A Szilikátipari Tudományos Egyesület lapja

építőanyag

Journal of Silicate Based and Composite Materials

A TARTALOMBÓL:

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Bakos József
(1933-2023)

Itt hagyott minket… csendben elaludt Egyesületünk „Nagy Öregje”, sokunk tisztelt és szeretett Bakos Jóskája.

Hatalmas életművet hagyott hátra, meghatározó személye volt a kibontakozó magyar építőanyag iparnak. A szigetelőanyagok gyártástechnológiája és termékfejlesztése területén alkotott maradandót.

1956-ban szerzett vegyészmérnöki diplomát a Veszprémi Vegyipari Egyetemen. Még ebben az évben előadóként kezdte pályáját a Külkereskedelmi Minisztériumban. Tehetsége hamar megmutatkozott és egy év után a Minőségi Ellenőrző Rt. mérnök-specialistájaként majd vegyi- és alapanyag osztályvezetőként dolgozott. Feladata volt a magyar külkereskedelemben (export-import) előfordult bányászati (ásvány-, szén, és kőolajbányászati) termékek, valamint a különböző vegyi- és alapanyagok (gyógyszeripartól-festékiparig bezárólag) minőségellenőrzése és vizsgálata. Ekkor dolgozta ki a matematika-statisztikai módszerre alapozva a vegyi- és alapanyagok mintavételi eljárását. Elsők között szorgalmazta a betonadalékok és egyéb építőkémiai vegyszerek bevezetését Magyarországon. A vegyészmérnöki oklevele mellé 1964-ben a Közgazdaságtudományi Egyetemen mérnök-közgazdász oklevelet szerzett.

A hét éves anyagvizsgálati munka és nagy tapasztalatgyűjtés után az érdeklődése az építőipari termékek, gyártástechnológiák és alkalmazástechnikák kutatása-fejlesztése felé fordult. 1964-től huszonöt éven át az Építőanyagipari Központi Kutató Intézet, majd Szilikátipari Központi Kutató- és Tervező Intézet tudományos munkatársa, 1970-től tudományos csoportvezetője volt. Rendkívül sokoldalú szakember volt Jóska. A hazai hő- és hangszigetelőanyag gyártás hosszútávú koncepciójának kidolgozásától kezdve az új típusú kötőanyagok, hő-hang- vízszigetelő és tűzvédelmi termékek fejlesztésén, nagyipari berendezések hő- és páratechnikai méretezésén át a magyar műszaki előírások, szabványok készítéséig sok területen dolgozott. Hőtechnikai méretezéseivel, szakértői tanulmányaival találkozhatunk a Paksi Atomerőmű 1-es blokkjának, A Tiszai Vegyi Kombinát, a Péti Nitrogénművek, a Dunai Kőolajipari Vállalat berendezéseinek dokumentációi között. A tervezők munkáját segítette a kerámia és téglaanyagok szorpciós és deszorpciós viselkedés új vizsgálati módszerének kidolgozásával.

Korán bekapcsolódott a hazai perlitvagyon szélesebb hasznosítási lehetőségének kutatásába. Ő elsősorban a technológia- és termékfejlesztéssel foglalkozott. Olyan perlitalapú szabadalmaztatott termékek kerültek ki a kezei közül mint, szórható tűzvédelmi szigetelés a Sziketherm, a tűzvédelmi lemezek a Szipernit és a Multisol, a bio termesztőközegek a Hanság gyöngye és a Construma nyagydíjas Naturalmix. A perlittel töltött falazóblokk találmánya jóval megelőzte saját korát, az ilyen elvek alapján gyártott falazóelemek most a legkorszerűbbek a szakmában.

A 37 szabadalmi jegyzése mellett 14 könyv szerzője, társszerzője volt, mint a Szilikátipar Kézikönyv, Építőanyagipari Praktikum, Építőanyagok, Szigeteléstechnika 1-2., Ember és Építési környezet stb. Közel 80 Publikációja jelent meg magyar, német, orosz, cseh szakmai folyóiratokban és további 32 nyomtatásban megjelent szakmai kiadványnak is szerzője volt. Külföldi kutatási anyagokat, szabványokat fordított angol német és spanyol nyelvről magyarra.

1968 óta tagja a Szilikátipari Tudományos Egyesületnek és 1976-tól az Építéstudományi Egyesületnek. Meghívott előadóként tanított a Veszprémi Egyetemen, a Budapesti Műszaki Egyetemen, a Miskolci Egyetemen és az Ybl Miklós Főiskolán. Az oktatói munkája részeként több jegyzetet is készített.

A tudományos tevékenység mellett az üzleti életbe is belekóstolva 4 évig irányította ügyvezetőként az Építőkémia Kft. munkáját 1993-as nyugdíjba vonulásáig. A nyugállomány nála nem a pihenésről szólt, szakértőként, tanácsadóként dolgozott tovább. Új építőanyagokat ragasztókat, fugázókat, önterülő padlókiegyenlítőket dolgozott ki. A Miskolci Egyetem korróziós szakértőjével együtt több évig a MOL Rt. szegedi, algyői gázüzemeiről készített szakvéleményeket a tartályok és csővezetékek állapotáról. (1997-2012-ig). Az Európai Uniós csatlakozás után a Szabványügyi Hivatal felkérésére több szabványt is lefordított pl.: az MSZ EN 13165 és az MSZ EN 131166 szabványokat. 1993 és 2005 között több új perlit-duzzasztó üzem gyártástechnológiáját, technológiai utasítását készítette el, segítve ezzel a hazai perlitduzzasztó ipar újraépítését. Ma Magyarországon nincs olyan duzzasztóüzem, amelyben tervezőként, szakértőként vagy szaktanácsadóként ne tevékenykedett volna.

Jóska ajtaja mindenki előtt nyitva állt, nemcsak műszaki-gazdasági problémával, hanem egy jó baráti beszélgetésre is sokan felkerestük.

A Pannon Egyetemtől 2006-ban az Aranydiplomáját, 2016-ban pedig a Gyémántdiplomáját vette át. A magyar építőiparért végzett sok évtizedes áldozatos munkájáért 2007. évi Építők Napján Miniszteri Elismerő Oklevéllel tüntették ki. Május 31-én töltötte volna be 90. életévét.

Drága Barátunk Jóska, emlékedet őrizzük! Nyugodj békében.

József Bakos
(1933-2023)

József Bakos "Jóska", the "Grand Old Man" of our Association, respected and loved by many of us, passed away quietly in April of this year.

Jóska was a key figure in the emerging Hungarian building materials industry. He made a lasting impression in the field of production technology and product development of insulating materials.

He obtained a degree in chemical engineering from the Veszprém University of Chemical Industry in 1956. In that same year, he began his career as an instructor at the Ministry of Foreign Trade. His talent soon became apparent, and within a year he was a Specialist Engineer, then a Department Manager for the Chemicals and Raw Materials Department of Quality Control Ltd, where he was responsible for the quality control and inspection of mining products (minerals, coal, and petroleum), as well as various chemicals and raw materials (from the pharmaceutical industry to the paint industry) in Hungarian foreign trade. During this time, he developed a sampling procedure for chemicals and raw materials. He was one of the first to advocate for the use of concrete admixtures and other building chemicals in Hungary. In addition to his degree in Chemical Engineering, he obtained a degree in Economics Engineering at the University of Economics in 1964.

After seven years of material testing work and accumulating a wealth of experience, his interest turned to the research and development of construction products, production technologies, and application techniques. For twenty-five years, he was a Research Fellow at the Central Research Institute for the Building Materials Industry from 1964, and then at the Central Research and Design Institute for the Silicate Industry, then scientific team leader from 1970. Jóska was an extremely versatile professional.

From the creation of the long-term concept of Hungarian material production for heat and sound insulation, through the development of new types of binders, heat-, sound-, waterproofing, and fire-protection products, to the authoring of technical regulations and standards, he worked in many different fields. His technical designs and expert studies can be found among the documentation of the equipment of the Paks Nuclear Power Plant, the Tiszai Vegyi Kombinát., the Péti Nitrogénművek, and the Dunai Kőolajipari Vállalat. He contributed to the construction of these plants by developing a new test method for the sorption and desorption behavior of ceramic and brick materials.

He got involved in the research for the wider utilization of Hungarian perlite from an early stage, with his primary focus being technology and product development. He created perlite-based patented products such as Sziketherm spray-on fire protection insulation, Szipernit and Multisol fire protection plates, and the Construma award winner Naturalmix organic growing media. The invention of the perlite-filled masonry block was well ahead of its time, masonry units manufactured based on these principles are at the forefront of the industry today.

In addition to his 37 patents, he was the author and co-author of 14 books. He published nearly 80 publications in Hungarian, German, Russian, and Czech professional journals and was the author of another 32 printed professional publications. He translated foreign research materials and standards from English, German, and Spanish into Hungarian.

He was a member of the Silicate Industry Scientific Association from 1968 and of the Architectural Association from 1976. He gave lectures as a guest speaker at Veszprém University, Budapest University of Technology, Miskolc University, and Ybl Miklós College.

In addition to his scientific activity, he was also Managing Director of Építőkémia Ltd. for 4 years until his retirement in 1993. For him, retirement was not about rest, he continued to work as a specialist and consultant. He developed new building materials, adhesives, grouts, and self-leveling floor levelers. Between 1997 and 2012, together with a corrosion expert from the University of Miskolc, he prepared expert opinions on the condition of the tanks and pipelines of MOL Ltd.'s gas plants. After Hungary joined the European Union, at the request of the Hungarian Standards Institute, he translated several standards, such as the MSZ EN 13165 and MSZ EN 131166 standards. Between 1993 and 2005, he created procedures and technological instructions for several new perlite expansion plants, helping to rebuild the Hungarian perlite industry. Today, there is no perlite expansion plant in Hungary that he did not contribute to in a designing or consulting capacity.

Jóska's door was always open for everyone, many of us visited him not only for advice on technical and economic problems but also for friendly conversations.

He received his Gold Diploma from Pannon University in 2006 and his Diamond Diploma in 2016. For his many decades of self-sacrificing work for the Hungarian construction industry, he was awarded a Ministerial Certificate of Appreciation on Builders' Day in 2007. He would have turned 90 on May 31.

Our dear friend Jóska, we will cherish your memory! Rest in peace.

