, it is necessary to be careful with the assumption that the replacement of fine particles is more appropriate than the replacement of coarse aggregate in concrete. Although the results of this research point to the confirmation of this premise, it can only be an extension of the expansion time horizon. However, this consideration needs to be verified by long-term testing or/and numerical methods.

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Appendix 3

Glass Waste Powder Utilization in High Performance Concrete

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Abstract: This paper deals with investigation of high-performance concrete (HPC) with full replacement of the silica powder by the waste glass powder. The silica powder was replaced by two types of the waste glass powder, originated from different sources (waste glass powder from grinding jewelry and milling of municipal waste glass). The properties of the waste glass powder were examined and compared with the silica powder. The mechanical and durability properties of three HPC mixtures were experimentally verified. The bulk density, flexural strength, and compressive strength were tested on beams 40 × 40 × 160mm at age 28 and 60 days and after 0, 25, 50, 75 and 100 freeze-thaw cycles. There were observed slightly worse properties of mixtures with the waste glass powder in comparison with reference HPC.

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GLASS WASTE POWDER UTILIZATION IN HIGH PERFORMANCE CONCRETE

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Abstract. This paper deals with investigation of high-performance concrete (HPC) with full replacement of the silica powder by the waste glass powder. The silica powder was replaced by two types of the waste glass powder, originated from different sources (waste glass powder from grinding jewelry and milling of municipal waste glass). The properties of the waste glass powder were examined and compared with the silica powder. The mechanical and durability properties of three HPC mixtures were experimentally verified. The bulk density, flexural strength, and compressive strength were tested on beams $40 \times 40 \times 160$ mm at age 28 and 60 days and after 0, 25, 50, 75 and 100 freeze-thaw cycles. There were observed slightly worse properties of mixtures with the waste glass powder in comparison with reference HPC.

Keywords: Waste glass powder, high performance concrete, durability, mechanical properties.

1. Introduction

High-performance concrete (HPC) becomes very popular. HPC has been mostly used in the precast industry, for pedestrian footbridges. Nowadays, HPC is used in buildings structures (skyscrapers) or in transportation structures (bridges) [1]. Due to its excellent mechanical properties the HPC structures could be more subtle. This could lead to the raw materials saving.

The properties of HPC are suitable in many ways such as mechanical and durability properties. HPC is also possible to use in aggressive environment with aggressive substances such as sulphates or chlorides. Permeability of HPC is also very low [2]. There is also the risk of carbonation of the concrete and further its corrosion due to presence of carbon dioxide in standard environment. For this reason, the utilization of HPC is appropriate as prevention against corrosion and concrete damage. Due to its excellent durability properties, the long lifespan of constructions is provided, despite exposure to aggressive conditions. The long lifespan and also lower material consumption of HPC structures is the main and most important advantages of this material. However, the primary raw materials which are used for HPC has high environmental impact such as CO_2 emissions, energy and raw material consumption. The impact on the environment is an important question. Nevertheless, new tendencies are heading towards sustainable building and ecological materials. This is the reason why it is appropriate time to think about improving HPC in an environmentally friendly way.

Silica powder, using as inner filler in HPC, is possible to replace with glass powder, because of similar properties. On one hand, the glass is a non-decomposable material which is necessary to landfilled. However, on the other hand, the material is almost 100% recyclable [3]. Recycling is the necessary attitude for the next years. Along with recycling it is desirable to minimize the amount of waste [4].

There are several studies [5–8], that examine the possibility of using glass waste as a partial replacement of aggregate in concrete. It is possible to replace coarse aggregate or fine aggregate. The replacement ratio depends on particles size due to possibility of alkali-silica reaction (ASR). It is important to notice that on basis of alkali-silica reaction are significant only aggregates with amorphous silica [9].

The utilization of waste glass as replacement of different constituents in concrete mixture has been investigated (aggregate replacement, inert filler, partial cement replacement etc.). The use of waste glass as partial replacement of coarse aggregate for ordinary concrete is possible way in some cases. There are several studies to examine a partial cement and quartz powder (fine fraction) replacement by waste glass powder in ordinary concrete or ultra-high performance concrete (UHPC) [8, 10]. The utilization of waste glass powder as partial replacement in HPC has not been completely explored yet. For this reason, the aim of this investigation was to prove the use of waste glass powder as full replacement of silica powder in HPC. The experiments were focused on a verification of mechanical properties and durability of HPC with waste glass powder. The results were compared with the reference sample containing silica powder.

2. Materials and Experimental Program

Samples of waste glass powder was collected and examined. There were two types of waste glass – milled waste glass from municipal waste and grinding glass. Analysis were made – granulometry and chemical analysis. After that, the grain curves were investigated and compared with the reference sample – silica powder. The same thing was made with chemical composition. After completing analysis of waste glass powder, high performance concrete was made. The basic recipe was optimized in previous research project, cf. Table 1. The optimized recipe is used as the reference sample (A). After that, the optimized basic recipe was changed – replacing silica powder with grinding glass (sample B), then with the milled waste glass from municipal waste (sample C). The weight of fine fraction stayed the same. There were two samples (B, C) which were examined and compared with reference sample (A). The differences were evident in the structure of concrete.

Component	Quantity (kg/m³)
Cement I 42.SR	680
Technical silica sand	960
Silica powder (ground quartz)	**325**
Silica fume (microsilica)	175
Superplasticizers	29
Water	171
TOTAL	**2340**

Table 1. Basic recipe of HPC – reference sample A.

Size of prepared samples for tests of mechanical properties was 40 × 40 × 160 mm. There were 54 samples made, 18 from each type. Samples 1–15 of each type was ready for tests after 28 days, samples 16–18 was ready for tests after 60 days. It was also meant to compare differences of the mechanical properties between 28-days-old concrete and 60-days-old concrete.

2.1. Tests of Mechanical Properties

Tests of mechanical properties were made using destructive methods. The tests were made on samples after 28 and 60 days. Prepared samples were examined to determine:

Compressive strength. The tested samples can be cubes, cylinders. In this paper, compressive strength was tested on fragments of samples 40 × 40 × 160 mm. The tested surface A_c was 40 × 40 mm. There are certain conditions to keep – about samples (EN 12350-1, EN 12390-1, EN 12390-2 or EN 12504-1), machine (EN 12390-4) and procedure.

Tensile bending strength. Tensile bending strength is described in ČSN EN 12390-5 [11]. The test is realized on block specimens with dimension 40 × 40 × 160 mm. Tensile bending strength is defined by three-point press according to ČSN EN 1015-11 [12]. The test is over after the sample breaks. The highest force registered during the test is used for calculation tensile bending strength. It is always necessary to test at least three samples.

Freeze-thaw resistance. The tested samples are 40 × 40 × 160 mm. This test was made following ČSN 73 1322. Cooling is done by air – 4 hours to −20°C and then 2 hours of warming up to 20°C. The samples were tested in 25, 50, 75 and 100 cycles.

3. Results and Discussion

The following chapters describe the results and discussion of all tests.

3.1. Chemical Analysis

Chemical analysis of samples A, B and C were examined during the spring of 2017. Table 2 summarize the results.

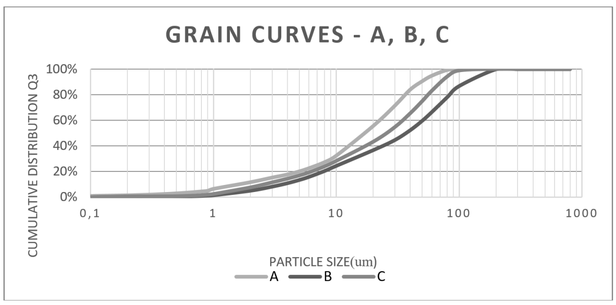
There are differences such as similarities in chemical composition. After checking amount of SiO_2 and NaO_2, CaO, it is possible to see difference in number – dozens of percent. Chemical composition has an impact to resulting properties. It is necessary to examine potential alkali-silica reaction. The topic of detailed examination of chemical composition could be used in the upcoming research.

Symbol	Sample A – reference sample	Sample B – Grinding glass	Sample C – Milled waste glass
SiO_2	85.730%	56.395%	55.740%
Fe_2O_3	0.677%	0.757%	1.044%
Al_2O_3	0.234%	3.260%	2.224%
NaO_2	< 0.014%	26.736%	19.220%
TiO_2	0.0654%	0.0453%	0.0748%
Ba	0.0322%	0.219%	0.1051%
P_2O_5	0.0244%	0.0868%	0.0589%
CaO	<0.0014%	3.0459%	11.490%

Table 2. Results of chemical analysis.

3.2. Particle Size Distribution

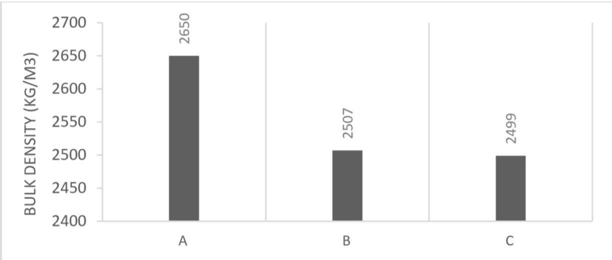
The size of particle has the main impact to the results. With the growing particle size increases the potential risk of ASR. It would be convenient to consider another milling or regrinding of the particles to achieve appropriate size in next research. The comparison of particle size is attached in Graph 1.



Graph 1. Comparison of particle size distribution.

3.3. Bulk Density

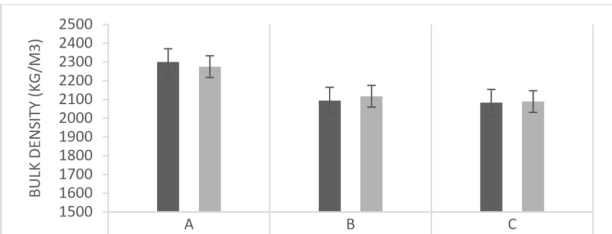
Bulk density of the samples could have the main impact to the results. The porosity in the sample can change the compressive strength or the tensile bending strength values. This research used the same weight amount of waste glass powder to replace silica powder. It would be appropriate to try another attitude in next research – based on bulk density, calculate the appropriate amount of the replacement.



Graph 2. Bulk density of the samples A, B and C – average values from 10 samples.

It is possible to see difference between samples B and C compared to sample A, cf. Graph 2. However, the difference is negligible – bulk density of sample B is 94, 9%, bulk density of sample C is 94, 3% compared to sample A – considered as 100%.

Bulk density of the concrete is calculated based on weight and volume. In Graph 3, note that the bulk density of the reference sample A is comparable with sample B and sample C.



	A	B	C
28 days	2300	2094	2083
60 days	2275	2117	2089

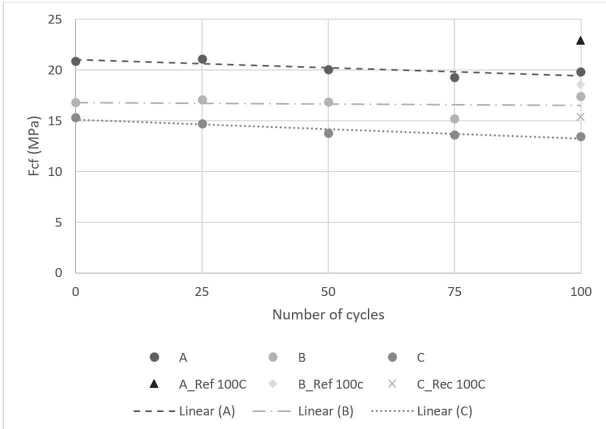
Graph 3. Bulk density of the concrete after 28 days and 60 days – average values from 3 samples.

Difference between samples B and C is less than 10% compared to reference sample A in all cases. Based on this knowledge, it is possible to compare the samples in following tests.

3.4. Tensile Bending Strength

Longer hardening time has a positive impact to the results – tensile bending strength increased after 60 days, cf. Graph 4. Nevertheless, the values between cycles are slightly different (with the increasing number of cycles the values are decreasing), but the impact of freezing cycles is not as big as the impact, for example, particle size or chemical composition.

Sample B achieved better results than sample C, it is probably caused due to the chemical composition. The values of sample B and C were 68%–88% compared to sample A (considered as 100%). However, it would be appropriate to work on utilization of both samples in HPC and try to improve the results.

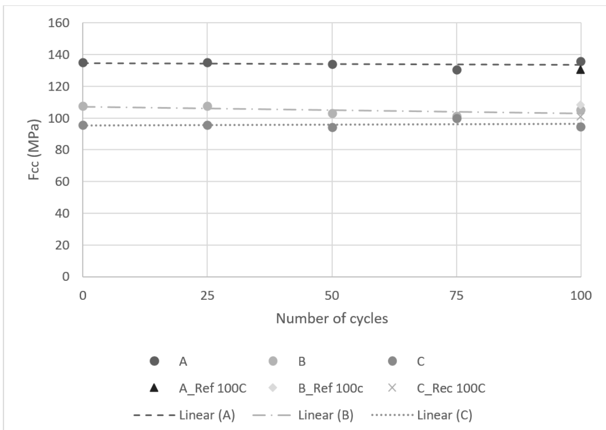


Graph 4. Comparison of tensile bending strength – average values from 3 samples.

3.5. Compression Strength

Compressive strength values showed positive impact of longer hardening time – the results are better after 60 days (expect sample A – although it is reference sample, in this case it is a negligible value). It would be appropriate to make the other tests based on longer hardening time in next years.

The compressive strength values after freeze-thaw resistance tests are satisfying, cf. Graph 5, the values of sample B and C range from 70% to 79% compared to sample A (considered as 100%). However, the values are decreasing (sample A, B, C) – it is unusual for HPC.



Graph 5. Comparison of compressive strength – average values from 3 samples.

4. Conclusions

Utilization of waste glass powder in high performance concrete was examined. Waste glass powder was used as replacement of silica powder in HPC. Mechanical and physical properties of concrete made with waste glass powder from different sources were investigated.

Two samples of high performance concrete contain waste glass powder were made, one sample of high performance concrete contains silica powder was made as well – the reference sample. Two waste glass powder samples were examined and compared to the reference sample.

First, the chemical composition was examined to find out the differences and similarities. There is a possibility to modify chemical composition to improve the results.

The particle size distribution was investigated, because the particle size has the main impact to the structure of the concrete and therefore the impact to the results as well. It would be appropriate to consider another milling to reach the right particle size – comparable to silica powder.

The bulk density of silica flour, glass powder and concrete was examined as well. The values were slightly different – it should not affect the results of the physical properties.

The tests to find out the compressive strength and the tensile bending strength were made. The results were compared to reference sample (contains silica powder).

There is a risk of an alkali-silica reaction, because of glass used in the HPC mixture. The freeze-thaw resistance tests confirmed that due to the dense HPC structure, the probability of the alkali-silica reaction was eliminated.

This study can be used as a basic for further work. The waste glass powder can be improved in different ways in next years and the utilization in HPC as inner filler is possible.

Acknowledgements

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Appendix 4

Ecotoxicity and Essential Properties of Fine-Recycled Aggregate

Authors: Mariaková, Diana; Mocová, Klára Anna; Fořtová, Kristina; Ryparová Pavla; Pešta Jan; Pavlů, Tereza

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Abstract: This article deals with the possibility of utilization of secondary-raw materials as a natural sand replacement in concrete. Four types of waste construction materials were examined—recycled aggregate from four different sources. The natural aggregate was examined as well as used as the reference sample. All the samples were tested to evaluate the water absorption, particle size distribution, and particle density. The basic chemical reactions in the view of ecotoxicology are investigated and measured based on Czech standards. Chemical analysis, Lemna growth inhibition test, freshwater algae, daphnia acute, and mustard germination toxicity test were made and discussed in this paper. Based on the physical and geometrical properties and ecotoxicology of examined waste materials, this work evaluated them as suitable for utilization in concrete as a sand replacement.

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Article

Ecotoxicity and Essential Properties of Fine-Recycled Aggregate

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Abstract: This article deals with the possibility of utilization of secondary-raw materials as a natural sand replacement in concrete. Four types of waste construction materials were examined—recycled aggregate from four different sources. The natural aggregate was examined as well as used as the reference sample. All the samples were tested to evaluate the water absorption, particle size distribution, and particle density. The basic chemical reactions in the view of ecotoxicology are investigated and measured based on Czech standards. Chemical analysis, *Lemna* growth inhibition test, freshwater algae, daphnia acute, and mustard germination toxicity test were made and discussed in this paper. Based on the physical and geometrical properties and ecotoxicology of examined waste materials, this work evaluated them as suitable for utilization in concrete as a sand replacement.

Keywords: chemical properties; recycled concrete aggregate; ecotoxicity

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1. Introduction

Tendencies toward the use of secondary raw materials have emerged in recent years, given the fact that the most used building materials are completely dependent in the production on primary materials. These sources are decreasing and due to their non-renewable disposition, the use of secondary raw materials is a logical step. However, when replacing, it is always necessary to consider the material being worked with and, with regard to the required properties, to select replaceable components and secondary materials that could be used. Nevertheless, the summarization of the material properties is only the second step, first it is necessary to take into account the properties of the secondary raw materials themselves.

Many studies describe the mechanical, physical, and durability properties of recycled aggregate (RA) originated from construction and demolition waste (CDW). The higher content of impurities and also mortar complicates the use of the fine fraction RA as a partial or full replacement of natural sand. For the coarse fraction, this problem is reduced [1]. This fact is one of the main reasons that keep the standard description of the use of recycled material as a substitute for sand in concrete. However, it is necessary to define a standard for the use of waste materials because of the fact that the extraction of sea sand has a negative impact on the environment—erosion by the sea is affected as well as the behavior of waves. Local ecosystems are generally negatively affected by sand mining [2].

However, most studies do not pay sufficient attention to the properties of waste raw materials themselves. The results of experiments on the waste may affect its overall utilization. According to the standards, it is possible to use recycled concrete aggregate (RCA) with a content of concrete particles above 70% as a partial replacement for gross natural aggregate (NA). However, this possibility is limited by the type of application [3,4].

Nevertheless, the utilization of another CDW types utilization is not defined in Czech standards yet (recycle masonry aggregate (RMA) or fine RA).

Previous research has verified the higher water absorption and lower density of RA. According to the previous studies, the water absorption of fine RCA ranges between 4.3% and 13.1% and the dry density of fine RCA ranges from 1900 to 2360 kg/m^3 [5]. The higher water absorption and lower density of RCA is caused by old mortar attached to the surface of original aggregate which is more porous and less dense than the aggregate particles [1]. This leads to a higher water absorption of RCA, which influences the effective water–cement ratio and has negative impact on the workability of the concrete mix. The main differences between RMA and NA are water absorption and particle density. The particle density of coarse RMA ranges between 2000 and 2500 kg/m^3 and ranges from 1800 to 2700 kg/m^3 for fine RMA [6–9], while the water absorption is several times higher (about 12–15% in various studies), which is about ten times higher than the water absorption of NA [6,10,11]. The higher water absorption of RMA is caused by more porous materials contained in this aggregate such as red bricks, aerated concrete, plasters, mortars etc.

Ecotoxicity is one of the indicators that can show the extent to which living organisms, or the entire ecosystem, can be affected [12]. Ecotoxicology is a science dealing with the impact of harmful substances on the environment. In particular, the toxic effect on organisms that must meet the given conditions during laboratory testing is investigated. It is necessary to deal with these properties, because from the point of view of the concept of circular economy, it is desirable to use the produced waste and re-involve it in the process. The evaluation of toxic effects can be performed by several methods, the evaluated criteria include, for example, mortality or the number of inhibited individuals. If it is not possible to evaluate these factors, other output data can be used, which are based on specific physiological characteristic of the organisms, such as growth of an individual or test colony or population can be considered as suitable parameters [13].

