



Kaunas University of Technology
Faculty of Civil Engineering and Architecture

Investigations on the Natural Zeolites Influence on Cementitious Products Properties

Master's Final Degree Project
Structural and Building Products Engineering (6211EX008)

Fallon Clare Manhanga

Project author

Prof. Dr. Žymantas Rudžionis

Supervisor

Kaunas, 2021



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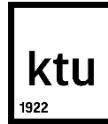
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**KAUNAS UNIVERSITY OF TECHNOLOGY
FACULTY OF CIVIL ENGINEERING AND ARCHITECTURE**

Task of the Master's final degree project

Study programme: Structures and Building Products Engineering

Topic of the project (English):

Investigations on the Natural Zeolites Influence on Cementitious Products Properties

Topic of the project approved by order of the dean No. _____

(English):

Investigations on the Natural Zeolites Influence on Cementitious Products Properties

(Lithuanian):

Gamtinių ceolitų įtakos cementinių gaminių savybėms tyrima

Parts of the degree project:

Introduction

x

Literature review

x

Research methodology

x

 Experimental research

 Analytical research

 Numerical research

 Economical part

Conclusions

x

Supervisor:

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Fallon Clare Manhanga. Investigations on the Natural Zeolites Influence on Cementitious Products Properties. Master's Final Degree Project / supervisor Prof. Dr. Žymantas Rudžionis; Faculty of Civil Engineering and Architecture, Kaunas University of Technology.

Study field and area (study field group): Engineering Sciences, Civil Engineering (E05).

Keywords: cementitious products, concrete, zeolite, density, compressive strength, adsorption, frost resistance, moisture content.

Kaunas, 2021. 62 p.

Summary

Climate change is a real issue these days, and as engineers, we always have to look for ways to improve the construction industry so that it doesn't promote the degradation of the environment. Concrete is the most common building product. From its production to use, it has a large negative impact on the environment.

It is important to find ways to reduce this impact, and one of the best is through production, namely the composition of concrete. Over the years, engineers have come up with innovative ways to reduce the use of cement in order to alleviate its impact on the environment.

Zeolites are a naturally found mineral and can function as a replacement, in small amounts, of cement. In this paper, the aim is to research the possibilities of replacing cement with zeolite but still achieving the required properties of concrete such as compressive strength, resistance to corrosion, water adsorption and more. Two types of the natural zeolite (clinoptilolite) with different particles size have been used (50 μ m and 200 μ m) and various test methods have been implemented to determine the effect of these two types of zeolite on cementitious products properties.

Fallon Clare Manhanga. Gamtinių ceolitų įtakos cementinių gaminių savybėms tyrima. Magistro baigiamasis projektas / vadovas Prof. Dr. Žymantas Rudžionis; Kauno technologijos universitetas, Statybos ir architektūros fakultetas.

Studijų kryptis ir sritis (studijų krypčių grupė): Inžinerijos mokslai, Statybos inžinerija (E05).

Reikšminiai žodžiai: : cementiniai gaminiai, betonas, ceolitas, tankis, gniuždomasis stipris, adsorbcija, atsparumas šalčiui, drėgmės kiekis.

Kaunas, 2021. 62 p.

Santrauka

Klimato kaita yra reali šių dienų problema, ir mes, būdami inžinieriai, visada turime ieškoti būdų, kaip pagerinti statybų pramonę, kad ji neskatinėtų aplinkos blogėjimo. Betonai yra labiausiai paplitęs statybos produktas, kuris nuo jo gamybos iki panaudojimo turi didelį neigiamą poveikį aplinkai.

Svarbu rasti būdų, kaip sumažinti šį poveikį, o vienas geriausių yra betono gamyba, naudojant mažesnę cemento kiekį. Per daugelį metų inžinieriai sugalvojo novatoriškų būdų, kaip sumažinti cemento naudojimą, kad būtų sumažintas jo poveikis aplinkai.

Ceolitas yra natūraliai randamas mineralas ir gali veikti kaip pakankamai efektyvus cemento pakaitalas. Šiame straipsnyje siekiama ištirti galimybes pakeisti cementą ceolitu ir tuo pačiu pasiekti reikalingas betono savybes, tokias kaip gniuždomasis stipris, atsparumas korozijai, vandens adsorbcija ir kt. Buvo naudojami dviejų tipų gamtinių ceolito (klinoptilolito) tipai (50µm ir 200µm vidutinio dalelių dydžio)) ir buvo panaudoti įvairūs bandymų metodai, siekiant nustatyti šių dviejų tipų ceolito poveikį cementinių gaminių savybėms.

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Introduction

As engineers, we are continually looking for ways to improve construction. Nowadays, there is a focus on sustainable engineering, and careful selection of building materials can aid in improving this area of engineering.

Amongst the primary building materials is cement, which is a binder. Binders are substances that adhere to other materials to form a bond, which should be permanent. Cement is used in unison with aggregates and, of course, water to form concrete: a composite material widely used in the construction industry because of its excellent mechanical and physical properties. [1]

Though concrete has such great benefits and essential use, it has disadvantages as seen with its negative impact on the environment as well as low mechanical durability resulting in shrinkage and corrosion. [1] Constantly, engineers are trying to improve concrete properties to increase durability and fight the effects it has on the environment.

The production of Portland cement is responsible for around 6% [1] of the total global emissions. In a time where we are currently fighting climate change, it is important to find ways to reduce the effects the construction industry has on our world. Hence, engineers look to building materials to aid in this. To tackle this problem, researchers look into enhancing the mechanical structure and durability of concrete structures. Another option is reducing the consumption, consequently the production, of Portland cement. This can be done by developing the particle packing density of the concrete and replacing Portland cement with natural pozzolans and/or pozzolanic industrial by-products such as fly ash, granulated blast furnace slag or silica fume. [1]

Zeolites are a pozzolan naturally found in the environment. They can be synthesised as well to form synthetic/artificial zeolites. Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4). They consist of channels and cages that allow for ion exchange and rapid absorption, which makes them beneficial substitutes of pozzolans. Zeolites can resist high temperatures, with the natural zeolites not changing structure, and can resist other environmental conditions that affect properties of materials.

Amongst the many uses of zeolites, the most common are water softeners in detergents, in agricultural processes, in production of petroleum, as removal of particles of radiation [2] and increasingly in the construction industry.

In this work, the uses of natural zeolites in the construction industry are discussed as well as what research can be conducted to improve on what fellow researchers have already concluded.

1. Types of Zeolites

Zeolites are naturally found materials used in many ways including, but not limited to, drying agents, catalysts, cement mixing materials and desalination agents. Zeolites can be classified as natural zeolites or synthetic zeolites. There are around 40 natural zeolites and around 150 synthetic zeolites. [1, 2]

Natural zeolites form in both volcanic and sedimentary rocks. Artificial/synthetic zeolites are made for specific purposes, the best-known being zeolite A, commonly used as a laundry detergent, zeolites X and Y, used for catalytic cracking. [1]

The main properties of zeolites include ion exchange, dehydration and hydration. The pores in zeolites contain charge balancing ions [1] that can allow for ion exchange. In natural zeolites, the structure will not change as ions exchange, even under high temperatures. Such a property can be used to soften water. Water can contain heavy metals, and this makes it dangerous for human consumption; hence, zeolites will remove magnesium and calcium in exchange with sodium making the water usable. The heavy metals can be collected and re-used. [1, 2] Zeolites allow for relatively low-cost adsorption, wide pH range and high performance in its different uses.

During dehydration, natural zeolites lose weight with increasing temperature, and this can help form lightweight concrete. [5] Synthetic zeolites do not lose weight but the structure of them changes. As the structure changes, it loses zeolitic properties. [1]

Zeolites can enhance the mechanical properties of concrete and mortar and their resistance to chemical and biological attacks. They can be used as supplementary cementitious material with benefits such as increasing durability and lowering the heat of hydration. [3]

In detergents, zeolites are used to remove calcium and magnesium and soften water so that these detergents can work better. How the zeolites work is that they trap magnesium and calcium ions that are plentiful in tap water then release sodium ions which soften water. [2]

Zeolites are also used in reducing or controlling odour, especially in cat litter. The porous structure of zeolites traps unwanted molecules of odour or other liquids. Other than this, they've been used to remove radioactive particles from nuclear waste. [2] This cleans up soils contaminated with heavy toxic metals. After the Fukushima nuclear disaster in 2011, in Japan, farmers spread zeolites on their fields to remove any radioactive particles that remained. Clinoptilolite Zeolite had a variety of roles in tackling the effects of the Chernobyl accident. Over 500,000 tons of Clinoptilolite Zeolite was shipped in from Ukraine, Georgia and Russia. The material was successfully used to decontaminate low-level radiation waters. [5]

Zeolites can be used as catalysts in producing drugs and petrol: they break down hydrocarbon into diesel and wax. Pores in a particular zeolite are of a fixed size and shape; hence, zeolite catalysts can work selectively on certain molecules. They can select the molecules they work on in other ways besides shape and size. Like all catalysts, zeolites are reusable over and over again. [2]

The general formula of zeolites is $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot nH_2O$ where M is the extra-framework cations K^+ , Na^+ , Ca^{2+} , Mg^{2+} and n and x are the number of water molecules.

2. Structure of Zeolites

Natural zeolites have a 3D honeycomb structure of hydrated crystalline aluminosilicates. They are formed of tetrahedral units linked together by sharing the four oxygen atoms. The ratio of Si/Al in zeolites varies between 1 and infinity with generally more polymorphs of SiO₂. When comparing with synthetic zeolites, natural zeolites have a lower Si/Al ratio as the structure cannot be altered or designed for a specific use. [1]

The framework of zeolites consists of passages and blockages or cages containing cations that balance charges. Cations, such as potassium, sodium, calcium and magnesium that can be replaced by extra cations, cannot affect the properties of zeolites because with temperatures from 500°C, water molecules can be removed from these channels or pores, and other cations can be introduced without changing the structure of zeolites.

Secondary building units are the different tetrahedral arrangements in zeolites. There are about seven different secondary building units categorised based on their Si and Al arrangements. Fig. 1. shows the secondary building units that can be found in zeolites based on Si and Al arrangements. The size of passages and cages in zeolites is contributed to the position, size and coordination of extra-framework cations. Dimensions of passages formed from 6, 8, 10, 12 and 14 oxygen atoms are between 3 and 10Å, where Å is 10⁻¹⁰ m or 0.1 nm. Controlling the openings in zeolites is possible through replacing cations. Presently, in initial experiments, I have used 200µm and 50µm zeolites and compared its effects on water/cement ratio. [1, 6]

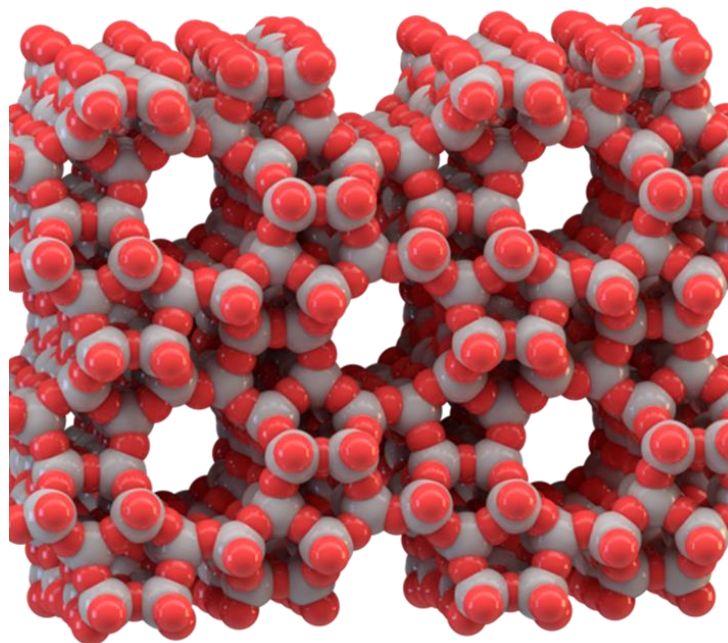


Fig. 1. 3D structure of zeolite [6]

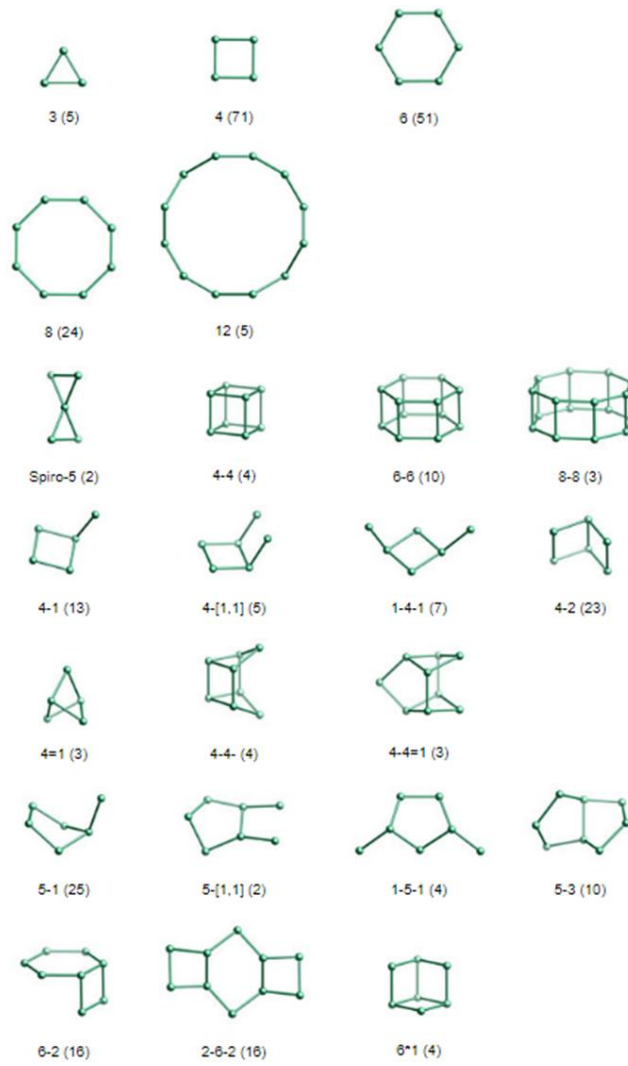


Fig. 2. Secondary building units in zeolites [7]

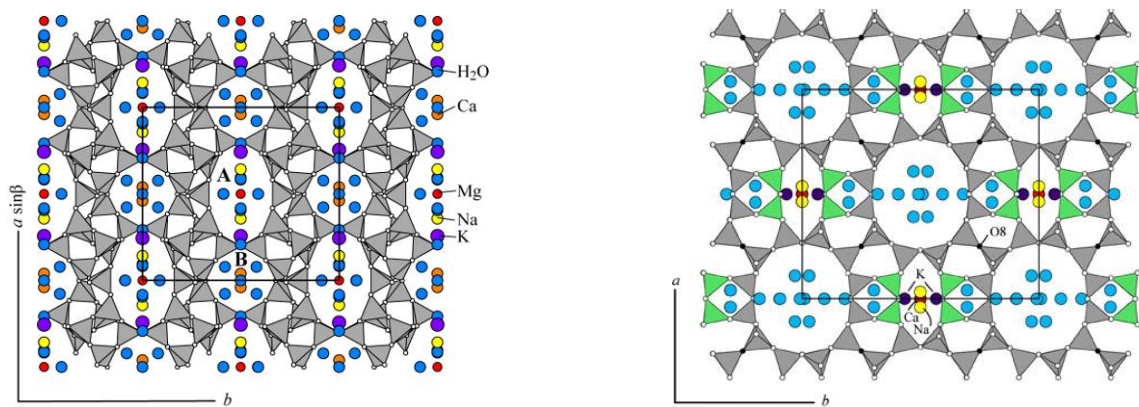


Fig. 3. Structure of commonly used zeolite (left) clinoptilolite, (right) mordenite [9]

3. Synthetic Zeolites

Synthetic zeolites are artificially made zeolites. Synthetic zeolites are usually created for specific purposes; hence, they are designed to suit a certain use. From the early 1950s, commercially significant zeolites A, X, and Y were discovered by Milton and Breck. These zeolites were synthesized from readily available raw materials at much lower temperature and pressure than used earlier. Many of the new synthetic zeolites had larger pore size than most of the known natural zeolites, allowing applications involving larger molecules.

Many zeolites can be synthesized with SiO_2 higher or lower than in nature for the same framework type. Higher SiO_2 generally gives greater hydrothermal stability, stronger-acid catalytic activity, and greater hydrophobicity as adsorbents. Conversely, lower SiO_2 gives greater cation exchange capacity and higher absorbance for polar molecules. Controlling the synthesis process optimizes a zeolite for different applications.

Synthetic zeolites may be a more attractive option where purity is an important part of a process. Natural zeolites may contain impurities making it difficult for certain applications. [1] Synthetic zeolites hold one important advantage over natural zeolites: they can be designed for a specific use. They do, however, have a poor performance when it comes to ion exchange, one of the most important properties of zeolites.

A method that can be used is hydrothermal synthesis. Amorphous reactants containing a silica source, an aluminium source, an inorganic cation, an organic structure-directing agent and water are mixed. The mixture undergoes an ageing process conducted either at room temperature or an elevated temperature to ensure adequate mixing and tuning. Then this aged mixture is put into a sealed, heated container and heated to the reaction temperature. After a certain synthesis period, the container is cooled down, and the crystalline product is recovered by separation, washing and drying. [11]

The synthesis can be conducted on a continuous or semi-continuous mode, which enhances the capacity, making it compatible for industrial applications.

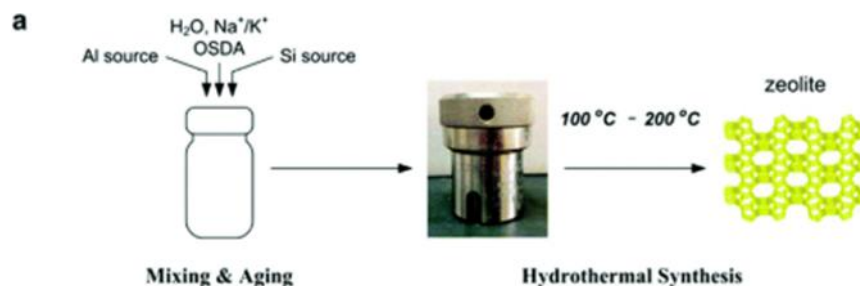


Fig. 4. Process of synthesising zeolites [11]

4. Natural Zeolites

Natural zeolites are also used for different purposes including water treatment; gas purification and construction as a pozzolanic additive in concrete production. Natural zeolites form on volcanic rocks due to the reaction between alkaline and groundwater. They can also be found in shallow marine basins but are not as pure as its synthetically made counterpart. Open-pit mining techniques are used to mine natural zeolites. The ore is blasted and stripped before processing (crush, dried or milled). Milled ore is shipped in bags or bulk. Crushed ore is screened to remove fine material for a more granular product. [10,12]



Fig. 5. Natural zeolite rock [12]

4.1. Applications of Natural Zeolites

Generally, several properties of concrete can be affected positively with the addition of zeolite: compressive strength, chloride permeability, frost resistance and shrinkage are among some of the main properties positively affected.

Important to note is that above 30% addition of zeolite, properties of concrete could decrease. [1]

4.1.1. Natural zeolites can be used as a pozzolan

Pozzolans are siliceous or siliceous and aluminous materials that react with water to form compounds having cementitious properties. Calcium hydroxide (CaOH) is formed during the hydration of cement in concrete. It has no cementitious properties; hence, it easily dissolves in water forming highly porous cement paste which can decrease the mechanical properties of concrete and consequently reduce its durability.

With the addition of zeolites, large pores and channels allow for rapid absorption of water and appropriate exchange of ions. In concretes with low W/C ratios, water is not enough for full hydration, and some cement has no use; hence, adding pozzolans in this portion of unused cement can improve the microstructure. Since zeolites are abundant in silicates and aluminates which react with the

calcium hydroxide to form tricalcium silicate (alite) and tricalcium aluminate, these products increase the density of concrete and reduce the number of pores in it.

In some studies [1], 10% and 15% weight of cement was exchanged by zeolite in the cement pastes. The compressive strength was tested, but it lowered by 1.18 and 1.55 times, respectively. [1] Despite these results, other works have shown that zeolite can increase the compressive strength. One trend that is apparent in the use of zeolites is that a higher percentage of zeolites by cement mass results in higher porosity and consequently, loss of strength.

Compressive strength, resistance to water permeability, sulfate attack, carbonation corrosion and freeze/thaw effects, which are all properties of concrete, have shown a positive result with the addition of zeolites. [1]

4.1.2. Natural zeolites can be used as internal curing agents

Curing is an important process during construction. Fresh concrete needs to be maintained at an optimum temperature and relevant moisture content for it to harden and achieve the required properties. When the water to cement ratio is less than 0.4, autogenous shrinkage occurs, and this can cause cracking, which leads to failure in concrete. Because zeolites can absorb water, they can help prevent autogenous shrinkage through the many water pockets, likewise, with drying shrinkage, where water evaporates reducing the volume of concrete. [1, 33]

4.1.3. Natural zeolites can be used as aggregates and air generating agents in lightweight concrete

In one study, replacing portions of fine aggregate with zeolite reduced the weight of samples and increased the thermal properties of concrete. Pre-wetting natural zeolites and heating them again has the possibility to form lightweight concrete.

It can also be suggested to use cementitious products containing zeolite for creating material which is sound insulating. [31] Normal concrete is dense, and the denser it is, the lower its acoustic properties. As such, creating a lightweight material that can offer the same or better properties than normal concrete would be very useful. Lightweight materials offer better sound insulating properties. A product that can be used in wall panels could prove efficient.