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CONTENT

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Durability of high-performance concrete to an attack by a mixture of sulfuric acid and acetic acid

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Abstract

Agrifood and industrial effluents, such as acetic acid (CH_3COOH) and sulfuric acid (H_2SO_4), are very aggressive media for concrete structures. The mixture of sulfuric and acetic acids (strong acid and weak acid) can be encountered in the environment due to industrial and agrifood effluents; the behavior of cementitious materials in particular high performance concrete under the combined effect of sulfuric (H_2SO_4) and acetic (CH_3COOH) acid is not studied until now. In this regard, the present study was devoted to investigating (i) the durability of two high performance concrete (HPC) based on maximum compactness granular mix with and without silica fume to the unique effects of two types of acid, sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH) and (ii) the durability of HPC with and without silica fume to the effects of a mixture of 5% H_2SO_4 and 5% CH_3COOH at an ambient temperature of 20±2 °C. The chemical resistance to acids was determined by monitoring the relative mass loss, compressive strength loss, and macroscopic changes (altered depth and porosity). A microscopy study including x-ray diffraction and scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) analysis was also performed. The experimental results showed very good compressive strength of HPC to the acid attack by CH_3COOH. The physico-mechanical properties were slightly influenced by the acetic acid attack. In contrast, the durability of HPC to attacks by H_2SO_4 and the mixture of the two acids (CH_3COOH) and (H_2SO_4) showed a remarkable modification in the initial properties of the HPC. The deterioration of HPC by the acid mixture was the most serious, with the maximum value of the mass loss reaching 6 times the mass loss due to acetic acid and almost twice the mass loss resulting from the sulfuric acid attack. X-ray diffraction analysis (XRD) showed the presence of calcium sulfate $CaSO_4{\cdot}2H_2O$ (gypsum) in the samples after the attack by sulfuric acid and after the attack by a mixture of the sulfuric acid and acetic acid.

Keywords: high performance concrete (HPC), durability, strong acid, weakacid, mixture of acids
Kulcsszavak: nagy teljesítményű beton (HPC), tartósság, erős sav, gyenge sav, savak keverék

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1. Introduction

An increase in damage to concrete structures by acids has been observed around the world, as a consequence of the increase in sources of acidic environments due to the evolution of urban and industrial activities. Acidic media can come, for example, from agriculture. Since cementitious materials are very sensitive when in contact with acidic environments, acid attacks on concrete is a very important subject to study [1], [2]. Many authors have been interested in the durability of cement materials to different types of acids with a solution pH of less than, equal to, or greater than 4 [3], [4]. Some authors have studied the effect of attacks by strong acids, such as sulfuric (H_2SO_4), hydrochloric acid (HCl), carbonic acid (H_2CO_3), and phosphoric acid (H_3PO_4) [8], on various cement materials, mortar, and concrete with no mineral additions[12], [13].

Other researchers have studied the harmful effects of organic acids. Those studies investigated the effect of a single acid or a mixture of two or more types of organic acids [3], [16].

The compound formed is calcium acetate salt, which is very soluble in water *Eq. (1)*; therefore, the porosity increases with an alteration of the concrete. The corrosion of concrete due to acetic acid can generally be characterized by the following reactions [5]:

$$2CH_3COOH+Ca(OH)_2 = Ca(CH_3COO)_2+2H_2O \quad (1)$$

Monteny et al [6] characterized the attack with sulfuric acid (H_2SO_4) by the following chemical reactions:

$$CaCO_3+H_2SO_4+2H_2O = CaSO_4{\cdot}2H_2O+H_2O+CO_2 \quad (2)$$

$$Ca(OH)_2+ H_2SO_4 = CaSO_4{\cdot}2H_2O \quad (3)$$

$$3CaO{\cdot}Al_2O_3{\cdot}12H_2O + 3(CaSO_4{\cdot}2H_2O) + 14H_2O = 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O \quad (4)$$

$$3CaO{\cdot}SiO_2{\cdot}3H_2O+H_2SO_4 = CaSO_4{\cdot}2H_2O+Si(OH)_4 \quad (5)$$

The primary reaction product manifested on the concrete surface is gypsum, which is associated with volume expansion *Eq. (3)* and can induce tensile stresses in concrete, resulting in cracking and spalling. Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite *Eq. (4)*, which has a larger volume increase than that of gypsum, thus leading to more micro- and macro- cracking. In addition, sulfuric acid decomposes the cementitious matrix

by decalcifying calcium silicate hydrate (C–S–H) *Eq. (5)*, thus contributing to strength loss [6].

Previous research

Achoura.D et al [8] found a reduction in the mechanical resistance of mortars based on blast furnace slag under the effect of attacks by different types of acids. The maximum decrease was observed in the samples immersed in the H_2SO_4 solution followed by hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and finally byacetic acid CH_3COOH. The attack by H_2SO_4 leads to the formation of gypsum and ettringite, the attack by hydrochloric acid HCl leads to the formation of calcium chloride and iron hydroxide, the attack by acetic acid CH_3COOH leads to the formation of calcium acetate, and the attack by phosphoric acid H_3PO_4 leads to the formation of calcium phosphate.

Ammonium nitrate (NH_4NO_3) is an aggressive agent for cement paste, of which an acceleration of Ca leaching was observed during attack. In addition, the degraded depth and the leached Ca linearly increased as a function of the square root of the immersion time of the samples in the Ammonium nitrate (NH_4NO_3) solution. An increase in water permeability and sample porosity after attack by Ammonium nitrate (NH_4NO_3) was noted for all samples [7].

Zivica.V [9] compared the aggressiveness of organic acids to that of inorganic acids. He demonstrated the aggressive power of acetic acid solution, which he compared to that of lactic acid.

We found in a previous study that the relative loss of mass of HPC under attack by a 4% sulfuric acid H_2SO_4 solution did not exceed 4%. Crystallization of calcium sulfate (gypsum) and thaumasite were detected by X-ray diffraction (XRD) at the end of the test [10].

Acid attack on high strength concrete with and without silica fume is mainly influenced by the type of acid even though they may have the same high concentration of 15%. Partial replacement of cement with silica fume up to 15% by weight caused no effect of the lactic acid ($C_3H_6O_3$) attack, reduced the HCl attack, and worsened the H_2SO_4 attack [11].

Kazuyuk et al [12] showed that using silica fume as a replacement cementitious material can increase sulfuric acid resistance. Zivica. V [13] reported that the use of chemically modified silica fume reduced the intensity of the hydrochloric acid attack. E. Hewayde et al [14] showed that the presence of silica fume in the concrete mixture had a minor effect on the resistance to the 7% H_2SO_4 solution. L. Mlinárik et al [32] studied the influence of combined of metakaolin and silica fume on the durability of mortars. The mortar specimens were exposed to two different types of acidic solutions, sulfuric acid and to acetic acid up to 390 days. The sulfuric acid caused increase in mass, the best results were provided by the metakaolin mixture. In acetic acid attack, the combined use of metakaolin and silica fume did not result better resistance, than for the other mixtures. On the other hand after almost one year of exposure, the differences are not significant.

Yasser Sharifi et al [15] studied the durability of mortars containing ceramic waste powder (CWP), like other cementitious materials, to attacks by sulfuric acid with a pH = 1.5. The cement was replaced with CWP powder in amounts of 0, 5, 10, 15, 20, and 25% (by weight of cement). This study presented the mechanical resistance tests, loss of mass of cement mortars, and a microstructure analysis (SEM and XRD). The results showed that mortar samples containing 5% CWP exhibited the lowest mass loss at all ages (0 days to 56 days). Crystallization of gypsum was observed by XRD in samples at the end of testing.

The addition of fly ash to mortars and concretes increased their chemical resistance to attacks by a mixture of organic acids (acetic acid CH_3COOH and lactic acid $C_3H_6O_3$), reducing the degradation of concrete and mortar samples compared to compositions without fly ash [16].

Sara Irico et al [17], studied the durability of two self-compacting concrete (SCC) by severe sulfuric acid attack at pH 2. The (SCC) types that are based on ordinary Portland cement (OPC) and granulometrically optimized blast-furnace slag cement was evaluated by three complementary tests that were performed in different research institutes. The use of granulometrically optimized slag cement provided a moderate increase of the concrete resistance against acid attack.

Compressive strength loss did not have a direct relation with mass loss of Self-consolidating concrete (SCC) specimens under sulfuric acid attack [18].

William G.Valencia-Saavedra et al [19], studied the acidic attack behaviour of alkali-activated concretes, based on a low-quality fly ash (FA), using as sources of calcium granulated blast furnace slag (GBFS) and Portland cement (OPC), which were incorporated in a 20% by weight proportion. A mixture of sodium silicate and sodium hydroxide was used as the activating solution. The specimens were exposed to solutions of sulfuric acid H_2SO_4 and acetic acid CH_3-COOH at concentration 1 M for 360 d. The results indicate that alkali-activated concretes show better performance compared with that of OPC. M. Nasir et al [28][29] combined blast furnace slag with silico-manganese fume to produce alkali-activated mortars. Slag free specimens were also studied. After exposure to H_2SO_4 (5%), they found that the slag free specimens exhibited high resistance attributed to the lack of Ca in silico-manganese fume. The blended specimens were reported to have underwent deal-umination along with gypsum formation which resulted in severe spalling.

L.Wu et al [29][30] found that adding up to 10% calcium aluminate cement had a positive impact on the H_2SO_4 (pH =2.0) resistance of alkali-activated metakaolin. This was attributed to the reduced volume of permeable voids and the enhanced neutralisation capacity. Khan et al [31] investigated the replacement of fly ash with waste glass (GP up to 40%) in alkali-activated fly ash/slag. They exposed mortars to H_2SO_4 (3%) and HCl (3%) for one year and found that waste glass improved the acid resistance in terms of the mass and strength losses observed. The inclusion of 10%–20% GP as a replacement of fly ash (FA) substantially reduced the physical, mechanical and microstructural damages of the specimens due to acid attack.

The effect of acid rain simulated by a mixture of sulfuric acid H_2SO_4 and nitric acid (HNO_3) was applied to concrete samples with a pH equal to 1. A slight increase in tensile strength was observed for immersion up to 10 days. Beyond 10 days, a decrease in tensile strength with increasing immersion time in the solutionwas observed [20].

The development of industrial, agricultural, food-processing activities, urban evacuations producing large quantities of effluents, these effluents are loaded mainly with organic acids and sulfuric acid used for the manufacture of fertilizers, also used in the petroleum industry…, thus the evacuation of waste water loaded with acetic acid used in cleaning products, certain medicines, food additives and preservatives, acid rain loaded with sulfuric acid, consequently, waste of great quantities loaded with acetic and sulfuric acid are stored before treatment in reinforced concrete structures, or evacuated into nature, and infiltrated under the foundations of the structures. Concrete structures exposed to these acid laden effluents are generally degraded very quickly. Acetic and sulfuric acids are aggressive environments for the cementitious matrix and the limestone aggregates, the salts resulting from the chemical reactions are soluble and insoluble salts (calcium acetate and calcium sulphate). The combined effect of attack by two sulfuric and acetic acids on a cementitious material little encountered in the environment, thus, it is not yet studied. In this respect, the study of the durability of cementitious materials, in particular HPC, under the combined effect of sulfuric and acetic acids is very important.

The originality of this research consists of studying the durability of HPC with and without silica fume to attacks by acid mixtures composed of acetic acid and sulfuric acid at a temperature of 20±2 °C in presence of low-pH solutions <4.

2. Materials and methods

2.1 Materials

2.1.1 Aggregates

The aggregates used to manufacture the different concrete compositions are of limestone origin of classes 0/4, 4/8, 8/16 and 16/20 with the addition of naturals and from rivers 0/4 in order to increase the compactness of the aggregates mixture and improve workability.

2.1.2 Cement and silica fume

The chemical analysis of cement and silica fume are summarized in *Table 1*.