Such great importance for the basic properties of selected waste raw materials is placed mainly due to their use in concrete. The aim of the research is to analyze the properties of waste materials from an environmental point of view, because in materials such as concrete, it is now desirable to use secondary raw materials that reduce the negative impact on the environment. The production of concrete itself is a great burden for the environment, because of the need to quarry of primary raw materials, often to transport these raw materials and further processing. It is also necessary to consider the amount of concrete produced in the construction industry and subsequently the waste in this sector. Construction waste is often landfilled, which seems to be an inappropriate choice because of the potential for toxicity of some materials. Another possibility is the recycling of waste materials, a suitable choice here also seems to be the overall evaluation of the life cycle to confirm the suitability of this solution [14].

The concrete composition is still developing. Many possibilities to substitute usual components of concrete have been evaluated in the past few years, and the utilization of secondary raw materials such as RA, blast furnace slag, fly ash etc. The use of RA from CDW as a partial or full replacement of aggregate in concrete is solved in terms of mechanical properties in various researches [10,11,15–17]. This approach is necessary to evaluate the strength of new concretes containing waste, because of the following use. Over the past decades, the properties of RA and their influence on concrete characterization has been tested and evaluated. The research has become complex in the last years because the use of RA as a replacement for natural aggregate (NA) in concrete in one of the most effective approaches how to use CDW in the recycle process. Because of constantly increasing concrete production, the amount of CDW is growing as well [18].

The properties of recycled aggregate, especially its quality, are the main indicators when used in concrete. Because of the frequent occurrence of impurities, there is a risk of decreasing mechanical properties of the concrete mixture. Generally, the RCA has lower particle density and higher water absorption, which is caused by the porous mortar which is attached in the original aggregate surface and water absorption influences the workability of fresh concrete mixture [1,5]. It is assumed that although the fine particles have a larger surface area, their contents could fill the space between the larger particles of the aggregate, which can eliminate the porosity. When using the fine fraction of RCA, problems also arise in terms of physical properties. Because of the high content of cement mortar, higher water absorption has to be discussed and this phenomenon also occurs with the partial replacement of RCA compared to reference concrete. Increasing the w/c ratio results in better processability of concrete mixture [5].

A study [19] dealt with the possible use of fine RCA in concrete. The results reached a possible substitution rate of up to 30%, nevertheless, the laboratory-prepared fine RCA was used in this study, which could have affected the results. The difference between laboratory-prepared fine RCA and fine RCA from CDW can be negligible, although particle sizes of 125 to 500 μm show a high content of cement mortar, which could lead to better mechanical properties of the concrete [18]. So far, the results of the studies are more with a decreasing trend—the compressive strength decreases to 70% of the reference concrete mixture when replacing NA with fine RCA. In the case of partial replacement (25, 50, and 75%), the values of compressive strength in the study [6] were similar, but in the case of full replacement, the lowest compressive strength was measured on the concrete sample.

The properties of RMA may adversely affect the workability of fresh concrete or the mechanical properties of concrete [19]. The composition can also have an effect, as there is a risk of impurities content in the RMA. The high water absorption is the key property in the RMA utilization in concrete. There are two possibilities to compensate higher water absorption of RA and it is necessary to find the optimal solution for practice. The possibilities are: during the mixture designing, it is necessary to take into account the pre-soaking of the aggregate into water (24 h before mixing) [7], or count with the use of an additional water during mixing itself [8]. Different studies [6–8] examined different amount of NA replacement rates, most studies show a decrease in compressive strength after 28 days depending on the increasing RMA replacement rates.

For all the mixtures containing RMA, the measured compressive strength increased after 90 days. This increase was higher compared to reference concrete sample containing NA. The reason for this phenomenon is given by, for example, the formation of pozzolanic reactions due to the presence of silica and alumina contents in the bricks used or a lower w/c ratio of concrete mixtures containing fine RMA [6]. This assumption was demonstrated by further studies where the w/c ratio was calculated from RMA water absorption. The results of these studies do not show any significant changes in the rate of strength development between the age of 28 and 90 days [7,8].

This article is proceeding the utilization of waste materials—in particular, the CDW. The research is focused on three types of RCA and one type of RMA from different sources. The planned use of these materials is in concrete as a natural sand substitute. However, the properties of CDW materials may be inappropriate, it is necessary to experimentally verify at least the essential properties such as particle size distribution, chemical composition, water absorption, or particle density of the recycled waste materials used in comparison with the reference sample (natural sand). Among other things, it is necessary to think about the suitability of use due to the possible toxic effects on natural organisms, the possibility of releasing toxic substances, etc.

The usual utilization of fine RA as backfilling layers in the Czech Republic leads to the toxic pollution in the environment. In addition, the previous investigation of the research group showed the satisfying results of mechanical properties of concrete with almost full replacement of natural sand by fine RA [20]. The published results showed that the mechanical and deformation properties of mixtures with the content of FRA were similar (fine RMA) or slightly better (fine RCA) in comparison with the reference mixture.

This research work has responded to previous results and dealt with the possible utilization of this waste materials with prediction of the chosen waste materials properties, which will fulfill the requirements for use in concrete especially in the vie w of ecology to show the advantages of this solution. Environmental impacts occur mainly during the integration of the components of concrete with rain or wind. These processes can cause degradation, as various substances can leach out due to the action of water and it is desirable that the waste materials used in concrete do not have a toxic effect on the environment. Therefore, the chemical composition and possible toxic effects must be investigated.

There are a number of factors that can affect the overall effect, such as contact time, porosity, or material damage, which only a small number of studies have examined these days [12]. This study works with the new assumption that the use of waste materials in concrete leads to their immobilization. The relative topic is also dealt with in another study [21], which brings new insights into the potential use of RA in concrete.

2. Materials and Methodology

2.1. Materials

Within the performed experiments, waste materials from CDW were used. The NA, which is widely used in concrete, was tested as a reference. The RA that has been tested should have properties comparable to natural sand, as the aim is to replace these primary raw materials in concrete with the secondary raw materials mentioned below. The RA originated from a recycling centers in the Czech Republic and had different origins:

(1) RA 1 was prepared from reinforcement concrete in the recycling center by the two-steps recycling process. The crushed and separated recycled aggregate of fraction 16/128 mm from the first step of recycling process was crushed and sieved to the fractions in the second step.
(2) RA 2 originated from highway and was partially prepared in the recycling center to fraction 64/128 mm. Afterwards, the fraction 64/128 was crushed and sieved into the fractions in the laboratory.
(3) RA 3 originated from the ground floor structures and was partially prepared in the recycling center to fraction 64/128 mm. Afterwards, the fraction 64/128 was crushed and sieved into the fractions in the laboratory.
(4) RA 4 originated from the masonry structures and contains mostly red bricks, mortar, and plasters. It was prepared from reinforcement concrete in the recycling center by the two-steps recycling process. The crushed and separated recycled aggregate of fraction 16/128 mm from the first step of recycling process was crushed and sieved to the fractions in the second step.

Two types of RA (RA 1 and RA 4) were modified by the two-step recycling process. In the first step, the CDW is crushed and separated to three fractions 0/4, 4/16, and 16/128 mm; the fraction 0/4 and 4/16 mm is separated and used as downcycling material for instance as backfilling material due to the unwanted impurities such as soil and dust. In the second step, the fraction 16/128 mm was crushed again and sieved to the fraction 0/4, 4/8, and 8/16. The content of unwanted impurities is reduced by this process. The recycling process of two other RAs (RA 2 and RA 3) was similar, however, the RA of fraction 64/128 mm from the first step of recycling process was finally crushed and sieved in the laboratory to fractions 0/4, 4/8, and 8/16 mm. Although three fractions of RA were prepared, only fraction 0/4 mm was studied in this investigation.

All the samples were used as a fine aggregate and the experiments were performed according to the valid Czech standards. The used samples are shown in Figure 1.

2.2. Physical and Geometrical Properties

All types of aggregates were used in natural humidity conditions. However, for the particle size distribution test the aggregates were dried until stabilization of weight and further tested according to the CSN EN 933-1 [22]. Limits are defined in CSN EN 12620 [23]. Water absorption and density were verified by the pycnometric method according to CSN EN 1097 [24].

(a) (b) (c)

Figure 1. Tested waste materials recycled concrete aggregate (RCA): (**a**) NA; (**b**) RA 1; (**c**) RA 4.

2.2.1. Fineness Modulus

Fineness modulus (FM) is informative property of aggregate used for determination of the degree of uniformity of the aggregate gradation. It is an empirical number relating to the fineness of the aggregate. The higher the FM is, the coarser the aggregate is CSN EN 12620 + A1 [3]:

$$FM = \frac{[(X_{>4}) + (X_{>2}) + (X_{>1}) + (X_{>0.5}) + (X_{>0.25}) + (X_{>0.125})]}{100} \quad (1)$$

where X is the sample of an aggregate retained on each sieve [3].

Fineness modulus of aggregate primarily describes the coarseness and fineness of fine aggregate (CSN EN 12620 + A1, 2008 [3]).

2.2.2. Fines Content

Determination of percentage of fines is based on the sieving test CSN EN 933-1 [22]. The requirements of the fines content in aggregate for concrete is listed in the Czech standard CSN EN 12620 + A1 [3]. According to this standard, the defined limit of maximal fines content in aggregate for concrete is 3% without further requirements.

Calculate the percentage of fines for dry method (f) passing the 0.063 mm sieve in accordance with the following Equation:

$$f = \frac{P}{M} \times 100 \quad (2)$$

where f is fines content (%), M is the mass of the test portion (kg), and P is the mass of the screened material remaining in the pan (kg) [25].

2.3. *Ecotoxicity Experiments*

Air-dried samples of 100 g were mixed with 1000 mL of H_2O and homogenized on an overhead shaker (7 rpm) for 24 h [26]. Consequently, the solid particles in leachates were settled for 10 min and the liquid phase was centrifuged (2360× g, 10 min, 25 °C) and filtered through a membrane paper with pores of 4 µm. pH and electrical conductivity was determined in the filtrated leachates at room temperature. All the leachates were prepared in two replicates. Selected elements (Cu, Ni, Zn, As, Cd, Cr, Sb, Ba, Hg, Pb, Se, B, Mo, V, Ca, Na) were determined using atomic absorption spectrometry with flame atomizer 280FS AA developed by Agilent Technologies, Inc. (Santa Clara, CA, USA) in leachates after acidification by HCl to pH of 2.0.

Ecotoxicological bioassays were performed with both untreated leachates and leachates amended with relevant inorganic nutrients according to control media of the given test species. pH adjustment was not included in the leachate's treatment.

2.3.1. Freshwater Algae Toxicity Test

Algal growth inhibition test was performed with freshwater green algae *Desmodesmus subspicatus*, strain Brinkmann 1953/SAG 86.81 which was obtained from CCALA, IBOT, AS CR (Trebon, Czech Republic) partly following the ISO guideline 8692 [26]. Bold Basal Medium (BBM; pH 6.6 ± 0.2) according to [27] was used as the control medium. For the test 25 mL Erlenmeyer flasks were filled with 15 mL of leachate/control sample and inoculated with pre-cultivated algae (80 000 cells per 1 mL). Samples and controls were represented by triplicates or quadruplicates, respectively. Flasks were covered with sterile cellulose cap and placed under stable temperature (23 ± 1 °C), light cycle (16 h of light period; 6000–8000 l×), and continuous shaking (130 rpm) for 72 h. Algal cell density was determined via cell counting using microscope and Bürker chamber (Hecht, Germany).

For chlorophyll content determination 9 mL of algae in uspension was isolated by centrifugation (14,780× *g*, 10 min, 4 °C), 8 mL of pure methanol was added to sediment and homogenized. In case of algae clusters formation, dispersion of the cells was eased by placing into cooled ultrasonic bath for 2 min. After three days of extraction (dark, 4 °C, daily homogenization), extracts were centrifuged (14,780× *g*, 10 min, 4 °C) and absorbance at 653 and 666 nm was measured using spectrophotometer UV-1900 developed by Shimadzu Corporation (Kyoto, Japan). Total chlorophyll content per volume unit was calculated according to [28].

2.3.2. Mustard Germination Toxicity Test

Germination test was performed with mustard (*Sinapis alba*), variety Severka C1. Seeds were obtained from Aros company (Prague, Czech Republic). Petri dishes (diameter of 9 cm) containing membrane paper soaked with 5 mL of medium/sample were prepared in triplicates (samples) or quadruplicates (controls). The control medium consisted of $CaCl_2 \cdot H_2O$~294 mg·L^{-1}; $MgSO_4 \cdot 7H_2O$~123.25 mg·L^{-1}; $NaHCO_3$~64.75 mg·L^{-1}; and KCl~5.75 mg·L^{-1}; pH of 7.8 ± 0.2 adjusted by 1 M HCl. 17 seeds of approximately 1.5 mm in diameter were placed in a regular net on the membrane paper. Covered dishes were stored under stable temperature (20 ± 1 °C) in dark for 72 h. After exposition, plant root length was determined.

2.3.3. Lemna Growth Inhibition Test

Duckweed assay was proposed by ISO guideline 20079 [29] using *Lemna minor*, strain Steinberg originated from Federal Environmental Agency (Berlin, Germany). Steinberg medium modified by Altenburg (pH 5.5 ± 0.2) [29] served as the control. The test was carried out in 150 mL beaker filled with 100 mL of sample/control medium. Samples and controls were represented by three and five replicates, respectively. Each vessel was inoculated with 10 fronds of duckweed of a similar total frond area and covered with transparent film. Test vessels were kept in a stable temperature (24 ± 2 °C) and exposed to a light cycle (5000–6000 l×; 16 h light/8 h dark).

The total frond area was determined by image analysis using NIS Elements (Version 5.20, Laboratory Imaging, Prague, Czech Republic). Growth rate (GR) was calculated from the values based on repeated measurements during the test exposure, i.e., 0th, 3rd, and 7th day. After the 7-day exposition, fronds were extracted by pure methanol (48 h; 4 °C, dark) and the total chlorophyll content was determined spectrophotometrically (Shimadzu UV-1900, Shimadzu Corporation, Kyoto, Japan) according to [28].

2.3.4. Daphnia Acute Toxicity Test

Acute toxicity assay was performed with *Daphnia magna* juveniles aged up to 24 h, which were hatched from ephippia obtained from Microbiotests Inc. (Mariakerke (Gent), Belgium). The experimental design was done following ISO guideline 6341 [30] with some adjustments. Fresh ADaM medium (pH~7.8 ± 0.2) prepared according to [31] was used as control sample.

Five juvenile individuals were transferred into 25 mL beakers with 20 mL of leachate or control sample, covered with transparent film and put under stable temperature (20 ± 1 °C) and light cycle (1000–2000 l×; 16 h light/8 h dark). Each sample was represented by four replicates, whereas controls by six replicates. The inhibition of daphnia mobility (viability) was observed after the 48 h exposition.

2.3.5. Evaluation of Ecotoxicity Data

In algae and duckweed growth rate (GR) based on cell number and frond area respectively was calculated using Equation.

$$r = \frac{\ln X_{t1} - \ln X_{t0}}{t_1 - t_0} \quad (3)$$

where r is growth rate per day, X_{t0} is value of the parameter in t_0 (d), and Xt_1—value of the parameter in t_1 (d). [29].

All the ecotoxicological data (algal and frond GR, root elongation, chlorophyll content and daphnia viability) were consequently expressed as the values of inhibition/stimulation in percentage, where tested organisms in leachates were compared to control organisms using the following Equation.

$$I = \frac{X_{c0-}\ X_{ci}}{X_{c0}} \times 100 \quad (4)$$

where I is inhibition/stimulation of growth (%), X_{c0} is average value of control, and X_{ci}—average value of sample i. [29].

EC50 values were calculated from the inhibition data for all ecotoxicity tests using nonlinear regression.

3. Results and Discussion

3.1. Physical and Geometrical Properties

In the previous studies, it was found that the dry density of fine RCA (recycled concrete aggregate) ranges between 1900 and 2360 kg/m^3 [5] and fine RMA (recycled masonry aggregate) between 2000 and 2500 kg/m^3 [9–11,32–34] which is generally lower than natural sand. The range of water absorption of fine RCA ranges between 4.3% and 13.1% [5] and RMA from 12% to 15% [8,32,33], which is more than ten times higher than natural sand.

In this study, granulometry, dry density and water absorption of one type of NA and four types of RA were examined and compared (Figure 2). All types of RA were prepared from construction and demolition waste and sieved into fraction of 0–4. All types of RCA contained more than 90% of recycled waste concrete (unbound natural aggregate and cement mortar) and RMA contained more than 70% of the waste masonry (red brick, aerated concrete, and plaster).

All tested properties of RA differed from NA, especially the water absorption capacity, which was more than ten times higher and ranged from 2.1 to 8.8% for fine fraction of RA, where the highest water absorption was measured for RA 1 originated from waste concrete from recycling center. On the contrary the lowest water absorption was evaluated for RA 3, which originated from demolished floor structures and was partially prepared in the laboratory. The water absorption of RA 3 was measured for fraction 0.063/4 mm and 1/4 mm to show the influence of fines particles of aggregate. The results of water absorption show the slight relation with the fineness modulus. This evaluation shows slightly lower water absorption of RCA [5] and significantly lower water absorption of RMA [8,32,33] in comparison with the results of previous studies. The decline of dry density of fine RCA in comparison with NA ranges between 7 and 20% and the decline of dry density of fine RMA in comparison with NA is 10%. These results correspond with the results of previous studies [9–11,32–34]. The higher density was measured for RA3 of fraction 1/4 mm. Furthermore, the RA contains more fine particles and has different granulometry in comparison with NA and two examined types of aggregate (RA 1 and

RA 2) does not meet the requirements in Standard [3] (see Figure 3). Therefore, the basic physical properties of aggregates (see Table 1) and the basic geometrical properties of fine aggregate (see Table 2) are presented to show the differences in the materials and its comparison with natural sand.

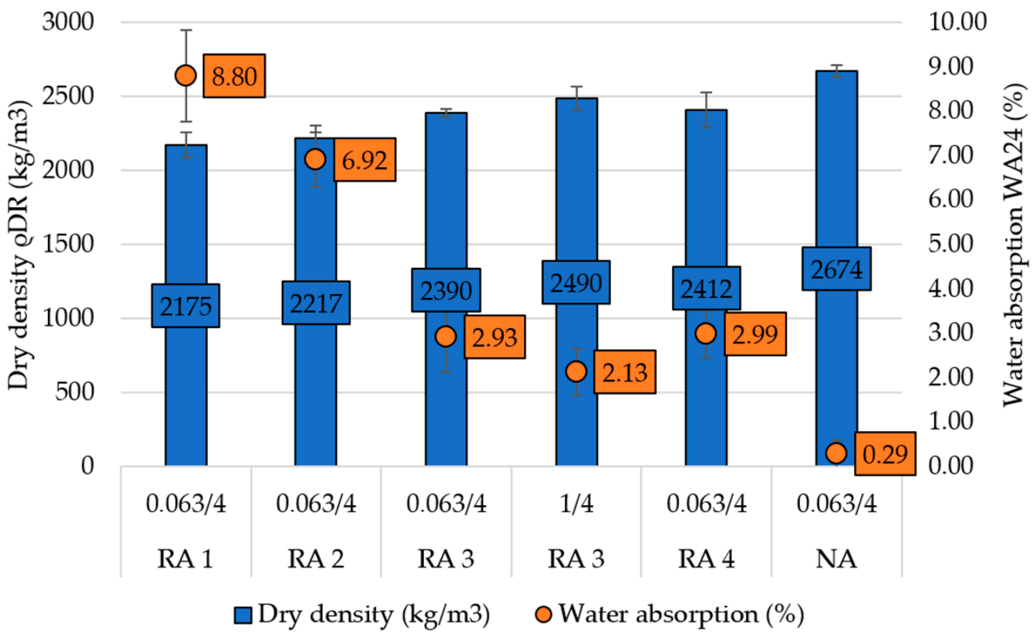


Figure 2. Oven-dry density and water absorption of aggregate according to CSN EN 1097-6.