Some researchers [32] have included rubber waste as an aggregate to improve the sound insulating properties of concrete. As seen from their results, increasing the rubber content by coarse aggregate significantly reduced the compressive strength of concrete amongst other properties such as durability. However, it was concluded that the lower dynamic modulus of elasticity, which shows a weaker bonding in the matrix, resulted in better sound insulation. [32] It could be investigated if combining zeolite and rubber waste could improve the overall performance of such a mix to promote better sound insulation, compressive and flexural strength as well as durability.

4.1.4. Natural zeolites can be used in heavy metal adsorption

Adsorption is the removal of substances from gaseous or liquid solutions. This is a selective process of certain substances from gases or liquids onto the surface of a solid substrate. [18]

The adsorbate is the material that is adsorbed by the adsorbent, and the adsorbent selects, in this case, the heavy metals. Van der Waals and electrostatic forces are responsible for the activity of adsorption. There is constant repulsion and attraction of molecules and surfaces allowing for adsorption to occur. [20] A large specific surface area is preferable for providing large adsorption capacity. The size of the pores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of pores is a valuable property. This makes zeolites an excellent adsorbent of ions because it offers this naturally huge pore size. Not only that, but zeolite can also be modified to fit the adsorbate molecules making it an even better material. [18]

Heavy metals have an effect on hydration of cement as they can affect the structure and permeability property during this process and ultimately the overall products of hydration. [17] Cement is the most adaptable binder currently available for the immobilisation of heavy metals. [17] Hence, it is important to try to improve the sustainability of use of cement, and zeolites are one way to do this as they are found naturally. Andrejkovičová et al. [19] looked into the effect of a natural zeolite called clinoptilolite, on mechanical performance and heavy metal's adsorption capacity of metakaolin-based geopolymers. Geopolymers are used because they achieve high early strength and are quite durable amongst other attractive properties. After experimentation, using X-ray diffraction, it showed that the geopolymers adsorbed the heavy metals Cu^{2+} Cr^{3+} and others, chromium being the last one adsorbed from a list of 5 heavy metals. The results indicated that adding 25% zeolite to geopolymers efficiently improved the adsorption capacity then allowing one to conclude that zeolites could allow formation of more eco-friendly materials that can treat water but still have high mechanical resistance. [19]

4.1.5. Aim of the work

The aim of this thesis is to determine what effect the naturally found zeolite, clinoptilolite, has on cement composites and to conclude on whether this effect could result in the creation of sustainable building materials which are in keeping with structural and durability requirements.

The following are the main tasks to be completed:

1. To determine how zeolite affects to the water requirement for normal consistency paste of cement and how the W/C ratio has a direct effect on the compressive strength of cement composites.
2. To determine the effect of zeolite on density and porosity as these properties have an effect on the performance of concrete.
3. To determine the influence of zeolite on compressive strength, flexural strength and specific strength of cement composites and to check the possibilities to use non-destructive testing methods for the prognosis of these composites' mechanical properties.
4. To determine the heavy metal adsorption capabilities of cement composites containing zeolite as removal of heavy metals from soils at construction sites is currently an expensive process.
5. To determine the frost resistance of cement composites containing zeolite.

5. Initial experimentation

The main aim of experimentation is to fulfill the requirements to achieve “green concrete”. Additionally, the research aims to further study the effects of natural zeolites on cementitious products and predict how effective the use of zeolites would be concrete production.

Various tests have been performed on products containing cement and different compositions of zeolite. The pozzolanic product that has been chosen is ZeoBau which is produced by a Slovakia based company called ZEOCEM. This product can be used for concrete production and other chemical building products. The benefits of this product include an improved stability of the mixture, better sulphate resistance (making it suitable for use in high sulphate environments), heavy metal ions are made inactive for reactions, and C_3A (tricalcium aluminate) content in cement is decreased which is vulnerable to sulphate attack. [20]

Samples of cement hardened paste with additions of zeolites have been made and tests for compressive strength, flexural strength and water/cement ratio have been conducted initially. Additionally, these samples were used to test for kinetics of water adsorption. Afterwards, more samples were created that contain an estimated water to dry product ratio of 0.39. These samples were then used to test the effect of zeolite on the temperature during hardening of samples. The test used for this was the semi-adiabatic test method. Also, compressive and flexural strength tests were conducted after 7 and 28 days to determine the effect of zeolite of two different specific area in cement hardened pastes. Lastly, samples containing chromium and a percentage of zeolite content were created and tested for compressive strength after different sets of days. These samples were washed out to determine the heavy metal adsorption properties of cement composites containing zeolite. Additionally, after 28 days, these samples were tested for frost resistance and consistency/quality through the ultrasonic pulse velocity method.

Two sizes of moulds have been used for testing. For the first few tests, moulds of 40x40x160mm have been used, and for the tests of heavy metal (chromium) adsorption, 70x70x70mm moulds have been made use of.

5.1. Water/cement ratio

Water/cement ratio is one of the most important properties of a concrete mix. It affects the workability of concrete as well as its strength and durability properties. In this thesis, it was first determined the water requirement at different percentages of zeolite by cement mass.

5.1.1. Methods

The testing equipment used was the VICAT apparatus for two different types of zeolites: 50 μ m and 200 μ m ZeoBau at 10, 20, 30 and 50% content in relation to cement. The decision to use different types of zeolite is to determine how the surface-area-to-volume ratio affects the properties of cement composites. The instrument is used to test the consistency of cement pastes and the initial and final setting time, but in this thesis, only the former will be tested. To use the apparatus to test for consistency, one should fill the mould with the paste and make the plunger just touch the top surface of the cement paste, then let it fall and note the amount of penetration. [21]

If the reading on the vertical scale is 5mm to 7mm, it means the cement paste is of normal consistency. [21] It was decided to begin with testing both types of zeolites for estimation of the W/C ratio requirement of normal consistency paste. Since zeolites have a high-water intake, the initial test was also used to determine this.

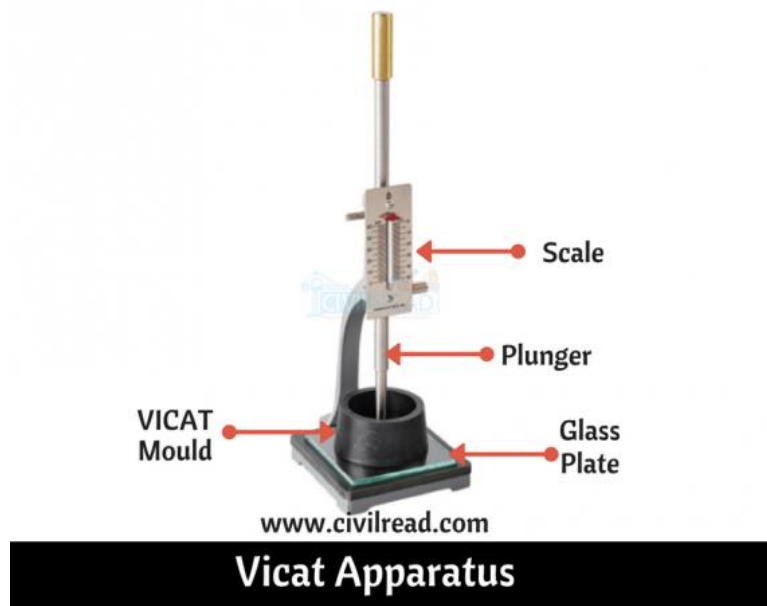


Fig. 6. Vicat apparatus for estimating W/C ratio for normal consistency cement paste

5.1.2. Results

As seen from the results in Table 1. and Table 2., increasing the content of zeolite by cement mass increases the water requirement for the paste for both types of zeolite (50 μ m and 200 μ m). As stated by Tran et al. [1], the introduction of zeolites to cement pastes decreases the workability of concrete, in this case cement paste. [1]

Additionally, based on current results, 50 μ m ZeoBau required slightly more water than 200 μ m ZeoBau, that is, between 0.5 and 1 % more. The results of this test clearly show the water absorption properties of zeolites. Their microporous structure allows trapping of water which means more water is required than a normal consistency paste with no zeolite. It allows expansion of the idea of the possibilities this water trapping ability has for the concrete industry. There are possibilities to counter autogenous shrinkage or promote internal curing. [1, 13] This also confirms that there is a larger water requirement for a smaller particle size because it has a higher surface area to volume ratio. Given that the 50 μ m ZeoBau required more water, it could lead one to assume that the reaction goes faster with this type of zeolite because of the lower surface-area-to-volume ratio. If the reaction occurs faster, higher levels of strength could be achieved at early stages than the 200 μ m ZeoBau, but as time goes on, the 200 μ m ZeoBau could achieve better results because it has a larger surface area for absorption. There are 4 times as many pores to trap water in the zeolites and this could improve those desirable properties such as internal curing to avoid autogenous or drying shrinkage. However, the strength could be lower because the composites could be more dense.

Table 1. Water content in relation to Zeolites 50µm Zeobau, %

Zeolite amount from cement mass, %	0	10	20	30	50
Water requirement for normal consistency paste, %	29.25	30.00	32.50	35.75	42.00

Table 2. Water content in relation to Zeolites 200µm Zeobau, %

Zeolite amount from cement mass, %	0	10	20	30	50
Water requirement for normal consistency paste, %	29.25	30.00	32.00	34.75	41.50

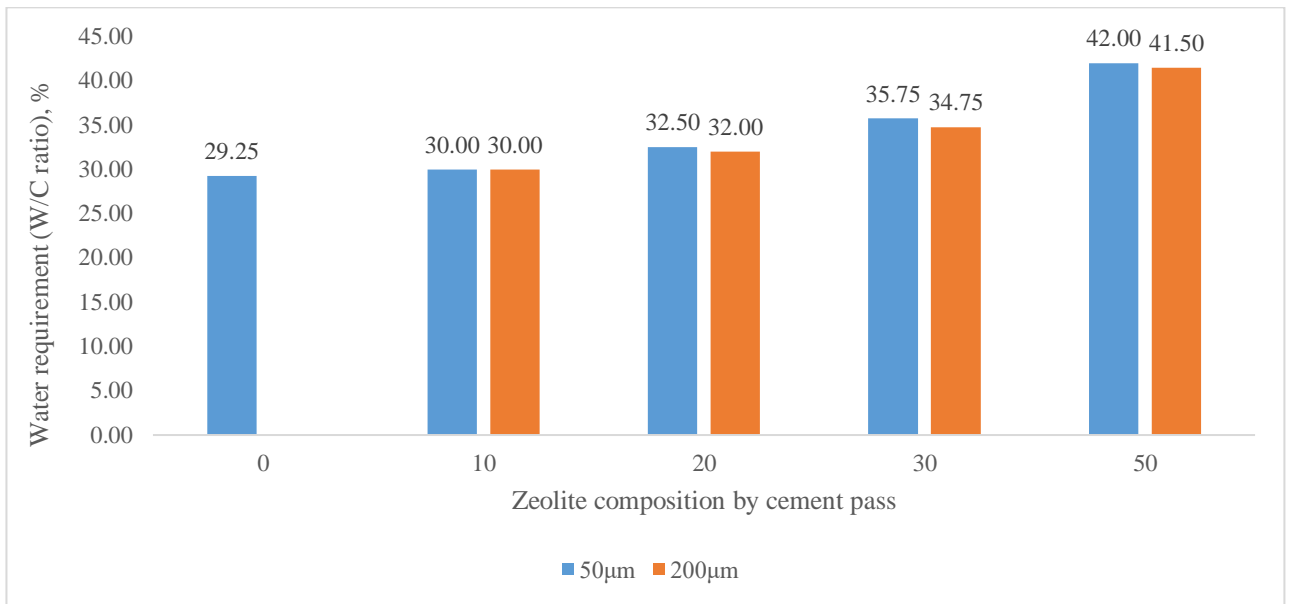


Fig. 7. Water requirement for normal consistency paste with part replaced with zeolite

5.2. Compressive, Flexural and Specific Strength

There was also determined the flexural and compressive strength of samples containing different amounts of zeolites by type at different intervals and amounts of water. In addition to compressive strength and flexural strength, it was also determined specific strength which is a material's strength (force per unit area at failure) divided by its density. It is also known as the strength-to-weight ratio or strength-to-mass ratio. Specific strength can be described as the length at which a column can support itself without breaking; hence, being also known as breaking length. [15] How useful materials with high specific strength are lies with how good they are at resisting corrosion. Carbon fibre reinforced composites are considered materials with high specific strength. [16]

5.2.1. Methods

A simple lab test using a compression test machine was conducted, likewise for flexural strength and the specific strength was calculated from these results. The mass and dimensions of each sample were

measured and recorded before the tests were conducted. The tests were conducted after 7, 14 and 28 and the results calculated and summarised in the following tables.

The specific strength was calculated using the formula below:

$$\text{Specific strength} = \frac{\text{Compressive strength}}{\text{Density}} \quad (1)$$



Fig. 8. Compression testing machine

5.2.2. Results

According to Tables 3, 4 and 5 which show results from tests conducted after 7 days containing 200µm ZeoBau, the flexural strength, compressive strength and specific strength all decrease with increasing percentage of zeolites. Although, it is noted that at 20% 200µm ZeoBau, the flexural strength increased to 2.62 N/mm² as compared to the 2 N/mm² at 10% which is an increase of 32%. According to Tran et. al, [1] the use of higher zeolite percentage by cement amount increases the porosity of the composite but decreases its compressive strength as seen in the results below.

Table 3. Flexural strength of 200µm samples after 7 days

Part of cement changed by zeolite, %	10	20	30	50
Flexural strength, f_t , N/mm ²	2.00	2.62	2.46	1.74

Table 4. Compressive strength of 200µm samples after 7 days

Part of cement changed by zeolite, %	10	20	30	50
Compressive strength, f_c , N/mm ²	64.80	47.80	38.40	21.80

Table 5. Specific strength of 200µm samples after 7 days

Part of cement changed by zeolite, %	10	20	30	50
Specific strength, kNm/kg	33.00	25.92	22.13	14.16

Next, similar tests were conducted for both samples with 50 μ m and 200 μ m after 14 days as summarised in the Table 6, 7, 8, 9, 10 and 11.

Table 6. Flexural strength of 50 μ m samples after 14 days

Part of cement changed by zeolite, %	20	30	50
f_i, N/mm²	2.68	2.64	1.95

Table 7. Compressive strength of 50 μ m samples after 14 days

Part of cement changed by zeolite, %	20	30	50
f_g, N/mm²	50.00	42.10	28.20

Table 8. Specific strength of 50 μ m samples after 14 days

Part of cement changed by zeolite, %	20	30	50
Specific strength kNm/kg	27.34	24.42	18.31

According to these tables, the flexural strength, compressive strength and specific strength all decrease with the increasing percentage of zeolites for 50 μ m ZeoBau. However, for the 200 μ m ZeoBau, it can be seen that there is a slight increase in the different strengths as compared to their values after 7 days. Of particular mention is 30% zeolite content by cement mass which has seen an increase for all strengths. The flexural strength increases by 16%, the compressive strength by 3.35% and the specific strength by 2%.

Table 9. Flexural strength of 200 μ m samples after 14 days

Part of cement changed by zeolite, %	10	20	30	50
f_i, N/mm²	3.42	2.78	2.86	1.96

Table 10. Compressive strength of 200 μ m samples after 14 days

Part of cement changed by zeolite, %	10	20	30	50
f_g, N/mm²	55.20	46.80	39.70	24.70

Table 11. Specific strength of 200 μ m samples after 14 days

Part of cement changed by zeolite, %	10	20	30	50
Specific strength kNm/kg	28.45	25.28	22.59	15.84

As seen by the above results, the flexural strength, compressive strength and specific strength all decrease with the increasing percentage of zeolites. Although comparing the compressive strength of the samples at the same percentage of ZeoBau though different particle size, we can see that the 50 μ m Zeobau has a higher compressive strength. At 20 and 30% zeolite composition, the compressive strength is 50MPa and 42.1MPa for 50 μ m Zeobau and 46.8MPa and 39.70MPa for 200 μ m. This may

conclude that the smaller particle size of zeolites yields higher compressive strength improving the properties of cement composites. However, it is noted that 200 μm yielded higher values of flexural strength at all compositions by cement mass of zeolite. It could also be that the 50 μm ZeoBau achieves a higher compressive strength only at earlier stages and could be surpassed by the 200 μm ZeoBau as time passes.

Once more, the samples were tested after 28 days and the results noted in Tables 12, 13, 14, 15, 16 and 17.

Table 12. Flexural strength of 50 μm samples after 28 days

Part of cement changed by zeolite, %	0	10	20	30	50
$f_i, \text{N/mm}^2$	3.54	3.77	2.78	2.86	1.96

Table 13. Compressive strength of 50 μm samples after 28 days

Part of cement changed by zeolite, %	0	10	20	30	50
$f_g, \text{N/mm}^2$	81.94	72.19	58.40	42.80	25.80

Table 14. Specific strength of 50 μm samples after 28 days

Part of cement changed by zeolite, %	0	10	20	30	50
Specific strength kNm/kg	39.53	36.36	31.47	24.84	16.76

According to these tables, increasing the percentage of zeolite reduces the compressive, flexural and specific strength. The sample without zeolite achieved better results than samples containing both types of zeolite. However, it can be noted that we can see a great increase in the values of compressive strength after 28 days. At each percentage of zeolite, a higher compressive strength was achieved than after 7 or 14 days. The compressive strength increased by 16.8% and 1.7% for 50 μm ZeoBau at 20 and 30% zeolite content by cement mass respectively. For the 200 μm ZeoBau, an increase of 9.6%, 8.5% and 13.4% can be seen at 10, 20 and 30% zeolite by cement mass.

Table 15. Flexural strength of 200 μm samples after 28 days

Part of cement changed by zeolite, %	10	20	30	50
$f_i, \text{N/mm}^2$	2.94	3.39	3.26	2.31

Table 16. Compressive strength of 200 μm samples after 28 days

Part of cement changed by zeolite, %	10	20	30	50
$f_g, \text{N/mm}^2$	60.50	50.80	45.00	27.10

Table 17. Specific strength of 200 μm samples after 28 days

Part of cement changed by zeolite, %	10	20	30	50
Specific strength kNm/kg	30.70	27.28	25.72	17.19

According to these tables, we can conclude that the compressive strength decreases with an increase in the percentage of zeolites additive although the value of compressive strength generally increases after 28 days. Also, as seen by the results, for 10 % and 20% zeolite composition, the compressive strength was 72.19MPa and 58.40MPa for 50 μ m then 60.50MPa and 50.80MPa for 200 μ m. This shows that the smaller the particle size of zeolite, the higher the compressive strength achieved. This then leads one to conclude that the high surface-area-to-volume ratio makes it possible to achieve higher compressive strengths; however, the flexural strength is higher for samples with a lower surface-area-to volume ratio. Though it is important to note that the strength decreases with increasing zeolite content, and hence, in the application in construction, engineers should be careful to accurately measure the amount of zeolite needed.