	CEM II/A 52,5	Silica Fume
SiO_2	19.58%	85%
Al_2O_3	4.52%	-
Fe_2O_3	2.76%	-
CaO	61.63%	-
K_2O	0.61%	-
Na_2O	0.09%	-
Na_2O-equ	0.50%	-
Loss on ignition	3.34%	-
MgO	1.75%	-
SO_3	2.59%	<2.5%
Cl^-	0.019%	<0.2%

Table 1 Chemical compositions of CEM II/A 52.5 cement and silica fume
1. táblázat A CEM II/A 52.5 cement és szilikapor kémiai összetétele

2.2 Formulation of high-performance concrete (HPC)

The HPC formulation method used was inspired by the HPC formulation method developed at the university of Sherbrooke [21] follows the same approach as the American standard ACI 211[22]. Overall, the formulation of HPC was based on a combination of empirical results and calculations based on the method of absolute volumes. Determination of the optimal dosage of the different granular classes used was based on the maximum compactness of the mixtures in the dry state. Combinations of aggregate mixtures were prepared; we started with binary mixtures, then ternary, quaternary, and ended with pentagonal mixtures. The maximum compactness in the dry state was observed for a pentagonal mixture. The determination of the dosage of superplasticizer MEDAFLOW 30 was conducted according to the grout method [21]. The main objective of the grout method is to experimentally determine the optimal dosage of superplasticizer (saturation dose) [21]. The compositions of the various concretes formulated, and which will be the subject of a characterization study both in the fresh and hardened state, are presented in *Table 2*.

Mix HPC	HPC	HPC FS
Crushed aggregat 16/20, kg/m³	432.05	426.21
Crushed aggregat 8/16, kg/m³	259.23	255.72
Crushed aggregat 4/8, kg/m³	388.84	383.59
Crushed limestone sand C0/4, kg/m³	344.22	339.59
Sand naturel R0/4, kg/m³	344.22	339.59
Cement, kg/m³	470	423
Silica fume, kg/m³	0	47
Water, l/m³	164.5	164.5
SP, kg/m³	5.64	8.46
e/c	0.35	0.38
e/l	0.35	0.35
Slump, mm	300	300

HPC: high performance concrete without silica fume
HPC FS: high performance concrete with silica fume

Table 2 Mix proportions and slump for high performance concrete (HPC)
2. táblázat Keverési arányok és süllyedés nagy teljesítményű betonhoz (HPC)

2.3 Test method

The test was devoted to investigating the durability of two high HPC with and without silica fume to the unique effects of two types of acid, sulfuric acid and acetic acid and the of mixture of 5% sulfuric acid and 5% acetic acid at an ambient temperature of 20±2°C. The test of chemical resistance to acid attack was carried out on two types of prismatic samples of dimensions 7x7x28 cm and cubic dimensions 10x10x10 cm. The shape, dimensions of the test pieces and the molds comply with European standard NF EN 12390-1 [23]. The acid concentration of the solutions was 5%; the test samples aged 56 days conserved in water were immersed in the solution in closed plastic tubs for 120 days. The solution was renewed every 15 days for the attack by sulfuric acid and the acid mixture, and renewed after 1 week for the attack by acetic acid. The samples were placed in a climatic chamber where the temperature was set at 20±2°C.

3. Results and discussion

3.1 Mechanical resistance of HPC before durability testing

The compression test was carried out on cubic specimens of dimensions 10x10x10 cm^3 cured for 1 week in water for 28 days and 56 days after demoulding.The three-point bending test was carried out on prismatic specimens 7x7x28 cm^3 aged 28 and 56 days. The compression and bending tests were carried out in accordance with the standards [24][25]. The results of the tests are the average values obtained on three test specimens. *Table 3* shows the evolution of the mechanical compressive strength and flexural strength, respectively.

Mix HPC	Compressive strength MPa		Flexural strength MPa	
Age	28 days	56 days	28 days	56 days
HPC	68.90	74.48	4.66	4.95
HPCFS	68.87	81.33	4.85	4.99

Table 3 Mechanical strength
3. táblázat Mechanikai szilárdság

3.2 PH evolution

Fig. 1 shows the change of pH of the acid solutions after immersion of the samples with and without HPC silica fume. According to the results, there is a rapid increase in pH for the acetic acid based solution because it reaches the value of 4 after 24 h of immersion of the samples. While, the pH values remained stable up to 10 days of immersion of the samples in solutions based on sulfuric acid and mixture of acids, the pH reached the value of 4 after 15 days. This can be explained by the phenomenon of the dissociation of strong and weak acids.

3.3 Exterior and interior appearance of the sample after the tests

Fig. 2 shows the appearance outside and inside the sample at the end of the trials.

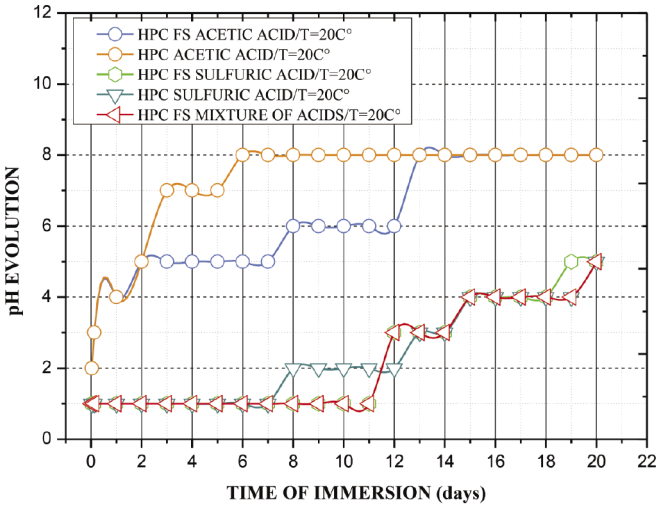


Fig. 1 pH evolution of acid solutions after sample immersion
1. ábra Savas oldatok pH-változása mintabemerítés után

Acetic acid

The test samples preserved in the acetic acid based solution were characterized by a smooth, clear, brown surface without cracks. After cutting the samples, no change was observed inside the HPC samples. The color change appears only on the surface (see *Fig. 2*).

Sulfuric acid and acid mixture: The test samples were characterized by a whitish appearance and a rough surface. Inside the samples, no degradation was observed (i.e., degradation appears only on the surface, see *Fig. 2*).

3.4 Altered depth

At the end of the test, the samples were sawn perpendicularly and sprayed with a solution dosed at 1% of phenolphthalein in order to check the healthy and degraded areas of the test pieces. The phenolphthalein test applied to the sections of the

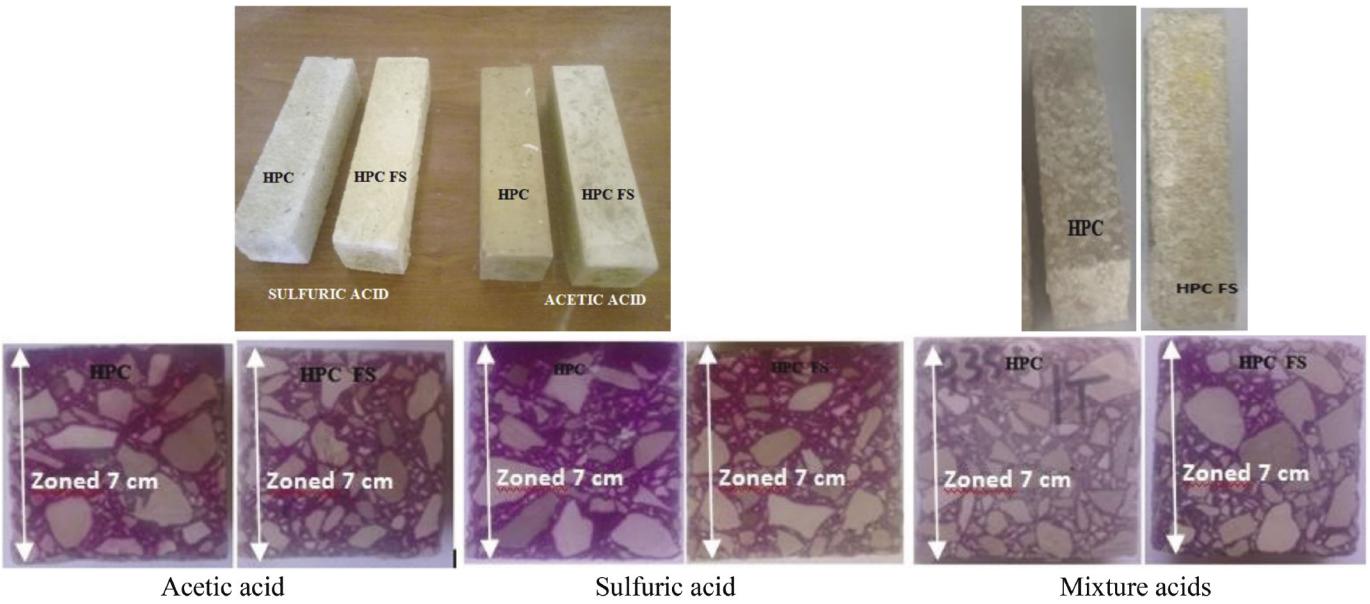


Fig. 2 Exterior and interior appearance after cleaning the samples sprayed the cut surface with phenolphtalein solution
2. ábra A minták külső és belső megjelenése tisztítás után, a vágási felületet fenolftalein oldattal permetezték be

samples at the end of the attack test by acetic and sulfuric acid showed the coloring of the entire sawn section (see *Fig. 2*). This was explained by the dissolution of the entire degraded surface of the samples. The histogram in *Fig. 3* shows the change in the altered depth. According to the results, the altered depth for the attack by acetic acid does not exceed a few micrometers for the two compositions of HPC, while the alteration of concrete by sulfuric acid reached 1.2 mm after 120 days of immersion of the samples in the aggressive solution. The curve in *Fig. 3* illustrates the longitudinal evolution of the altered depth of the different compositions of the HPC tested in the acid mixture; the range of its variation was between 1.5–2 mm.The layer of corrosion products on the surface of HPC increased faster in the solution of sulfuric and mixture acids than in the solution of acetic acid. this is explained by the formation of gypsum $CaSO_4{\cdot}2H_2O$ on the surface of the sample, which results from the reaction of sulfuric acid, calcite $CaCO_3$ and portlandite $Ca(OH)_2$.

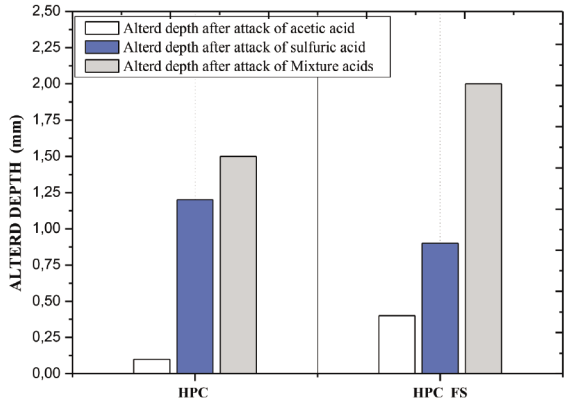


Fig. 3 Altered depth
3. ábra Változott mélység

3.5 Mass loss

The cumulative mass loss at each month (^{TM}Mt) was calculated by:

$$\delta M_t = \left(\frac{M_t - M_i}{M_i}\right) \times 100 \qquad (6)$$

M_t: Mass at time t (kg).
M_i: Initial mass before exposure to acid (kg).