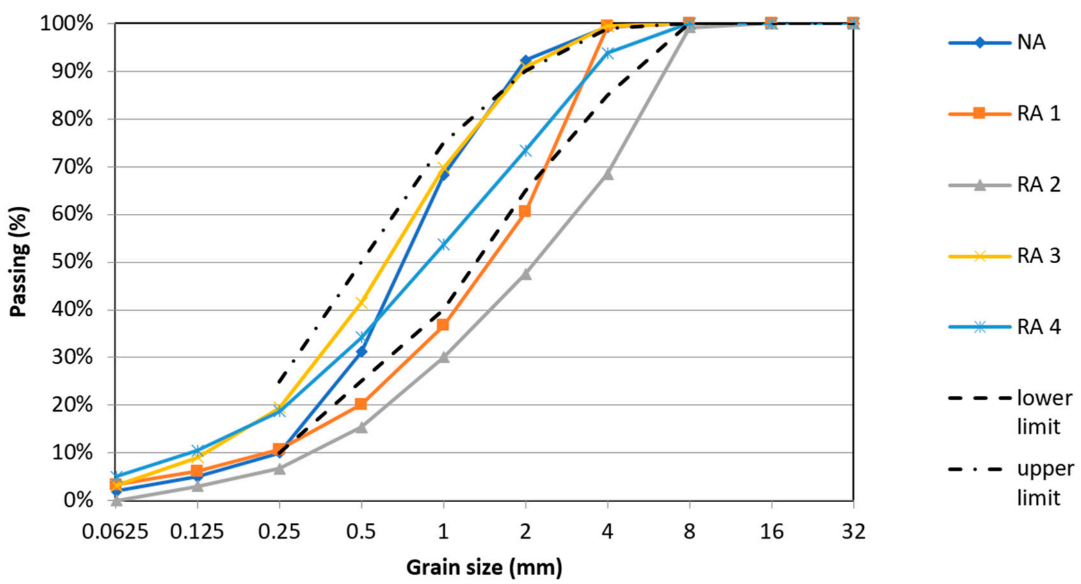


Figure 3. The particle size distributions of natural aggregate (NA) and RCA (grain size 0/4 mm) according to CSN EN 933-1.

Table 1. Basic geometrical properties.

Physical Properties	NA 0/4 mm	RA 1 0/4 mm	RA 2 0/4 mm	RA 3 0/4 mm	RA 4 0/4 mm
Fineness modulus	2.10	2.90	2.57	1.92	2.53
σ	0.06	0.03	0.08	0.88	0.14
Content of fines	2.0%	3.4%	3.1%	3.2%	5.1%
σ	0.2%	0.0%	0.8%	1.7%	1.1%

Table 2. Basic physical properties.

Type of Aggregate	Fraction (mm)	Oven-Dry Density (kg/m^3)		Water Absorption (%)	
		ρ_{RD}	σ	WA_{24}	σ
NA	0.063/4	2674	38	0.29	0.31
RA 1	0.063/4	2175	87	8.80	1.03
RA 2	0.063/4	2217	89	6.92	0.60
RA 3	0,063/4	2390	29	2.93	0.80
RA 3	1/4	2490	81	2.13	0.53
RA 4	0.063/4	2412	118	2.99	0.56

3.2. Ecotoxicity

Results showed different leaching behavior of the tested samples (Tables 3 and 4). All of the leachates were alkaline; from weakly basic NA to strongly basic RA 2. Similarly, the electrical conductivity varied. Very low ions content was found in NA which reflected the inert character of this material. The conductivity values of RA 1 and RA 4 were relatively close to the values of the control media of test organisms whereas RA 2 and RA 3 showed very high levels. As Table 3 shows, the selected heavy metals were at very low concentrations or under the detection limit in all the samples. For instance, zinc which plays an important role as a microelement for photosynthesis, homeostasis, and growth of microalgae [35] was far below the Zn concentration in BBM medium [27]. In RA 2 leachate barium content (1.056 mg·L^{-1}) was approximately 5–10 times higher in comparison with the other samples. However, concentrations below 5 mg·L^{-1} in freshwaters were found safe for duckweed [36] and acute toxicity for crustacean and green algae was observed in concentrations higher than 10 5 mg·L^{-1} [37] On the contrary the content of sodium and calcium was significant and showed the biggest differences among the leachates. The Ca content in RA 1 (80.08 5 mg·L^{-1}) was equal or similar to the Ca content in Steinberg and ADaM media whereas in RA 2 (660.57 5 mg·L^{-1}) the Ca content was 8–13 times higher.

Table 3. Basic chemical properties.

Chemical Properties		NA	RA1	RA2	RA3	RA4
Leachates	pH	8.1 ± 0.6	10.3 ± 0.0	12.2 ± 0.0	11.7 ± 0.1	8.6 ± 0.0
	el. conductivity (µS·cm^{-2})	27 ± 3	545 ± 13	7150 ± 80	2730 ± 10	1129 ± 6
Element (mg/l)	Ca	3	80.08	660.57	146	216.98
	Na	1	13.733	8.83	9.92	20.71
	As	<0.4	<0.4	<0.3	<0.3	<0.4
	Zn	0.027	~0.012	~0.011	~0.008	0.023
	Cu	<0.01	~0.02	<0.02	<0.02	~0.02
	Cr	<0.05	~0.05	~0.1	<0.05	<0.05
	Ba	<0.1	<0.1	1.056	~0.2	<0.1
	Se	<0.4	<0.4	<0.5	<0.5	<0.4
	Pb	<0.04	<0.04	<0.06	<0.06	<0.04
	Hg	<0.001	<0.001	<0.001	<0.001	<0.001

Table 4. Properties of control media.

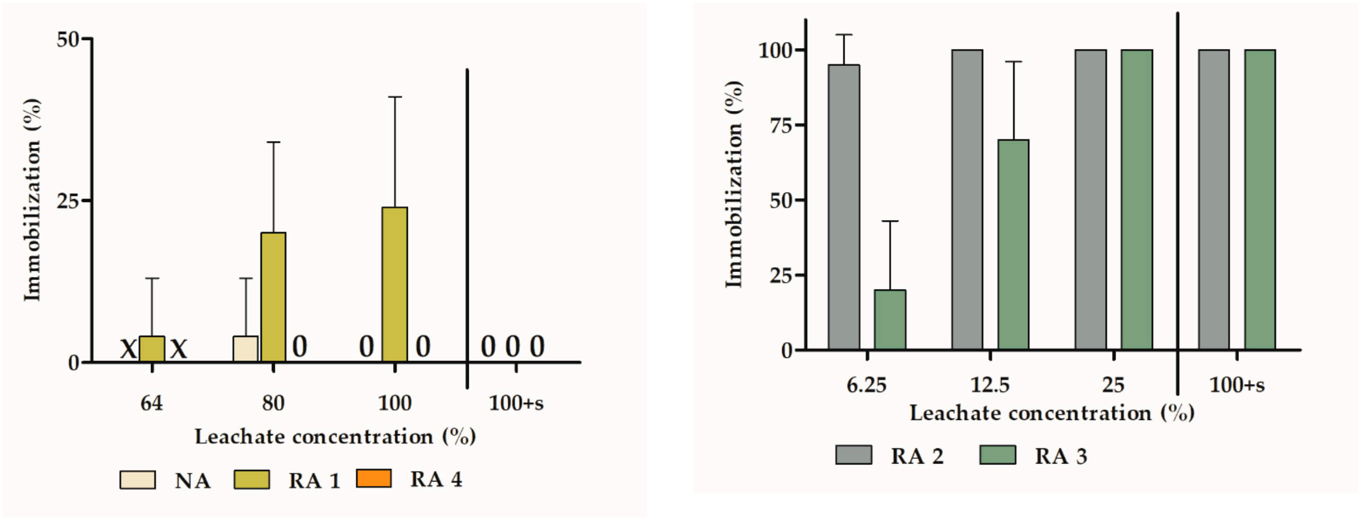
Properties. of Control Media		*Lemna*	Algae	*Sinapis*	Daphnia
	pH	5.5 ± 0.1	6.6 ± 0.1	7.8 ± 0.2	7.8 ± 0.2
	el. conductivity (µS·cm^{-2})	977 ± 15	853 ± 12	625 ± 7	829 ±15

The response of the model organisms to the tested samples is shown in Figure 4. Generally, exposure to RA 4 leads to the lowest effect on test organisms with no effect on daphnia (Figure 4a) and only slight reduction of mustard root length (Figure 4c) and duckweed chlorophyll content (Figure 4f). The growth and chlorophyll reduction in both algae and duckweed (Figure 4b,e and Figure 5b,e,i) in non-treated 100% NA leachate was caused by the lack of minerals. However, there was no growth reduction after addition of nutrients or dilution of the non-treated leachates to 80%. In RA 1 leachate (non-treated and 80% dilution) growth inhibition effect was observed which was caused probably because of the higher pH of the sample (Table 3). Further dilution of the leachate led to pH decrease and no-effect or stimulation of the organisms' growth. For the ecotoxicity comparison EC50 values were calculated for leachate concentration in % (Table 5). Classification of ecotoxicity level was done according to [38]. The calculated EC50 values of NA, RA 1, and RA 4 were higher than the concentrated leachates. Thus, according to [38] these samples were classified as non-toxic.

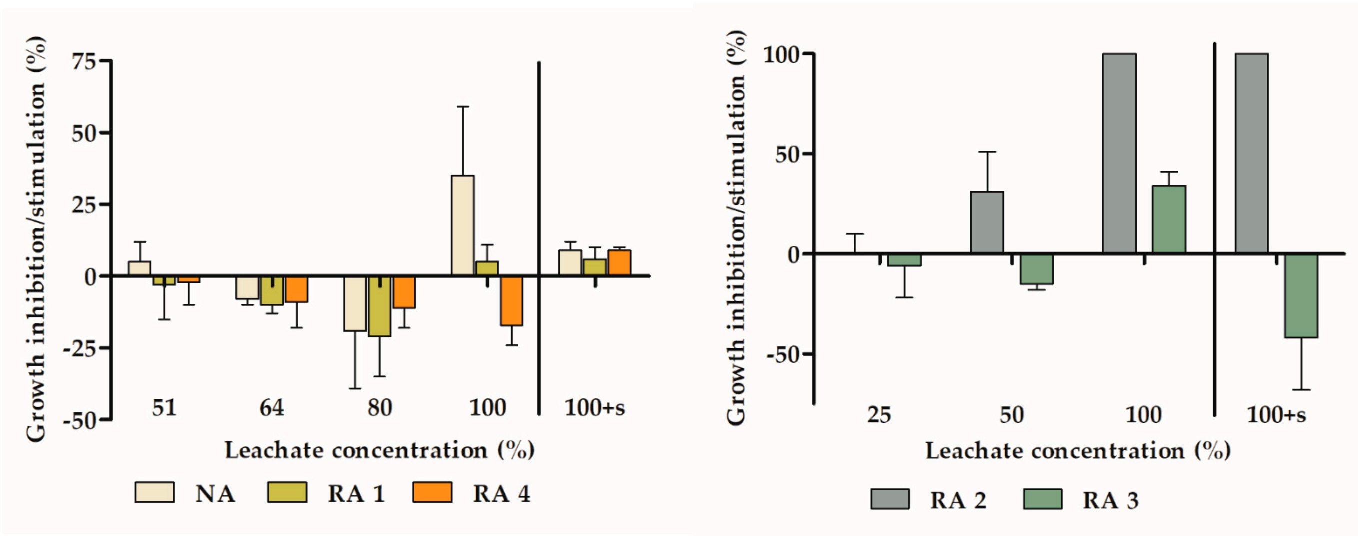
In RA 2 and RA 3 samples both untreated and nutrients-amended non-diluted leachates the lethal effect was observed for all the test organisms except for mustard (Figures 4 and 5e,g). Because of higher toxicity effect, different dilution rates had to be performed in these leachates. Inhibitory or toxicity effect was shown mainly in duckweed growth, chlorophyll and especially daphnia. According to [38] these leachates were classified as inhibitory—mild toxic (Table 5). The ecotoxicity of concrete leachates can result both from toxic compounds presence and alkalinity [12,39,40]. Besides the high conductivity in RA 2 and particularly RA 3 (Table 4) the pH values remained highly alkaline even after dilution of the original leachates unlike in the case of NA, RA 1, and RA 4 samples. In accordance with our previous study [41] we hypothesize that the high conductivity might contribute to the buffering capacity of the leachate and thus maintain the toxicity of the samples with time and/or dilution. As a most probable reason of the alkalinity was the high content of calcium ions, however, this statement will have to be verified in the further testing.

The most sensitive bioindicator of ecotoxicity was daphnia which was already recommended for ecotoxicological assessment of concrete leachates [39,42]. Our study also confirmed duckweed as a suitable plant test organism because of its sensitivity where toxic effect can be detected on both morphological and biochemical level and various symptoms such as necrosis can be observed. Because of the photo-documentation of the test plants, the behavior of the sample within time can be also monitored, e.g., precipitation of the salts in leachates, especially in variants with nutrient addition or those with high conductivity values (Figure 5c).

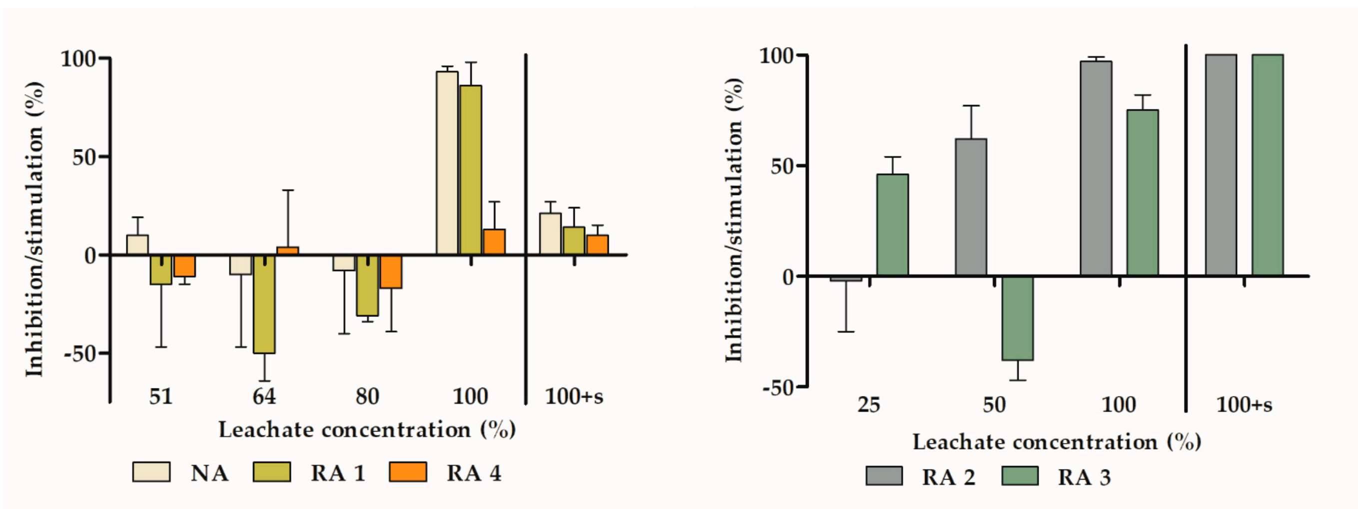
Based on the ecotoxicity results, the samples RA 2 and RA 3 are suitable to verify the prediction that use of waste materials in concrete can lead to their immobilization. These samples were picked because of their properties, especially higher toxicity level (inhibitory—mild toxic), but other aspects should also be considered. RA 3 with lower water absorption and higher bulk-density also fulfills the limits of current standards in particle size distribution.



(**a**)

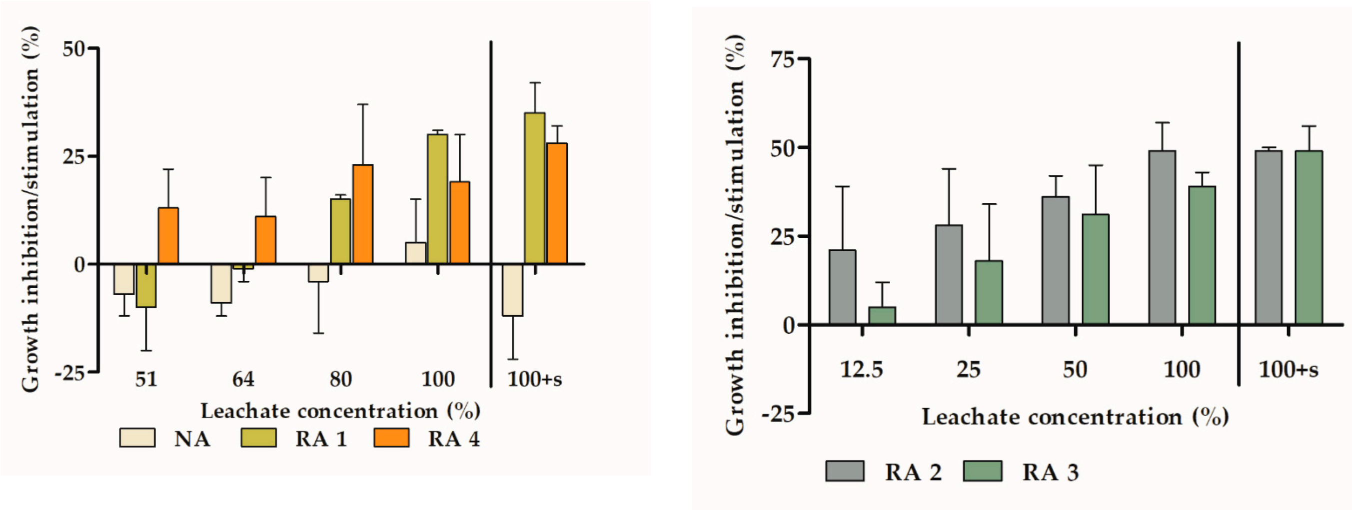


(**b**)



(**c**)

Figure 4. *Cont.*



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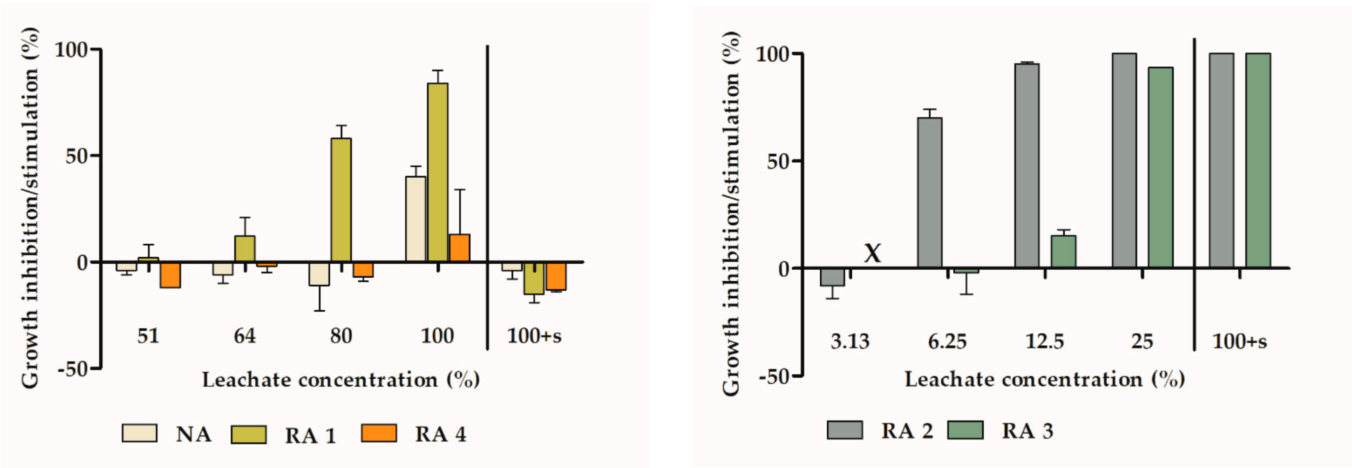
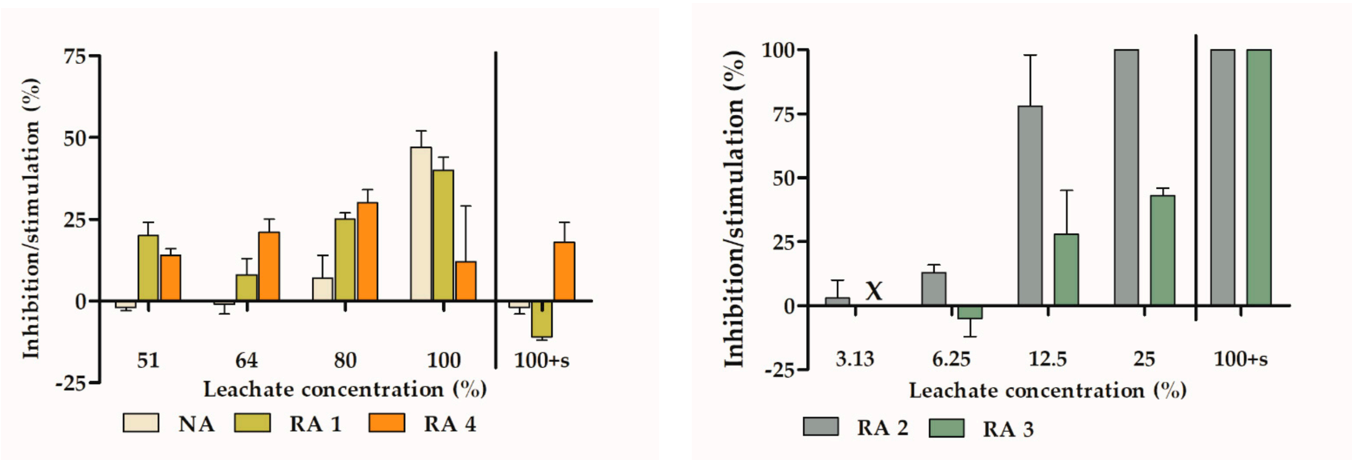


(**e**)



(**f**)

Figure 4. The results of ecotoxicity experiments: (**a**) Daphnia immobilization, (**b**) algae growth rate, (**c**) algae chlorophyll content, (**d**) mustard root elongation, (**e**) *Lemna* growth rate, (**f**) *Lemna* chlorophyll content. X—not determined, 0—zero values, 100 + s—leachates amended with nutrient salts.