Additionally, if cementitious products that have been made with a variable W/C ratio are compared to those that have been made with a constant W/C ratio, it can be seen that the flexural strength is higher for samples made with a constant W/C ratio. However, for the compressive strength, having a variable W/C ratio results in higher compressive strength although it decreases with the addition of zeolite. The W/C ratio that was kept constant was 0.39. This could be attributed to internal curing. [1, 22, 33]

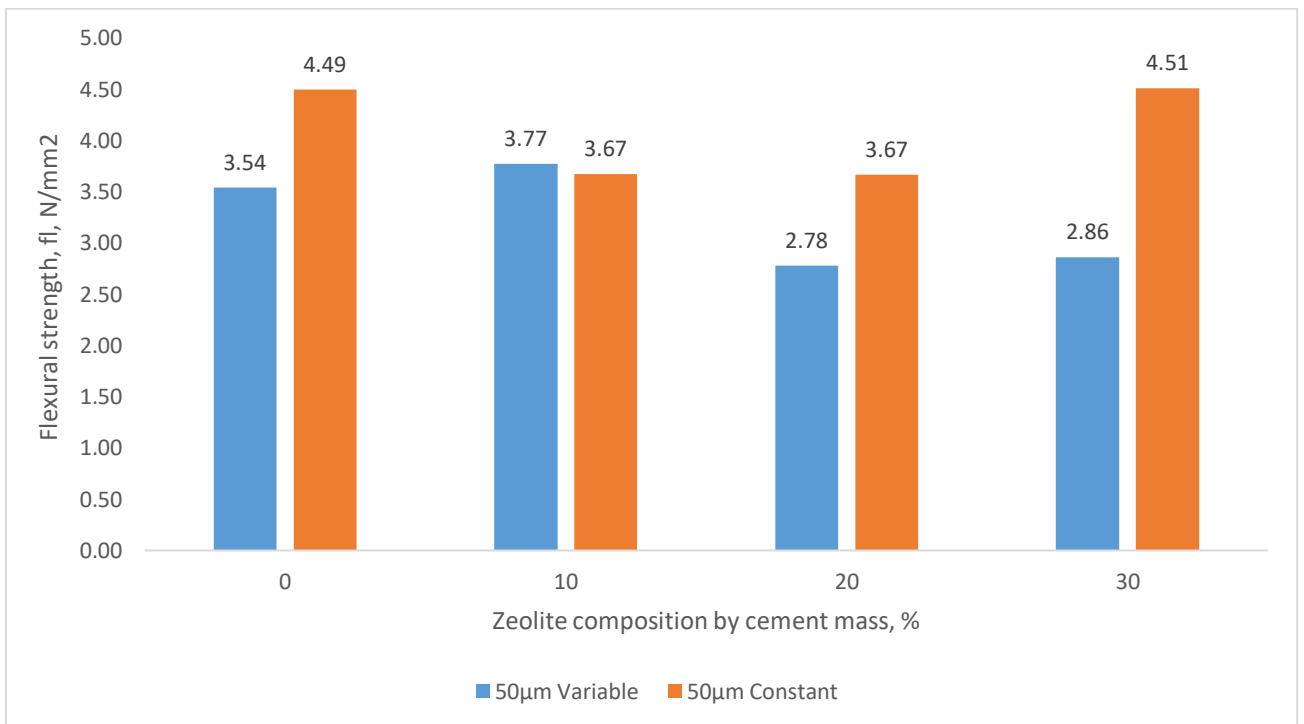


Fig. 9. Graph showing flexural strength of samples after 28 days with variable and constant W/C ratio for 50 μ m ZeoBau

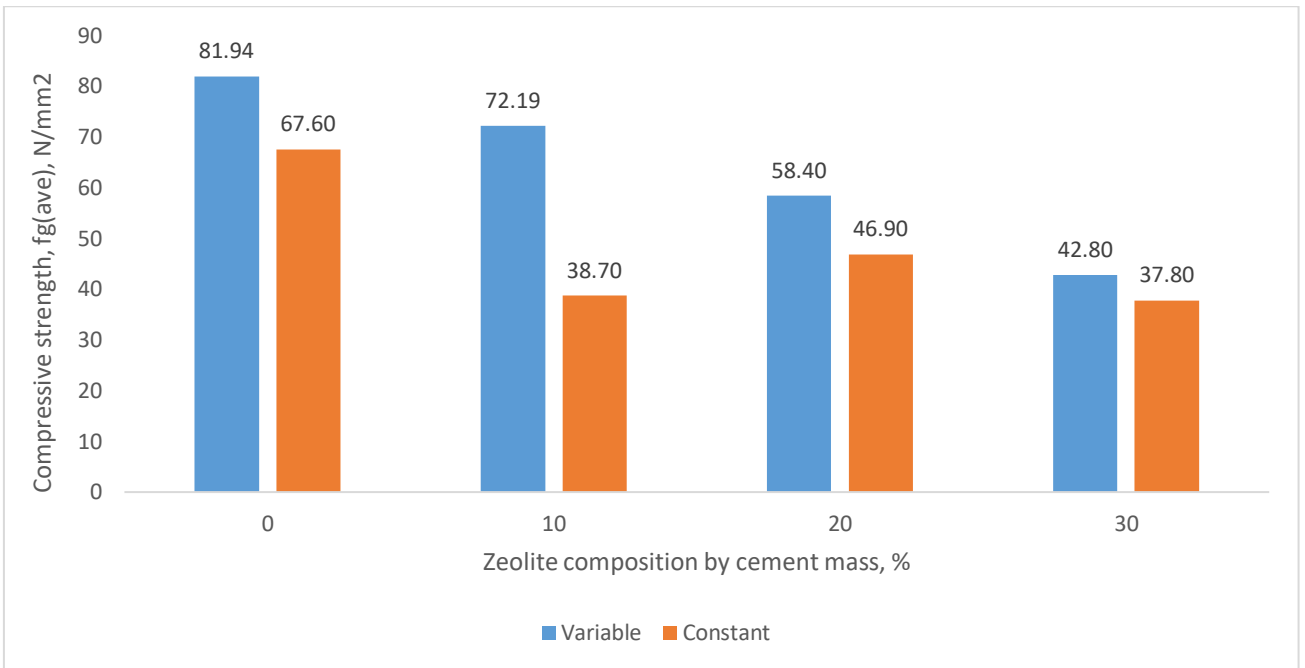


Fig. 10. Graph showing compressive strength of samples after 28 days with variable and constant W/C ratio for 50µm ZeoBau

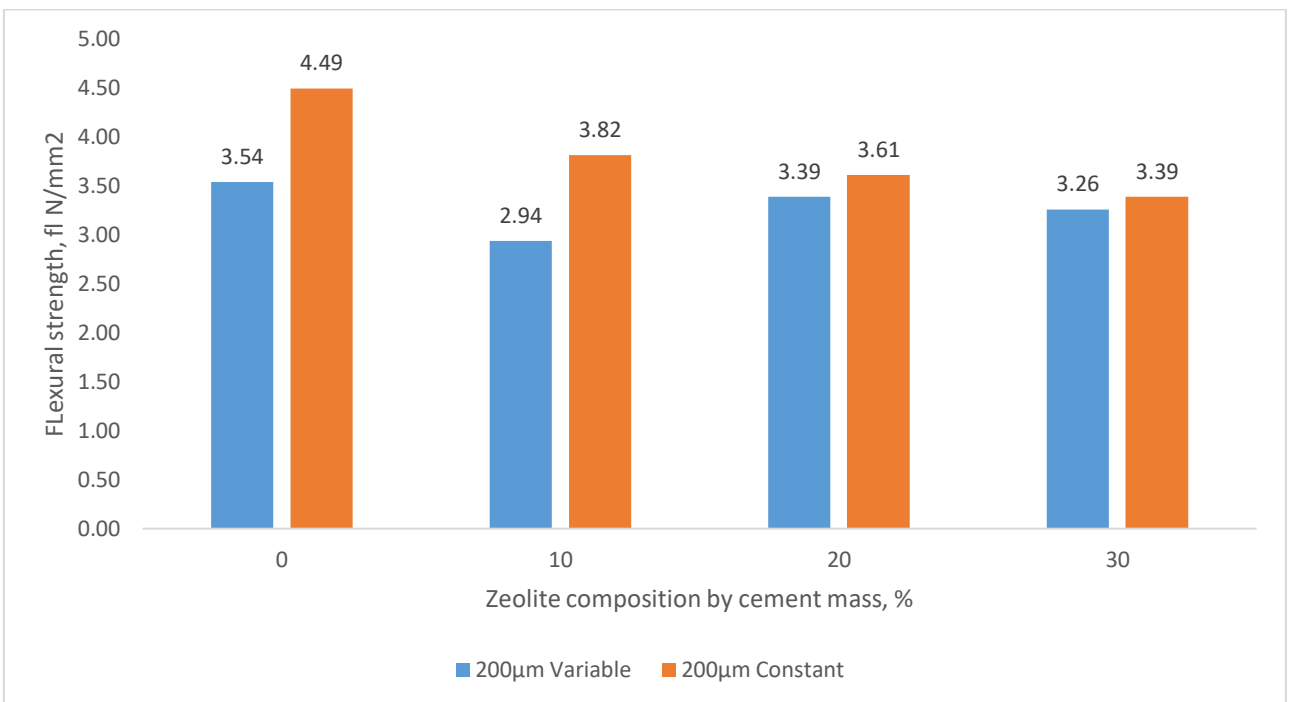


Fig. 11. Graph showing Flexural strength of samples after 28 days with variable and constant W/C ratio for 200µm ZeoBau

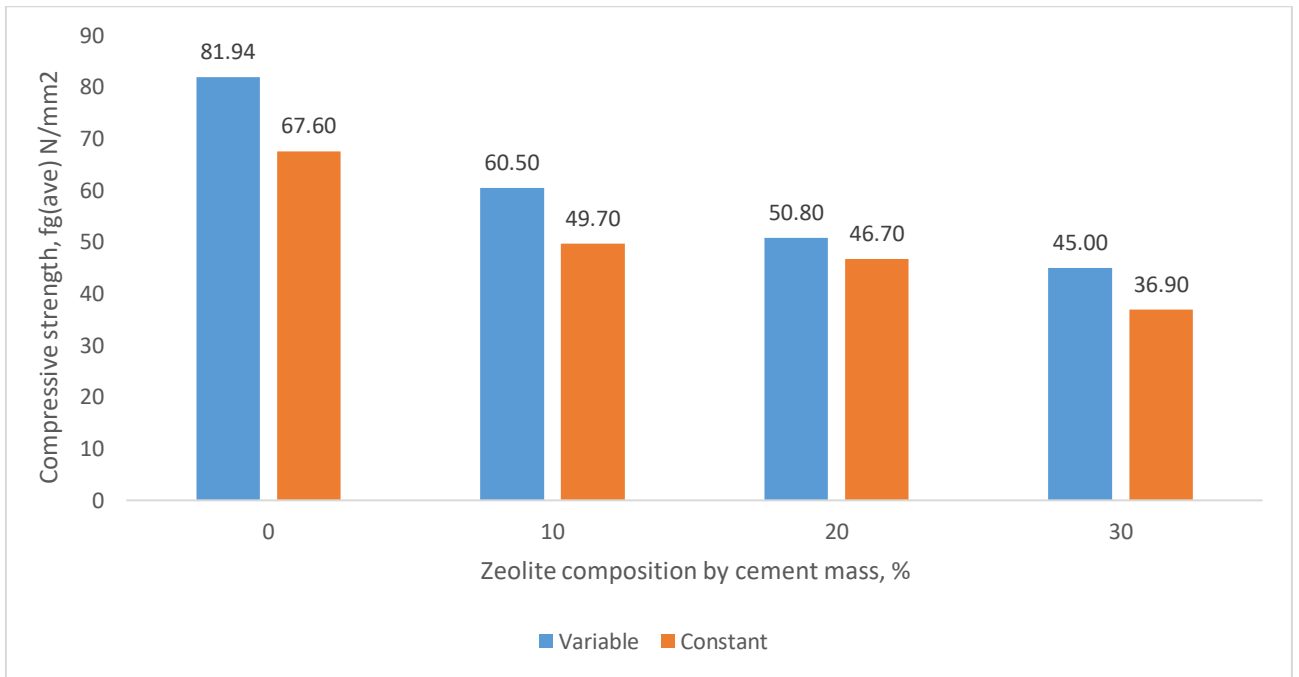


Fig. 12. Graph showing compressive strength of samples after 28 days with variable and constant W/C ratio for 200 μ m ZeoBau

As seen from the results in graphs in Fig. 9, 10, 11 and 12, a lower W/C ratio resulted in higher compressive strength. At 0% zeolite and 29.25% W/C ratio, the compressive strength was 81.94 MPa; at 20% zeolite by cement content and 32.0% W/C ratio, the compressive strength for 50 μ m and 200 μ m ZeoBau was 58.40 MPa and 50.80 MPa respectively. This goes to show the effect of W/C ratio on cementitious products' properties and how important it is to design concrete with the right mixture. When the mixture is designed for each composition, we can see that higher compressive strengths are achieved than when a method of one-size-fits-all is used. At each percentage of zeolite content, a higher compressive strength was achieved with a varied W/C ratio. The compressive strength decreased by 21.7%, 8.8% and 22% for 10, 20 and 30% zeolite content by cement mass when the W/C ratio was kept constant.

Zhutovsky and Kovler [33] also found that reducing the water to cement ratio decreased drying shrinkage. They concluded that the internal curing capabilities of concrete improve when the W/C ratio is decreased, and this means that cracking sensitivity is improved. [33] It was also said that although this internal curing has negative effects on compressive strength at early ages, the effect starts to fade as time progresses. [33] This could lead us to assume that with the current tests for the effect of zeolites, the results could match the control sample after some time making it possible to create "green" concrete that has similar strength and durability properties to normal concrete. As it can be seen, at 20% zeolite by cement mass at 14 days, 50MPa compressive strength was achieved then 58.40 MPa after 28 days for 50 μ m. The increase in strength can also be noted in 200 μ m zeolite.

5.3. Moisture content and Density

When concrete has very low W/C ratios, it increases its chances of autogenous shrinkage. [1, 33, 34] Autogenous shrinkage occurs when the volume within the concrete continues to change because of

the hardening process. This shrinkage excludes the effect of loads imposed on the structure and only takes into account the process of hardening. This is why curing is an important process during construction. It is necessary to maintain moisture in the structures to avoid cracking.

Tran et al. [1] also discussed the internal curing capabilities that zeolites promote when added to concrete samples. Since zeolites have water trapping abilities, they can be used to maintain a good moisture content within the concrete as it hardens, lessening the effects of shrinkage. Yang et al. [22] also investigated the effect of natural zeolite as an internal curing agent and discovered that adding 20% zeolite by amount of cement leads to higher internal relative humidity (90.4%) during the first 7 days as compared to that of the control sample (78.1%). [22]

5.3.1. Methods

As an additional test for this thesis, the possibility of using zeolite as a curing agent was tested. For this test, the samples were weighed, then dried at 50°C. Afterwards, they were weighed again, and the moisture content was calculated and tabulated below. The moisture content shows how much moisture was retained in the sample after drying. It allows one to conclude on the water trapping ability and resistance to drying shrinkage of samples containing zeolite.

5.3.2. Results

These two tables show the density and moisture content of the samples. As seen from the results, the higher the zeolite content, the higher the moisture content, generally. This goes to prove the water trapping capabilities of zeolites. As this is the case, zeolite can be incorporated in concrete samples to be used as an internal curing agent and minimise the self-desiccation of concrete. [1, 22, 33, 34] The smaller capillaries that external curing cannot reach can remain moisturised by the presence of water molecules trapped in zeolite particles. [1]

Table 18. Results of humidity test of cementitious samples with 50µm ZeoBau

Part of cement changed by zeolite%	Wet Density, kg/m ³	W, %	Dry Density, kg/m ³
0	2072.8	4.9	1976.0
10	1985.5	5.6	1880.2
20	1855.6	4.4	1777.4
30	1722.7	5.6	1631.3
50	1539.7	7.4	1433.6

Table 19. Results of humidity test of cementitious samples with 200µm ZeoBau

Part of cement changed by zeolite%	Wet Density, kg/m ³	W, %	Dry Density, kg/m ³
0	2072.8	4.9	1976.0
10	1970.5	3.7	1900.2
20	1862.1	4.6	1780.2
30	1749.7	5.0	1666.4
50	1576.5	6.5	1480.3

Additionally, we can also see the density of the samples generally decreases with increasing zeolite content. We can also see that the lowest dry or wet density falls in the range of lightweight concrete, which is 1440 to 1840 kg/m³. Further studies can be conducted to determine if higher compressive strength can be reached with this lightweight concrete that contains zeolite. Engineers are constantly trying to improve the properties of concrete to decrease the effects the industry has on the environment, so as seen by the results here, zeolites could prove a useful component in lightweight concrete.

It can be seen in one study [34], which used lightweight aggregates to improve moisture absorption, that it is possible to effectively reduce drying shrinkage. Linking that with this thesis, we can say that further research is required into the effects of adding zeolite to improve the quality of concrete and reduce overall drying shrinkage effects.

6. Final experimentation

After having completed initial testing to determine in which direction to expand the topic, it was decided to conduct more tests using zeolite at different compositions. Additional tests include a slump test, compressive, flexural and specific strength tests, a semi-adiabatic test, adsorption using leaching tests as well as tests for consistency of concrete using ultrasonic pulse velocity.

6.1. Slump test

The slump test is used to test the workability and consistency of fresh concrete before it is left to set.

6.1.1. Methods

Having initially created samples with different W/C ratios, final tests were decided upon with a determined W/C ratio. To determine the final W/C ratio, an optimum was selected from initial test data using the VICAT method. Having analysed those results, it was determined that starting from 0.36 W/C would be good, then from there, increase the water content until a desirable workability of cement paste was achieved. Below is a photograph of the mini slump test conducted for the sample paste with 100% cement content (no zeolite) and a W/C ratio of 0.39.



Fig. 13. Photo showing slump of cement paste with no zeolite

As seen in the above photograph, the cement paste produced was highly viscous but will prove to be the right W/C ratio to use when zeolite is included in the mixture. To better compare results, the composition of zeolite chosen for experimentation are 0%, 5%, 10%, 20% and 30% mass by cement. This was so chosen because as previously seen, increasing the content of zeolite beyond 30% generally decreases the compressive strength of the samples, which is our most desirable property. For each of these percentages of zeolite, 50 μ m and 200 μ m ZeoBau has been used and a Swedish cement (Cem I). The results of the slump can be seen below:

6.1.2. Results

Table 20. Slump test for samples with different zeolite compositions

Zeolite composition (%)	50 μm ZeoBau slump (cm)	200 μm ZeoBau slump (cm)
0	16.5	16.5
5	8	10.5
10	8	10
20	8.3	8.5
30	8	7.65

The photos below show the slump of samples containing 5%, 10%, 20% and 30% zeolite content by cement mass. As one can see, the slump significantly decreases with the addition of zeolites, meaning the workability of these cement hardened samples decreases, thus proving its water absorption capabilities. Additionally, the required consistency was achieved, and as a result, it can be concluded that the 0.39 W/C ratio is sufficient for creating samples at the same water ratio but different percentages of zeolite by cement mass.



Fig. 14. Photo showing slump of cement paste containing 5% zeolite by mass



Fig. 15. Photo showing slump of cement paste containing 10% zeolite by mass



Fig. 16. Photo showing slump of cement paste containing 10% zeolite by mass

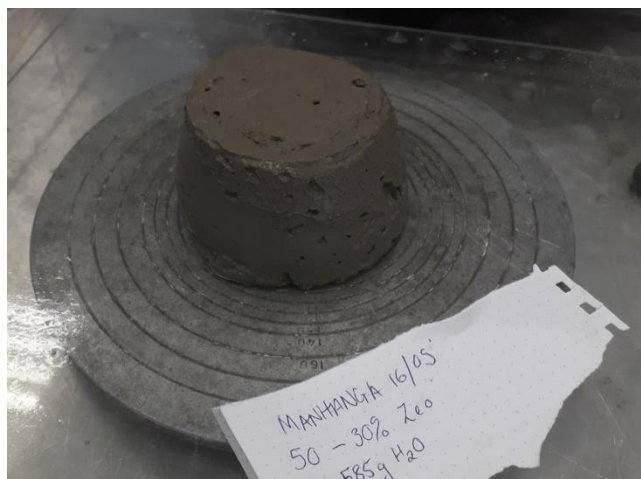


Fig. 17. Photo showing slump of cement paste containing 10% zeolite by mass

6.2. Compressive, flexural, and specific strength tests

These samples containing the same W/C ratio were tested for compressive strength, specific strength and flexural strength after 7, 28 and 76 days.

6.2.1. Methods

The samples were weighed and the dimensions measured. They were then tested using the strength testing machine and results were recorded as follows.

6.2.2. Results

As seen in the graph below (Fig. 18.), the flexural strength generally increases with increasing zeolite content by cement mass. It can be seen that 50 μ m ZeoBau achieves a higher flexural strength which can lead us to conclude that a smaller particle size provides better properties of cement composites. The flexural strength is higher by 61 times for the 50 μ m ZeoBau at 5% zeolite and 44 times higher than the 200 μ m ZeoBau for 10 and 20% zeolite content respectively.

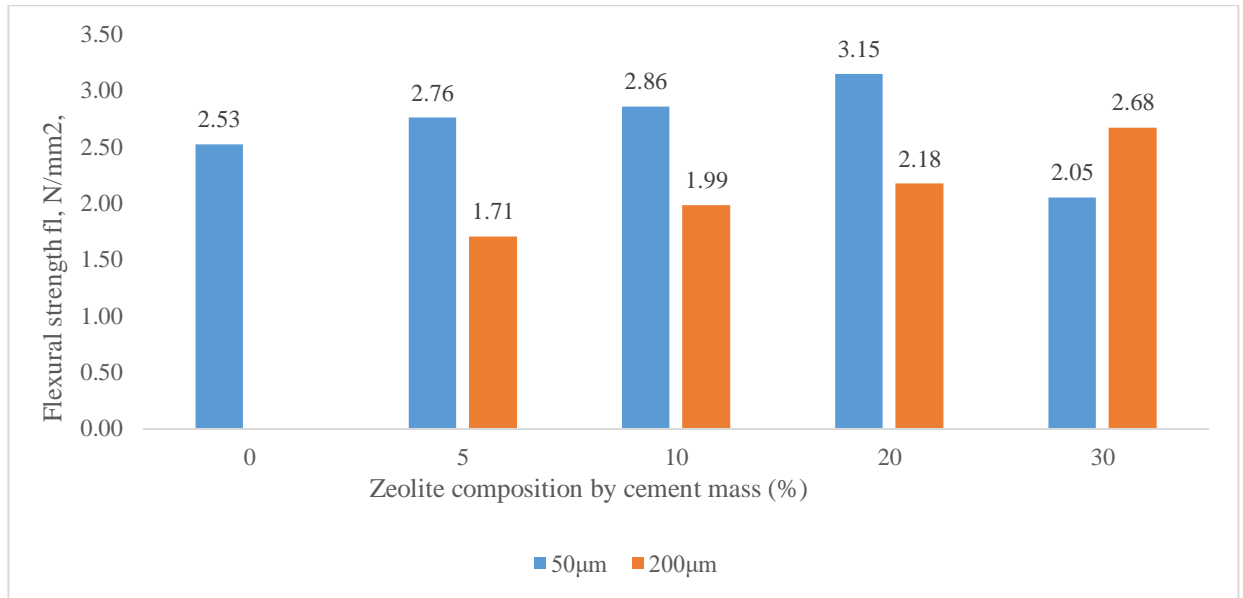


Fig. 18. Graph showing Flexural strength of samples after 7 days for 50 μ m and 200 μ m ZeoBau

Looking at the graph below (Fig. 19), we see that the compressive strength of samples generally decreases with increasing zeolite content by cement mass. At 5% zeolite content, the compressive strength decreased by 13% comparing with the samples that does not contain zeolite. However, it is noted that at 20% for 50 μ m, the strength increased slightly as compared to 10%. At 30% and more zeolite content by cement mass, the compressive strength generally decreases, which other researchers have concluded as well.