Fig. 4 shows the evolution of the variation rates of the masses of the different compositions of HPC tested in an aggressive solution of acids: acetic acid, sulfuric acid, and acid mixture.

- **Acetic acid:** In the first month, the mass losses are almost identical for the two compositions with and without silica fume. From the second month of the acid attack, it is observed that the mass loss is slightly lower by the incorporation of silica fume in the composition of HPC. The mass losses do not exceed 1.5% after 120 days of immersion in the acid solution. The loss of mass in the specimens is mainly due to dissolution of the calcium upon exposure to acetic acid.
- **Sulfuric acid:** The maximum mass losses were observed in the compositions with silica fume; its maximum value reached 5% after 120 days of immersion of the samples in the acid solution, the differences are not significant. These mass losses were noted to be significant compared to samples attacked by acetic acid.
- **Acid mixture:** The results show an increase in the mass loss of the samples as a function of the duration of the immersion of the samples in the acid mixture solution. The maximum mass loss is 10.26% after 120 days of immersion of the samples with silica fume in the acid mixture solution. This marked increase in mass loss is mainly due to with the reduction of the pH, results from the addition of sulfuric acid.

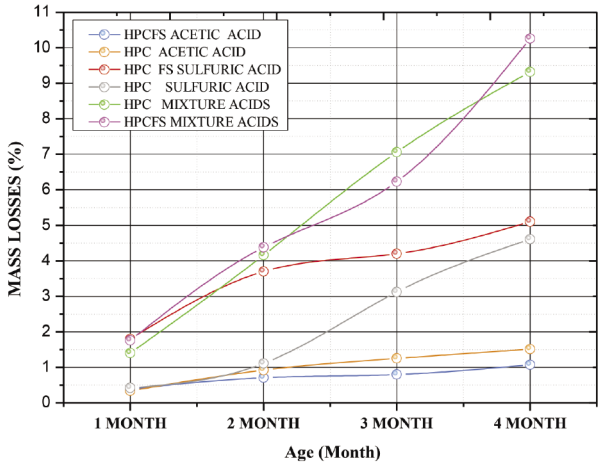


Fig. 4 Relative mass losses
4. ábra Relatív tömegveszteségek

The attack of HPC with sulfuric acid causes mass loss of the order of 5%, i.e., 3.4 times the mass loss resulting from the attack of acetic acid after 120 days in the solution. While the deterioration of HPC by the acid mixture was noticed, the maximum value of the mass loss reached 9.39%, which is 6 times the mass loss by the aggression of acetic acid and almost twice the mass loss resulting from the aggression of sulfuric acid (see *Fig. 5*). The increase in mass loss recorded to attack by the mixture of acids can be explained by the decrease in pH during the fifteen days, and therefore the increase in the speed of deterioration of the samples.

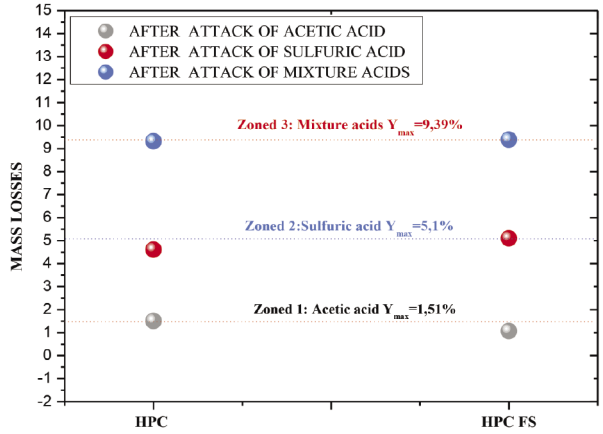


Fig. 5 Relative mass loss
5. ábra Relatív tömegveszteség

3.6 Porosity accessible to water

The histogram of *Fig. 6* shows a slight increase of the porosity accessible to water samples before and after the attack by acetic acid, sulfuric acid, and the acid mixture. A slight increase in the porosity of the HPC was observed after attack by the acids. According to the results illustrated in *Fig. 7*, the maximum increase in porosity of HPC without silica fume does not exceed 0.56% compared to the value of the initial porosity before immersion of the samples in the acid solution. This value is 0.65% for HPC with silica fume. The measurements of porosity have shown that HPC formulated has good resistance to attack by acids, and this thanks to its dense structure.

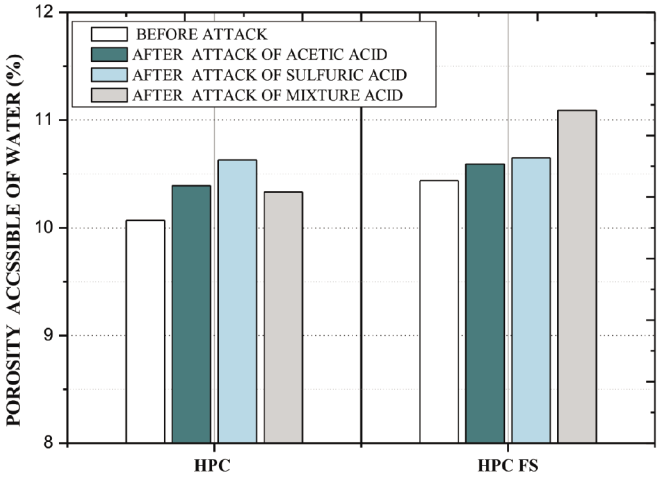
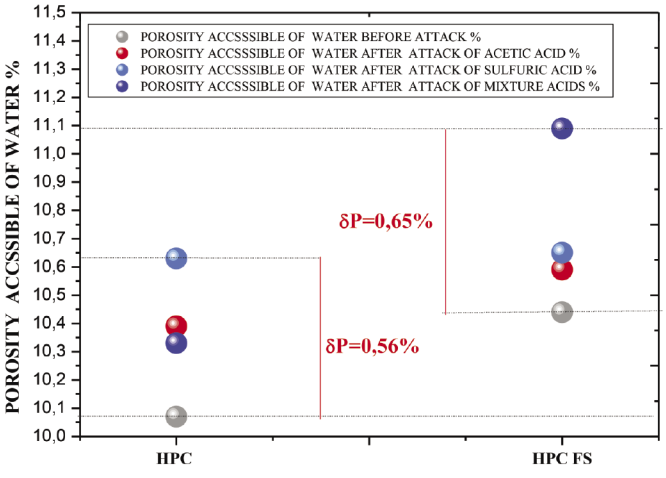


Fig. 6 Porosity accessible to water of the specimens before and after the attack
6. ábra A próbatestek víz számára hozzáférhető porozitása a savazás előtt és után



Fig, 7 Variation of Porosity accessible to water
7. ábra A víz számára elérhető porozitás változása

3.7 Compressive strength

The histogram in *Fig. 8* shows the variation in the compressive strength of HPC compositions tested before and after attack by both acetic and sulfuric acid and also for the acid mixture over 120 days. It can be seen that the compressive strength of the HPC samples under the attack of acetic acid is slightly changed; the maximum reduction rate is $\delta\sigma$ = 3.73% (see *Fig. 9*). A remarkable drop in compressive strength was recorded for the HPC immersed in a solution of sulfuric acid and the acid mixture. The decrease of the compressive strength reached $\delta\sigma$ = 46% after the attack by sulfuric acid and $\delta\sigma$ = 54.35% after the attack by the acid mixture despite the sample cores remaining healthy and degradation appearing only on the surface. This result can be explained by the importance of surface degradation, which decreases the toughness of the material and, consequently, the ease of the propagation of cracks at the moment of crushing of the test pieces, which accelerate the rupture of the material.

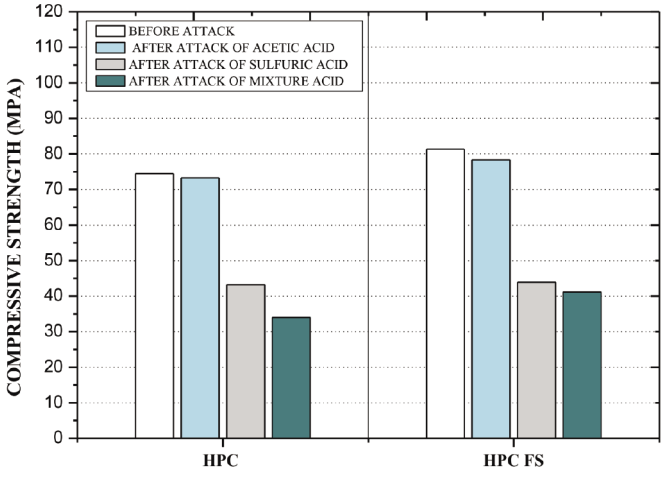


Fig. 8 Mechanical compressive strength
8. ábra Mechanikai nyomószilárdság

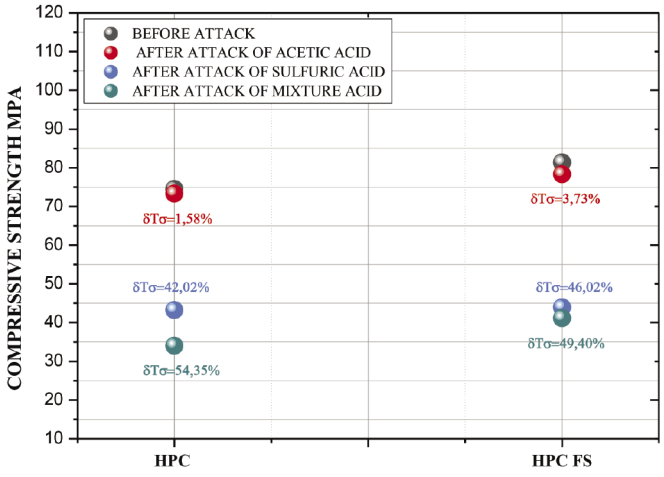


Fig. 9 Variation of compressive strength
9. ábra A nyomószilárdság változása

The formulated HPC compositions exhibit very good resistance to attack by sulfuric acid despite the fact that the aggregates used are reactive. The relative mass loss does not exceed 5% after 4 months of immersion in the dosed solution of 5% sulfuric acid. A comparison of the results obtained by some authors, in the framework of studying the durability of HPC to attacks by sulfuric acid, are summarized in the following: Shweta Goyal [26] studied the durability of HPC to attacks by sulfuric acid with a solution concentration of 1%. These HPC were formulated with and without 5% silica fume substitution, with granite-type crushed aggregates and natural river sand. According to the results obtained by Shweta Goyal [26], the relative mass losses reached 7% after 4 months of immersion

in the dosed solution of 1% sulfuric acid for composition M2-II (composition with 5% silica fume, w/c= 0.35, compressive strength R_{c28} = 83.5 MPa, slump = 20.4 cm). E. Hewayde [14] showed that the relative mass loss for a HPC reached 19% after 61 days of immersion of the samples in a solution of 3% sulfuric acid and 30% after 61 days of immersion of the samples in a 7% sulfuric acid solution, although this HPC was made of siliceous aggregates (composition with and without silica fume 15%, w/c = 0.35, R_{c28} = 57.6 MPa and 68 MPa, slump = 5 ± 1 cm). R. Sri Ravindrarajah [11] performed research on the durability of high performance concrete based on silica fume to attack by sulfuric acid. The concentration of the acid solutions was maintained at 15%. The results showed that the incorporation of silica fume had a negative effect for the attack of HPC by sulfuric acid; the maximum mass loss for the HPC reached 20% after 30 days of immersion in the aggressive solution.