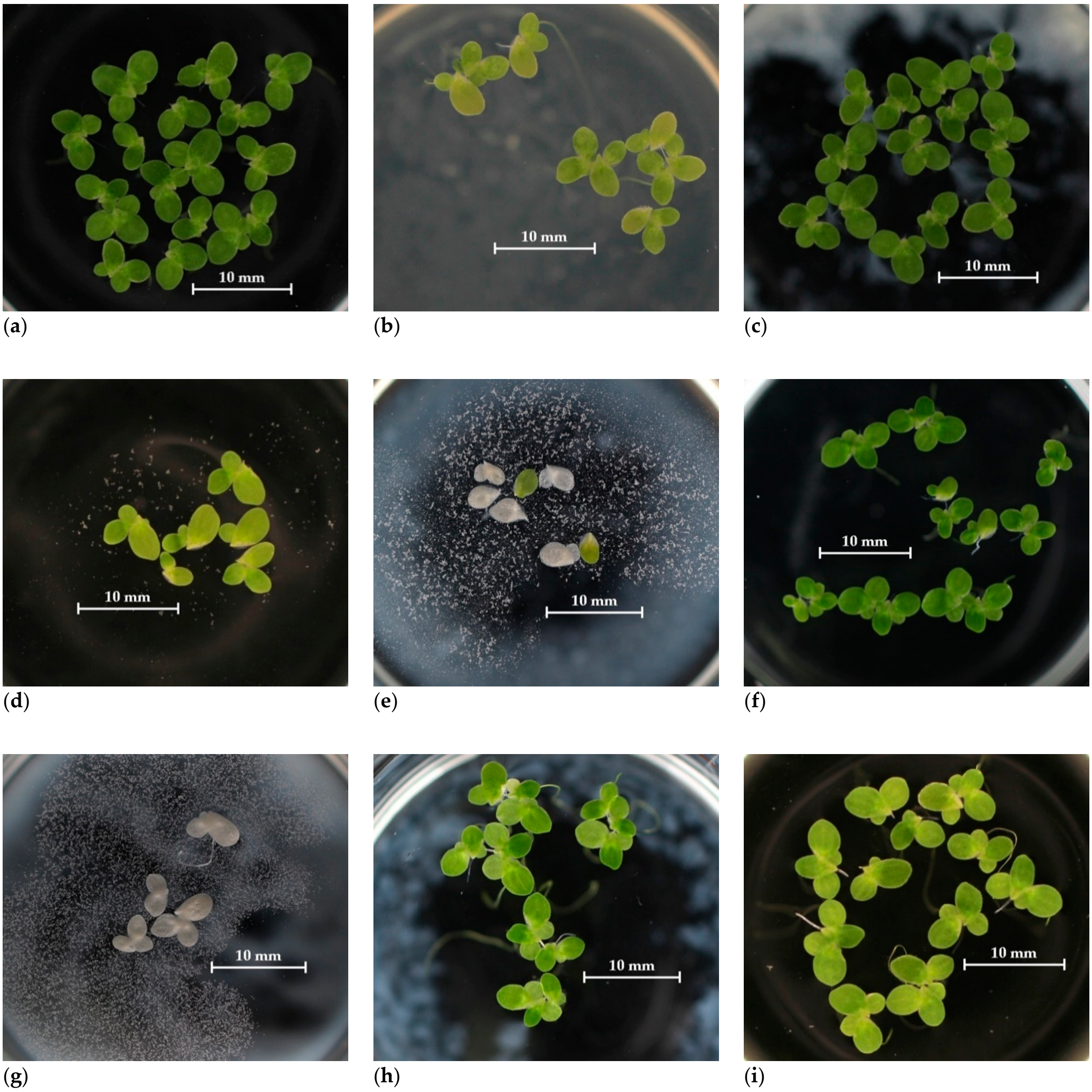


Figure 5. Test plants photo-documentation: (**a**) control, (**b**) NA—100%, (**c**) NA—salts, (**d**) RA 1—100%, (**e**) RA 2—12.5%, (**f**) RA 2—1.56%, (**g**) RA 3—100 + s, (**h**) RA 3—12.5 %, (**i**) RA 4—100%.

Table 5. EC50 values and ecotoxicity assessment of leachates. GR—growth rate; chl—chlorophyll content; TC—toxicity class.

Type of Aggregate	Daphnia	Sinapis	Algae GR	Algae Chl	*Lemna* GR	*Lemna* Chl	Toxicity Level
NA							
EC50	>100	>100	~100	~97	~100	>100	
TC	A1	A1	A2	A2	A1	A1	non-toxic
RA 1							
EC50	>100	>100	~100	~99	78	>100	
TC	A2	A3	A2	A2	A3	A2	non-toxic
RA 2							
EC50	~5	>100	~54	~49	~6	9	
TC	C	A3	A3	B	C	C	Inhibitory—mild toxic
RA 3							
EC50	~7	>100	>100	~95	16	26	
TC	C	A3	A1	B	B	B	Inhibitory—mild toxic
RA 4							
EC50	>100	>100	>100	>100	>100	>100	
TC	A1	A2	A2	A2	A1	A2	non-toxic

4. Conclusions

This research examined and discussed the experimental verification of physical and geometrical properties of recycled concrete aggregate from four different sources. Tested samples (RA 1–4) were measured and compared with the reference samples (NA). The ecotoxicity tests were made to verify the impact of harmful substances to environment. Based on provided experiments, the final conclusions are summarized in the following points:

- The water absorption of RA 1–4 is up to ten times higher than NA. The highest absorption was measured on RA 1, the lowest on RA 3.
- The highest density was measured on RA 3, which corresponds with the lowest water absorption measured on this sample.
- Samples RA 1 and RA 2 provided higher number of fine particles in the particle size distribution and the limits of the current standards have not been fulfilled.
- Ecotoxicity of the tested leachates increased from non-toxic effect in NA, RA 1, and RA 4 to inhibitory effect or mild toxicity in RA 2 and RA 3 in following order:

$$\text{NA} \sim \text{RA 1} \sim \text{RA 4} < \text{RA 3} \leq \text{RA 2} \tag{5}$$

The novelty of this study is in the effort to create a comprehensive analysis of potential environmental threats in the ecotoxicology point of view considering the physical and geometrical properties of RA. This work presents the results of the effect of waste materials on leachates and ecotoxicity. Because of the higher mortality of the tested organisms, landfilling of these materials is not appropriate. A more suitable variant seems to be the use in concrete because of the new assumption that the use of waste materials in concrete leads to their immobilization. This assumption is verified in a follow-up research.

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Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflict of interest.

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Appendix 5

Ecotoxicity of Concrete Containing Fine-Recycled Aggregate: Effect on Photosynthetic Pigments, Soil Enzymatic Activity and Carbonation Process

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Abstract: Recycling materials such as masonry or concrete is one of the appropriate ways to reduce the amount of disposed construction and demolition waste (CDW). To verify the overall environmental benefits of recycled concrete, this work deals with the ecotoxicity of recycled concrete as well as the potential environmental impacts of their life cycle. Additionally, impacts related to carbonation of concrete are considered in terms of durability and the effect of potential CO2 absorption. Concrete containing fine recycled aggregate from two different sources (masonry and concrete) was experimentally investigated at the biochemical level and compared with reference samples. Leaching experiments are conducted to assess physicochemical properties and aquatic ecotoxicity using water fleas, freshwater algae and duckweed. Consequences such as the effect of the material on soil enzymatic activity (dehydrogenase activity), photosynthetic pigments (chlorophylls and carotenoids) and the carbonization process are laboratory verified and included in comparison with theoretical life cycle assessment. In conclusion, the ecological soundness of the recycled concrete was verified and its overall potential impact on the environment was lower compared to the reference concrete.

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Ecotoxicity of Concrete Containing Fine-Recycled Aggregate: Effect on Photosynthetic Pigments, Soil Enzymatic Activity and Carbonation Process

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Abstract: Recycling of materials such as masonry or concrete is one of the suitable ways to reduce amount of disposed construction and demolition waste (CDW). However, the environmental safety of products containing recycled materials must be guaranteed. To verify overall environmental benefits of recycled concrete, this work considers ecotoxicity of recycled concrete, as well as potential environmental impacts of their life cycle. Moreover, impacts related with carbonation of concrete is considered in terms of durability and influence of potential CO_2 uptake. Concrete containing fine recycled aggregate from two different sources (masonry and concrete) were examined experimentally at the biochemical level and compared with reference samples. Leaching experiments are performed in order to assess physicochemical properties and aquatic ecotoxicity using water flea, freshwater algae and duckweed. The consequences, such as effects of material on soil enzymatic activity (dehydrogenase activity), photosynthetic pigments (chlorophylls and carotenoids), and the carbonation process, are verified in the laboratory and included in the comparison with the theoretical life cycle assessment. As a conclusion, environmental safety of recycled concrete was verified, and its overall potential environmental impact was lower in comparison with reference concrete.

Keywords: recycled concrete; carbonation; life cycle assessment

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1. Introduction

Construction and demolition waste (CDW) constituted approximately 35.9% of the total waste production in the EU in 2018. CDW, as one of the highest waste streams, consists of materials like red bricks, mortar, masonry, and concrete, which can be recycled and used as secondary raw materials. This approach reduces not only waste but also the demand for primary resources. However, there is a risk of using recycled materials with content, which is potentially harmful to human health or the environment. Therefore, prior to their use, the ecotoxicity of such materials must be tested using ecotoxicological bioassays and their potential environmental impact should be assessed.

To evaluate the ecotoxicological impact of concrete containing recycled materials, bioassays according to the European law system can be performed. These tests are designed to determine the potential influence of various chemicals or their mixtures, along with the transport from the source to the reservoir. To model this transport, the leachates of considered materials are prepared. However, just the impact caused by bioavailable chemicals can be evaluated using these tests.

Ecotoxicity of construction waste or materials was assessed in previous studies, which were carried out with a simple test design, such as the freshwater algae growth test, seed germination test, crustacean acute assay, marine bacteria bioluminescence test, or the yeast growth test [1–5]. Nevertheless, tests with these organisms are focused on the influence of chemicals on water ecosystems only.

Green plants (algae, aquatic and terrestrial plants) are usually examined not only at morphological level, such as growth rate or yield. Photosynthetic pigments represent the most typical chemicals in plants. Chlorophylls are closely related to primary production, while carotenoids serve as protection against adverse effects of the environment. Both groups of pigments are known to be sensitive to contamination, alkaline pH, and consequently oxidative stress [6–8]. With a significant decrease in chlorophyll, it is likely that plant growth will also decrease. An increase in total carotenoids indicates internal oxidative stress, which can result from lack of nutrients, heavy metal accumulation, and other stresses associated with the formation of reactive oxygen species (ROS) [9].

Impacts on soil ecosystems can be assessed using tests focused on nonspecified microbial communities where a selected metabolic activity is determined. Soil enzymes are produced mainly by bacteria and fungi, and are suitable for the determination of various external effects on the soil microbiota [10]. Various methods for the determination of soil enzymes, such as oxidoreductases, hydrolases, transferases, etc., have been described [10], but the most often found soil enzymes belongs to the group of dehydrogenases (DHA). In contrast to most soil enzymes, DHA are intracellular, and so DHA can be used as an indicator of living (active) cells [11].

Besides ecotoxicological impact, other environmental impacts, such as an impact on climate change, should be assessed. The impact of CO_2 emissions is one of the most discussed issues in the European Union. The EU aims to reduce CO_2 emissions values by 40% by 2030 [12]. Moreover, up to 9% of CO_2 emissions are directly related to the construction industry, and about 3% specifically to concrete [13]. This is also associated with a large amount of energy consumption, which is spent on the construction process (from material production, building the construction, construction life, and also demolition). This amount is estimated to be up to 40% of total energy consumption [14].

On the other hand, one of the beneficial influences of concrete is the absorption of CO_2 during a slow process called carbonation, in which CO_2 reacts with the cement matrix, mainly portlandite. Limit conditions for this reaction are the environment, the amount of carbon dioxide in the air, and the type of concrete (great influence, e.g., porosity) [15–20]. The CO_2 and moisture of the environment neutralize concrete by forming calcium carbonate and reducing alkaline balance, which means that the initial properties are rapidly changing during the carbonation process. During the reaction, the pH values decrease from 12–12.5 to 9, and as a result the protective properties of the material are weakened and a suitable environment appears for the development of corrosion [21]. These effects decrease the quality and possible utilization of concrete, and so the speed of carbonation is used to characterize the concrete quality. Thus, many researchers have stated that the durability of concrete is better with slower carbonation speed [22,23]. However, even concrete with a higher speed of carbonation can be used in some applications. Thus, subsequent absorption of CO_2 by concrete should be assessed as a potential benefit and compared with other environmental impacts in the life cycle of concrete.

Potential environmental impacts caused by recycled concrete can be assessed using the Life Cycle Assessment (LCA) method. The LCA is used to analyze not only the life cycle of the concrete itself, but also material and energy flows between the concrete and the environment, as well as the impact of these flows. In life cycle assessment, it is necessary to take into account the issue of care for the structure at the end of its life, and also benefits such as CO_2 uptake.

This study aims to verify the environmental safety of different types of concrete containing recycled aggregates in two strength classes. Each strength class had its own reference sample (control) with which the recycled mixtures were compared. These environmentally friendly mixtures have been designed with regard to the properties of individual materials and are intended for use in the construction sector, for example, as the foundations of buildings. In addition to the influence of leachates on aquatic plants and invertebrates, this research deals with the determination of photosynthetic pigments and impact on soil enzymes. Recycled concretes were exposed to the carbonation test, to analyze the impact of the environment on the samples. The rate of CO_2 absorption was measured according to the valid Czech standard ČSN EN 12390-12 (73 1302) [24]. Following the gained practical knowledge from laboratory experiments, the theoretical level was evaluated in the form of life cycle analysis.

2. Materials and Methodology

2.1. Materials

This work is based on the solid foundations of previous research, which verified the chemical analysis and ecotoxicity of selected waste materials from different sources [25]. The authors investigated four types of waste materials, and after evaluation and verification, two types were picked and used in this investigation as a substitute for natural aggregate. Natural aggregate concrete (NAC), which contains natural aggregate, was used as a reference sample in both strength classes.

Two types of strength class were tested to compare the properties:

- Strength class I—corresponds to ordinary concrete in strength class C16/20
- Strength class II—corresponds to ordinary concrete in strength class C25/30

In each strength class was the reference sample containing natural aggregate and two types of samples with recycled aggregate. Therefore, there were a total of three samples in each strength class (reference sample and two mixtures with recycled aggregate). Thus, a total of six mixtures were tested (two strength classes of three mixtures each).

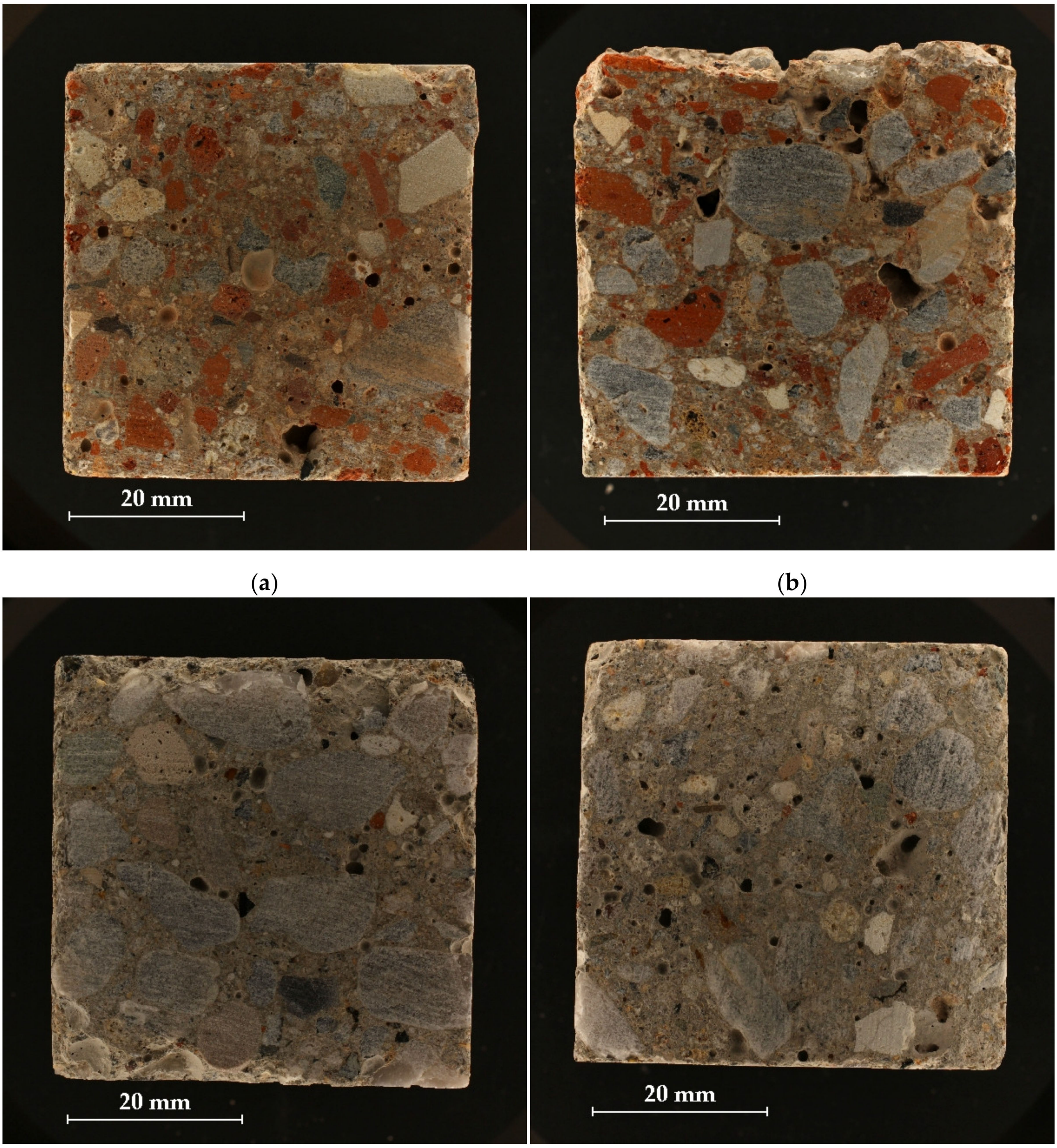
The first type of recycled aggregate used originates from masonry structures and contains mainly red bricks, mortar, and plasters (RA4) [25]. It was prepared from reinforcement concrete at the recycling center using the two-step recycling process and used in recycled masonry aggregate concrete (RMAC) in this research. This type of concrete was made in two mixtures with different strength classes (RMAC-I, RMAC-II).