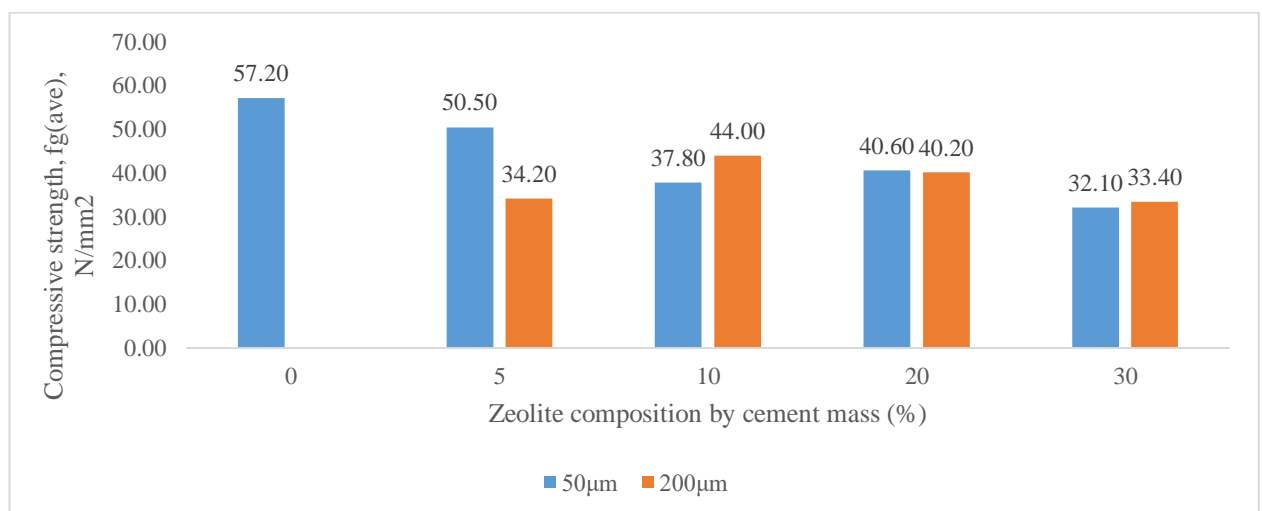


Fig. 19. Graph showing compressive strength of samples after 7 days for 50 μ m and 200 μ m ZeoBau

The specific strength of samples also generally decreases with increasing zeolite content, but it is noted that for 200 μ m, we see an increase at 10% and likewise at 20% for 50 μ m (Fig. 20). With these results, the ability of zeolites to add to the corrosion resistance property of samples is questionable. The presence of more capillaries and adsorption pockets can lead to internal corrosion.

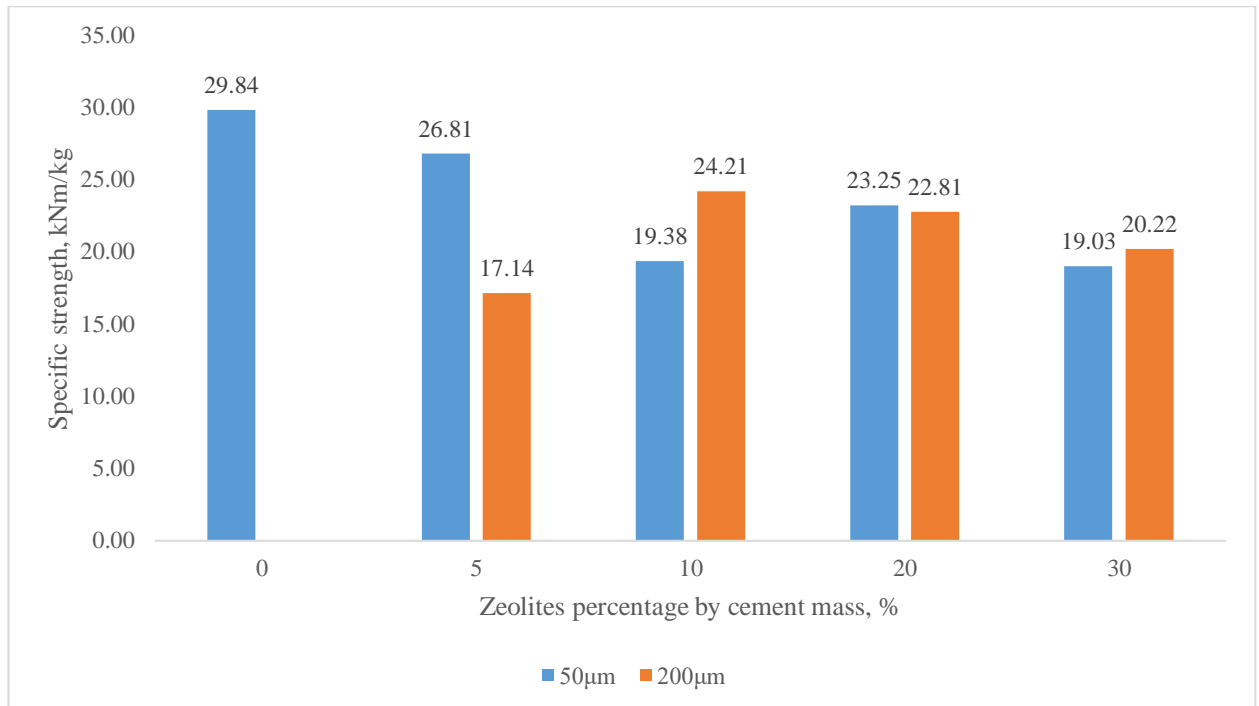


Fig. 20. Graph showing specific strength of samples after 7 days for 50 μ m and 200 μ m ZeoBau

After 28 days, the same tests were conducted on the samples.

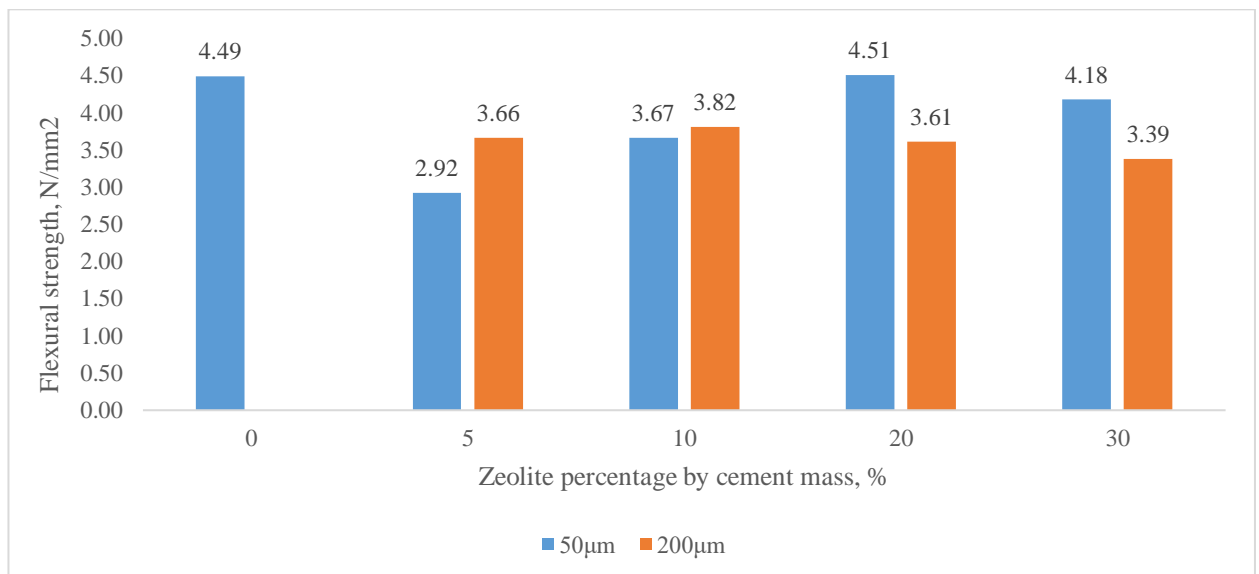


Fig. 21. Graph showing Flexural strength of samples after 28 days for 50 μ m and 200 μ m ZeoBau

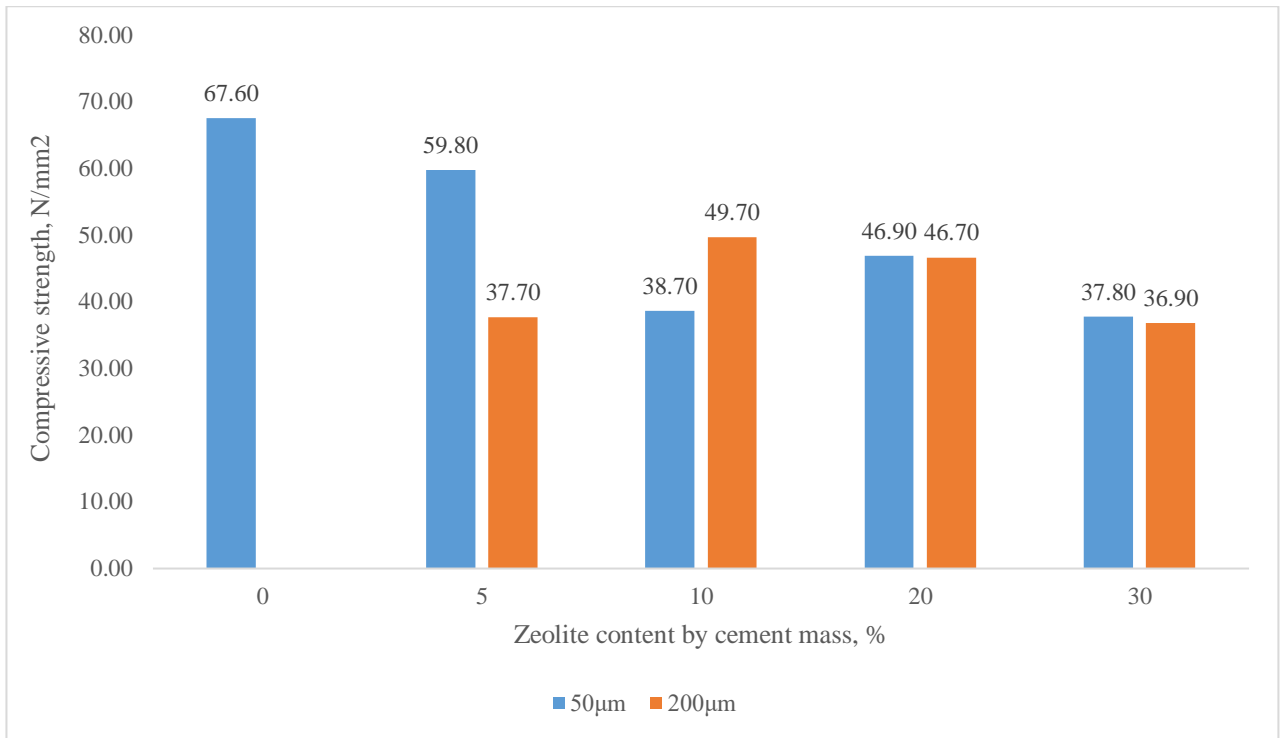


Fig. 22. Graph showing compressive strength of samples after 28 days for 50µm and 200µm ZeoBau

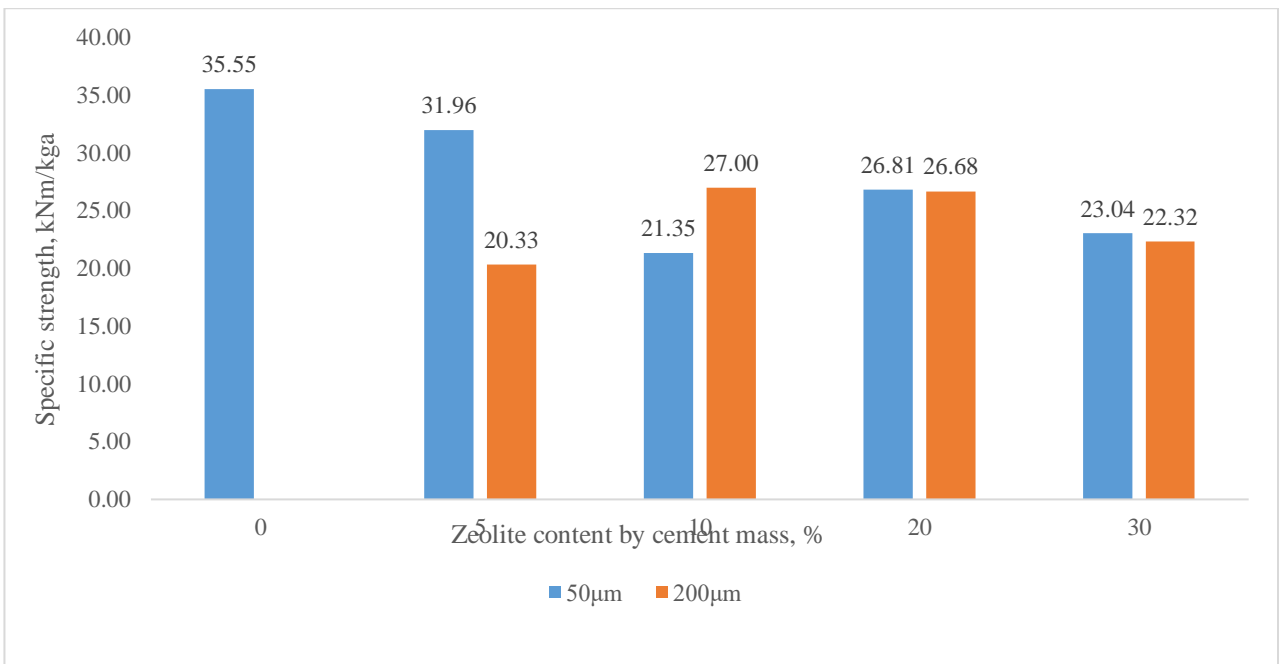


Fig. 23. Graph showing specific strength of samples after 28 days for 50µm and 200µm ZeoBau

As seen from the figures above (Fig. 21, 22 and 23), in all cases, the strength of the samples improved after 28 days. The flexural strength is higher in samples containing 50µm. It is, however, noted that at 20% zeolite content by cement mass, the compressive strength achieved after 28 days is almost the same. This then supports the conclusion to use 20% zeolite content for the adsorption of heavy metals test. The specific strength calculated after 28 days also supports this decision as the results are quite similar.

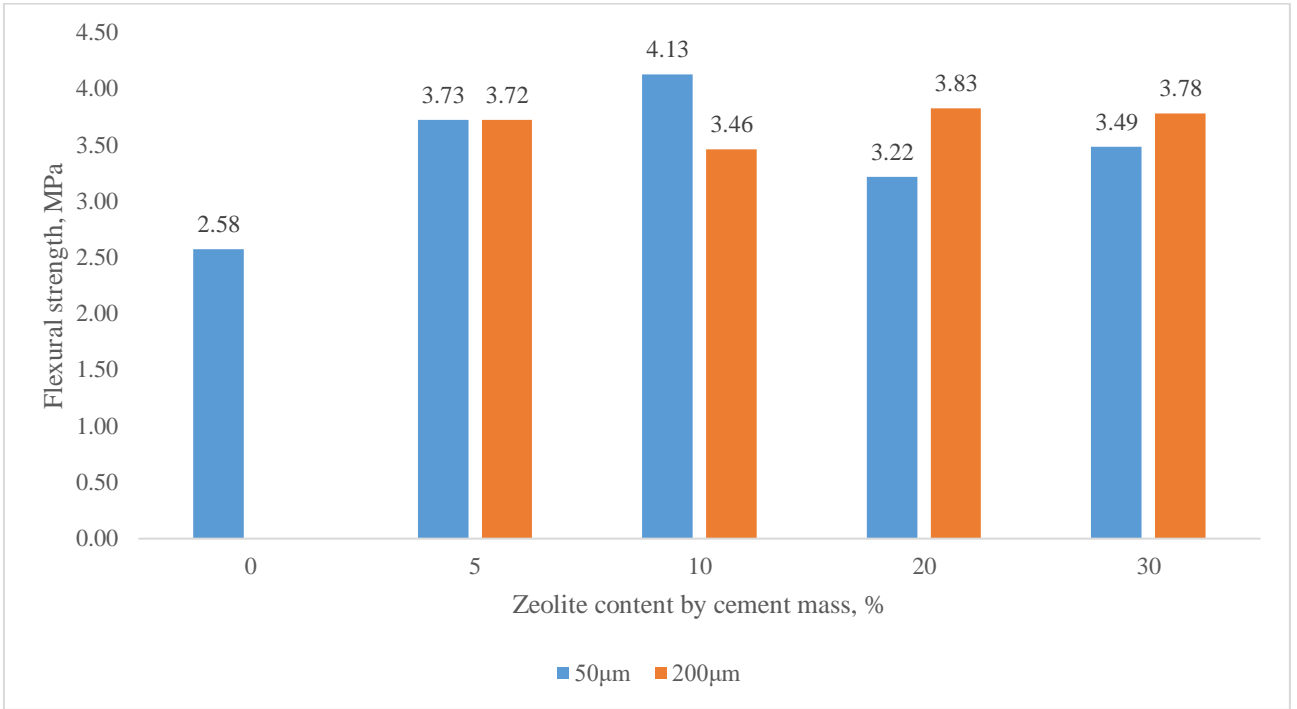


Fig. 24. Graph showing Flexural strength of samples after 76 days for 50µm and 200µm ZeoBau

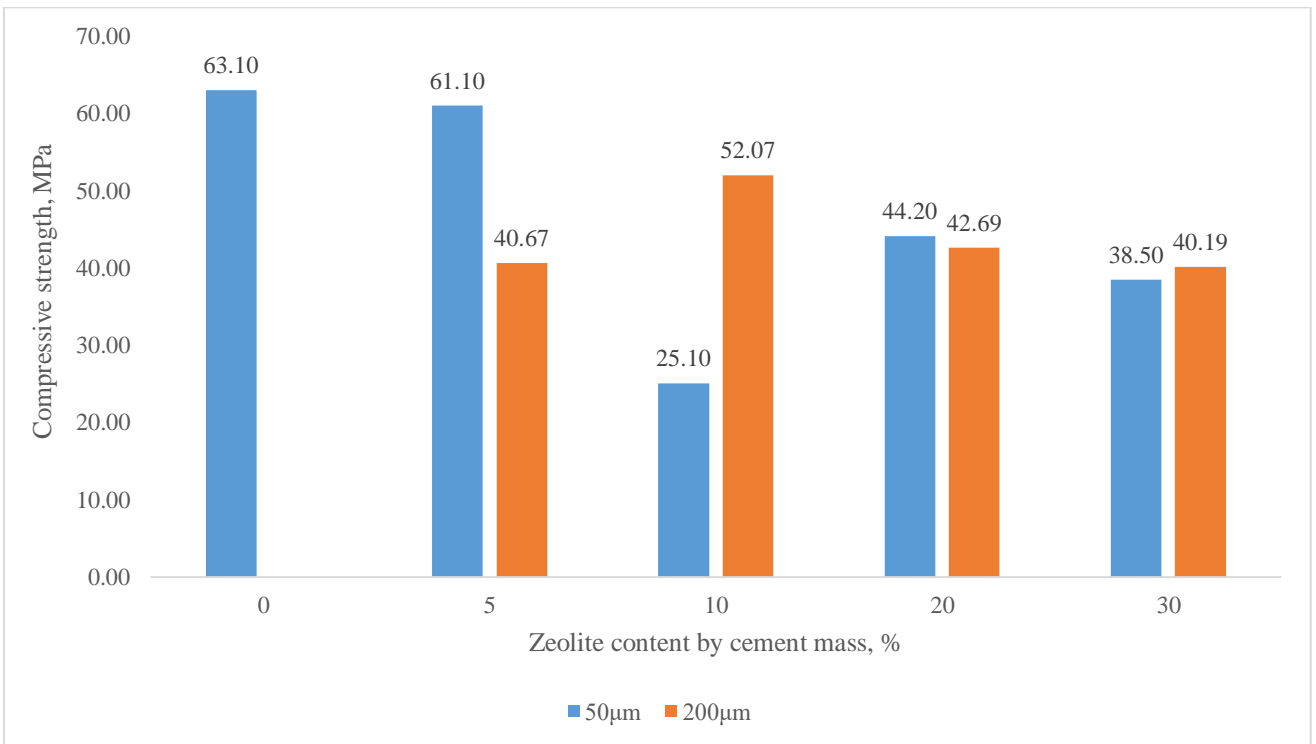


Fig. 25. Graph showing compressive strength of samples after 76 days for 50µm and 200µm ZeoBau

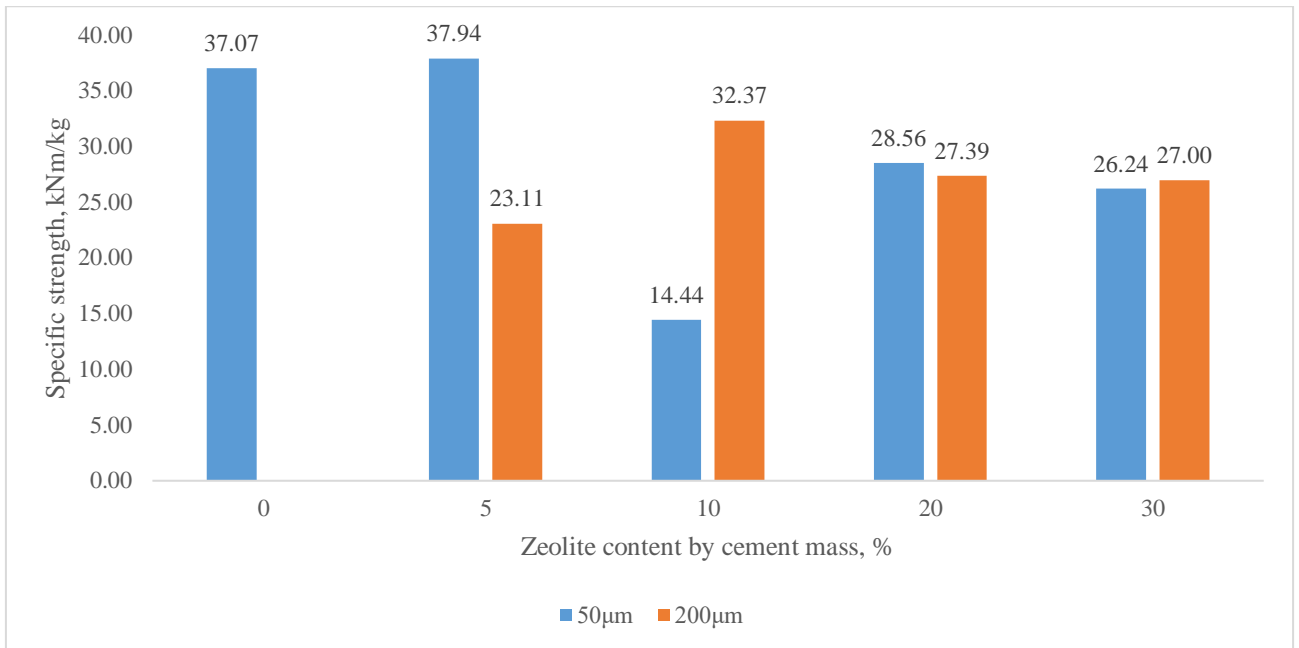


Fig. 26. Graph showing specific strength of samples after 76 days for 50µm and 200µm ZeoBau

The cement composites were also tested after 76 days. For 50µm ZeoBau, the compressive strength increased by 2% to 61MPa for 5% zeolite content. For the 200µm ZeoBau there can be seen a general increase in compressive strength after 76 days. The strength increased by 7.9%, 4.8% and 8.9 % for 5, 10 and 30% zeolite content by cement mass respectively. It can be concluded that the compressive strength generally decreases with increasing zeolite content, but overtime, the strength increases and urges closer and closer to the control sample.