The good resistance to attacks of sulfuric acid observed for our HPC, results from the use of granular mixture with maximum compactness, the latter minimizes the speed of deterioration of material and consequently its lifespan.

	Mass loss (5% Acid) sulfuric Research		Mass loss (1% Acid sulfuric) Shweta Goyal [26]		Mass loss (3% acid sulfuric) E. Hewayde [14]		Mass loss (15% acid sulfuric) E. Hewayde [14]	
	HPC	HPC FS	HPC	HPC FS	HPC	HPC FS	HPC	HPC FS
After 30 days	0.42%	1.8%	-2%	-2%	10%	10%	20%	14%
After 60 days	1.11%	3.7%	5%	3.5%	18%	19%	-	-
After 90 days	3.12%	4.2%	7%	6%	-	-	-	-
After 120 days	4.61%	5.1%	11%	7%	-	-	-	-

Table 4 Comparison of the results
4. táblázat Az eredmények összehasonlítása

4. Microstructure analysis by SEM/EDS and XRD after attack by acids

Microstructure analysis by SEM/EDS and by XRD were carried out at the end of the acid attack tests in order to verify all types of modification within the material at the microscopic scale. We chose the composition HPC FS for our microscopic study, from the cut of the sample sawn perpendicularly. The results obtained are as follows:

4.1 Acetic acid

The SEM image in *Fig. 10a* shows that the HPC FS sample always remained healthy with very little appearance of micro-cracks and small pores characterized by lengths of a few micrometers. According to the EDS atomic spectrum, HPCFS contains peaks of Ca, O, and C, which are the main elements in the composition of hydrates and calcium acetate resulting from the reaction of portlandite and calcite with acetic acid. Another smaller scale SEM image was taken on the same sample. *Fig. 10b* shows crystallization of a dense regular texture in sheets with very little crystallization from a gel. Since the EDS analysis shows the richness of the sample by calcium and a low percentage of silicon SiO_2, we believe this is the crystallization of portlandite with very little of the calcium acetate crystallizing in the pores. An X-ray diffraction analysis was performed on a ground sample (in average sample) in order to further validate the results obtained by EDS. *Fig. 11* shows the spectrum of HPCFS obtained by XRD. According to the results, the components detected by XRD are calcite $CaCO_3$, silicon SiO_2, and calcium silicate $CaSiO_3$. Calcium acetate is not detected in this analysis; this can be explained by its solubility in water.

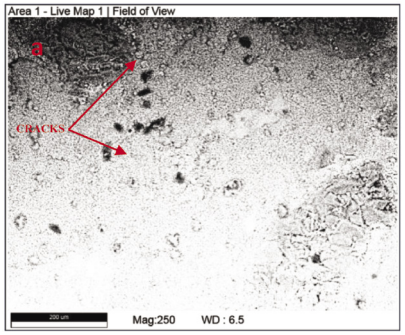
4.2 Sulfuric acid

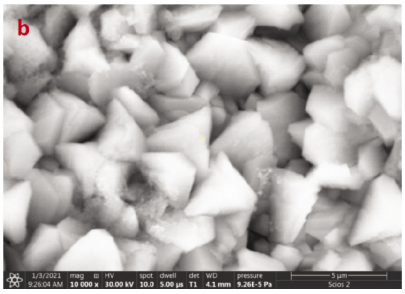
The presence of a few long micro-cracks in the paste and in the limestone aggregates was observed in the HPC FS sample. These micro-cracks were characterized by lengths of the order of 600 µm (see *Fig. 12a*). EDS analysis shows that the HPC FS sample contains peaks of Ca, O, Si, Al, and C, which are the main components in the composition of hydration products. The absence of sulfur (S) was noted in the EDS analysis. Sulfur is a major component in the composition of ettringite and gypsum. In contrast, the second full-scale SEM image shown in *Fig. 12b* shows the crystallization of hydrates and gel. For this purpose, XRD analysis was performed to confirm the results; actually, according to the spectrum in *Fig. 13*, the XRD analysis detects the crystallization of calcium sulphate $CaSO_4 \cdot 2H_2O$ (gypsum) and calcium-aluminum-silicate-hydrate $CaAl_2Si_2O_8 \cdot 4\ H_2O$ (gismondine [27]) within the material.

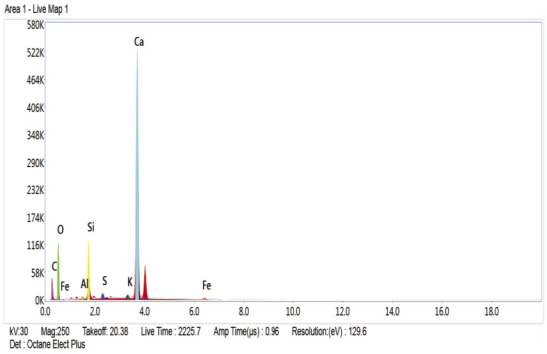
4.3 Acid mixture

After observing the SEM image presented in *Fig. 14a*, we noticed the appearance of a large field of micro-cracks at the level of the paste, at the level of the calcareous aggregates, and at the interface of the paste aggregates siliceous. The lengths of the micro-cracks exceeded 600 µm. The EDS spectrum of HPCFS contains peaks of Ca, O, Si, Al, and C, which are the main building blocks of hydration products and calcium acetate. As in the single attack by sulfuric acid, there is no sulfur in the EDS analysis. The large scale SEM image shown in *Fig. 14b* also shows gel crystallization within the sample, which we believe to be hydrates and $CaSO_4 \cdot 2H_2O$ (gypsum). However, the XRD analysis in *Fig. 15* detects the crystallization of calcium sulfate $CaSO_4 \cdot 2H_2O$ (gypsum) and calcium-aluminum-silicate-hydrate $CaAl_2Si_2O_8 \cdot 4\ H_2O$ (gismondine [27]) within the ground concrete sample.

The salts, which were detected only by X-ray diffraction analysis on the ground sample, can be explained by the crystallization of salts on the surface of the sample.







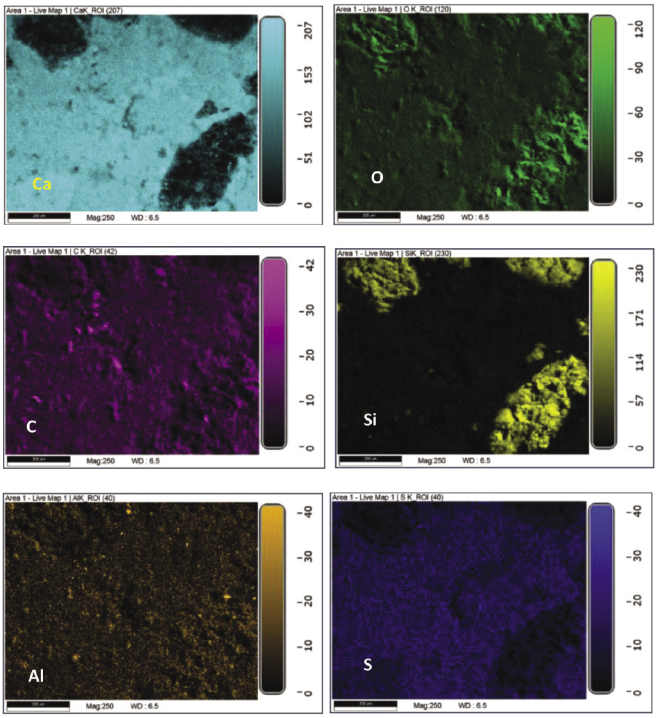


Fig. 10 SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a solution of 5% acetic acid

10. ábra SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5%-os ecetsav oldatba való merítés után

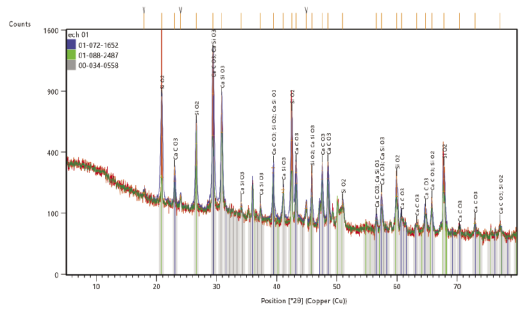
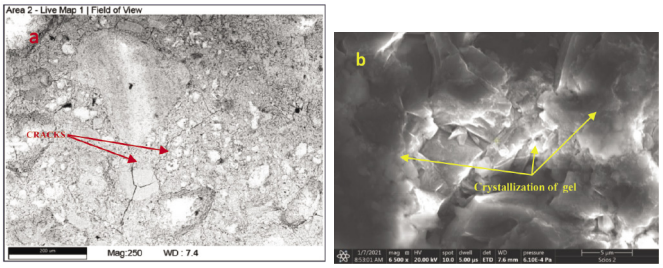
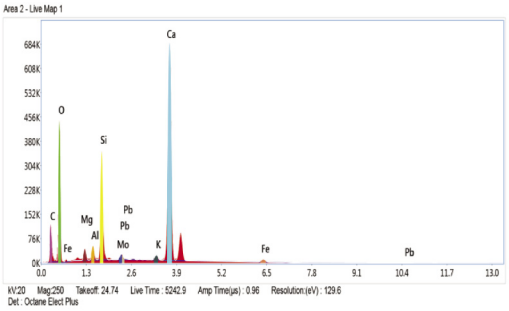


Fig. 11 XRD observation for the HPC FS sample after 4 months of immersion in a solution of 5% acetic acid

11. ábra XRD megfigyelés a HPC FS mintánál 4 hónapig 5%-os ecetsav oldatba való merítés után





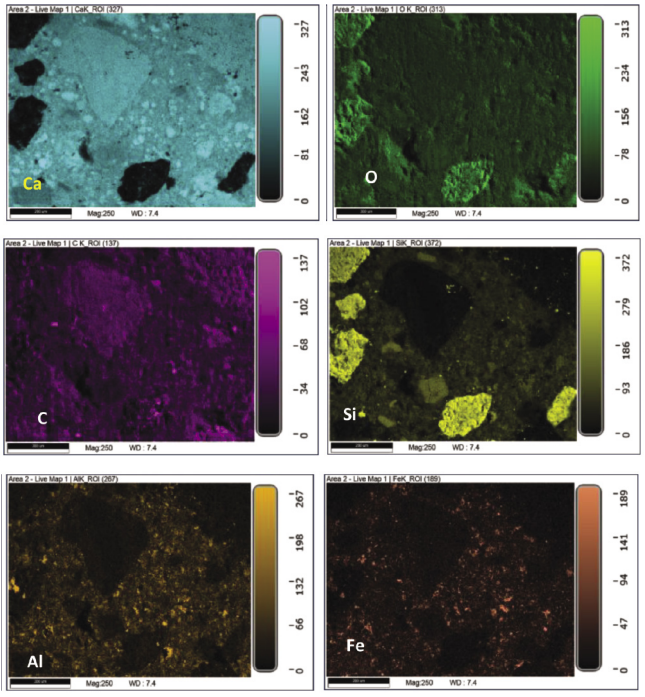


Fig. 12 SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a 5% sulfuric acid solution