The second type of aggregate used was prepared from reinforcement concrete in the recycling center by the two-step recycling process (RA1) [25]. The crushed and separated recycled aggregate of fraction 16/128 mm from the first step of the recycling process was crushed and sieved into fractions in the second step. Two concrete mixtures containing RA1 were prepared (RCAC-I, RCAC-II).

In general, six concrete mixtures were made and tested in the field of ecotoxicity at the biochemical level with regard to environmental impacts; specifically, a comparison of actual exposure and potential life cycle was examined.

- NAC-I, as a reference concrete sample for strength class C16/20
- RMAC-I, as recycled concrete containing RA4, strength class C16/20.
- RCAC-I, as recycled concrete containing RA1, strength class C16/20.
- NAC-II, as a reference concrete sample for the C25/30 strength class
- RMAC-II, as a recycled concrete containing RA4, strength class C25/30
- RCAC-II, as recycled concrete containing RA1, strength class C25/30.

The tested samples containing recycled aggregates are shown in Figure 1.



(a) (b) (c) (d)

Figure 1. Tested samples containing recycled aggregates: (**a**) RMAC I, (**b**) RMAC II, (**c**) RCAC I, and (**d**) RCAC II.

2.2. Methodology

In this research, recycled aggregate was used that has been tested in previous research [25] with the aim of proving the possibility of replacing normally used raw materials in concrete with secondary raw materials. On the basis of the results from previous research, materials were selected and concrete mixtures were designed, which were subsequently exposed to the experiments on the basis of the international standards. All samples were tested according to the valid Czech standards as well.

2.3. Ecotoxicology

2.3.1. Chemical and Ecotoxicological Analysis of Leachate

The concrete cubes were leached as described in [26]. The concentrations of Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Ba, Hg, and Pb were determined in leachates acidified to pH 2.0 using inductively coupled plasma optical emission spectrometry (Integra 6000, GBC, Melbourne, Australia).

Aquatic ecotoxicity tests were performed with non-treated leachates in the concentration range from 510 to 1000 $mL.L^{-1}$, and nutrient-amended leachates diluted 10 times (100 + n $mL.L^{-1}$). The water flea (*Daphnia magna*) acute immobilization test followed the methodology described in [26]. The algal toxicity test using *Desmodesmus subspicatus* and the duckweed (*Lemna minor*) test were conducted according to [25] with minor changes. In algae, growth rate was determined based on optical density measurements at 750 nm using a UV/VIS spectrophotometer UV-1900 (Shimadzu Corporation, Kyoto, Japan).

2.3.2. Determination of Photosynthetic Pigments

In the algal and duckweed test, the total chlorophyll a + b (Chls) and total carotenoid (Cars) content was determined after the exposition and growth rate determination.

First, 10 mL of algal suspension was transferred to 15 mL Falcon tubes and centrifuged (2360× *g*, 10 min, 4 °C). The supernatant was disposed of and 5 mL of 99.5% methanol (Lach-Ner) was added. The samples were homogenized in a vortex homogenizer for 15 s and placed in an ultrasound bath with ice-cooled water for 15 min. The extracts were homogenized again and centrifuged (2360× *g*, 10 min, 4 °C). The absorbance in the supernatants was determined at 470, 653, and 666 nm. Total chlorophylls and carotenoids were calculated according to [27] and expressed as pigment content per unit of algal suspension volume and as the Chls/Cars ratio.

In the duckweed test, the total frond material from a test vessel was transferred to a 15 mL centrifugation tube, covered with 3–8 mL of pure methanol (according to the total frond amount) and placed in the dark and 4 °C for 24–48 h. After extraction, the samples were centrifuged (2360× *g*, 10 min, 4 °C) and the absorbance in the supernatants was determined at 470, 653 and 666 nm. Total chlorophylls and carotenoids were calculated according to [27] and expressed as pigment content per unit of frond area and as the Chls/Cars ratio.

The absorbance was determined using the UV/VIS UV-1900 spectrophotometer (Shimadzu, Kyoto, Japan).

2.3.3. Soil Enzymatic Test

To determine the influence on soil enzymes, leachates were added to Lufa soil 2.4, characterized as clayey loam type (LUFA Speyer, Speyer, Germany). Fifty grams of air-dried soil were properly mixed with 15.3 g of nondiluted and untreated leachate in a sterile glass jar to achieve 70% WHC. Pure distilled water was used as a control sample. The containers were covered with sterile aluminum and placed under stable conditions (20 °C, light cycle 16 h/8 h; 1000 lux). The samples were left without humidity treatment for 56 days. Dry mass content (DM), pH, and soil dehydrogenase activity were determined 7, 28, and 56 days after soil contamination.

For the DM content, approximately 2.5 g was dried at 105 °C for 2 h and weighed. For this measurement, two replicates were prepared. DM was calculated as the fresh mass/dry mass ratio. The soil pH was determined in soil suspensions in 0.01M $CaCl_2$, as described in [28].

Soil dehydrogenase activity (DHA) was determined using triphenyltetrazolium chloride (TTC; Sigma-Aldrich) as a substrate for the reaction. The procedure followed ISO Guideline No. 23753-1 [29] with some adjustments. For each sample, 2.00 ± 0.05 g was transferred to a sterile glass tube and 2 mL of 1% TTC solution in Tris buffer (pH of 7.8) was added. Each sample was prepared in triplicate, plus one blank (2.00 ± 0.05 g of soil, 2 mL of Tris buffer). The samples and blanks were carefully homogenized for 10 s and placed on a dark thermostat (25 °C) for 20 h. After that, each sample was extracted using 10 mL of 99.5% acetone (Lach-ner) and homogenized three times, every 60 min. Finally, the extracts were centrifuged (2360× *g*, 10 min, 4 °C) and the absorbance at 485 nm was determined (UV/VIS spectrophotometer (Shimadzu, Kyoto, Japan). The DHA was expressed as the amount of product formation, i.e., triphenyltetrazolium formazan per soil DM and time. Consequently, the data obtained were compared to the control values and recalculated as % inhibition/stimulation, as described in [26].

2.3.4. Statistical Analysis and Data Evaluation

A one-way ANOVA was performed on all ecotoxicity data sets. Normality was tested using the Shapiro–Wilk test. ANOVA was followed by Tukey's post-hoc test to determine significant differences between samples. The nonparametric Kruskal–Wallis test followed by Dunn's post-hoc test was used when the data did not meet the normal distribution. Ecotoxicity based on EC50 and NOEC values was evaluated according to the scale formulated in a previous study [26]. All statistical analysis was performed using GraphPad Prism, v9.1 (GraphPad Software, San Diego, CA, USA).

2.4. Carbonation Testing Process

Concrete structures need to be durable to ensure that service life is achieved; This plays a significant role in resistance to corrosion. This phenomenon is caused by carbonation; consequently, carbonation behavior is an important attribute to measure.

The simplified carbonation reaction of concrete:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \quad (1)$$

The Czech standard ČSN EN 12390-12 (73 1302) describes the carbonation resistance of concrete using test conditions that accelerate the rate of carbonation [24]. The method used in this research is inspired by this standard, but the conditions were slightly different.

Czech Standard ČSN EN 12390-12 (73 1302)

This document quantifies the carbonation resistance of concrete. The test conditions used an accelerated the rate of carbonation. The experiment is carried out under controlled exposure of carbon dioxide to an increased level after 28 days of hardening concrete samples. The carbon dioxide concentration should be within ±0.5% by volume of the target value.

For each test, the reference sample of concrete should be used. Samples for one test should be made from one concrete mixture. The concrete cubes are cast and cured for 28 days (in accordance with EN 12390-2 [30]), then placed in a storage chamber with carbon dioxide under normal conditions: 1 013 mbar at 25 °C, temperature 20 ± 2 °C, relative humidity 57 ± 3. In addition, 0.8 g of phenolphthalein powder was dissolved in a solution of 70 mL of ethanol and 30 mL of deionized water. Phenolphthalein was used as an indicator.

After the exposure period, which is 28 days, the carbonation depth is measured at three points on each of the four faces of the cube. To locate these points, the length of the edge is divided into four equal distances. Three samples of each mixture were measured and the mean carbonation depth at time t in mm was calculated as a result.

2.5. Life Cycle Assessment

To analyze the environmental performance of the described mixtures from the perspective of their entire life cycle, the life cycle assessment (LCA) method was applied as an analytical tool [31], which is used primarily to assess the environmental impacts caused by processes throughout the life cycle of a product or service according to the international standards ISO 14 040 and ISO 14 044 [32,33]. According to these standards, the LCA method consists of four steps: definition of goals and scope, inventory analysis, impact assessment, and interpretation.

Taking into account the scope and other conditions for the environmental assessment described in EN 15 804 + A2 for construction products [34], the LCA method was used to evaluate all elementary flows, including the inputs and outputs of materials and energy to the environment in the phases of raw resource production, transport of resources to the facility, production of ready mix concrete, and disassembly of concrete and its disposal in landfill.

2.5.1. System Boundaries and Functional Unit

The environmental impacts of the mixtures were related to the declared unit, which was defined as 1 m^3 of the concrete mixture. The system boundaries of the compared concrete mixtures include raw material supply (cement production, water production, production of primary or recycled aggregate), transport of resources to a facility, mixing of materials, and their transport to site. The phase of use of concrete mixtures was not included according to EN 15 804 + A2. The boundaries of the system also include the end-of-life phase (EoL), which consists of the excavation of concrete in the process of deconstruction, the transportation and demolition of concrete waste in the landfill, and the disposal of waste in the landfill. The investigated system boundaries are described in Figure 2.

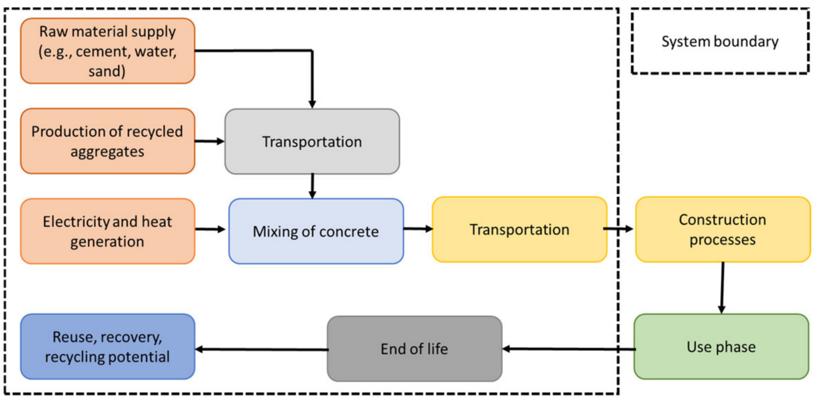


Figure 2. Description of the boundaries of the system.

2.5.2. Life Cycle Inventory

To create the environmental model of the life cycle of the mixtures, GaBi software was used [35]. The mixtures were modelled according to the proportions described in Table 1. To model upstream processes, generic data from the GaBi database were used to describe the environmental impacts of resource production [36]. In addition, the end-of-life processes of concrete were modelled using the mentioned generic data. The energy supply was modelled using the Czech energy mix according to data from the reference year 2016. The transport processes were modelled as transporting on a 50 km distance using a truck trailer (EURO 3, up to 28 t gross weight).

Table 1. Composition of concrete mixes.

Material (kg)	I			II		
	NAC	RMAC	RCAC	NAC	RMAC	RCAC
Cement	260	260	260	300	300	300
Nature Sand	709	-	-	671	-	-
Gravel 4/8	38	-	-	28	-	-
Gravel 8/16	1092	766	949	1139	822	994
Recycled Aggregate 0/4	-	971	843	-	920	800
Water	169	187	186	165	182	181

2.5.3. Influence of Carbonation

As an alternative scenario, the CO_2 uptake potential in concrete was calculated according to EN 16 757 [37]. The expected service life of concrete blocks made of the considered mixtures was assumed to be 50 years. The maximum theoretical uptake of CO_2 was estimated for the cement used as 0.49 kg CO_2/kg of cement. The assumed degree of carbonation was estimated at 0.85 on the basis of the potential future use of concrete as a foundation structure, which will be covered by ground.

2.5.4. Environmental Assessment

To evaluate the impacts of inputs and outputs on the environment, these elementary flows were classified and characterized using the Product Environmental Footprint 3.0 method [38]. This impact assessment method is recommended by the European Commission and uses several environmental indicators [39].

2.5.5. Normalization and Weighting

Taking into account the spectrum of environmental indicators, the results were normalized and weighted to obtain a single score evaluation of the mixtures considered. Normalized values were calculated by dividing the indicators' results by normalized contributions for each indicator according to the normalization data set described in the PEF 3.0 method [39]. Similarly, the weighted values were calculated by multiplying the normalized results using weighting factors. Weighing is used to express the relative importance of each indicator. The data set of the weighing indicators is based on expert opinion and is described in the PEF 3.0 method [39].

3. Results

3.1. Physicochemical Properties of Concrete Leachates

Table 2 shows the results of the chemical analysis of the leachates. Mn, Co, Ni, Cu, As, Se, Mo, Cd, Ba, Hg, and Pb were below the detection limit; Cr was found only in NAC I. The main elements found in the leachates were Ca, K, and Na, while the concentration of Mg, Al, Fe, Zn, and Sr was below 0.5 mg.L^{-1}. The chemical composition of the leachates was generally relatively similar. Only Zn content showed different patterns, with the highest content in RMAC I and the lowest content in NAC I. All leachates had similar pH (10.5–10.7), as well as electrical conductivity (162–232 µS.cm^{-2}). The initial pH value decreased to 7.5–8.4 after both dilution and seven-day exposure under the light cycle and 24 ± 1 °C in the duckweed assay (Supplementary Materials, Table S1).

Table 2. Physicochemical properties of leachates.

Element (mg.L^{-1})	I			II		
	NAC	RMAC	RCAC	NAC	RMAC	RCAC
Na	3.04 ± 0.05	3.96 ± 0.09	<2.5	<2.5	4.16 ± 0.17	<2.5
Mg	0.20 ± 0.01	0.29 ± 0.01	0.24 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	0.20 ± 0.01
Al	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	17.27 ± 0.32	15.66 ± 0.63	14.20 ± 0.46	14.03 ± 0.49	19.19 ± 0.32	12.82 ± 0.11
Ca	28.85 ± 0.23	29.44 ± 0.95	24.68 ± 0.49	21.19 ± 0.59	19.75 ± 0.33	22.13 ± 0.49
Cr [1]	<0.5	0	0	0	0	0
Fe	~0.04	~0.08	~0.03	~0.02	~0.04	~0.02
Zn [2]	~0.008	0.182 ± 0.007	0.016 ± 0.001	0.033 ± 0.001	0.055 ± 0.002	0.015 ± 0.001
Sr	<0.03	~0.08	~0.03	~0.03	~0.03	~0.03
pH	10.7 ± 0.1	10.6 ± 0.1	10.7 ± 0.1	10.6 ± 0	10.6 ± 0.1	10.5 ± 0.1
el. conductivity (µS.cm^{-2})	225 ± 12	232 ± 24	191 ± 11	183 ± 6	211 ± 38	162 ± 17

[1] Limit value in waste leachates 7 mg.L^{-1}. [2] Limit value in waste leachates 20 mg.L^{-1}.

3.2. Aquatic Ecotoxicity

Basic ecotoxicity tests performed with water flea, algae, and duckweed showed similar dose-response patterns in all leachates (Tables S2–S4). The duckweed growth rate was the most sensitive endpoint, while the algal growth was the least sensitive.

For most samples, NOEC was found to be 800 mL.L^{-1} in the acute test for algae and water fleas, and 640 mL.L^{-1} in the growth rate of duckweed. Therefore, according to ecotoxicity indexes, all leachates were classified as non-toxic (Table 3).

Table 3. Ecotoxicity assessment of concrete leachates: EC50 with 95% CI (confidence interval) and coefficient of determination (R^2), NOEC values. GR—growth rate; TC—toxicity class [26]; n.c.—not calculable. EC50 and NOEC values are expressed in mL.L^{-1}.

Concrete Mix	Value	Water Flea	Algae GR	Duckweed GR	Toxicity Level
NAC I	EC50	931	>1000	870	
	CI 95%	890–n.c.	-	833–912	
	R^2	0.89	0.80	0.94	
	NOEC	800	800	640	
	TC	NT-1	NT-1	NT-2	Non-toxic
RMAC I	EC50	929	>1000	896	
	CI 95%	894–n.c.	-	838–966	
	R^2	0.96	-	0.86	
	NOEC	800	800	640	
	TC	NT-1	NT-1	NT-2	Non-toxic
RCAC I	EC50	>1000	>1000	911	
	CI 95%	n.c.	-	864–971	
	R^2	0.69	0.77	0.92	
	NOEC	800	800	640	
	TC	NT-1	NT-1	NT-2	Non-toxic
NAC II	EC50	>1000	>1000	844	
	CI 95%	-	-	829–861	
	R^2	0.11	0.82	0.99	
	NOEC	640	800	510	
	TC	NT-2	NT-1	NT-2	Non-toxic
RMAC II	EC50	992	>1000	926	
	CI 95%	976–n.c.	n.c.	909–943	
	R^2	0.94	0.76	0.99	
	NOEC	800	800	640	
	TC	NT-1	NT-1	NT-2	Non-toxic
RCAC II	EC50	>1000	>1000	928	
	CI 95%	-	-	895–966	
	R^2	0.65	0.77	0.95	
	NOEC	800	800	640	
	TC	NT-1	NT-1	NT-2	Non-toxic

3.3. Photosynthetic Pigments

The evaluation of photosynthetic pigments in algae and duckweed was in accordance with observations at the morphological level. As shown in Tables 4 and 5, the pigment ratio (total chlorophyll/total carotenoids) was significantly reduced only in non-diluted leachates in algae, and in 800 and 1000 mL.L^{-1} in duckweed with two exceptions (in NAC-I and RMAC-I diluted to 800 mL.L^{-1}, the change in pigment ratio was not significant). The change in pigment ratio was caused by a decrease in both chlorophylls and carotenoids in algal suspension, where the negative effect of concentrated leachates was more pronounced in chlorophylls than in carotenoids (Figures 3 and 4). The change in the pigment ratio in duckweed was caused by a decrease in total chlorophyll and an increase in total carotenoids at the same time (Figures 5 and 6). The highest carotenoid content per frond was found in duckweed exposed to nondiluted NAC I leachate, which led to the lowest Chls/Cars ratio (Table 5).