6.3. Density and Moisture content test

Additionally, the density and moisture content were determined after 7, 28 and 76 days, results of which are shown in the tables below.

6.3.1. Methods

As initially conducted in chapter 5.3, the samples were weighed, and dimensions recorded to determine the density before and after drying. The samples were dried in the oven at 100°C.

6.3.2. Results

As seen by the tables below, the water content and density generally decreased after 28 days comparing with the data for 7 days. However, we can see that for 20% zeolite, the density increased after 28 days. Also, it retained a higher moisture content as compared to other percentages of zeolites. Again, at 30% the results show a decrease, continuously proving that from 30% and beyond, the effects of zeolites on cementitious products' properties decrease.

Table 21. Density and water content for samples containing 50µm 7 days

Zeolite content by cement mass, %	0	5	10	20	30
Ave. density, kg/m ³	1916.11	1883.04	1947.63	1744.83	1686.26
W, %	17.6	17.4	17.9	17.9	16.3
Dry density, kg/m ³	1629.35	1603.95	1651.93	1479.92	1449.92

Table 22. Density and water content for samples containing 50 μ m after 28 days

Zeolite content by cement mass, %	0	5	10	20	30
Ave. density, kg/m ³	1901.79	1869.88	1814.58	1749.85	1642.39
W, %	15.9	15.9	16.5	16.7	15.4
Dry density, kg/m ³	1640.89	1613.36	1557.58	1499.44	1423.21

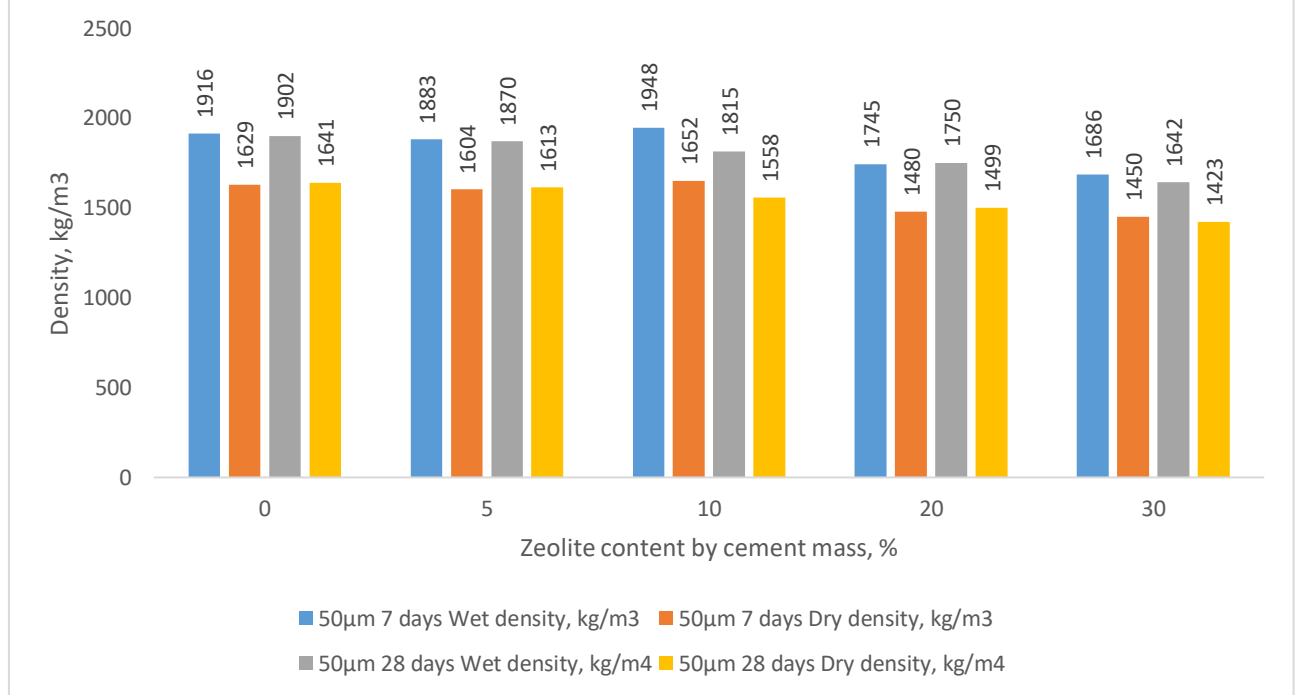


Fig. 27. Density for samples containing 50 μ m ZeoBau after 7 and 28 days

Table 23. Density and water content for samples containing 200 μ m after 7 days

Zeolite content by cement mass, %	0	5	10	20	30
Ave. density, kg/m ³	1916.11	1994.60	1818.60	1763.13	1652.17
W, %	17.6	16.9	16.2	15.7	16.1
Dry density, kg/m ³	1629.35	1706.24	1565.06	1523.88	1423.06

Table 24. Density and water content for samples containing 200 μ m after 28 days

Zeolite content by cement mass, %	0	5	10	20	30
Ave. density, kg/m ³	1901.79	1853.77	1839.98	1748.68	1652.17
W, %	15.9	15.4	15.7	15.2	15.1
Dry density, kg/m ³	1640.89	1606.39	1590.30	1517.95	1435.42

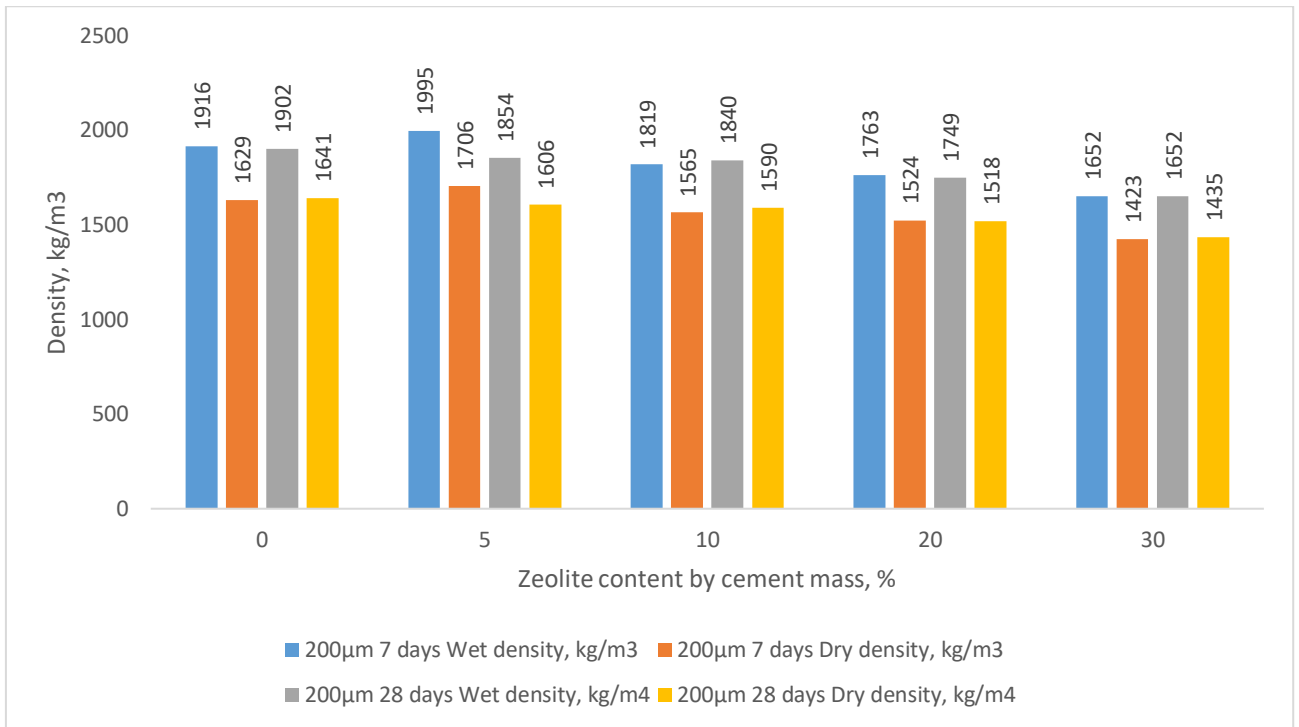


Fig. 28. Density (wet and dry) for samples containing 200µm ZeoBau after 7 and 28 days

For the 200µm ZeoBau, the density is generally lower than that of 50µm. However, at 20% we achieve closely related results after 28 days. The water content in 200µm is generally lower than that of 50µm which shows that the particle size of zeolite chosen has a significant effect on the results produces. The larger the particle size, the smaller the surface area to volume ratio. This then reduces the overall adsorption properties as there's less "pockets" to be used to trap water. When there is less water trapped, the risk of internal shrinkage increases. [22]

6.4. Semi-Adiabatic test

It is important to understand the hydration process because it shows the properties of a concrete mix. It has an effect of workability, setting behaviour, strength and pore structure development, which is important in this case when testing the effect of zeolite. The results of such a test can help determine how a concrete mix, in this case a cement paste, will perform.

6.4.1. Methods

To analyse the results, the 'derivatives' method has been used which defines the initial setting time as the time at the peak of the second derivative of temperature versus time function. The final set time is then the time corresponding to the peak of the first derivative of temperature versus time function. This method works well but is very sensitive to changes in the environment; hence, the testing procedure must be done very careful, limiting the effect of the environment.

The results were recorded after 46.5 hours.

6.4.2. Results

As seen from the table of results, adding zeolites gradually increased the initial setting temperature. The highest recorded was for 20% zeolite content, which is the optimum zeolite content going forward in testing procedures. Use of 30% zeolite recorded the lowest final setting temperature which indicates that there is less hydration and ultimately a lower compressive strength. As previously determined in the compressive strength test, this is the case. The highest strength in this case (Fig 22) is achieved at 5% zeolite content by cement mass.

Table 25. Table of results of hydration of cement paste with different amount of 50um zeolite

Composition	Initial setting time, min	Initial setting temperature, °C	Final setting time, min	Final setting temperature, °C	Delay in setting time, min
CEM I 42.5R + 0 % ZEO	71	25.33	512	50.13	-
CEM I 42.5R + 5 % ZEO	71	25.99	548	52.20	36
CEM I 42.5R + 10 % ZEO	93	26.83	546	49.66	34
CEM I 42.5R + 20 % ZEO	83	27.03	572	44.60	60
CEM I 42.5R + 30 % ZEO	39	24.08	570	38.36	58

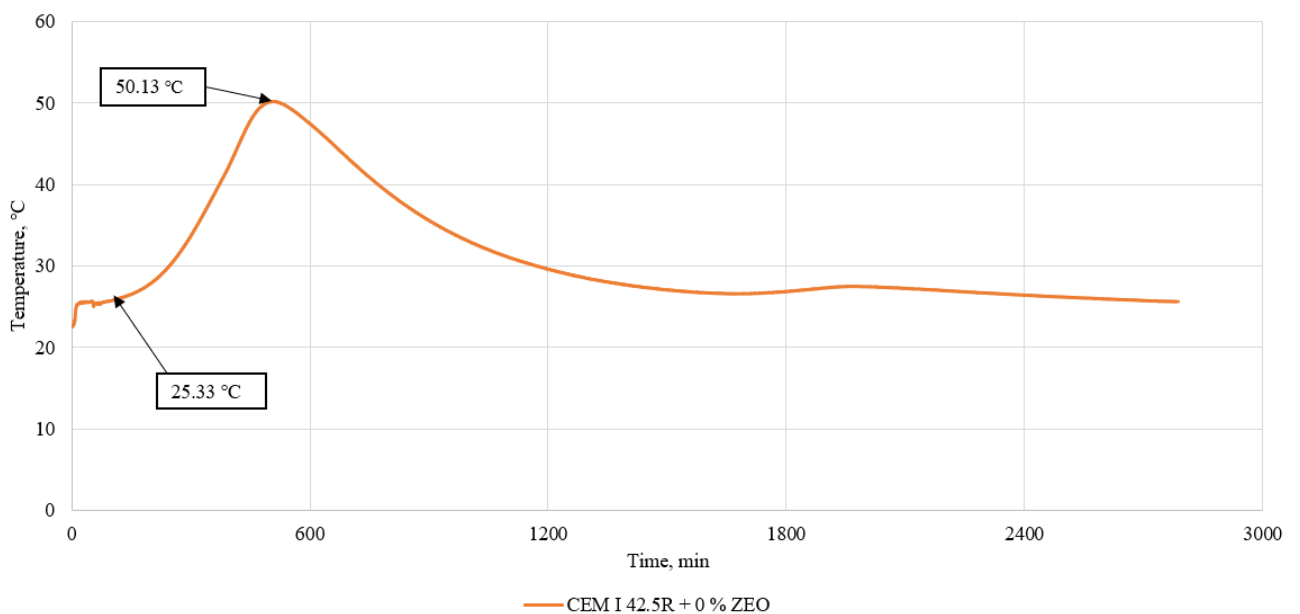


Fig. 29. Graph showing the hydration of cement paste with no zeolite added

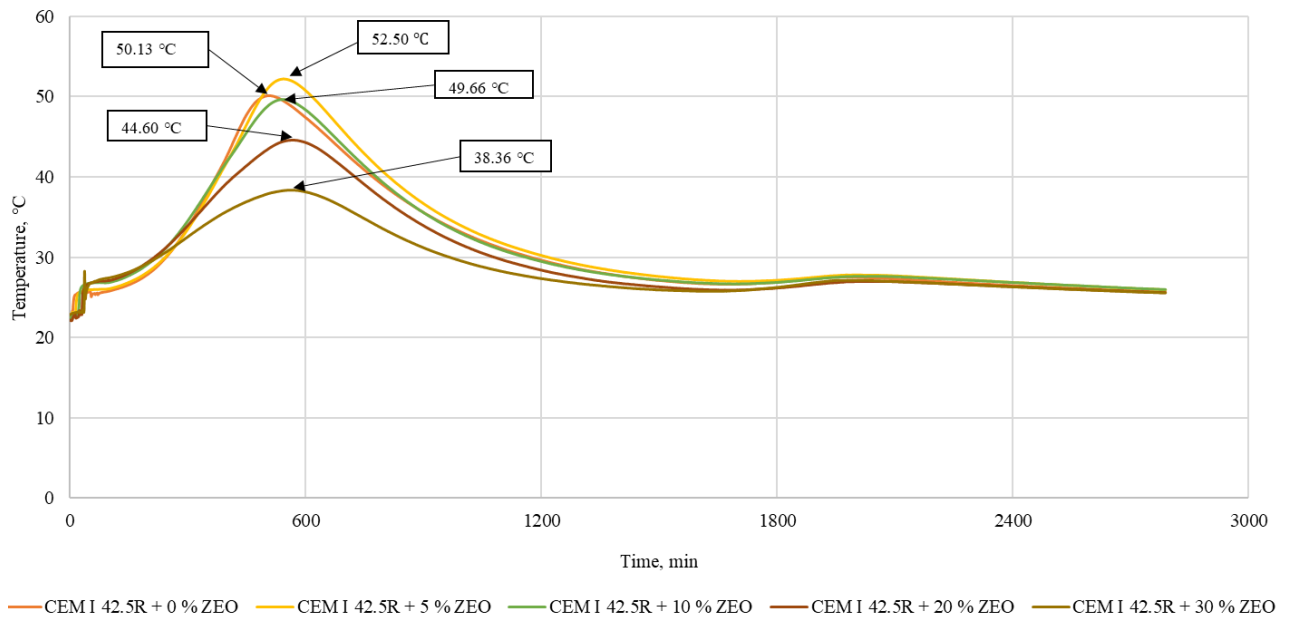


Fig. 30. Graph showing the hydration of cement paste at different percentages of 50µm zeolite

Table 26. Table of results of hydration of cement paste with different amount of 200µm zeolite

Composition	Initial setting time, min	Initial setting temperature, °C	Final setting time, min	Final setting temperature, °C	Delay in setting time, min
CEM I 42.5R + 5 % ZEO	101	26.83	554	53.54	42
CEM I 42.5R + 10 % ZEO	56	23.33	575	53.16	63
CEM I 42.5R + 20 % ZEO	62	23.18	593	45.66	81

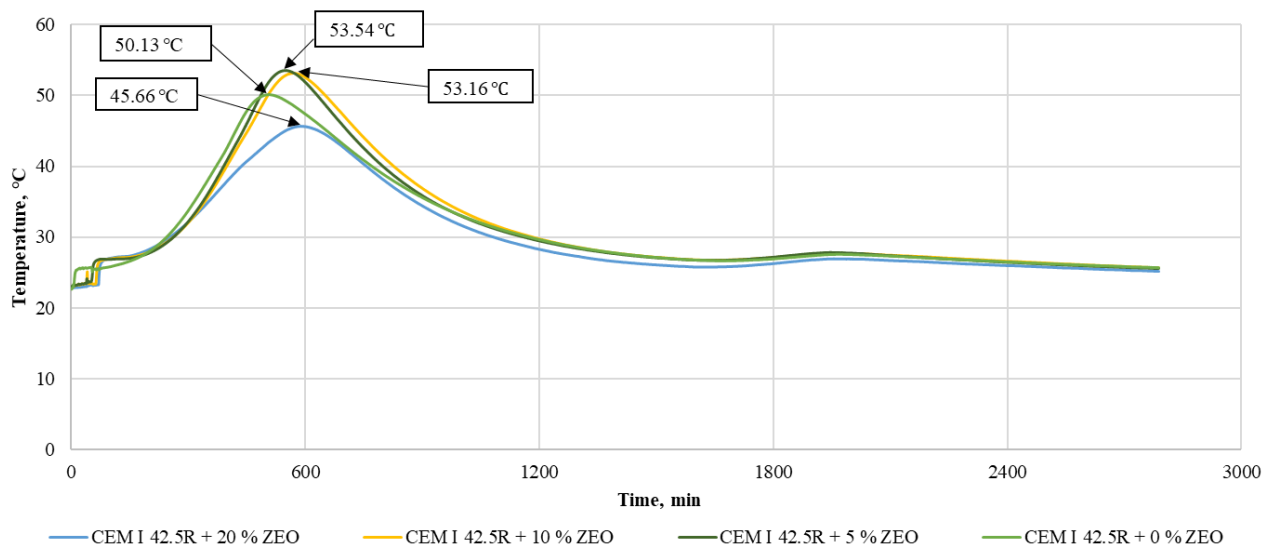


Fig. 31. Graph showing the hydration of cement paste at different percentages of 200µm zeolite

Comparing the result of the 200 μm and 50 μm ZeoBau, it can be seen that at similar percentages of zeolite content, the 200 μm began hydration at a lower temperature than that of the 50 μm . The initial setting time was also lower for the 200 μm . This goes to show that the 50 μm has a better surface area to volume ratio and can extend the hydration time. However, it is also noted that the 200 μm had higher final setting temperatures at every percentage of zeolite. This means that it would result in better compressive strength. Also, it can be seen that at 20% zeolite content, the results are very similar, and this is shown in the compressive strength tests conducted previously.

6.5. Adsorption of heavy metals using a leaching test

As noted earlier, zeolites have been used for heavy metal adsorption. Heavy metals can be very hazardous to health and could complicate constructions of structures. It is important that these harmful metals like lead, zinc and chromium be removed from naturally found sources such as water or soil. Common removal methods of heavy metals from aqueous material include membrane filtration, activated carbon adsorption and electrocoagulation; however, their applications may be limited in some areas. [35] Engineers are constantly looking for more cost-effective methods to use in the waste-removal industry.

Andrejkovičová et. al. [19] showed that adding 25% zeolite to geopolymers efficiently improved the adsorption capacity. It was found out by X-ray diffraction that geopolymerisation with the inclusion of zeolites results in an increased compressive strength. [19] This could allow one to conclude that zeolites could promote use of more eco-friendly materials that can adsorb heavy metals but still have high mechanical resistance. The applications could be in environments where concrete is required but there is high heavy metal content, for example, in water treatment facilities or in natural soils.