12. ábra SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5%-os kénsavoldatba való merítés után

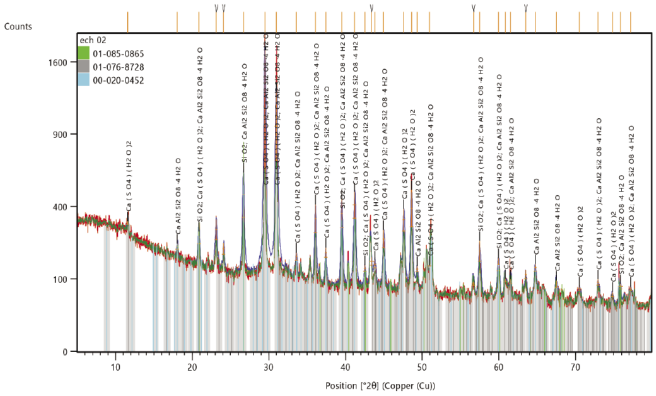
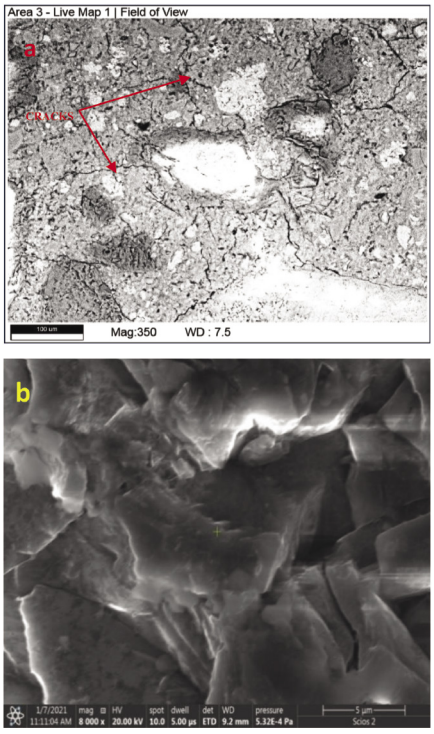


Fig. 13 XRD analysis on the HPC FS sample after 4 months of immersion in a 5% sulfuric acid solution

13. ábra XRD analízis a HPC FS mintán 4 hónapig 5%-os kénsavoldatba való merítés után



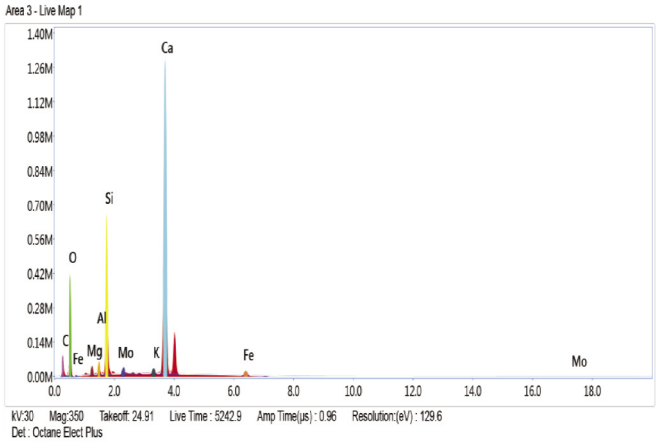


Fig. 14 SEM observation accompanied by EDS analysis for the HPC FS sample after 4 months of immersion in a solution based on 5% acetic acid and 5% sulfuric acid

14. ábra SEM megfigyelés kíséretében EDS analízis a HPC FS mintánál 4 hónapig 5% ecetsav és 5% kénsav alapú oldatba való merítés után

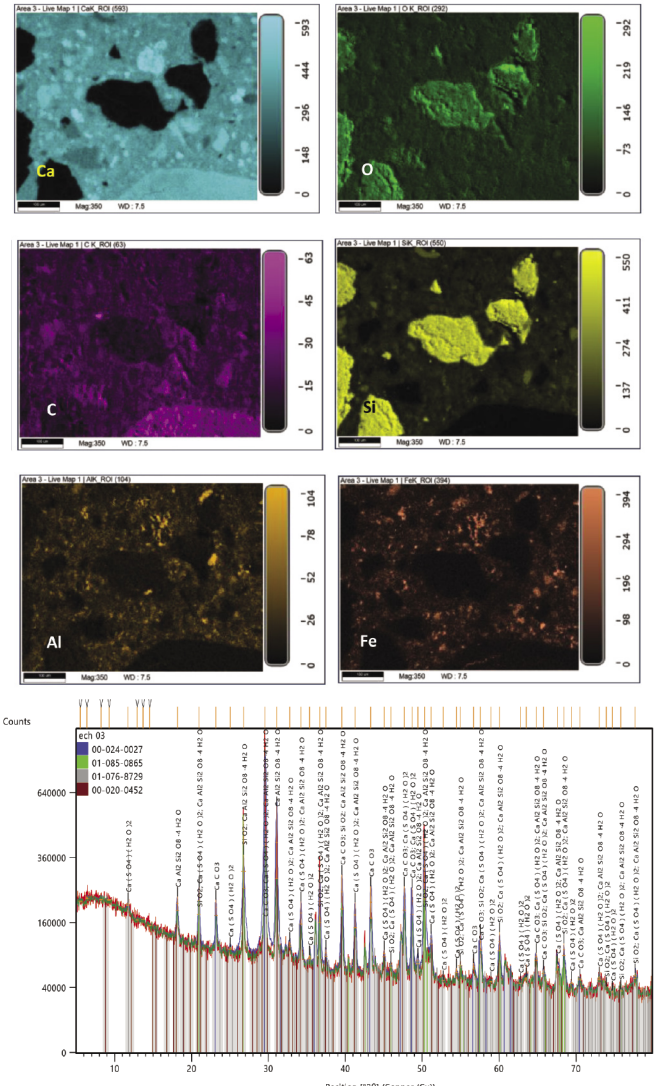


Fig. 15 XRD analysis on the HPC FS sample after 4 months of immersion in a solution based on 5% acetic acid and 5% sulfuric acid

15. ábra XRD analízis a HPC FS mintán 4 hónapig 5 % ecetsav és 5% kénsav alapú oldatba való merítés után

5. Conclusions

This work was focused on evaluation of durability of HPC under the single and combined effect of two types of acetic and sulfuric acids which are encountered in the environment. A comparative study was presented after the presentation of the results. From the obtained results following conclusions can be drawn:

- The study of the durability of different compositions of HPC formulated to the unique attacks of acetic and sulfuric acids showed us that the chemical and mechanical resistance of HPC was slightly affected by the attack of in the solution of acetic acid dosed 5%; while a remarkable drop in the physico-mechanical characteristics were observed for the attack of sulfuric acid. The rate of reduction of the compressive strength reached 46% and the relative loss of mass reached 5%. HPC made in the context of this study show very good resistance to attack by sulfuric acid, although the

aggregates used responsive, and that compared to other results obtained by the researchers.

- The durability tests of HPC to attacks by a mixture of acids (acetic and sulfuric) at an ambient temperature of 20±2 °C showed an increase in the weathering rates or the rates of mass change at the end of the test to be almost double that compared to attacks by sulfuric acid and six times higher compared to attacks by acetic acid. A considerable drop in compressive strength was observed in all HPC compositions tested.
- The use of silica fume in HPC somewhat reduces the intensity of the acetic acid attack. The relative losses of the masses were observed to be minimal compared to the samples formulated without silica fume, the differences are not significant.
- In contrast, the addition of silica fume in HPC decreases the chemical resistance to the attack by sulfuric acid and the acid mixture. The maximum values of the relative mass losses were obtained for the samples attacked by a mixture of sulfuric and acetic acid.
- The microstructure analysis performed on the HPC FS sample after the attack with acetic acid, sulfuric acid, and the mixture of the two acids showed the following:
- The HPC FS sample after the acetic acid attack was characterized by a dense microstructure with the appearance of very few micro-cracks. No salt was detected by XRD, this can be explained by the solubility of calcium acetate in water.
- The presence of long micro-cracks and the crystallization of calcium sulfate ($CaSO_4 \cdot 2H_2O$) (gypsum) and gismondine ($CaAl_2Si_2O_8 \cdot 4\ H_2O$) within the HPC FS sample were detected by XRD at the end of the sulfuric acid attack. The modifications in the microstructure of HPC FS are the causes of the modification of the physico-mechanical characteristics of the sample (increase in porosity accessible to water and decrease in compressive strength).
- A significant development of micro-cracks within HPC FS after the attack by a mixture of acetic acid and sulfuric acid was observed compared to the appearance of the samples after the single attack of the two acids. As in the case of the sulfuric acid attack, crystallization of calcium sulfate ($CaSO_4 \cdot 2H_2O$) (gypsum) and gismondine ($CaAl_2Si_2O_8 \cdot 4\ H_2O$) was observed in the HPC FS sample by XRD. The remarkable changes in the microstructure justify the drop in strength resulting from the combined effect of the acetic acid and sulfuric acid.

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Welcome notes to XVIII ECERS

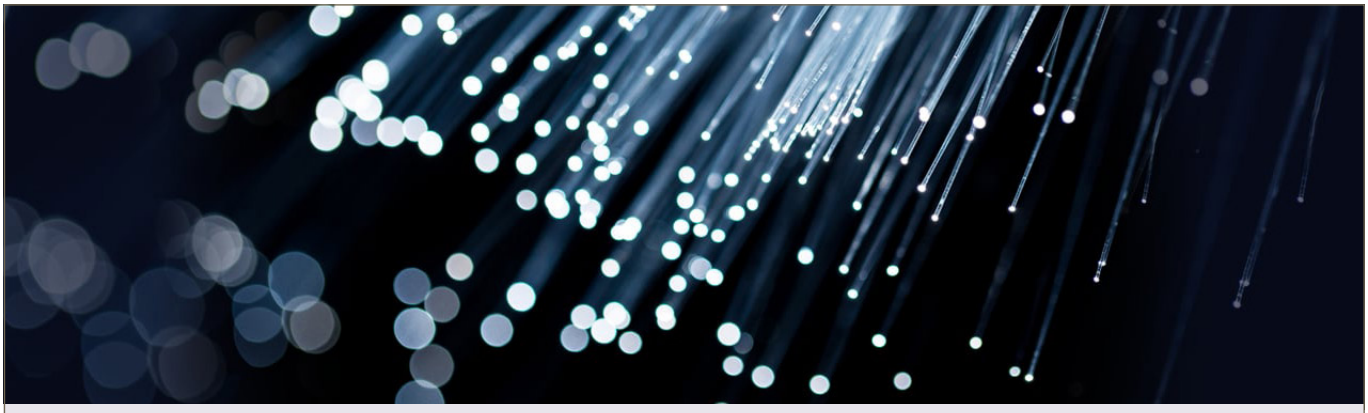
The XVIII[th] Conference of the European Ceramic Society will take place in Lyon, on 2-6 July 2023.