Table 4. Total chlorophyll to total carotenoid ratio in algae (mean values ± SD). 100 + n—leachates (100 mL.L^{-1}) amended with nutrients. The letters indicate significant differences between the values (post-hoc test; α = 0.05) within the same column (uppercase) and within the same row (lowercase).

mL.L^{-1}	I						II					
		NAC		RMAC		RCAC		NAC		RMAC		RCAC
0	A	5.6 ± 0.4	A	5.6 ± 0.4	A	5.6 ± 0.4	A	5.6 ± 0.4	A	5.6 ± 0.4	A	5.6 ± 0.4
640	A	5.5 ± 0.1 a	A	6.0 ± 0.2 a	A	5.4 ± 0.2 a	A	6.2 ± 0.1 a	A	5.4 ± 0.7 a	A	6.3 ± 0.1 a
800	A	5.1 ± 0.2 a	A	5.8 ± 0.8 a	A	5.1 ± 0.2 a	A	5.8 ± 0.3 a	A	5.6 ± 0.1 a	A	5.9 ± 0.1 a
1000	B	1.9 ± 0.1 a	B	1.7 ± 0.2 a	B	1.8 ± 0.1 a	B	2.0 ± 0.1 a	B	1.9 ± 0.2 a	B	1.8 ± 0.2 a
100 + n	A	5.4 ± 0.2 a	A	5.7 ± 0.2 a	A	5.2 ± 0.0 a	A	5.9 ± 0.1 a	A	5.5 ± 0.1 a	A	5.9 ± 0.1 a

Table 5. Total chlorophyll to total carotenoid ratio in duckweed (mean values ± SD). 100 + n—leachates (100 mL.L^{-1}) amended with nutrients. The letters indicate significant differences between the values (post-hoc test; α = 0.05) within the same column (uppercase) and within the same row (lowercase).

mL.L^{-1}	I						II					
		NAC		RMAC		RCAC		NAC		RMAC		RCAC
0	A	7.9 ± 0.2	A	7.9 ± 0.2	A	7.9 ± 0.2	A	7.9 ± 0.2	A	7.9 ± 0.2	A	7.9 ± 0.2
510	A	7.0 ± 0.3 a	A	7.0 ± 0.5 a	A	7.6 ± 0.6 a	A	7.2 ± 0.2 a	A	7.0 ± 0.3 a	A	8.1 ± 0.4 a
640	A	7.9 ± 1.0 a	A	7.4 ± 0.3 a	A	7.7 ± 0.5 a	A	7.1 ± 0.3 a	A	7.1 ± 0.4 a	A	7.0 ± 0.3 a
800	A	6.9 ± 1.0 a	A	7.0 ± 0.9 a	B	5.1 ± 0.1 b	B	4.6 ± 0.2 b	B	4.4 ± 0.1 b	B	4.4 ± 0.1 b
1000	B	1.5 ± 0.1 b	B	3.8 ± 0.5 a	C	3.9 ± 0.4 a	B	3.2 ± 0.7 a	B	3.8 ± 0.1 a	C	2.8 ± 0.2 ab
100 + n	A	8.2 ± 0.1 a	A	7.7 ± 0.2 a	A	8.6 ± 0.3 a	A	8.1 ± 0.3 a	A	8.3 ± 0.3 a	A	8.1 ± 0.1 a

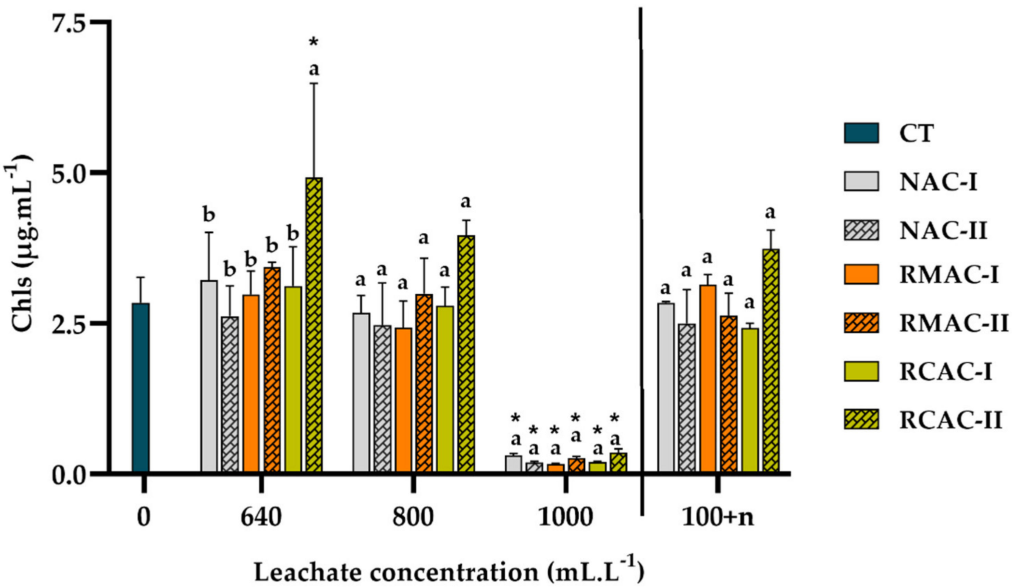


Figure 3. Mean (±SD) total chlorophyll (a + b) content in algal suspension. CT (control)—Bold's Basal medium. 100 + n—leachates (100 mL.L^{-1}) with amended nutrients. Lowercase letters indicate significant differences between samples of a given concentration, and asterisks (*) indicate significant differences between sample and control (post-hoc test; α = 0.05).

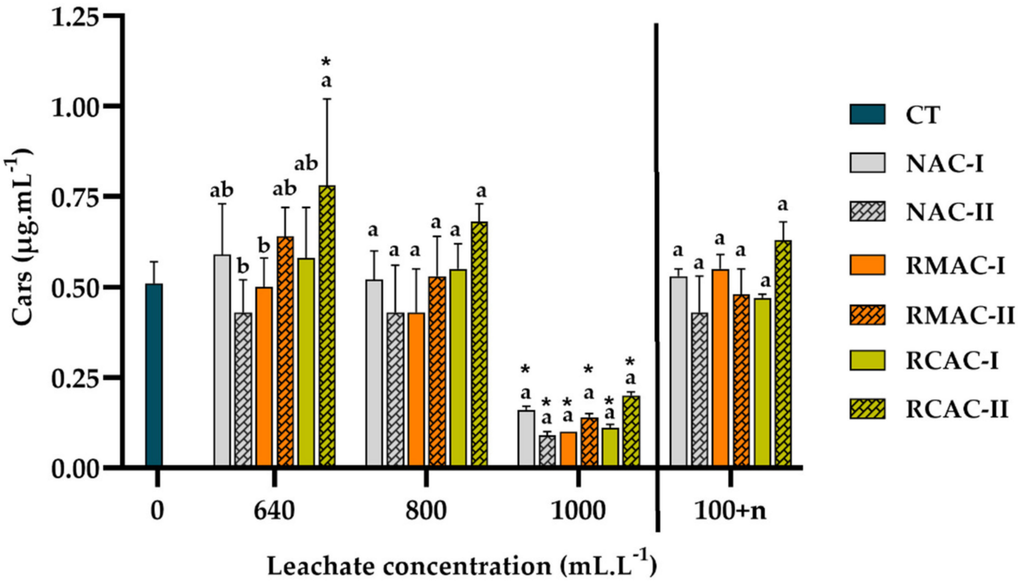


Figure 4. Mean (±SD) total carotenoid content in algal suspension. CT (control)—Bold's Basal medium. 100 + n—leachates (100 mL.L^{-1}) with amended nutrients. Lowercase letters indicate significant differences between samples of a given concentration, and asterisks (*) indicate significant differences between sample and control (post-hoc test; α = 0.05).

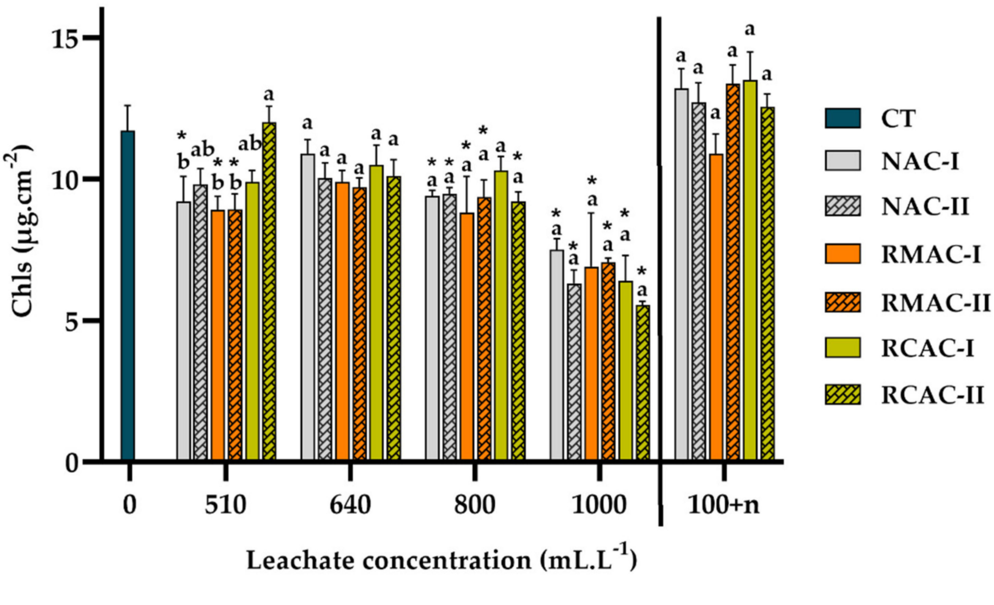


Figure 5. Mean (±SD) total chlorophyll (a + b) content in duckweed. CT (control)—Steinberg medium. 100 + n—leachates (100 mL.L^{-1}) with amended nutrients. Lowercase letters indicate significant differences between samples of a given concentration, and asterisks (*) indicate significant differences between sample and control (post-hoc test; α = 0.05).

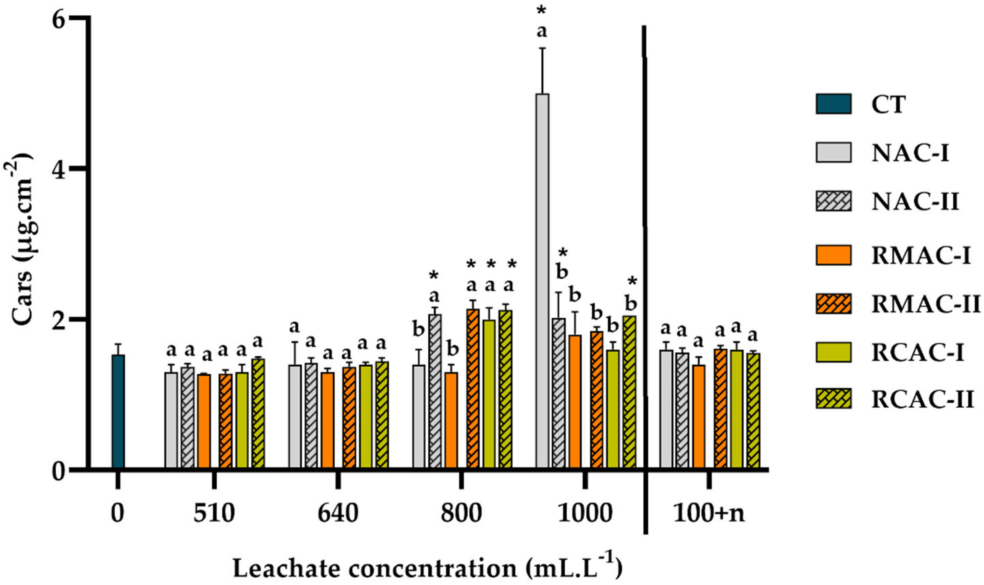


Figure 6. Mean (±SD) total carotenoid content in duckweed. CT (control)—Steinberg medium. 100 + n—leachates (100 mL.L^{-1}) with amended nutrients. Lowercase letters indicate significant differences between samples of a given concentration, and asterisks (*) indicate significant differences between sample and control (post-hoc test; α = 0.05).

3.4. Soil Dehydrogenase Activity

The results of DHA in the soil are summarized in Figure 7. With a few exceptions, the enzymatic activity was slightly stimulated in soils amended with leachates. Stimulation was more pronounced in soils amended with concrete leachates of strength class I. However, the differences among samples, as well as the stimulation, were usually not significant. RMAC II was the only leachate that caused slight inhibition in all measurements, while soils contaminated with NAC I leachate changed their reaction from significant stimulation (−11% and −10% after 7 and 28 days, respectively) to low inhibition (5%) at the end of the exposure. The highest stimulation was observed in soil contaminated with RMAC I leachate after seven days (15%). Generally, it can be said that undiluted leachates did not significantly affect soil microbial activity, or caused a slight increase of up to 15%. The pH of the soil mixtures was relatively similar to that of the control soils (Table S5). The soil pH ranged between 5.7 and 6.0 after seven days and dropped to 5.3–5.6 after 56 days of exposure; therefore, according to the soil pH [29], all samples and the control remained acidic during the whole experiment.

3.5. Carbonation Effect

There are four basic stages of carbonation; most structures reach the maximum of the second stage. The amount of calcium carbonate formed does not completely characterize the carbonation stage [40]. By finding out in what form $CaCO_3$ is present, it is possible to characterize the carbonation process and, at the same time, assess the situation of carbonated concrete. Studies that consider concrete carbonation in general show that concretes of the lower strength class (C16/20) reach deeper carbonation depths compared to the higher strength class (C25/30) [40–42]. This fact is also connected with factors such as porosity and density beside concrete strength [43–45]. Research dealing with carbonation effect has proved that with increasing porosity and density, the carbonation effect is decreased. This phenomenon is also confirmed in this research (Figure 8). The purple-red color adheres to the noncarbon part of the sample, where the concrete is highly alkaline. There was no coloration in places with reduced concrete alkalinity. Mixtures NAC-I, RMAC-I, and RCAC-II have shown deeper penetration compared to the corresponding higher-class concrete (NAC-II, RMAC-II, and RCAC-II). Carbonation depth was determined by image analysis using NIS Elements (v5.20, Laboratory Imaging, Prague, Czech Republic).

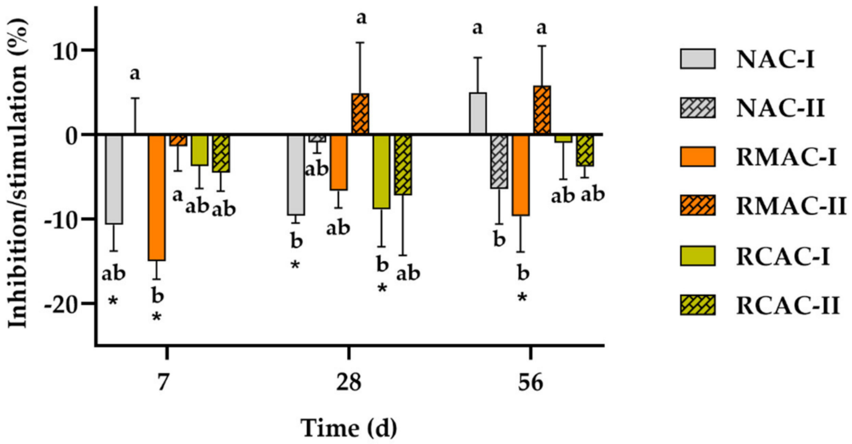
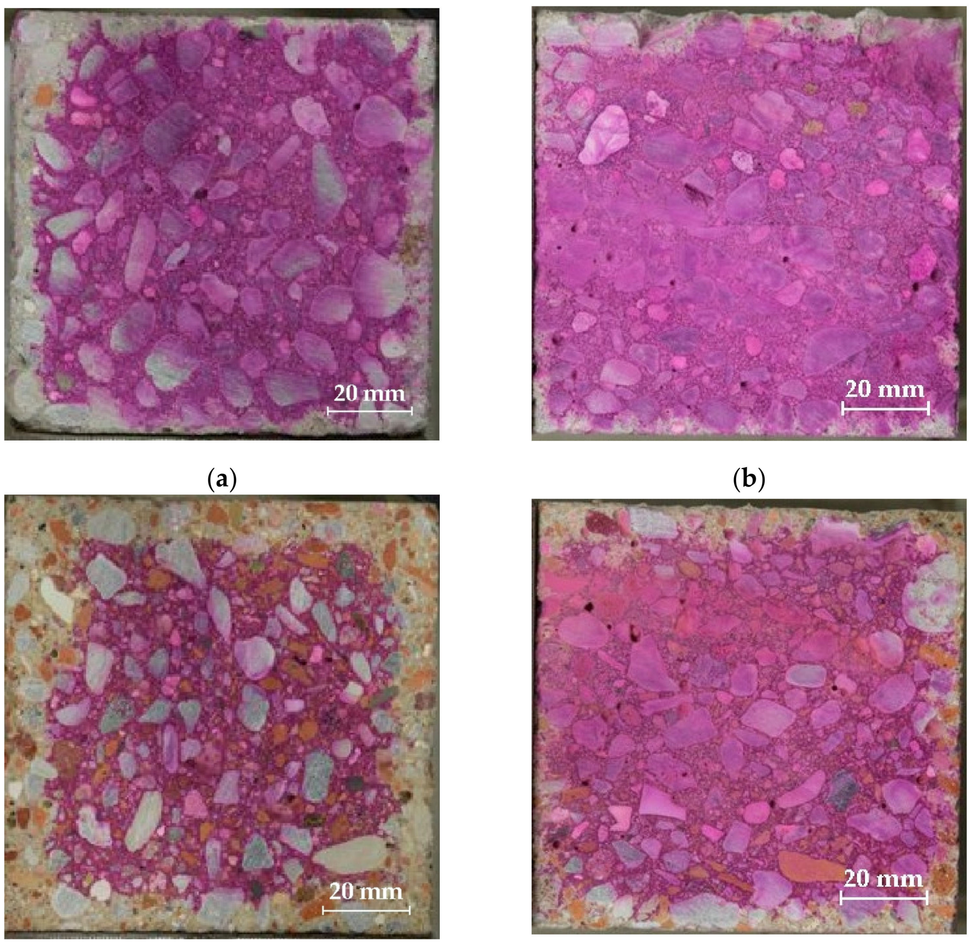
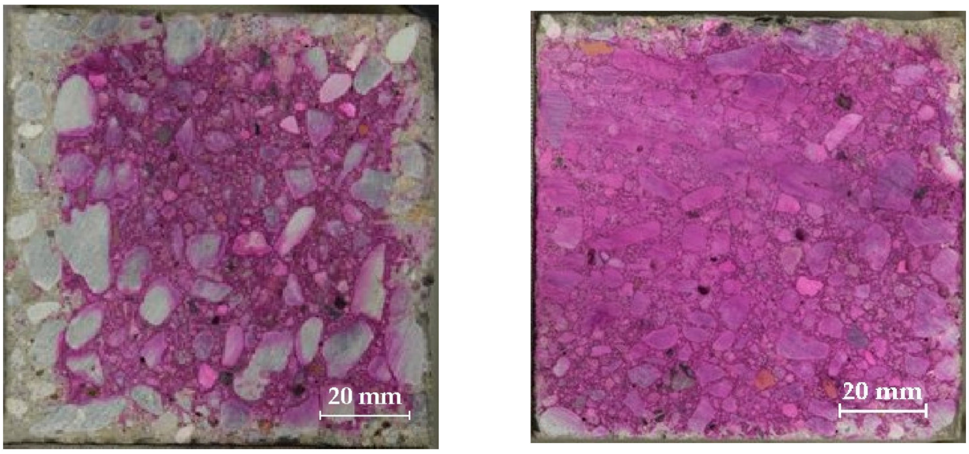


Figure 7. Mean (±SD) inhibition/stimulation of soil dehydrogenase activity measured in soil contaminated with leachates after 7, 28 and 56 days. Different letters indicate significant differences among samples within a given time point. Asterisks (*) indicate significant differences between the sample and control, that is, zero values (post-hoc test; α = 0.05).