6.5.1. Methods

To conduct the leaching and adsorption tests, chromium of 50g/l concentration has been used. The type of chromium is hexavalent chromium, which is commonly found in drinking water, soils and more. It is important to use as cost efficient methods as possible and in this case, it has been decided to use the Atomic Absorption Spectroscopy equipment - Shimazu AA-7000 (Fig.). This equipment is used to detect metals in a sample and measure concentration of the sample. Free atoms are generated in an atomiser and absorb radiation at different frequencies. These atoms are exposed to ultraviolet light or visible light and reach higher energy levels. The analyte concentration is then determined from the amount of absorption. It is important to note that this equipment records atoms at their ground state. [36] Concentration can then be deduced from curves that are in relation to known concentrations.

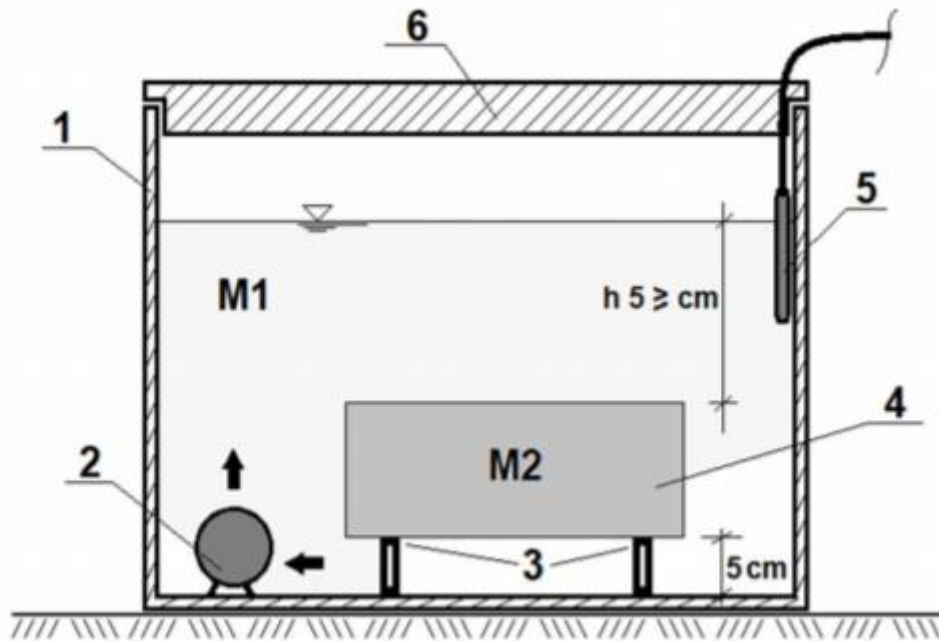


Fig. 32. Heavy metal leaching from a compacted soil test pilot plant scheme.

- 1 - polyethylene container
- 2 - water pump which keeps the water circulating
- 3 - support structure; however, in the case of the testing done, the sample was suspended with string from the top and elevated to 5cm from the bottom
- 4 – sample containing chromium (heavy metal)
- 5 - thermostat to maintain a constant temperature which was omitted in this test
- 6 – cover to stop water from splashing

To collect liquid with leached material, the sample was suspended with string in the container. Then, the amount of distilled was calculated at a ratio of volume of sample to liquid of 1:15, which amounted to 5.3L of water. The pump was then fixed to the container to avoid movement and allowed to circulate the water. This circulation was left for 24 hours. After this time, the liquid from the leaching test was collected into containers for a future X-ray diffraction or Atomic Absorption Spectroscopy test. The latter is desirable as it is a lower-cost testing method than XRD.

Samples containing no zeolite, 20% of 50 μ m and 20% of 200 μ m have been used. Concentrations of chromium used were 1g/kg, 3g/kg and 6g/kg grams. The water cement ratio was maintained at 0.39. The moulds chosen were of 7.07 x 7.07 x 7.07cm. The dry products (cement and zeolite) were mixed then the water and chromium were mixed into one container. That solution was then mixed with the dry products and poured into forms. The forms were covered with plastic to avoid evaporation of chromium. To conduct the investigation, 500 ml of leached water solution have been taken. The concentration of the solution was increased by evaporation at 30-40 $^{\circ}$ C until 25ml. The concentration of the liquid increased by 25 times.

Some of the samples were then tested for compressive strength after 7 days and 28 days. The rest of the samples were left for leaching and frost resistance tests after more days.



Fig. 33. Atomic Absorption Spectroscopy equipment (Shimadzu AA-7000)

6.5.2. Results

After 7 and 28 days, the compressive strength was determined, and the results were as follows:

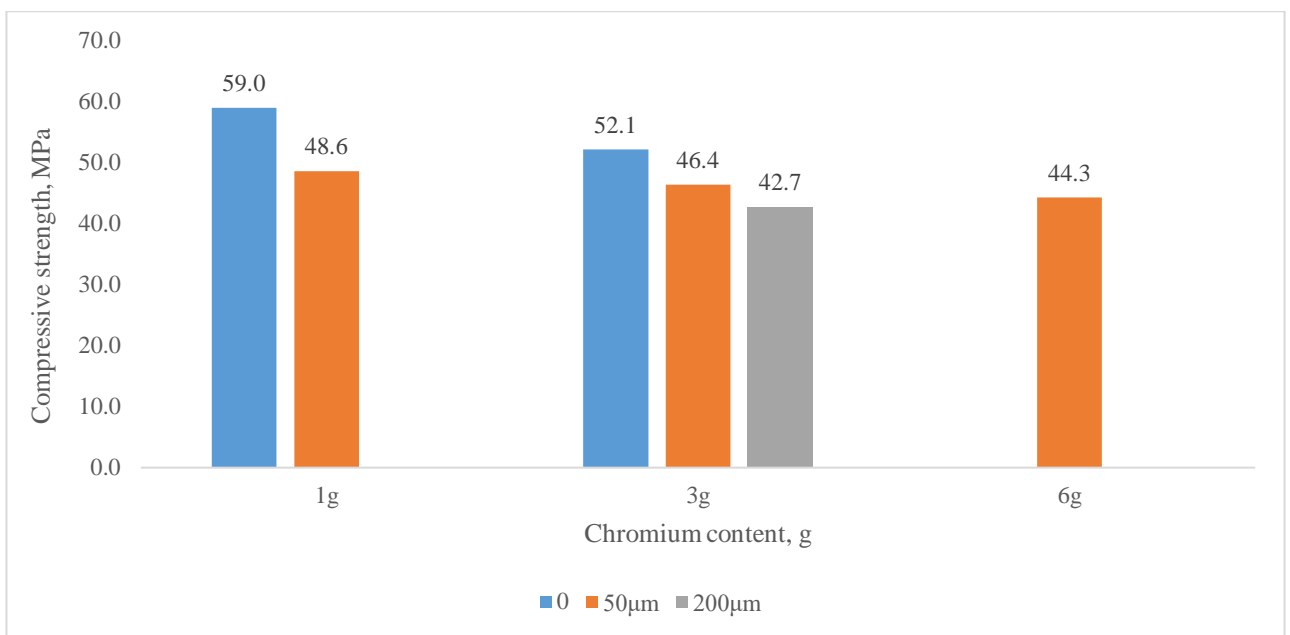


Fig. 34. Graph showing compressive strength after 7 days of samples containing different types of zeolite and amount of chromium.

As seen in Fig 24. and Fig. 25, the compressive strength decreased with the addition of zeolite as seen in earlier tests. In addition, the strength decreased with increasing chromium content. How chromium content may affect the compressive strength remains to be concluded on as well as the heavy metal adsorption with different types of zeolite at different concentration of chromium. This test was conducted using Atomic Absorption Spectroscopy.

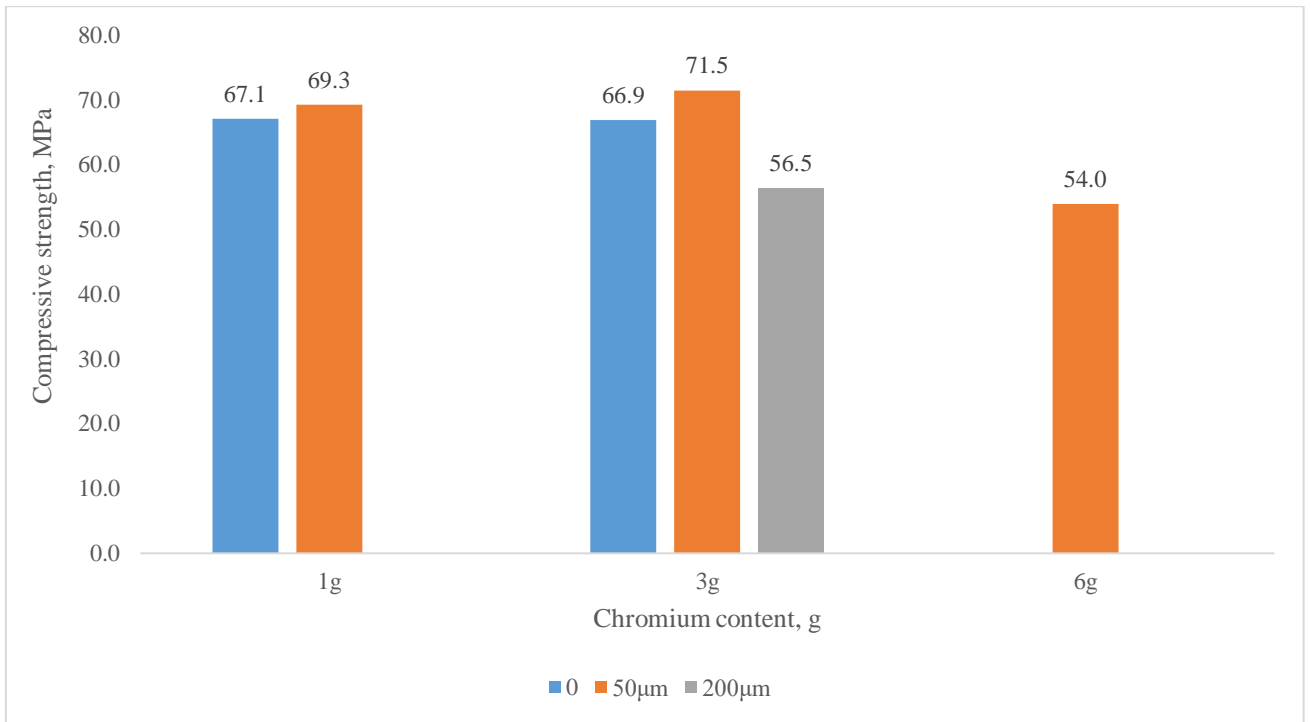


Fig. 35. Graph showing compressive strength after 28 days of samples containing different types of zeolite and amount of chromium.

It can also be noted, in consistency with previous tests, that the compressive strength of samples containing zeolites increases with age. As can be seen above, the samples containing zeolite achieved results similar to the control sample which contained no zeolite. For 50µm ZeoBau, the highest strength of 71.5 MPa was reached, which was a 25% increase from 7 days. Also, reverting to the initial testing data, at 20% zeolite by cement mass for 50µm ZeoBau, it was achieved a compressive strength of about 46 MPa after 28 days whereas, for the sample with no zeolite, it was achieved a strength of about 67 MPa.

This result of strength could be solely attributed to the addition of zeolite, but it is yet to be finalised once it is determined how the adsorption of heavy metals has affected the compressive strength. if at all. Additionally, the density of these samples was determined.

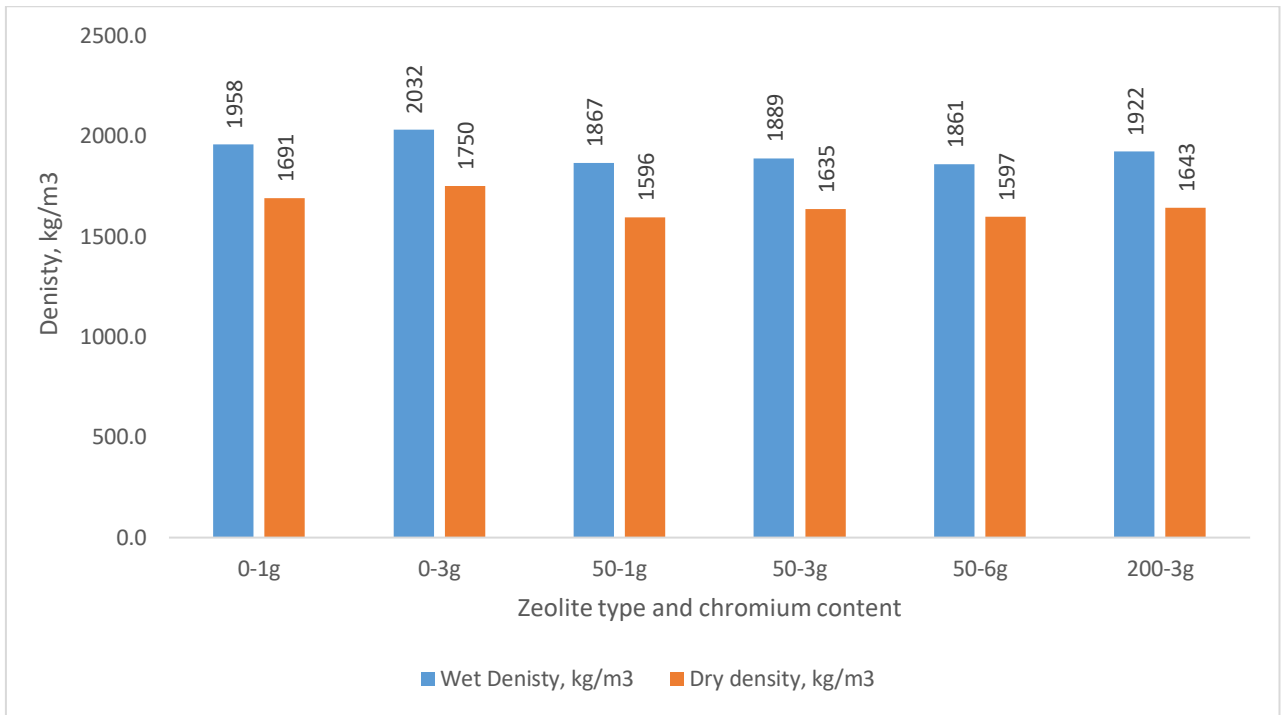


Fig. 36. Graph showing wet and dry density of samples after 28 days containing different types of zeolite and amount of chromium.

It can be seen that the dry density was almost the same for all concentrations of chromium in the samples containing 20% zeolite. Additionally, samples containing zeolite are consistent with lightweight concrete even with the inclusion of heavy metals.

More tests were conducted after 63 days and the results are as follows. As seen with Fig. the highest compressive strength was achieved with 50 μ m zeolite. It is, however, noted that for other samples, the compressive strength decreased.

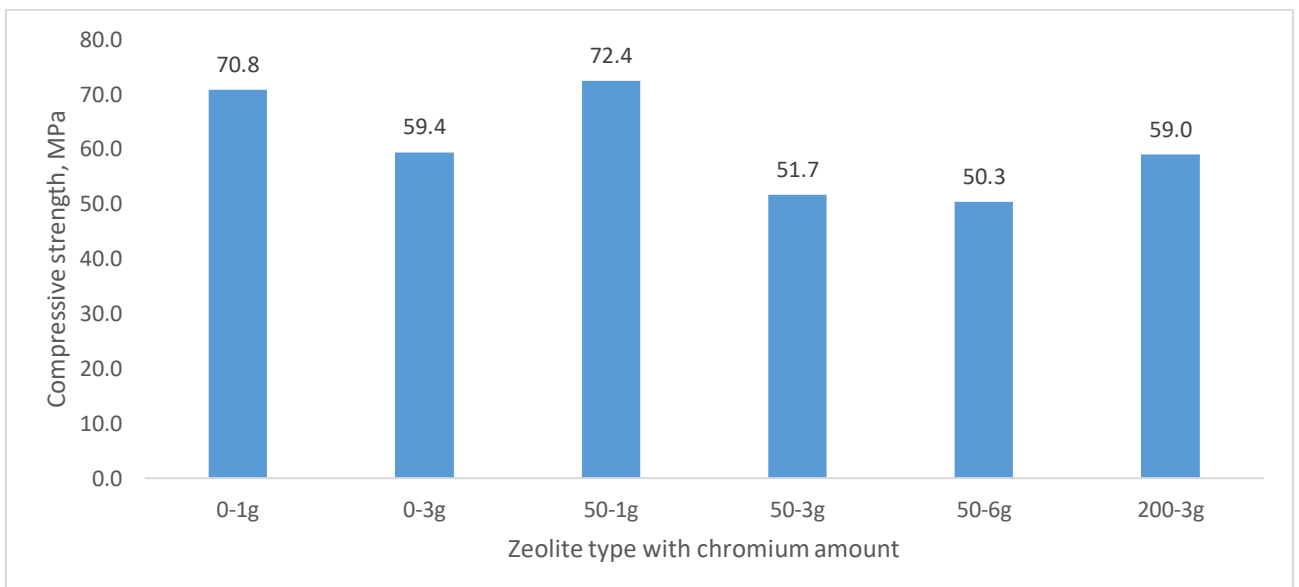


Fig. 37. Graph showing compressive strength after 63 days of samples containing different types of zeolite and amount of chromium.

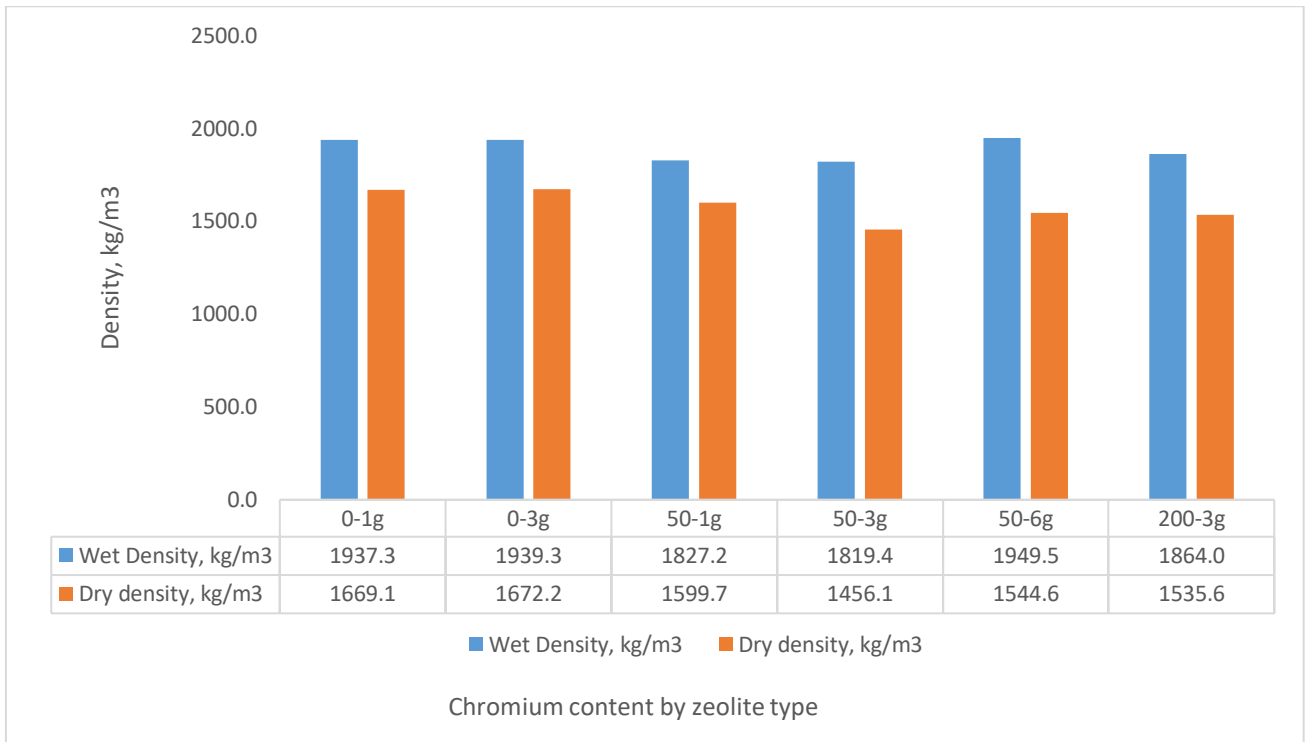


Fig. 38. Graph showing density after 63 days of samples containing different types of zeolite and amount of chromium.

The density and specific strength results are consistent with the previous set of results were the density decreases with increasing amount of zeolite by cement mass. Additionally, the density decreases with age. However, it must be noted the wet density is not far off from the normal range of lightweight concrete. The specific strength which was, in previous test, decreasing with increasing zeolite content has shown a slightly different result with the 7 x 7 x 7cm samples. As seen below, the highest specific strength is achieved with a 50µm zeolite sample.