Lyon, where the Rhône and the Saône rivers meet, has always been a city of exchanges and industrial development, with major historic landmarks. 'Lugdunum' was founded in 43BC by the Romans and served as the capital of Gaul. It was also famous, as the world capital of silk, during the French Renaissance. Lyon's cuisine is famous all over the world, the cinema was invented by the Lumiére brothers in this City of Lights, surrounded by prestigious wine areas where you can taste Beaujolais, Burgundy and Côtes-du-Rhône, not far from the Alps and of course Mont Blanc. Lyon is also the city of cutting edge industry and engineering, especially in the fields of chemistry and materials, bio-technology and medicine, mobility systems, with numerous schools and faculties created to answer technological and societal needs.

Thus, it is a great pleasure to welcome ceramists in the City of Lights, to share the latest discoveries in ceramic science and technology, reconnect with colleagues from around the world, in a convivial conference atmosphere. The conference, hosting ceramic experts from industry and academia, offering a unique opportunity to participate in an international event covering the development and applications of ceramic-based systems.

In addition to the now traditional symposia dealing with innovative processing, thermo-mechanical properties, modelling and ceramics for different high-tech applications, emphasis will also be given to advanced characterization techniques, silicate-based ceramics and materials for building applications, as well as the place of ceramics in necessary sustainable development. Lyon has been growing and evolving for 2,000 years: it is today a leading sustainable destination. Therefore, intent on reducing our environmental impact, we will make this XVIII[th] ECerS conference a truly "think green" event.

www.ecers2023.org



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Investigation of waterproof concrete with crystal and zycosilic technologies in the executive levels of the building

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Abstract
According to the properties of concrete, it is necessary to upgrade this material. In areas such as construction. Concrete has many pores and increases the amount of water penetration. One of the ways to make waterproof concrete is to use crystal and zycosil technology. The details of this technology are expressed in the form of scientific texts and images. In this article, a descriptive-analytical research method has been used. The purpose of study is to provide methods to prevent water from entering the concrete. This issue increases the architectural quality of concrete buildings. It can also be concluded that using waterproof concrete with this technology is important. This material prevents the building from damaging chemical reactions caused by water penetration. Finally, this material increases the quality of the building in execution.
Keywords: concrete crystallization, construction implementation, nanotechnology, Waterproof concrete, water penetration prevention, zycosil technology
Kulcsszavak: betonkristályosodás, építési kivitelezés, nanotechnológia, vízálló beton, vízbehatolás elleni védelem, zikozil technológia

1. Introduction

Concrete has entered the world of construction as an important material. According to studies, a new generation of concrete was introduced to the architecture [1]. Building materials have internal cracks. Water penetration is also a problem resulting from this issue. Waterproofing is a type of operation that makes the material impermeable to water. The health of concrete structures depends on some things, like the destructive reactions that occur during the life of the structure. All these reactions need water as a reactant, so if water penetration is reduced, and these reactions will be reduced [2]. Concrete penetration is one of the most important challenges of working with concrete. Researchers consider a parameter related to the health of concrete in operating [3]. Concrete elements have been more important than its components like cement and water. Due to the applications of concrete in different conditions, additives are used. Other important materials must be used to waterproof the concrete. This material closes the pores of the concrete. These materials must be present in some steps, like the hydration reactions and formation of the cement. This issue causes it to crystallize in the pore wall. Zycosil nanotechnology is the first cost-effective and friendly technology. Which is offered in both powder and liquid forms. Which is used as the best waterproof filter to fill the empty micro-spaces of the concrete. According to the introduction, waterproof concrete with crystal and zycosil technology has many advantages. If you use this waterproof concrete, you can improve the quality of the buildings, waterproof concrete is recommended in countries with heavy rainfall. Because it reduces building damage and increases its life.

2. Problem statement

What are the advantages and using waterproof concrete in the construction of buildings? Can the use of waterproof concrete technology in architecture increase their lifespan? Is it appropriate to use this type of concrete in the Iranian construction industry?

3. Research methods

In the present study, a descriptive-analytical research method has been used. Taking into account library studies, the required information has been collected. This information is about concrete with crystal and zycosilicate technology in the building. This article examines the details of making waterproof concrete with new technology.

4. Research history

Mehdi Rahimi Asl and Amirhosein Alizade in 2011, wrote an article. The titles are Crystal Waterproofing Technology and ZYCOSIL (ZYCOSIL), in marine environments studied waterproof concrete. In this article, it is stated that due to many studies, and tests on concrete samples with different percentages of disturbances of elements. We came to the conclusion that crystalline chemicals improve the strength of concrete and increase the period of use of the building [4].

Abbas Doagu in 2015, in an article examined the performance of Zycosil in concrete. It is stated that the Zycosil mechanism is a phenomenon of nanotechnology of waterproof concrete, with resistance to water penetration has caused a period of

operation of structures, such as enhancing the facade of the building [5].

Hamed Javadi Tazehkand and Karim Naqdi in 2016, studied the waterproofing of concrete. This technology uses crystal and zycosil technology in Sarein urban area. This article states that construction materials are in contact with atmospheric factors. Today, with the knowledge of the latest technologies, it has introduced two products. They are crystal and zycosil technology [6].

Mohammad Reza Shojaei in this article, it is stated that water is one of the destructive factors of facades. Waterproofing makes the material impermeable to water. Zycosil has a significant role in waterproofing surfaces. achieving stability and improving the quality of the urban landscape [7].

5. Check concrete

Concrete in a broad sense refers to any material that is composed of a cementitious adhesive. This is one of the most used building materials. A variety of building materials have long been used by humans. Concrete is actually man-made. A very hard body is made from a combination of a certain amount of cement, sand, gravel, water, air. In small and insignificant tasks, concrete mixing is done. But, mechanical devices are used to produce concrete in large volumes [8]. Concrete has different types including plain, reinforced, prestressed, prefabricated, and also lightweight, polymer, waterproof and so on. To have types of concrete, chemical additives are used, that these materials are used in the structure of concrete, such as lubricating, bubbling, retarding, crystallizing additives, improving quality, and improving performance. Concrete has several advantages such as easy access to its components, easy transport, and also easy molding and formability, high compressive strength and so on. But concrete has disadvantages such as low tensile strength, high porosity and permeability. Cracking due to drying after concreting has been eliminated with significant technological advances. In construction, use of concrete is very common, and it can be used in the execution of foundations, buildings and structures. In general, the implementation of concrete in the building includes three main stages. They are reinforcement, formwork and concreting.

6. Waterproofing methods for concrete

There are various methods for waterproofing concrete. Some of them are old and traditional and some of which are modern. Especially nanotechnology in which water can't reach the interior of the concrete structure. From the beginning, they don't reach the underlying layers. Such as the use of coatings (PVC), which are called waterproofing products. In other methods, the concrete structure becomes impermeable using chemical additives. And prevents moisture from advancing. According to *Fig* 1, the waterproof system is activated by the entry of moisture. In the absence of water and moisture, the concrete is not waterproof. Crystallization and zycosil technologies are examples of this method. They are useful for permeable products. Infiltrators are soluble monomeric materials. And have two types of non-reactants such as oils and types of substrates reactants [2].

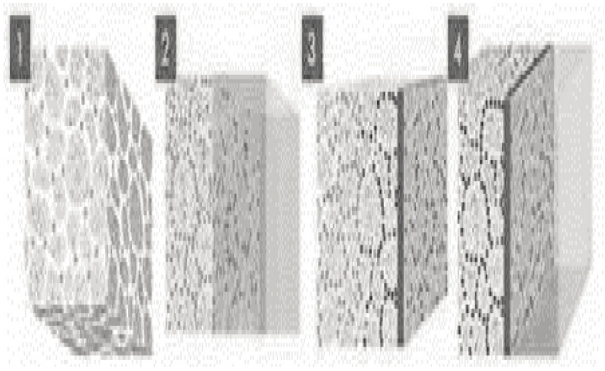

Fig. 1 Steps of forming waterproof concrete with reactive permeable products
1. ábra A vízálló beton kialakításának lépései reaktív permeábilis termékekkel

7. Waterproof concrete with crystallization technology

Crystal is a unique chemical solution for waterproofing, protecting and regenerating concrete. Crystalline concrete is the most active chemical product with a crystalline waterproofing system. And it is activated when mixed with water. This creates a reaction in the concrete and prevents water and any other liquid [9]. This type of innovation in the executive part of the building is available in three forms, covering structures, dry matter of horizontal surfaces and composite in time [10]. This valuable technology is inspired by the lotus leaf mechanism. This means that it has advantages, such as hydrophobicity of concrete and also preventing the entry of chemicals into it [6]. According to *Fig 2*, it takes time to convert the primary concrete to crystal concrete, and this structural change is not in place.

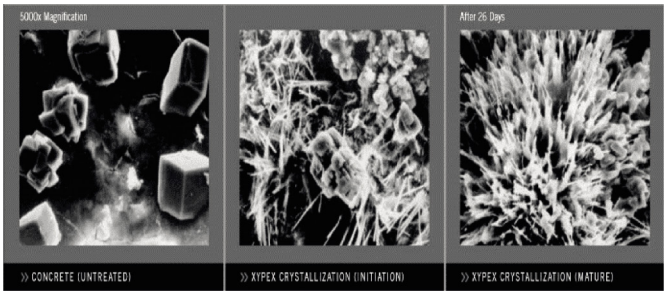

Fig. 2 Stages of crystallization of concrete
2. ábra A beton kristályosodásának szakaszai

8. Waterproof concrete with zycosil technology

Zaydex has recently developed a waterproofing product in India called Zycosil, which reacts with the inorganic substrate of the material. Zycosil is an organosilicon product that forms a nanometer-sized particle size in water as shown in *Fig. 3* and penetrates deep into the pores of the material and becomes part of it, making the building material highly water repellent. This product has outstanding features such as long life of twenty to thirty years, environmental friendliness due to the very low entry of biomaterials into the atmosphere and dissolution in tap water, its use with brushes and rollers and therefore easy work with it.

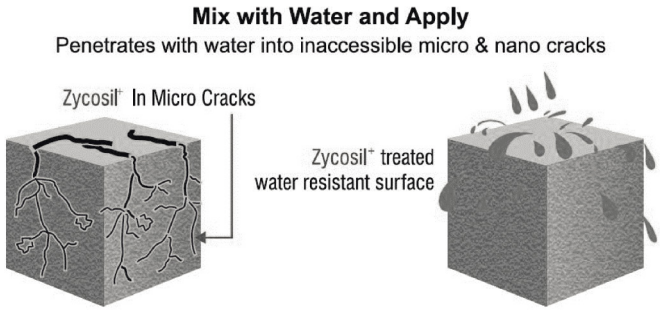

Fig. 3 How Zycosil works
3. ábra Hogyan működik a Zycosil

9. Advantages Of Waterproofing Concrete

Waterproof concrete prevents the penetration of water into the structure. It can also be used to prevent corrosion of steel used in concrete. It's important to prevent freezing and whitening of concrete in cold seasons. These advantages have increased the quality, stability and strength of concrete. It is also ready for various construction operations.