(**a**) (**b**) (**c**) (**d**)

Figure 8. *Cont.*



(**e**) (**f**)

Figure 8. Samples after carbonation test colored with phenolphthalein: (**a**) NAC-I, (**b**) NAC-II, (**c**) RMAC-I, (**d**) RMAC-II, (**e**) RCAC-I, and (**f**) RCAC-II.

The results of the carbonation depth are summarized in Table 6. The NAC-I value 4.41 mm was more than one and a half times higher compared to the same mixture in the higher concrete class NAC-II 2.65 mm. This trend appears similarly in the other mixtures as well, but the ratio increases from 1.6 to 2.9 with RMAC, and to 3.6 with RCAC. In general, the deepest penetration was observed in RMAC in both evaluated grades (10.04 mm and 3.37 mm). However, the RCAC-I was extremely high compared to that of NAC-I. Meanwhile, RCAC-II (with the value 2.45) was almost comparable with NAC-II (2.65).

Table 6. Average carbonation depth results of samples tested containing natural and recycled aggregate.

Mean Carbonation Depth (mm)	I			II		
	NAC	RMAC	RCAC	NAC	RMAC	RCAC
d_1	2.99	12.69	9.66	2.50	1.18	2.56
d_2	6.82	8.41	7.99	5.25	3.74	1.87
d_3	3.66	7.35	6.27	0.34	3.37	4.10
d_4	4.17	11.73	12.14	2.50	6.25	1.30
d_k	4.40 ± 1.45	10.04 ± 2.22	9.01 ± 2.16	2.65 ± 1.74	3.37 ± 1.79	2.45 ± 1.05

3.6. Results of Environmental Assessment

The environmental assessment was performed using the LCA method and the potential environmental impacts were calculated using PEF 3.0. The results of this assessment are given in Table 7.

Taking into account the climate change (total) indicator, which describes the potential impact on one of the key categories, mixtures with natural aggregates cause a higher impact than mixtures with recycled aggregates in the same strength class. Similarly, NAC has a greater impact in most categories. This is affected by the dominant influence of cement. Mixtures in the same strength class are designed with the same amount of cement, so their potential impact is mainly affected by this. However, there is also the influence of the beneficial impact of recycled aggregates, which are used as replacements for natural gravel in the mixture.

In comparison of the two types of recycled aggregates, recycled concrete aggregate has a more beneficial impact than recycled masonry aggregate. This is mainly affected by the higher amount of iron scrap, which can be recycled from concrete structures with steel reinforcement.

Table 7. Results of the selected impact indicators for 1 m^3 of concrete mixtures; the environmental impact assessment was carried out according to the PEF 3.0 method.

	I			II		
	NAC	**RMAC**	**RCAC**	**NAC**	**RMAC**	**RCA**
Acidification (Mole of H+ eq.)	9.96×10^{-1}	8.99×10^{-1}	8.64×10^{-1}	1.06	9.66×10^{-1}	9.34×10^{-1}
Climate Change—total (kg CO_2 eq.)	3.21×10^{2}	2.59×10^{2}	2.21×10^{2}	3.54×10^{2}	2.95×10^{2}	2.59×10^{2}
Climate Change, biogenic (kg CO_2 eq.)	3.62×10^{-1}	3.18×10^{-1}	3.69×10^{-1}	3.88×10^{-1}	3.47×10^{-1}	3.95×10^{-1}
Climate Change, fossil (kg CO_2 eq.)	3.20×10^{2}	2.58×10^{2}	2.20×10^{2}	3.53×10^{2}	2.94×10^{2}	2.58×10^{2}
Climate Change, LULUC (kg CO_2 eq.)	6.12×10^{-1}	6.35×10^{-1}	6.95×10^{-1}	6.29×10^{-1}	6.51×10^{-1}	7.09×10^{-1}
Ecotoxicity, freshwater—total (CTUe)	1.71×10^{3}	1.39×10^{3}	1.57×10^{3}	1.77×10^{3}	1.47×10^{3}	1.65×10^{3}
Eutrophication, freshwater (kg P eq.)	1.07×10^{-3}	7.31×10^{-4}	8.75×10^{-4}	1.12×10^{-3}	7.91×10^{-4}	9.28×10^{-4}
Eutrophication, marine (kg N eq.)	3.42×10^{-1}	3.25×10^{-1}	3.30×10^{-1}	3.59×10^{-1}	3.43×10^{-1}	3.48×10^{-1}
Eutrophication, terrestrial (Mole of N eq.)	3.76	3.59	3.66	3.95	3.78	3.85
Human toxicity, cancer—total (CTUh)	9.03×10^{-8}	4.41×10^{-8}	2.19×10^{-8}	9.24×10^{-8}	4.87×10^{-8}	2.77×10^{-8}
Human toxicity, non-cancer—total (CTUh)	6.75×10^{-6}	5.62×10^{-6}	5.31×10^{-6}	7.12×10^{-6}	6.05×10^{-6}	5.76×10^{-6}
Ionising rad., human health (kBq U235 eq.)	6.49	4.83	6.29	6.99	5.41	6.80
Land use (Pt)	5.57×10^{2}	4.66×10^{2}	5.30×10^{2}	5.88×10^{2}	5.01×10^{2}	5.63×10^{2}
Ozone depletion (kg CFC-11 eq.)	3.73×10^{-7}	2.53×10^{-7}	3.13×10^{-7}	3.85×10^{-7}	2.71×10^{-7}	3.28×10^{-7}
Particulate matter (Disease incidences)	1.12×10^{-5}	6.37×10^{-6}	5.74×10^{-6}	1.20×10^{-5}	7.43×10^{-6}	6.83×10^{-6}
Photochem. ozone form., hum. health (kg NMVOC eq.)	8.52×10^{-1}	7.98×10^{-1}	7.80×10^{-1}	9.02×10^{-1}	8.51×10^{-1}	8.35×10^{-1}
Resource use, fossils (MJ)	2.08×10^{3}	1.31×10^{3}	9.71×10^{2}	2.17×10^{3}	1.44×10^{3}	1.12×10^{3}
Resource use, mineral and metals (kg Sb eq.)	3.05×10^{-5}	6.43×10^{-5}	1.81×10^{-4}	3.30×10^{-5}	5.68×10^{-5}	1.67×10^{-4}
Water use (m^3 world equiv.)	1.27×10^{3}	7.67×10^{2}	8.40×10^{2}	1.31×10^{3}	8.35×10^{2}	9.03×10^{2}

LULUC–Land use and land use change

4. Discussion

4.1. Impact of Chemical Composition on Leachate Ecotoxicity

Except for reference samples, the concentration of leached elements from concrete cubes was significantly lower compared to leaching patterns of homogenized recycled aggregates, as expected (Table 2, [25]). However, the general proportion of leached elements was similar for primary materials and construction applications. Heavy metals which are non-essential for organisms, i.e., hazardous at any concentration (As, Ba, Cd, Hg, Ni, and Pb), were below the detection limit. Ca, Na, and K that belong to the main metals released in concrete leachates [4] are not considered toxic; in fact, quite the opposite, as they are essential mineral macroelements that are included in the culture media for both crustacean and aquatic plants [46–48]. Mg, Fe and Zn represent other mineral nutrients required especially by plants. However, Zn is included in risk metals and therefore has to be analyzed in wastewaters, sludge or waste leachates [49,50]. Moreover, secondary salinization of surface waters and soils caused by increasing concentration of ions including Na^{+}, Mg^{2+}, Ca^{2+}, K^{+} and Fe ions together with climate change is an issue of growing concern [51–53]. In this study, the essential minerals were often below the concentration required in growth media.

The results from ecotoxicity tests indicate that the high growth inhibition/immobilization in original untreated leachates was caused most particularly by lack of nutrients. This can be considered as a favorable result because abundant elements in eluates entering aquatic or terrestrial environment can cause ecological imbalance [54,55].

4.2. Selection of Leaching and Ecotoxicity Testing Design

Various leaching test methods have been reported from batch tests in one stage, percolation tests, and long-term tests with leachant renewal [56]. For the leaching experiment, we have chosen the simple batch design in one stage that was already applied in the previous study [26] to compare the ecotoxic potential of recycled glass waste in the form of homogenized material and its subsequent use in concrete cubes. This 24-h leaching design was also chosen to prevent potential metal sorption on glass vessels, change of the leachate pH in time, biocontamination, as well as potential biodegradation of the leached compounds.

Ecotoxicity tests are usually based on a simple experimental design with acute exposure that provide quick screening of potential environmental risks. However, acute exposure which usually lasts several hours to several days is suitable mainly for detection of larger amounts of hazardous substances affecting living organisms. To detect the potential risk of lower concentrations of toxicants, chronic ecotoxicity tests may be used. Such methods are time-, space- and sample-consuming, and thus can be problematic for routine application. The use of semi-chronic tests provides a suitable solution.

Ecotoxicological impact of concrete leachates is usually tested by a set of two or three aquatic bioassays. In consumers, the most popular test is immobilization of freshwater or marine crustaceans [1–5,57,58]. The embryonic stage of zebrafish eggs (*Danio rerio*) represents another possibility of how to avoid problematic animal models, as the early developmental stage is not protected by regulatory framework [59]. In the inter-laboratory study, tests with zebrafish eggs was applied, but was evaluated as the least sensitive model [57]. Marine luminescent bacteria *Aliivibrio fischeri* (previously *Vibrio fischeri*) is often used in concrete leachate testing [1,57,60] as the test design is simple, short-term (30 min exposure), and easy to perform using modern luminometers [61]. Heisterkamp et al. [57] reported the bacterial luminescent test as the most sensitive for construction product evaluation. Plant models can be examined at both the individual (lethality, necrosis) and population (reproduction) levels, making them semi-chronic tests. At the same time, additional endpoints at the biochemical level [9,60] can be determined. As duckweed and unicellular algae reproduce asexually, they represent genetically homogeneous plant material and have another advantage over seed germination tests [9].

4.3. Photosynthetic Pigment Ratio as Stress Indicators in Aquatic Plants

Aquatic plants growing in metal-contaminated waters are able to accumulate heavy metals [62]. Besides the negative effect on plant growth, metal contamination also causes oxidative stress, as reported for duckweed exposed to Cd, Cu, Cr, and Hg [63,64]. Oxidative stress in aquatic plants can be detected by increased activity of antioxidative enzymes, malondialdehyde, or changes in total carotenoids content [64,65]. However, deficiency of essential metals such as Cu also has a negative impact on photosynthetic pigments [66]. Duckweed exposed to heavy metals in industrial wastewater was more seriously affected at the morphological level (growth rate based on the frond number and weight) than in the chlorophyll content [9]. This is in agreement with our results (Table S4, Figure 5).

Another task is to determine how the pigment content is expressed. Calculation per weight unit or frond area may be subject to error in the event that the water content in the fronds differs or the fronds overlap. The effect of heavy metal pollution in wastewaters lead to changes in chlorophyll a and b, and the total carotenoids exceeded the total chlorophyll content in duckweed, which indicated internal oxidative stress [65]. Hence, Chls/Cars ratio can be easily used for comparison among various samples and control. In this study, a significant decrease of Chls/Cars was generally in accordance with significant growth inhibition in duckweed (Table 5, Table S4). Besides, by determination of the pigment ratio, both the actual state of the plant and the prediction of the future plant response can be considered.

Traditional algal assays are often based on indirect estimation of biomass or population growth through cell counting under a microscope, flow cytometry, or optical density measurement [67,68]. These approaches do not take into account the cell size and the cell quality, including colour, i.e., pigment profile.

Direct biomass determination on the cell dry mass basis is usually impossible due to the very low dry matter content. At the same time, the extraction of photosynthetic pigments enables the quantification of algal production at the biochemical level (Chls/mL), and the level of stress pronounced by changes in Cars. Another guideline for measuring aquatic ecotoxicity describes the determination of chlorophyll a in algae using ethanol extraction [69]. However, as summarized in [70], hydrophilic carotenoids are not easily extracted by ethanol. Osorio et al. reported acid-free methanol as a suitable solvent for quantitative extraction for carotenoids in various macro- and micro-algae [71]. For this reason, a similar approach for pigment extraction and measurement as applied in the duckweed assay was chosen in the algal experiment also.

4.4. Effect of Leachates on Soil Dehydrogenase Activity

Soil represents an important part of the environment. The balanced functioning of soil is strongly dependent on the soil microbial community. Soils are considered one of the sinks for various kinds of pollutants, including those coming from the construction sector [72]. The release of alkalizing compounds from cement and concrete contributes to the increase of soil pH [73]. Soil pH was reported to be a significant factor influencing the composition of the soil microbiome [74]. Our hypothesis was that the addition of leachates into natural soil would lead to a change in microbial activity in response to metal input. This was observed in most samples, especially seven days after soil contamination (Figure 6). The slight stimulation effect is not surprising, since the total amount of metals leached from concrete was relatively low. Leachate alkalinity also did not affect soil pH significantly, although the pH value decreased slightly over time (Table S5). As the stimulation/inhibition effect of concentrated concrete leachates on DHA was very low (though significant in several cases), addition of diluted leachates was not tested. To our knowledge, there is no study on the addition of concrete leachate to soil. Soil enzymes were not inhibited in soils located near landfills or soils amended with landfill leachates [75,76].

The DHA experiment was performed using only one selected type of an acidic soil material. However, soils located in urban sites vary in physicochemical characteristics [77] and thus may give different results. Furthermore, impact on other components of the soil ecosystem, plants and invertebrates may be also included. The performed type of experiment was the first of its kind due to the untraceable studies in this field. Thus, more research is necessary on terrestrial ecotoxicology of construction products.

4.5. Impact of the Carbonation Process on Concrete

The real trigger mechanism is water and oxygen, which means the process of carbonation itself (high CO_2 content) does not cause corrosion. Carbonation is one of the chemical mechanisms that can cause concrete failure, and one of the main factors effecting the process is relative humidity of the environment. In a wet environment (humidity higher than 95%), the carbonation process is inefficient or not going at all [45,78]. However, structures in a very dry environment (relative humidity up to 30%), as well as structures fully immersed in water, show no signs of carbonation or corrosion. This is caused by the absence of oxygen to fill the capillary pores [23]. The definition of the effect of relative humidity on the carbonation process in concrete is an important topic in the scientific field; the research in this area is examined by Matoušek et al. [40]. According to [40], the carbonation process is more intense between 50 and 95% of relative humidity, and between 75 and 95% strongly unsolicited [42]. However, the reduction of concrete alkalinity could be (beside carbon dioxide) caused by nitrogen oxides or sulfur dioxide, which are also pollutants affecting concrete. This scenario could appear with outdoor exposure.

Some studies have also shown refinement of pore structure, but this factor was dependent on the relative humidity. However, the research [78] validates that carbonation of concrete before its utilization could lead to a decrease in water absorption as well. These conclusions are also connected with better durability, e.g., freeze-thaw resistance, which is an important factor for concrete structures in general.

Another factor that affects the carbonation depth could be a higher cement ratio. Studies have shown that carbonation on these samples was negligible [21,79]. This study confirms the prediction that concrete in the lower strength grade has deeper penetration and the extent of carbonation is more significant. However, phenolphthalein as an indicator reveals that the pH level is in fact below 9 (not the real carbonation depth) [79,80].

When dealing with cement, there is also the possibility of using alkali-activated materials. There are studies [81,82] dealing with a high MgO ratio in in alkali-activated slag.

With hydrotalcite as the main secondary product, this can effect and reduce the carbonation process, and this whole case can lead to an increase of the durability of concrete [82].

If focusing purely on carbonation without corrosion, e.g., reinforcement, the process can be considered environmentally beneficial. Carbon dioxide absorption by concrete structures can reduce these emissions. With regard to this theory, it can be said that the recycled concrete that has been investigated in this work will hold more CO_2 than conventional reference concrete in the same strength grade. The usual CO_2 content in the air is 0.03% by volume, depending on the area. In cities, this number could be up to three times higher [42].

In general, based on the results of this research, the investigated recycled concretes can be evaluated as suitable for use in concrete structures that will not have a negative environmental impact higher than similar reference concretes of the same strength class.

4.6. Environmental Assessment of the Alternative Scenario Considering CO_2 Uptake

The alternative scenario describes the potential of concrete mixtures to capture CO_2 as a consequence of carbonation. The approach for this calculation is described in Section 2.5. In this chapter, the assumed factors for the calculation were described to characterize the potential of the mixtures to take up CO_2. The results of the calculation of the total potential uptake are described in Table 8.

Table 8. The potential total CO_2 uptake calculated for concrete cubes (a = 1 m) that have 5 m^2 of the surface below the ground, according to EN 16757.

	NAC I	RMAC I	RCAC I	NAC II	RMAC II	RCAC II
Total CO_2 potential uptake (kg CO_2 per cube)	4.21	4.21	4.21	3.53	3.53	3.53

The calculated uptake contribution can be used as a benefit of the concrete structure, and it can be declared together with the results of the environmental assessment of the entire life cycle. However, assumptions describing expected service life or future utilization or the surface of the cube available for carbonation are highly uncertain. Therefore, the results of this calculation are stated as an alternative scenario which describes the possible use of such concrete. Furthermore, the potential total CO_2 uptake is not considered in comparison with the total impact in the category of climate change, which is mainly influenced by cement production.

Carbonation of concrete also continues after its service life and CO_2 can be absorbed in recycled concrete aggregate. After gridding of recycled concrete to particle size 0–40 mm, the rate of CO_2 can reach even 5.5% of overall CO_2 emissions realized during the life cycle of concrete [83]. The amount of absorbed CO_2 after four months, in which concrete is crushed into the typical size of concrete aggregate, can reach even 20% of the total amount of CO_2 realized during calcination of used cement [84]. A similar result was reported by Yang et al., who calculated the CO_2 uptake during life expectancy of 40 years and recycling span of 60 years as 18–21% of the CO_2 emissions from the production of ordinary Portland cement [85].

4.7. Overall Potential Impact on the Environment

Based on the normalized and weighted results, the overall potential impact can be calculated, and the sums of normalized and weighted results are presented in Figure 9. The highest environmental impact is related to the considered life cycle of NAC II. Mixtures with the same strength class, which were designed with the use of recycled aggregates, cause a smaller potential impact. The same relation is seen among the mixtures designed for the lower strength class.