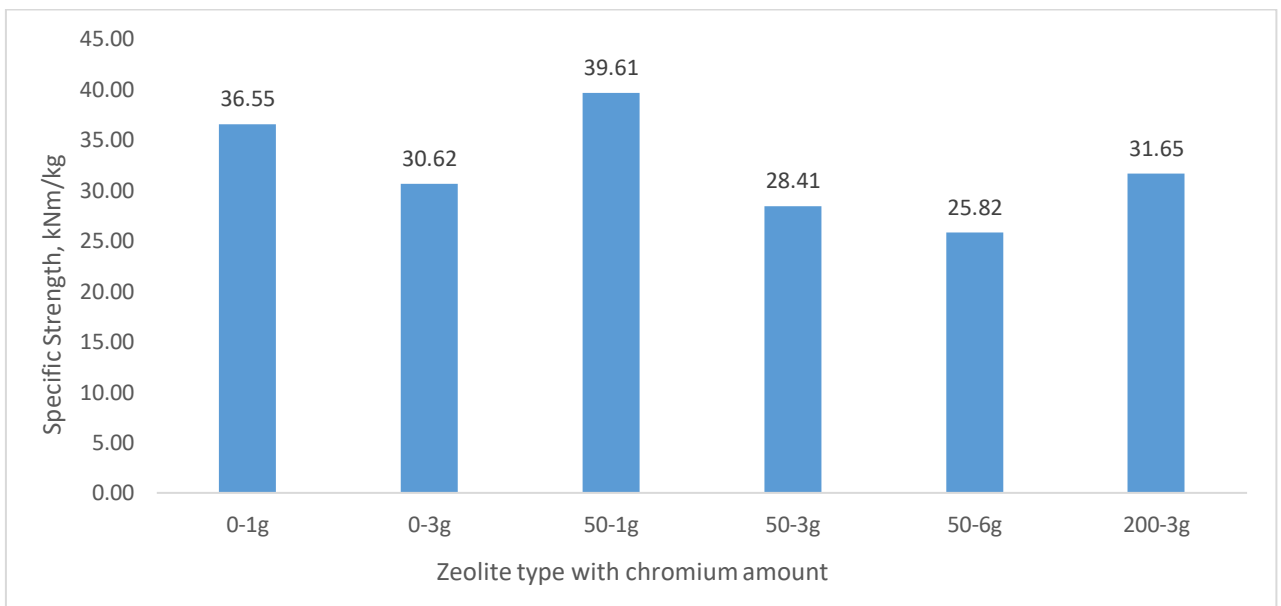


Fig. 39. Graph showing specific strength after 63 days of samples containing different types of zeolite and amount of chromium.

Table 27. Table of results of leaching of chromium from samples containing zeolite at 20%

Sample marking	Concentration of chromium in the sample g/kg	Concentration of chromium in the sample g/l	Concentration of chromium in the sample mg/l	Concentration of chromium in the liquid of leached water mg/l	Reducing of chromium concentration in the leached water in times
0 – 1 g Cr	1	0.5991	599.14	7.35	81.5
0 – 3 g C	3	1.7941	1794.05	8.49	211.2
50 – 1 g Cr	1	0.6251	625.12	2.19	285.1
50 – 3 g Cr	3	2.0603	2060.27	13.07	157.7
50 – 6 g Cr	6	3.8844	3884.40	106.17	36.6
200 – 3 g C	3	1.9536	1953.59	6.37	306.7

What can be seen from this table of results is that when the concentration of chromium is increasing, the reduction of chromium content in the leached water becomes less effective. However, it can be seen that it still meets the requirements of the Lithuanian Hygiene norms (HN60:2004). The requirement of HN60:2004 is that the chromium content in the leached water should not exceed 100 mg/l, which, in this case, is evident. The exception, however, is when 6g/kg of chromium concentration is used. It is seen that the amount of chromium in the leached water is 106.17mg/l which surpasses that of the requirement – 100 mg/l. What must be clearly noted is that the amount of zeolite present was 20% of the cement content. It can be estimated that with an increase in zeolite content, even by 5 %, the effectiveness of chromium absorption could increase.

For the sample containing 1g/kg or chromium, at the same concentration of chromium, which was calculated by simple proportion, it's seen that the sample containing 50µm zeolite had the lowest concentration in the leached sample at 2.10mg/l This goes to show the heavy metal adsorption abilities that zeolite could promote. Comparing the samples containing 3g/kg of chromium content at the same amount of concentration in the sample, it can be seen (Fig. 41.) that the sample containing 200µm zeolite had the lowest concentration of chromium in the leached water.

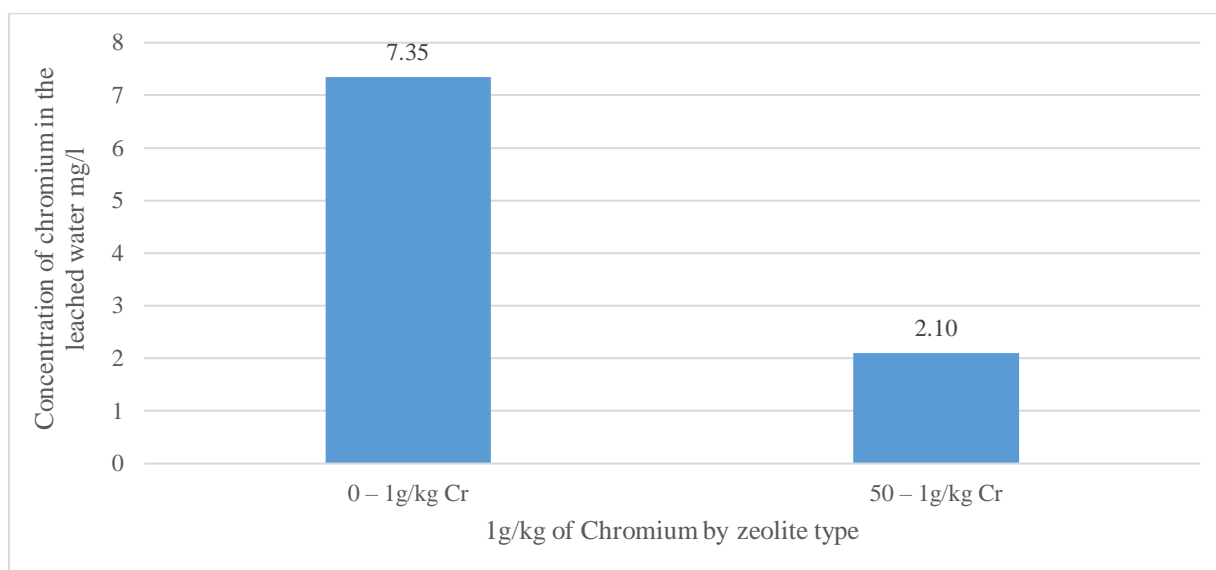


Fig. 40. Graph showing specific strength after 63 days of samples containing different types of zeolite and amount of chromium.

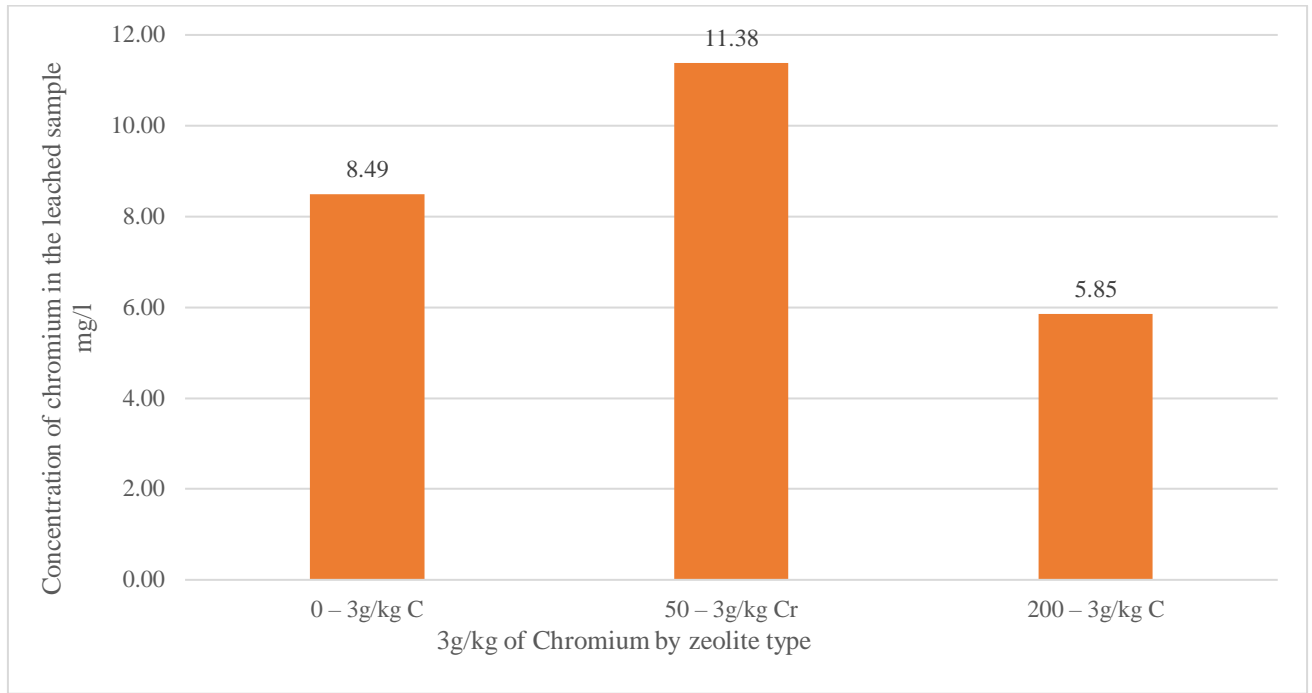


Fig. 41. Graph showing specific strength after 63 days of samples containing different types of zeolite and amount of chromium.

6.6. Dynamic Modulus of Elasticity and Ultrasonic Pulse velocity

The ultrasonic pulse velocity test, henceforth referred to as UPV, is a non-destructive test method which is used to determine the quality of concrete. UPV has a correlation with compressive strength, modulus of elasticity and density; therefore, it is heavily influenced by porosity and cracking in a sample.[37] Zeolites, when added to concrete, increase the general porosity. As such, it can be expected that with the presence of zeolites, lower UPV values will be reached in turn resulting in lower compressive strength but having the possibility to create lightweight concrete which could be used as a sound insulating material. Other researchers [38] have concluded that both UPV and compressive strength of concrete increase with age.

The modulus of elasticity is the relationship between stress and strain of a material. In other words, it is the resistance to deformation of a sample. [39] This modulus of elasticity can be determined by physically loading a material. However, dynamic elastic modulus of elasticity is determined from a non-destructive test method. Once this is determined, a formula is used to determine the static elastic modulus then results are plotted to determine the compressive strength.

6.6.1. Methods

To determine the dynamic modulus of elasticity, the method of resonant frequency has been used. The testing equipment used for this is the Erudite MkIV for resonant frequency. A sample was fixed onto the equipment and subjected to a frequency. The results were recorded in kilo-hertz (kHz). The dynamic elastic modulus (E_d) was then calculated using the following formula:

$$E_d = 4 \cdot n^2 \cdot l^2 \cdot \rho \quad (2)$$

where n = frequency, l = length of the sample and ρ = density of the sample.

Once the dynamic elastic modulus was determined, the static elastic modulus was then calculated using two formulas for comparison.

$$E_c = 1.25 \cdot E_d - 19 \quad (3)$$

and

$$E_c = 1.04 \cdot E_d - 4.1 \quad (4)$$

The first formula is not suitable for very rich concrete with cement content more than 500kg/m^3 and lightweight concrete but both formulas have been used for comparison of results. [39] The dynamic modulus can allow one to determine the relative durability of concrete exposed to different conditions because it changes depending on the quality of concrete. [39]



Fig. 42. Resonant frequency test equipment – Erudite MkIV



Fig. 43. Handheld ultrasonic pulse velocity tester

6.6.2. Results

The following are graphs showing the correlation between the ultrasonic pulse velocity (UPV) and the dynamic modulus of elasticity (E_d) for samples containing different amounts of 50 μ m and 200 μ m zeolite.

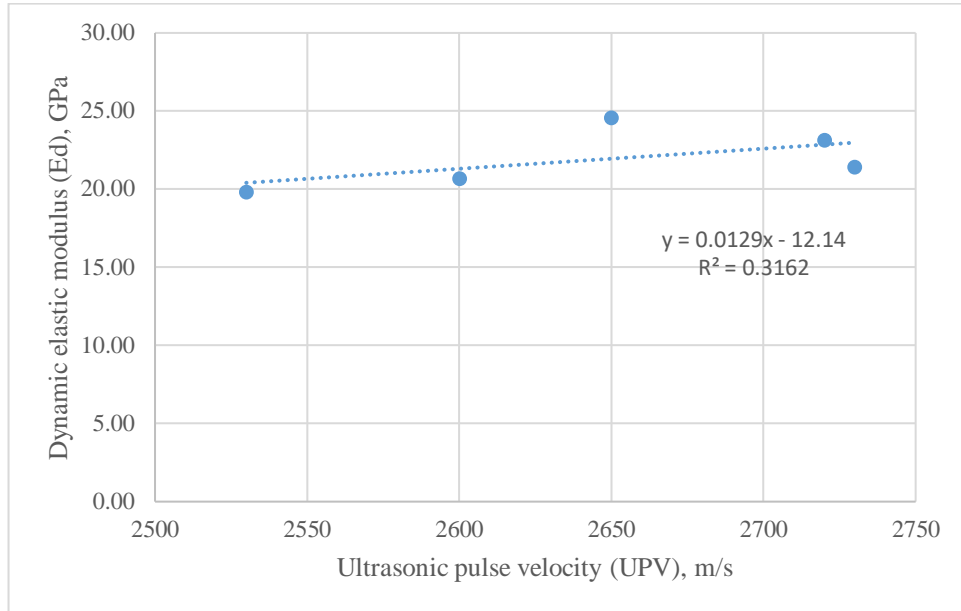


Fig. 44. Correlation between the elastic modulus and the ultrasonic pulse velocity for increasing amount of 50 μ m zeolite

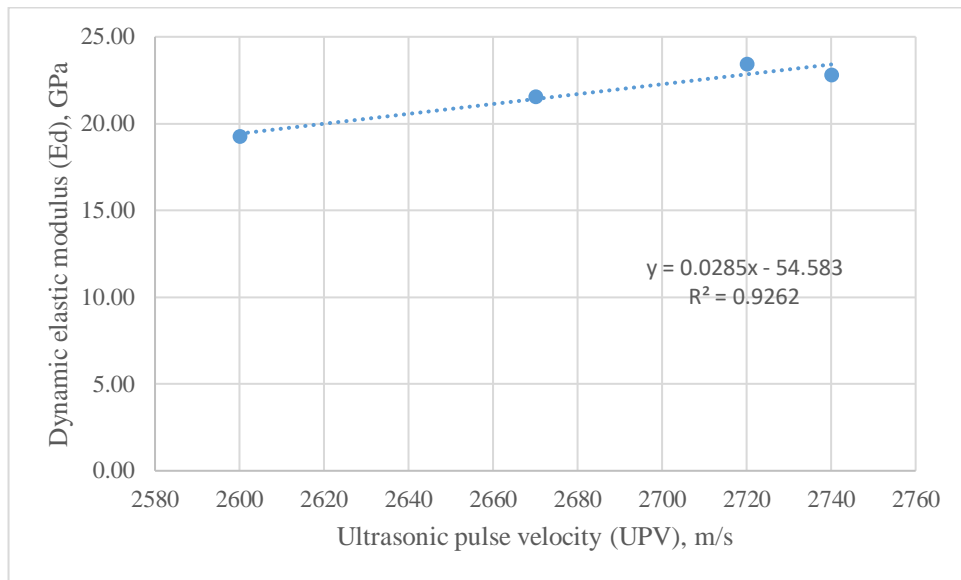


Fig. 45. Correlation between the elastic modulus and the ultrasonic pulse velocity for increasing amount of 200 μ m zeolite

As seen from the graphs above, an increase in UPV results in an increase in the dynamic modulus which goes to confirm the relationship that E_d depends on the quality of the concrete. It is also interesting to note that the correlation was better for the samples containing 200 μ m zeolite.

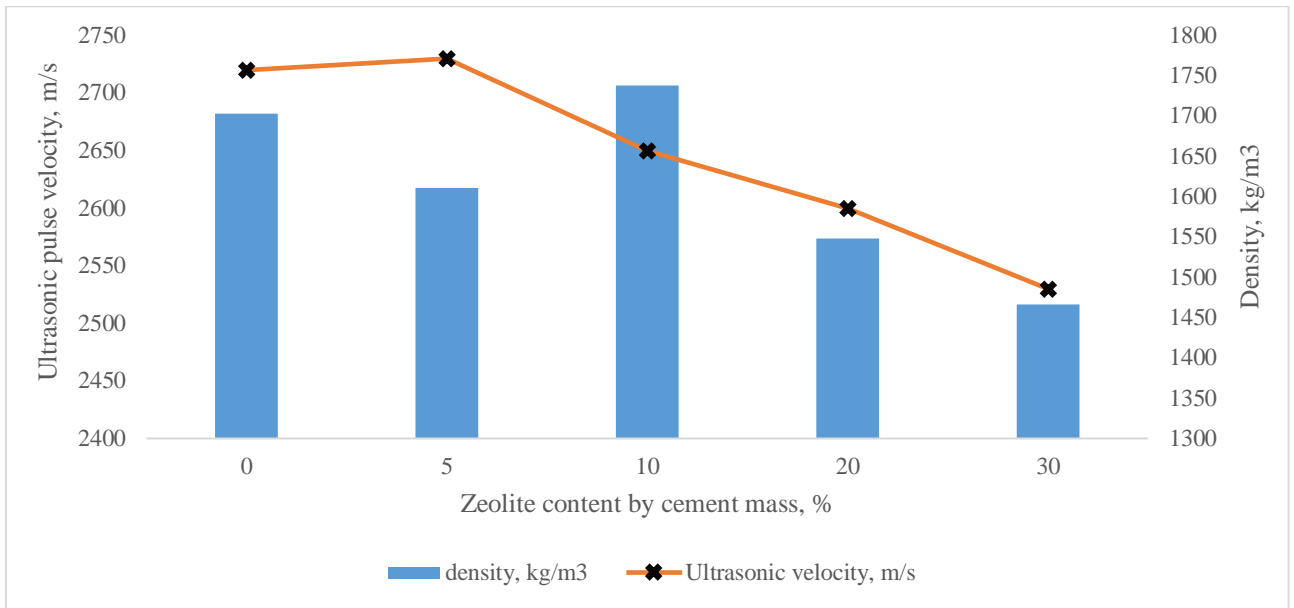


Fig. 46. Correlation between density and UPV for increasing amount of 50µm zeolite

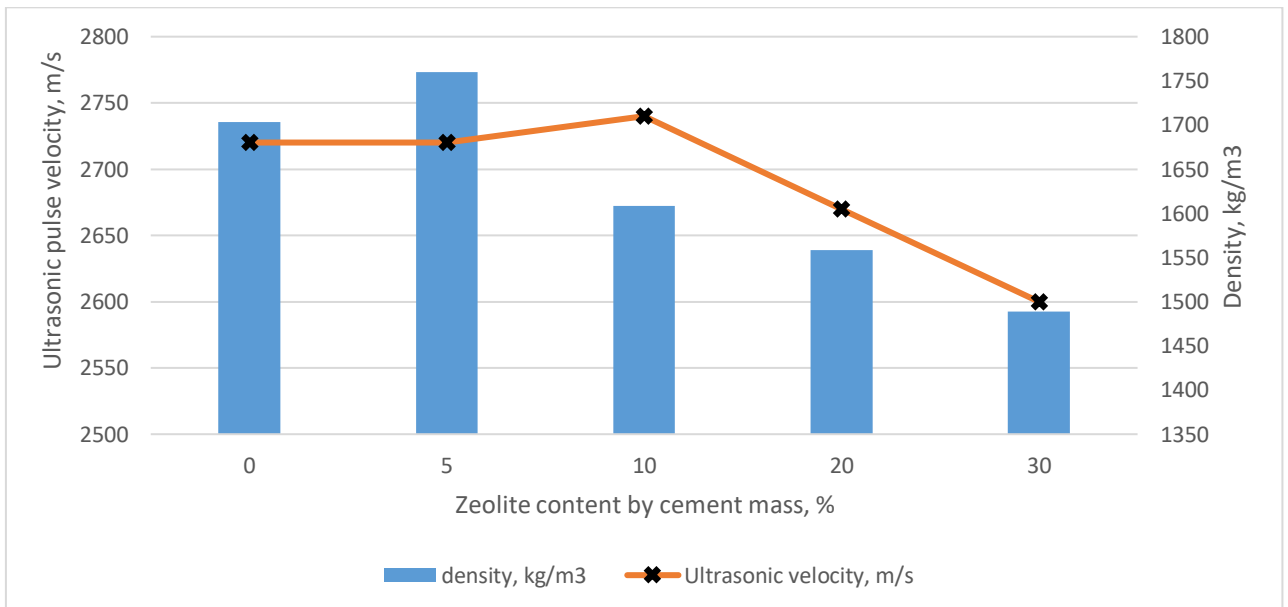


Fig. 47. Correlation between density and UPV for increasing amount of 200µm zeolite

In Fig. x and x, it can be seen that density and UPV are related. As the density decreased, so too does the UPV for increasing amount of zeolite. This means that we achieve concrete that is more lightweight. One could also conclude that the samples are in correlation with the standardised values of UPV and density for lightweight concrete. As seen by the two graphs above, the correlation is better for 200µm Zeobau which could lead us to conclude that this set of results will have a prediction of the compressive strength closely matching the measured compressive strength.

As seen in Fig x, the UPV of normal concrete is usually in the range of 3.5 to 4.5 km/s. Based on the results of the test conducted, it can be seen that the values of UPV range from 2.5 to 2.74 km/s. This can lead to the conclusion that the quality of the samples is low. However, it must be considered that the density falls in the range of 1440 and 1840 kg/m³, which is the required density for lightweight

concrete. Further studies would need to be conducted to determine how a sample mix can be adjusted to achieve a better-quality concrete.