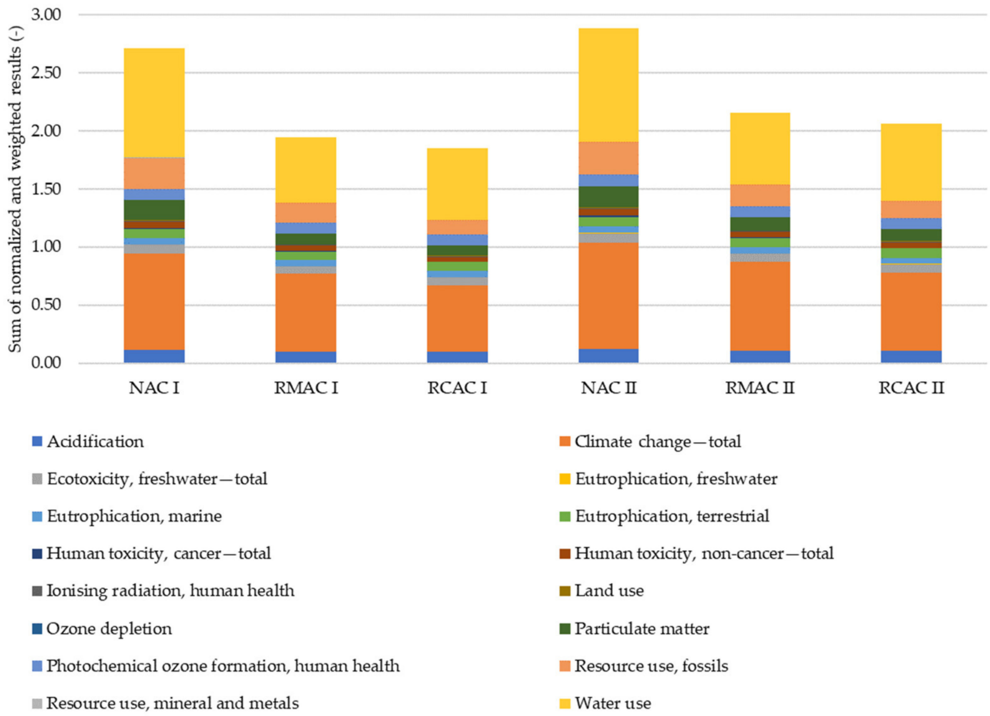


Figure 9. Sum of normalized and weighted results calculated using the PEF 3.0 method.

Regarding the comparison of mixtures containing recycled concrete aggregate and recycled masonry aggregate, the lowest overall impact is reached in the case of RCAC mixtures. The similar conclusion was reported by Marinkovic et al., who, in two scenarios, in which recycled aggregate and natural aggregate concrete were compared, calculated that lower normalized and weighted results of environmental indicators was reached by recycled aggregate concrete [86]. In addition, a study published by Colangelo et al. shows that concrete with 25% recycled aggregates is the best solution from an environmental point of view [87].

The overall impact is significantly affected by the contribution in the water use category. The impact in this category is caused mainly by gravel production, and the production of recycled aggregates has a beneficial impact in this category. This beneficial impact represents the environmental credits, which are connected to the recycling of iron scrap from construction and demolition waste.

Another important contribution to the overall impact is related to the results in the climate change category. The major impact in this category is caused by the production of cement.

5. Conclusions

In this study, the experimental verification of the reaction between concrete and the environment, from the biochemical level up to the mechanical and theoretical levels, was performed. Laboratory leaching experiments that determine the toxic effect of the concrete structure on the environment (water and soil) were combined with evaluation of the environment (air or water) on the concrete structure, through the carbonation process. All of the obtained experimental data were then theoretically compared with results of the life-cycle assessment.

As a conclusion of the observation at both the ecotoxicological and biochemical levels, it is possible to say that all assumptions were confirmed. With a smaller surface, the leachability of both toxic compounds and trace elements also decreases. The effect of concrete leachates on photosynthetic pigment ratio (Chls/Cars) was in accordance with the effect on plant growth. Addition of leachates to natural soil had a very low effect on soil

DHA and did not change soil pH. Hence, from an ecotoxicological point of view, concrete containing fine recycled aggregate does not disturb the balance in the ecosystem and is as nontoxic as reference samples.

At the same time, some types of recycled concrete (mainly RCAC-II) have been proven to reach carbonation depths similar to those of the reference sample, while RMAC-I and RMAC-II showed a deeper penetration of CO_2. In general, it is possible to say that, based on the performed experiments and assumptions from foreign studies, the increasing depth of carbonation with the decreasing strength class was confirmed, regardless of whether it is a reference concrete with natural aggregates or concrete with recycled aggregates.

The potential scenario of CO_2 uptake is evaluated in the LCA, and the captured CO_2 value was evaluated as negligible compared to the value of CO_2 in cement production. However, the assumption of CO_2 capture could be useful given the effort to eliminate environmentally non-friendly materials, such as cement in concrete production, and replace them with waste or recycled materials.

After an overall evaluation of the LCA, recycled concrete (RMAC-I, RCAC-I, RMAC-II, RCAC-II) were evaluated as more environmentally friendly compared to the reference samples (NAC-I, NAC-II). These results will be used as a basis for the subsequent verification of other specific properties of recycled concrete with the aim of implementing them in the industry sector.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su14031732/s1, Table S1: pH of the leachates (mean values ± SD) at the end of the duckweed toxicity test (after 7 days of exposition). 100 + n—leachates (100 mL.L^{-1}) amended with nutrients; Table S2: The results of the water flea toxicity tests. Mean (±SD) values of immobilization (%). 100 + n—leachates (100 mL.L^{-1}) amended with nutrients. The letters indicate significant differences between values (post-hoc test; α = 0.05) within the same column (uppercase) and within the same row (lowercase), and the asterisks indicate differences between sample and control (zero values); Table S3: The results of algae toxicity tests. Mean (±SD) values of inhibition/stimulation (%) of growth rate based on optical density at 750 nm. 100+n—leachates (100 mL.L^{-1}) amended with nutrients. Negative values indicate growth stimulation. The letters indicate significant differences between values (post-hoc test; α = 0.05) within the same column (uppercase) and within the same row (lowercase), and the asterisks indicate differences between sample and control (zero values); Table S4: The results of duckweed toxicity tests. Mean (±SD) values of inhibition/stimulation (%) of the growth rate based on the total area of the frond. 100 + n—leachates (100 mL.L^{-1}) amended with nutrients. Negative values indicate growth stimulation. The letters indicate significant differences between values (post-hoc test; α = 0.05) within the same column (uppercase) and within the same row (lowercase), and the asterisks indicate differences between the sample and control (zero values); Table S5: pH (mean values ± SD) measured in soils amended with leachates after 7, 28, and 56 days.

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Appendix 6

Influence of the use of waste glass from photovoltaic panels in high-performance concrete in the fire resistance test

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Abstract: The combination of highly durable material with recycled material expresses the idea of sustainable construction. The primary raw materials used for the production of concrete need a large amount of primary energy; it is possible to replace them with a more environmentally friendly version - waste materials from construction and demolition waste. Waste materials and their usability in concrete should be examined in terms of tests outside the classic durability and strength experiments. The paper focuses on the behavior of concrete samples with waste glass from photovoltaic panels exposed to high temperatures corresponding to fire. The loading is done according to the standard temperature curve ISO 834. The influence of fire on the microstructure of concrete samples - the development of cracks and the cohesion of concrete was monitored. The condition was compared with the reference concrete sample

Influence of the use of waste glass from photovoltaic panels in high-performance concrete in the fire resistance test

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Abstract. The combination of highly durable material with recycled material expresses the idea of sustainable construction. The primary raw materials used for the production of concrete need a large amount of primary energy; it is possible to replace them with a more environmentally friendly version - waste materials from construction and demolition waste. Waste materials and their usability in concrete should be examined in terms of tests outside the classic durability and strength experiments. The paper focuses on the behavior of concrete samples with waste glass from photovoltaic panels exposed to high temperatures corresponding to fire. The loading is done according to the standard temperature curve ISO 834. The influence of fire on the microstructure of concrete samples - the development of cracks and the cohesion of concrete was monitored. The condition was compared with the reference concrete sample.

INTRODUCTION

In the last few years, problems related with the global increase of waste are increasing. According to the latest data from the Czech Statistical Office (from 2019), up to 41% of this waste is generated during construction activities (construction, demolition, reconstruction, etc.) [1].

Almost 10.9 thousand tons of the produced waste is glass. Recycling is a term that the general public generally associates with glass and already has a very broad meaning. Glass from municipal waste is reusable in the form of glass bottles and these days it taken as a standard that each new glass bottle is made from up to 60% of recycled glass. However, the process is repeatable for a limited time, after that the glass is mostly put into a landfill due to the unsolicited impurities [2].

Nevertheless, there are other possibilities to recycle glass. The use in concrete is suitable because of lower demands on purity of glass. Cleanliness could be lower while used waste glass in concrete mixtures.

This research deals with the glass component of photovoltaic panels, which was evaluated on the basis of previous research as suitable for use in concrete as a substitute for silica flour and fine sand as well. While the average lifetime of crystalline silicon photovoltaic panels is 25-30 years [3], the service life of the first generation of photovoltaic panel systems made and used in the Czech Republic is coming to an end. Due to the specific chemical composition (ie high aluminum content), landfilling is an inappropriate approach. The proper recycle technology is necessary to find for processing used photovoltaic panels [4].

It is the chemical composition and its specification in research that have raised many questions that need to be answered before moving on to the next phase (design of specific design applications and their testing). This work focuses on the behavior of such treated concrete samples at high temperatures corresponding to fire. The aim of the test was to describe the different behavior of test specimens made of HPC with an admixture of glass dust from photovoltaic panels exposed to high temperatures compared to a reference specimen made of simple HPC.

This study should only serve as a basis for concluding that it is safe and reliable in terms of fire safety with regard to concrete containing photovoltaic glass. It is necessary to be aware of the risks associated with the use of waste materials and to verify, in particular, the environmental impact and toxicity, given the efforts being made to reduce the use of primary raw materials not only because their resources are depleted but also because of environmental risks.

MATERIALS AND METHODS

For the preparation of concrete mixtures, materials were used according to the basic recipe, which was developed at the Department of Civil Engineering, Faculty of Civil Engineering, CTU [7]. The basic materials used include Portland cement 42.5R, natural sand 01/06 and 06/12, quartz flour, microsilica, superplasticizers and water. The quartz flour was replaced in 100% by weight by waste glass from photovoltaic panels. At the same time, microsilica was omitted in the mixture with photovoltaic glass, which in combination with photovoltaic glass created a chemical process that caused the degradation of concrete samples in the form of cracks [8].

A description of the materials used and the composition of the tested concretes is given in Table 1.

TABLE 1. Composition of tested concrete mixtures

Component	REF kg/m^3	PP kg/m^3
Portland cement I 42,5	680	680
Natural sand 01/06	480	-
Natural sand 06/12	480	480
Silica flour	325	-
Photovoltaic panels glass powder	-	325
Photovoltaic panels glass sand 01/06	-	480
Microsilica	175	175
Superplastificators	29	29
Water	171	171

REF concrete mix with the composition see above was used as a reference mix. By replacing the fine fraction of natural sand and quartz flour with waste glass from photovoltaic panels, a PP mixture was developed.

FIRE RESISTANCE TEST

The test was performed on the basis of a test regulation, which is based on the conditions of large-scale tests for testing fire resistance ČSN EN 1363-1 and ČSN 1365-2 [5,6]. The aim of the test was to describe the different behavior of test specimens from HPC with an admixture of glass dust from photovoltaic panels exposed to high temperatures compared to a reference specimen from plain HPC. ISO 9705 Reaction to fire tests - Room corner test for wall and ceiling lining products - Part 1: Test method for a small room configuration can be considered as a related test [9]. To perform this test, the anteroom in front of the fire chamber and under the exhaust bell for the Room Corner Test was defined. This space dimensions and equipment comply with the requirements of ISO 9705-1 [9]. A fire furnace developed in a fire laboratory for medium-sized fire experiments was placed in this space. The furnace has the following parameters:

• bright internal dimensions: 1200 × 800 × 800 [mm]

• simple cladding with cement fiber boards, th. 15 [mm]

• ventilation conditions: natural inlet and outlet openings in longer walls 300 × 100 [mm]

• dimensions of the sand burner: 300 × 100 × 100 [mm]

• flue gas: propane 2.5, net calorific value 46.4 [MJ / kg]

PILOT TEST

A total of 2 concrete samples were tested during the fire experiment. They were hung in the combustion chamber by means of a threaded rod (ø8 mm), penetrating the ceiling structure of the furnace. The threaded rods were fixed to steel profiles secured to the upper face of the furnace supporting structure (steel steel 40/40 mm) (Figure 1). The threaded rods were protected in the combustion chamber by thermal insulation made of mineral fiber to prevent them from being damaged by the increased temperature.

The output of the sand burner is automatically increased during the test according to a predetermined program, which is to ensure temperatures close to the standard temperature curve according to ISO 834 inside the furnace without flammable elements [10].

$$T = 345 \cdot log(8 \cdot t + 1) + 20 \quad (1)$$

The supplied samples are non-flammable, and it can be assumed that the resulting average temperature in the furnace will be within the specified limits of the standard temperature curve.

The temperature, which is compared with a standard temperature curve, is determined by the arithmetic mean of the four thermocouples in the upper part of the furnace marked Ts, a - Ts, h:

• thermocouples Ts, a – Ts, e are placed at a distance of 200 mm from longer and shorter walls, at a height of 100 mm below the upper surface of the furnace;

• thermocouples Ts, f – Ts, h are placed at a distance of 200 mm from longer and shorter walls, at a height of 200 mm above the floor

The measured quantities are only the temperatures in the combustion space in the furnace.

The test is terminated after 30 minutes followed by data collection for 10 minutes. The experiment is terminated earlier if the test specimens are destroyed or fall off the structure, fixing the specimens under the furnace ceiling.

The subject of the test was two test samples with different HPC recipes for comparison purposes. Test sample No. 1 (PP) was made of a concrete mixture of HPC with a mixture of glass dust from photovoltaic panels. Test sample No. 2 (REF) is then made of a standard concrete mixture, which serves as a reference. The aim was to expose the test specimens to a standard fire over their entire surface (Figure 1) and to observe the difference in their behavior at elevated temperatures. See Figure 2 for the location of the test specimens in the fire furnace.

FIGURE 1. Test specimens before the fire resistance experiment.

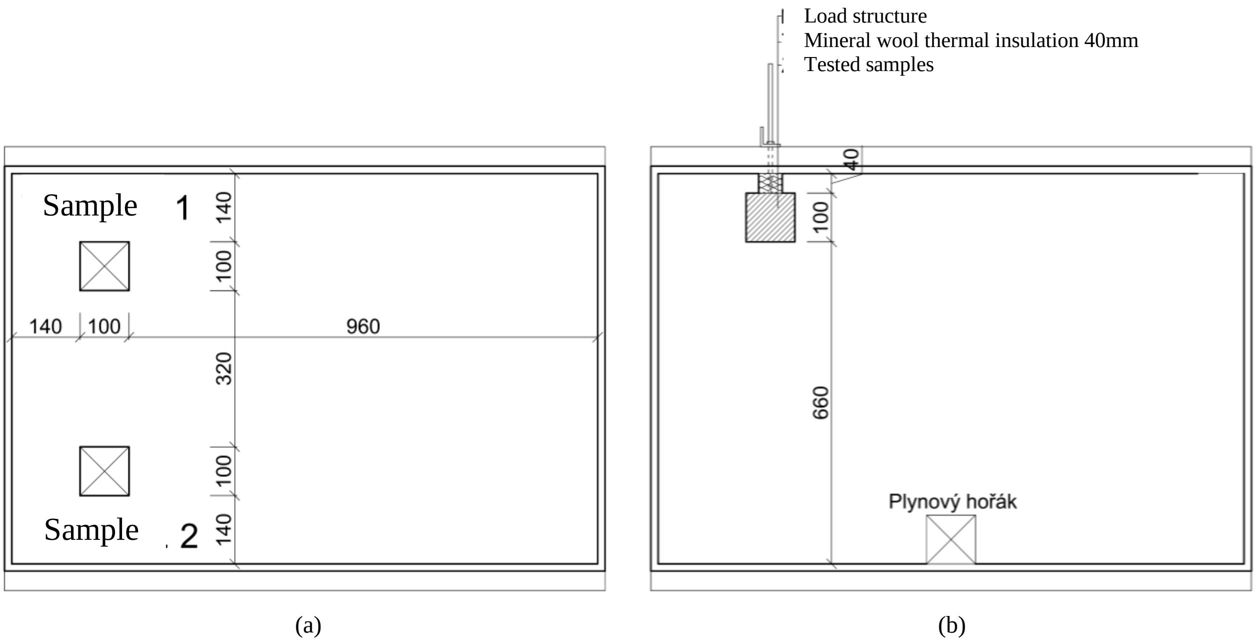

FIGURE 2. Position of test specimens in the fire furnace: (a) location of test specimens in the combustion chamber (floor plan); (b) placement of test specimens inside the furnace (section).

During the experiment, the concrete layers of Reference Test Sample No. 2 (REF) were gradually split. The beginning of the splitting of the concrete layers was about 5 minutes. Test sample No. 1 (PP) did not show any non-standard behavior caused by high temperature, there was no splitting of the concrete layers or its destruction. Figure 3. shows the course of temperatures inside the furnace during the experiment in comparison with the nominal standard temperature curve according to ISO 834 [10].

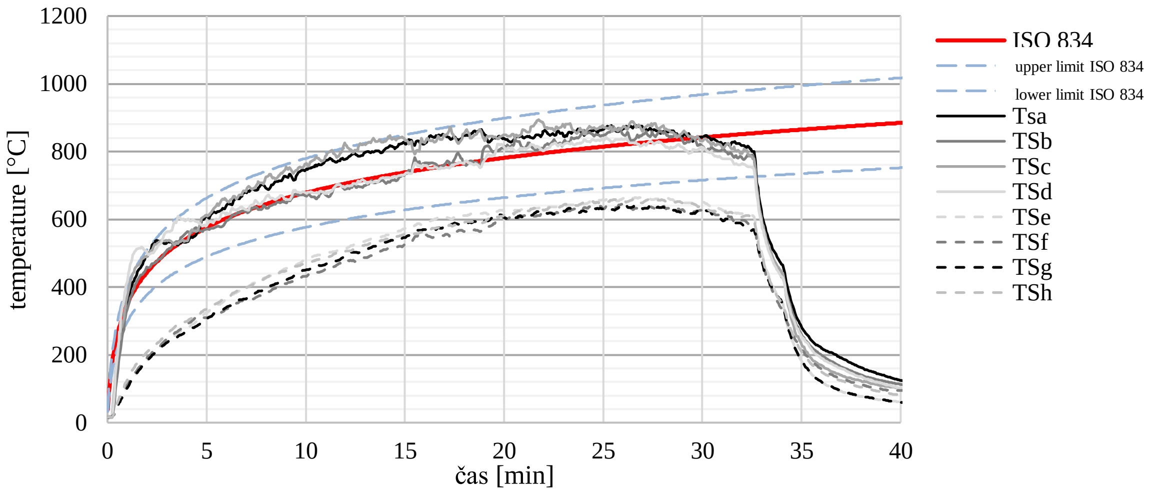

FIGURE 3. The course of temperatures inside the furnace in comparison with the nominal standard temperature curve ISO 834.

FIGURE 4. Tested samples after the fire resistance experiment.

Compared to the planned 30 minutes, the test ended at 33.5 minutes with an interruption of data recording at 40 minutes. During the experiment, the concrete layers were massively split off in test sample No. 2 (REF) and, as a result, it broke and fell off the suspension structure (Figure 4). Test Sample No. 1 (PP) did not show negative behavior caused by elevated temperature throughout the experiment. From about 27 minutes, the combustion gas level dropped below the level where the mass flow meter is able to supply the required amount of gas and the resulting power and temperatures decreased, however, the measured temperatures did not fall below the lower limit of the ISO 834 standard temperature curve [10].

CONCLUSIONS

The work, which we deal with in the research, has the basic goals of saving sources of non-renewable raw materials, preventing and solving problems associated with the generation of waste and, depending on that, use waste glass in concrete. It is therefore necessary to meet research goals that can help realize these ideas. In addition to environmental and chemical parameters, the basic goals also include physical properties. Fire resistance is one of the fundamental research issues in the field of concrete with waste components in general, and therefore the aim of this research was to expose test specimens to standard fire over their entire surface and to monitor the development of their behavior at elevated temperatures. Significant differences were noted, and while from the reference HPC REF sample, the concrete layers began to massively split and fall off the structure, the new PP mixture did not show any non-standard behavior in response to elevated temperature throughout the experiment. This knowledge positively contributes to the possibility of further research and development of mixtures of this type - containing recycled and waste materials.

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