Pulse Velocity	Quality of Concrete
>4.5 km/s	Excellent
3.5 – 4.5 km/s	Good
3.0 – 3.5 km/s	Doubtful
2.0 – 3.0 km/s	Poor
<2.0	Very poor

Fig. 46. Table of relation between pulse velocity and quality of concrete

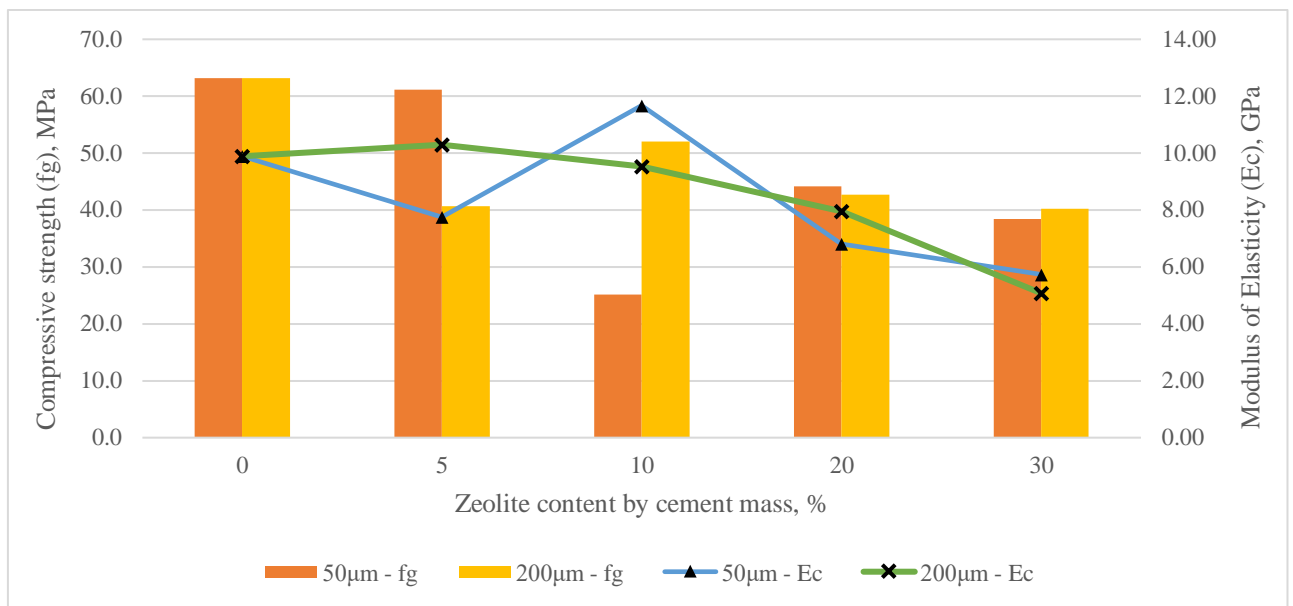


Fig. 48. Correlation between zeolite content, static elastic modulus and compressive strength for $E_c = 1.25 \cdot E_d - 19$

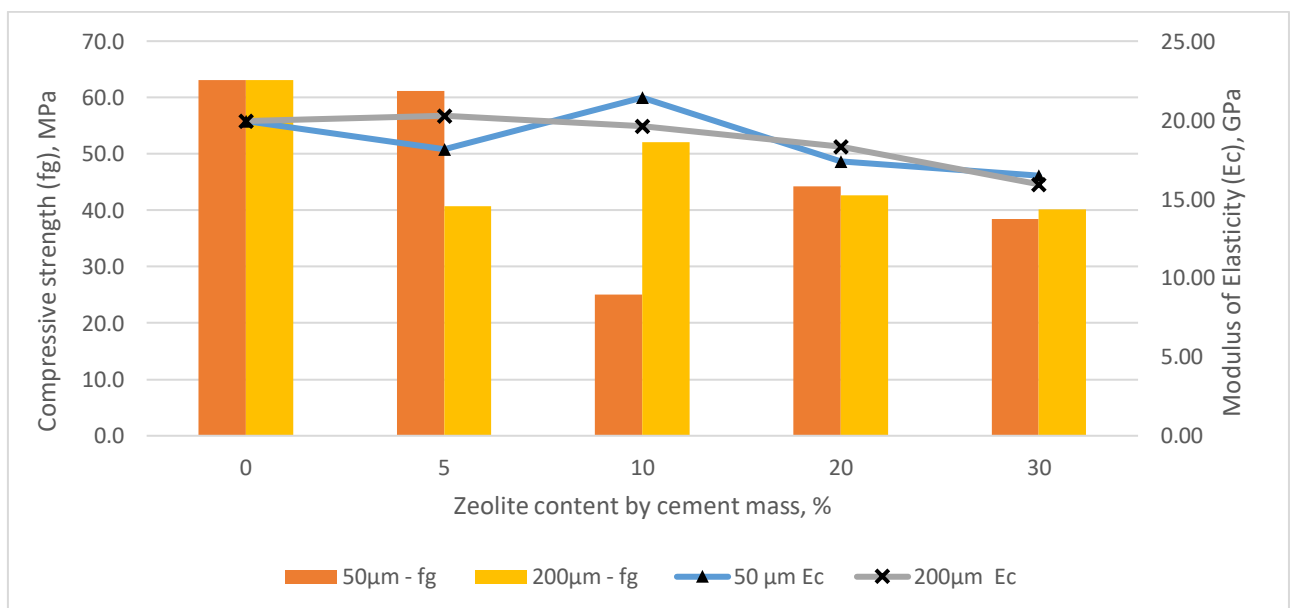


Fig. 49. Correlation between zeolite content, static elastic modulus and compressive strength for
 $E_c=1.04 \cdot E_d \cdot 4.1$

6.7. Frost resistance test

It is important to determine how concrete samples behave when exposed to freeze-thaw cycles. Concrete is normally used in areas where it is exposed to external climate changes. As a result, a concrete must be designed with the consideration of this. If concrete is not resistant to frost, it will not be durable. As such is the case, experimentation has been conducted to determine if zeolites can improve the frost resistance of cementitious products.

6.7.1. Methods

The samples of 7 x 7 x 7cm containing chromium have been immersed in water and put into a freezer to determine frost resistance. Dövgan et al. [23] concluded that the use of zeolite to replace a part of the cement content along with a plasticiser resulted in a reduction of porosity while maintaining the strength of the sample as well as the resistance to climatic changes such as freeze-thaw cycles. It is yet to be concluded on the samples created for testing.

The testing procedure includes immersing samples in water after recording their initial mass. Then, it should be continuously observed if any cracks appear in the samples. Once there is visible damage, the samples are weighed, and the mass changes are analysed to determine the samples' frost resistance.

6.7.2. Results

The samples of 7x7x7cm have been exposed to 54 freeze-thaw cycles. The initial and final mass have been recorded. It can be seen that the density of 0-3g/kg Cr, 50-3g/kg Cr and 200-3g/kg Cr has increased by 0.2, 0.6 and 1.1% respectively. In order to determine the effect of freeze-thaw cycles, the mass losses must be determined. As a result, the samples need to be exposed to more cycles to come up with more conclusive results. The samples were exposed further to freeze-thaw cycles. The total the samples have been exposed to is 108 freeze-thaw cycles. What can be seen is that for 0-3g/kg Cr, 50-3g/kg Cr and 200-3g/kg Cr, the mass increases by 0.38, 0.65 and 0.68% respectively, which isn't much. One could conclude that the samples are fairly resistant to frost because the mass did not increase significantly and there were no visible cracks.

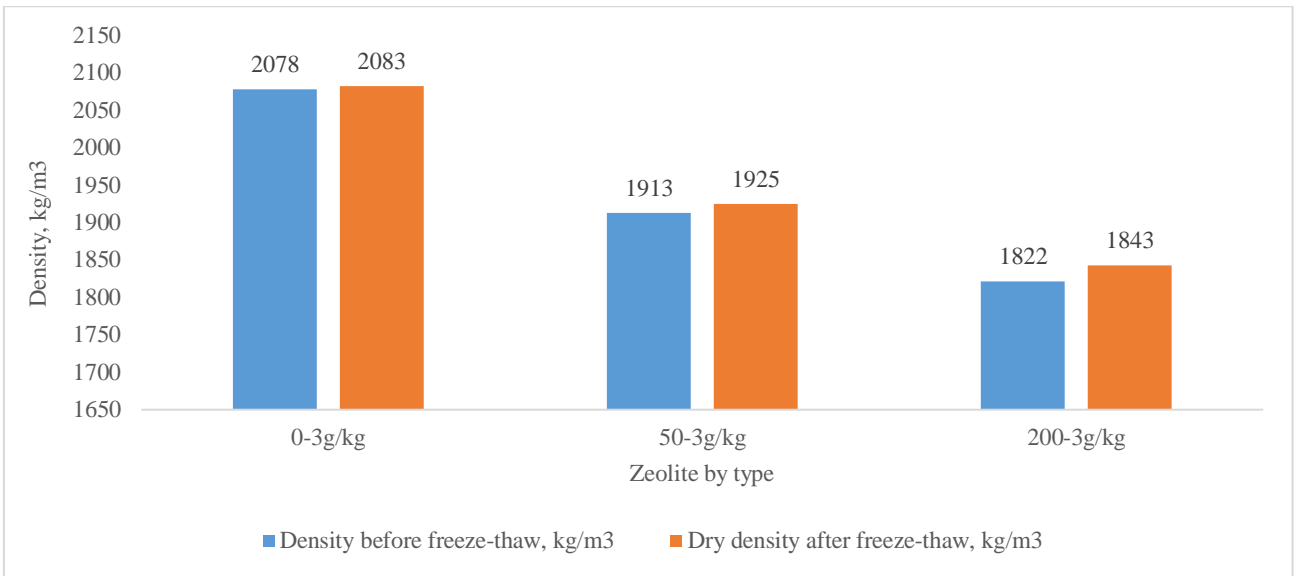


Fig. 50. Density of samples containing chromium exposed to 54 freeze-thaw cycles

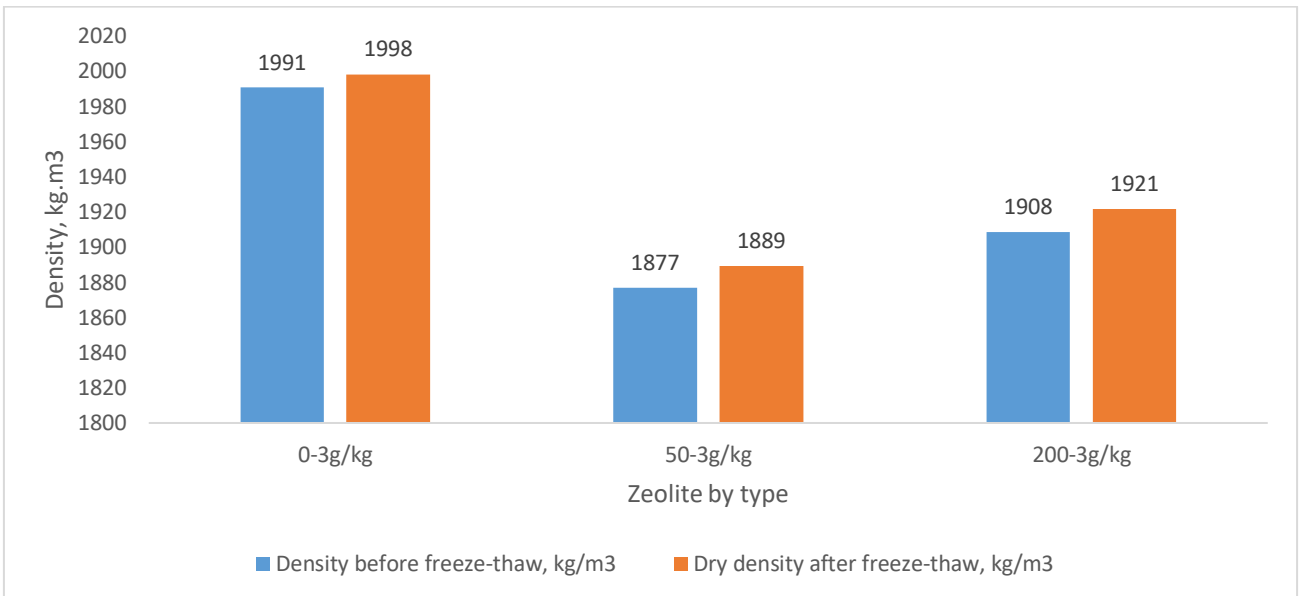


Fig. 51. Density of samples containing chromium exposed to 108 freeze-thaw cycles

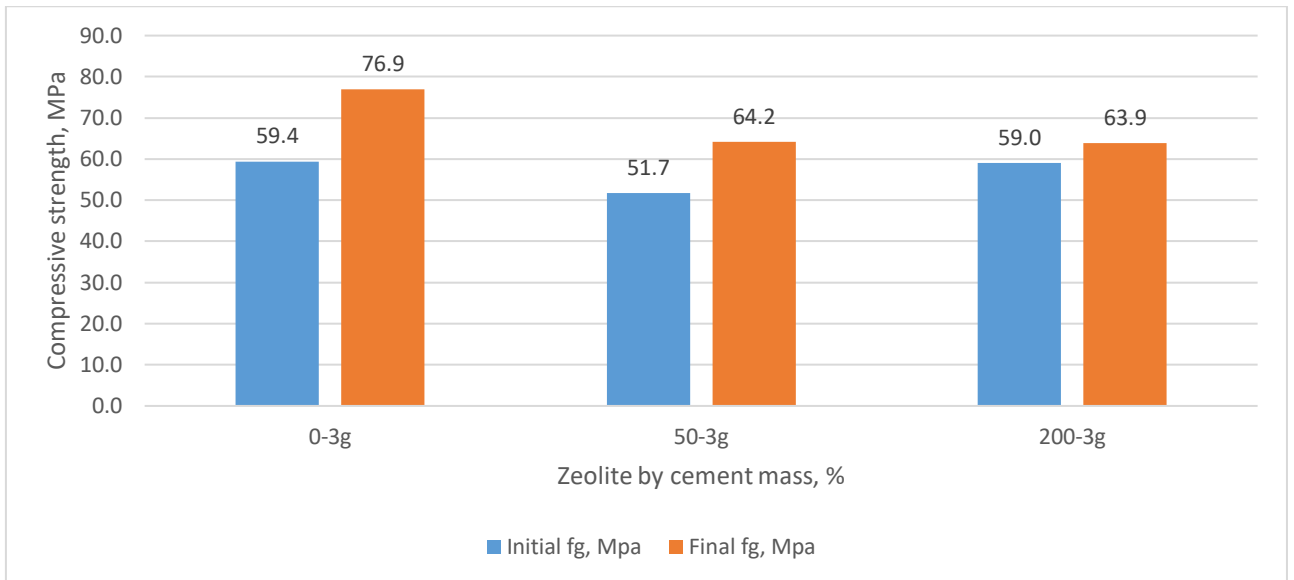


Fig. 52. Compressive strength of samples containing chromium exposed to freeze-thaw cycles

The compressive strength at 0-3g/kg Cr and 50-3g/kg Cr have increased by about 29 and 24% respectively in comparison to the initial samples that were not exposed to freeze-thaw cycles. For 200-3g/kg Cr, the compressive strength only increased by 8.4%. The increase in density and compressive strength may be owed to the presence of zeolites since they have the ability to trap molecules in their microcapillaries. However, it must be noted that with zeolites, the compressive strength is lower than that of the sample with no zeolites. This is the same for density. What can be concluded from this is that the presence of zeolites means the sample requires more water; hence, the effects of freeze-thaw cycles could be less.

Conclusions

1. Cementitious products that are made with a part of the cement replaced with zeolite require a higher W/C ratio. The higher the zeolite content, the higher the water requirement. As such, when the W/C ratio is higher, properties such as compressive strength are decreased because the material created becomes generally less dense. The results showed that when the W/C ratio is chosen according to material composition, the strength achieved is better than using a constant W/C ratio. At each percentage of zeolite content, a higher compressive strength was achieved with a varied W/C ratio. The compressive strength decreased by 21.7%, 8.8% and 22% for 10, 20 and 30% zeolite content by cement mass when the W/C ratio was kept constant comparing with a variable W/C ratio. Therefore, it is important to determine a good W/C ratio depending on the desired properties.
2. The particle size of the zeolite type has an effect on the properties of cementitious products. The smaller the particle size, the higher the water requirement because of the surface area to volume ratio. As seen in the tests conducted in this thesis, the 50 μm zeolite required between 0.5 and 1% more water for every percentage of zeolite content by cement mass. Therefore, it is important to determine what particle size of zeolite could result in better compressive strength and durability of a concrete. The larger the particle size, the smaller the surface area to volume ratio. This then reduces the overall adsorption properties as there's less "pockets" to be used to trap water. When there is less water trapped, the risk of internal shrinkage increases.
3. The compressive strength of concrete containing zeolites generally decreases with increasing zeolite content; however, it is noted that with age, it is possible to achieve higher compressive strengths because the pozzolanic reaction is going slowly. As it was noted, for 20% zeolite by cement mass at 14 days, 50MPa compressive strength was achieved then 58.40 MPa after 28 days for 50 μm . For the 200 μm ZeoBau, there can be seen a general increase in compressive strength after 76 days. The strength increased by 7.9%, 4.8% and 8.9 % for 5, 10 and 30% zeolite content by cement mass respectively. It can be concluded that the compressive strength generally decreases with increasing zeolite content, but overtime, the strength increases and urges closer and closer to the control sample. This trend is also shown in the samples that were made for the purpose of the leaching test. The compressive strength increased by nearly 30% after 63 days as compared to the initial testing.
4. Specific strength was also determined which sometimes shows how good a material is at resisting corrosion. The specific strength of stainless steel is about 63 kN·m/kg and of normal concrete is estimated at 5.22 kN·m/kg. Comparing this with the results determined in this thesis, it can be seen that higher specific strengths of cement composites have been achieved and a slight addition of zeolites results in values higher than normal concrete. The specific strength for samples containing 50 μm zeolite and 200 μm zeolite increased with time. Comparing 7 days to 28 days, it could be seen that the specific strength increased by 10 - 21%, an increase of 19% being recorded at 5% zeolite by cement mass for both the 50 μm and 200 μm zeolite. However, it is noted that beyond 10% addition, generally, the specific strength is decreases with increasing zeolite content.
5. The density of the samples is affected by the amount of zeolite added. The more zeolite added, the lower the density of the concrete. A lower density ultimately results in lower compressive strength which is generally consistent with the results provided. It is also important to note that the general densities determined in this thesis fall in the range of lightweight concrete (1440-1840kg/m³). As such, it could be further researched whether samples containing zeolite could be used as a sound insulation material for walls, for example.

6. The final setting temperature is also affected by the presence of zeolite. At every increase of zeolite percentage by cement mass, a lower setting time was achieved. A lower setting time results in a lower compressive strength, which matches the results of density and compressive strength.
7. The ultrasonic pulse velocity (UPV) of normal concrete is usually in the range of 3.5 to 4.5 km/s. Based on the results of the test conducted, it can be seen that the values of UPV range from 2.5 to 2.74 km/s. This can lead to the conclusion that the quality of the samples is low. However, it must be considered that the density falls in the range of lightweight concrete even in the presence of a heavy metal. Further studies would need to be conducted to determine how a sample mix can be adjusted to achieve a better-quality concrete.
8. The size of the pores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of pores is a valuable property. This makes zeolites an excellent adsorbent of ions because it offers this naturally huge pore size. Heavy metals have an effect on hydration of cement as they can affect the structure and permeability property during this process and ultimately the overall products of hydration. When the water to cement ratio is less than 0.4, autogenous shrinkage occurs, and this can cause cracking, which leads to failure in concrete. When the concentration of chromium is increasing, the reduction of chromium content in the leached water becomes less effective. However, it can be seen that it still meets the requirements of the Lithuanian Hygiene norms (HN60:2004). The requirement of HN60:2004 is that the chromium content in the leached water should not exceed 100 mg/l, which, in this case, is evident. The exception, however, is when 6g/kg of chromium concentration is used. It is seen that the amount of chromium in the leached water is 106.17mg/l which surpasses that of the requirement – 100 mg/l. For the sample containing 1g/kg of chromium, at the same concentration of chromium, which was calculated by simple proportion, it's seen that the sample containing 50 μ m zeolite had the lowest concentration in the leached sample at 2.10mg/l and the sample with no zeolite had 7.35mg/l. This goes to show the heavy metal adsorption abilities that zeolite could promote. For the samples with 3g/kg of chromium content at the same amount of concentration in the sample, it can be seen that for 200 μ m, the lowest concentration was achieved at 5.85mg/l compared to the one with no zeolite at 8.49mg/l.
9. The samples were exposed to freeze-thaw cycles. The total the samples have been exposed to is 108 freeze-thaw cycles. What can be seen is that for 0-3g/kg Cr, 50-3g/kg Cr and 200-3g/kg Cr, the mass increases by 0.38, 0.65 and 0.68% respectively, which isn't much. One could conclude that the samples are fairly resistant to frost because the mass did not increase significantly and there were no visible cracks.
10. The possible challenge with the decreasing compressive strength is one that needs further investigation. As concluded by other researchers, increasing zeolite content beyond 30% reduces compressive strength though increasing other properties. Knowing how useful natural zeolites are and considering their sustainable benefit more, it is needed to carry out more experiments with different zeolites and cement mixtures to try to immobilize dangerous substances (such as hard metals) in the structure of concrete while maintaining or also improving on the other properties that had more positive results. This could prove very useful in areas where construction needs to be done but the quality of soil is poor because of the heavy metal content.

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