10. Uses of waterproof concrete in construction

This type of concrete is used in various construction operations. There are no restrictions on its implementation. Some buildings need waterproof concrete for special weather. Such as buildings that are located in humid climates and high annual rainfall. In these structures, the outer shell and the foundation are in direct contact with water, so the use of waterproof concrete in their structure plays an important role, this type of concrete used in water structures, such as dams, water canals and other structures built in water. In this paper, the use of waterproof concrete in residential buildings is considered. We are in a lot of contact with them every day. Waterproof concrete with crystal and zycosil innovation, like other types of concrete, it has been applicable in construction projects. And there is no need to use special rules and maintenance points are enough. And concrete execution should be observed like other types of concrete.

11. Conclusions

From this research, it can be concluded that knowledge and use of this concrete is essential. And its implementation at the executive levels of the building is very important. Because most concrete buildings are affected by heavy annual rainfall. And over time, chemical reactions with water and sulfate lose their quality. This issue can cause irreparable financial and human losses to building users. But this, like other construction problems, has been controlled by advances in technology. Technologies such as crystallization and zycosil are emerging. And help the construction industry by forming waterproof concrete.

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Steel fibre-reinforced concrete: review

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Abstract
The studies on fibre-reinforced concrete are vast, with different fibres used, cement types, binders' proportions, additives, and admixtures. Steel fibres (SFs) are the most used fibres when it comes to tensile strength. The paper gives a basic understanding of the behaviour of SFs as a reinforcing element. The SFs properties (shape, aspect ratio, and volume fraction) are highly effective in improving the steel fibre-reinforced concrete (SFRC). The addition of SFs changes the mixture and enforces new conditions for mixing it and what proportions to use. SFRC has proven a better performance in toughness as the energy absorption and ductility of the SFRC have improved; post-cracking strength has also seen improvements as the SF that have a sufficient bond with the matrix are able to bridge the cracks and transfer the stresses also the improvements of the mechanical properties of the SFRC and the flexural strength being the most sensitive to the SFs addition.
Keywords: fibre-reinforced concrete (FRC), steel fibre-reinforced concrete (SFRC), mechanical properties steel fibre, concrete, bond strength, aspect ratio, SF shape, volume fraction, workability
Kulcsszavak: szálerősítésű beton (FRC), acélszálerősítésű beton (SFRC), acélszálak mechanikai tulajdonságai, beton, tapadási szilárdság, méretarány, SF alakja, térfogat százalék, bedolgozhatóság

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1. Introduction

The usage of fibres as reinforcement existed prior to the rebar reinforcement. The Mesopotamia civilisation was one of the oldest in the world. About 5,500 years ago used fibres (straw) were used to reinforce the building material (adobe clay) [1] in order to improve its properties. Concrete, one of our current building materials, is a brittle material with low tensile strength and a low strain capacity. A material with good tensile properties is added to the concrete to overcome these properties in concrete. Fibres used in cement-based composites are thin, short, and primarily made of steel, glass, and polymer or derived from natural materials. The fibre reinforcement may be used in the form of three-dimensionally randomly distributed, where the fibre distribution in different orientations significantly affects the reinforcement efficiency. Steel has proven to be a good material for tensile reinforcement in concrete. The common use of steel is in reinforcing bars, where the steel reinforcing bars are placed in the tensile zone of the concrete.

Fibres alone are not enough to improve the overall capacity of the concrete; SFs cannot work as a replacement for the primary reinforcement in most cases. Still, they improve some properties in concrete and create a material that behaves differently. The amount of fibre added to the concrete recipe is measured as a volume fraction. As the SFs volume fraction increases, the SFs are closer. This can cause "balling", but when the volume is controlled, and the SFs are correctly mixed, it will help manage the cracks by bridging them and transferring the stresses.

The usage of SFs started in the early 20th century. Within the mid of century, the science community started to study the possibility of the usage of fibres to improve concrete properties. Nowadays, there are codes that deal with the usage of SFRC, such as (NZS 3101 (2006), DafStb, Fib Model code, CECS 38:93, and RILEM TC 162-TDF). While the codes are not covering a wide range of applications, there is a driving force to improve our understanding of fibres as a reinforcing element. The addition of SFs in concrete increases its flexural toughness, energy absorption capacity, ductile behaviour prior to the ultimate failure, reduced cracking, and improved durability. This paper tries to cover a basic understanding and consideration to keep in mind when dealing with SFRC.

2. Steel fibres

A considerable number of fibres can be used to improve the concrete properties. With different fibres, we get different properties. A combination of fibres can also be used to get improvements from the added fibres' properties. The most used material of fibres is steel, as the steel holds desirable properties in tensile strength. The paper aims to narrow the fibres to steel and discuss the effect of the addition of SFs in concrete. It is necessary to mention some parameters of the types of SFs and the effect of each fibre type before the generalisation of the SFs as a part of concrete.

The bond between the steel fibre and the concrete regulates how well the materials are working together and the stresses transferred between the steel fibre and the matrix surrounding it. The most common failure for SFs is a pull-out failure [3], where the loss of bond between the SFs and the matrix happens. The bond strength (the highest value for the bond stresses) depends on physiochemical adhesion and friction at the interface, and mechanical anchorage [4], the mechanical anchorage, which is responsible for a significant part of the strength reached, is much better for deformed

shapes than undeformed. It is worth mentioning that the use of straight fibres is very low, and the most used one is the hooked-end [5], as the cost of creating these deformations controls the price of the fibre.

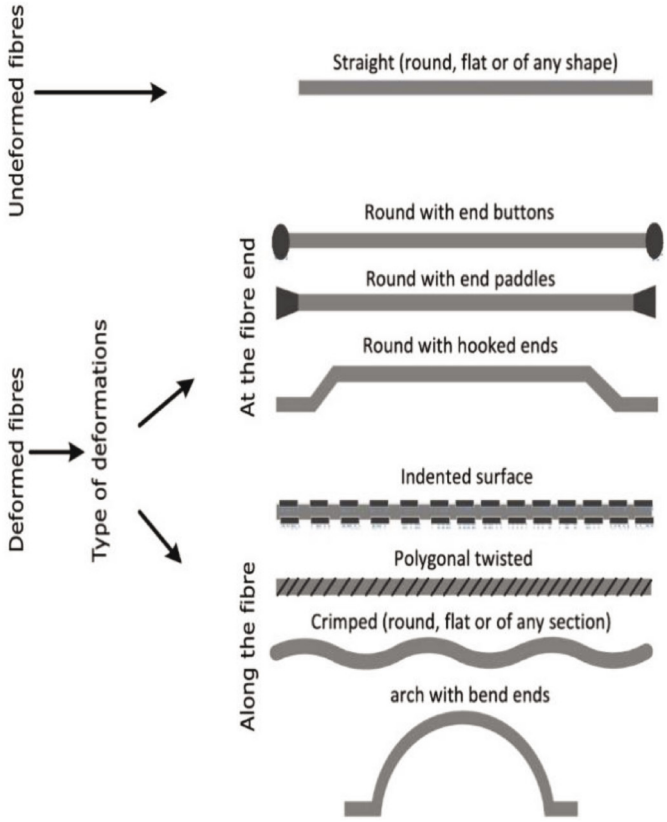

Fig. 1 Steel fibres' most common shapes [2]
1. ábra Az acélszálak leggyakoribb alakjai [2]

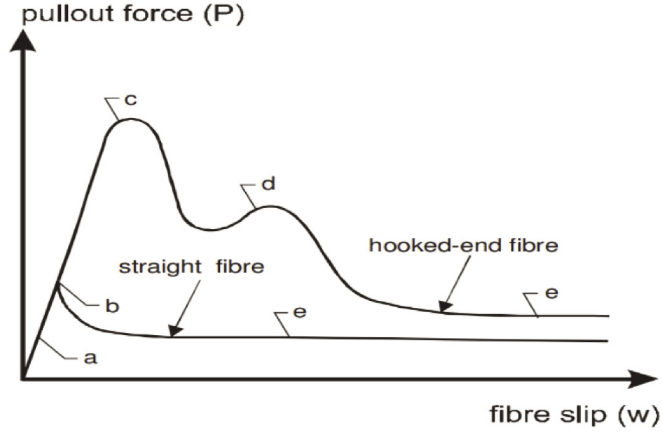

Fig. 2 Pull-out behaviour of straight and hooked-end fibres [6]
2. ábra Egyenes és kampós végű szálak kihúzási viselkedése [6]

Shapes are essential in defining the extent the fibres affect the overall properties. It has been noticed that the mechanical properties vary significantly with the same fibre's volume and different geometries [7]–[9]. The fibre's diameter (equivalent diameter for non-circular) and length influence how well the mixture can be mixed, its workability and much more, but both are dealt with as one parameter (aspect ratio), the ratio of length to diameter (l/d). The amount of fibre used in the volume (volume fraction) highly affects the properties. These three parameters can provide a guideline on what SFs to choose.

A study was done on the stress-strain curves under compression for SFRC to study the volume fraction and aspect ratio. It was found that the slope of the descending part of the stress-strain curve decreases if the fibre fraction is increased with a constant aspect ratio, and the same if the aspect ratio is increased and kept the volume fraction constant [10]. Also, it was noted that the slump decreases with the increase of either the volume fraction or the aspect ratio [11]. In another way, the area under the stress-strain curve increases with respect to both volume fraction and aspect ratio. It's worth mentioning the reinforcing index, which is a parameter used to combine both the volume fraction and the aspect ratio into one standard parameter. The reinforcing index depends on the weight fraction (representing volume) and the aspect ratio [10].

Shape

The bond is an interface between the matrix surrounding the fibre (the interfacial transition zone) and the fibre itself. Similar to the bonds between the plain bars or the deformed bars and the matrix, the bond between the fibres and the matrix is made of physicochemical adhesion and friction that will be affected by the surface properties of the fibre and a mechanical interlock affected by the shape.

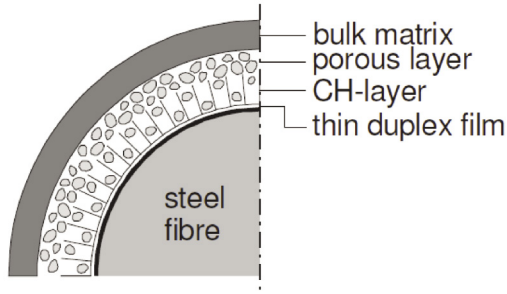

Fig. 3 Transverse cross-section of the interfacial transition zone ITZ [6]
3. ábra Az ITZ határfelületi átmeneti zóna keresztmetszete [6]

Adhesion and friction are the types of bonds controlling the bond strength for straight fibres (undeformed), assuming no bending or pre-deformation has happened. Where the efficiency of the bond depends on the continuity of the interfacial transition zone, on the other hand, the mechanical anchorage, which is a significant influencer of the bond strength, is mainly affected by the shape (deformations). The studies show that the deformed shapes behave better than straight ones [7]–[9], [11].

Volume fraction

The volume to be used in the concrete mixture affects the cost and degree of fibres modification on the concrete. Volume fraction affects mixing, placing, and the hardened concrete performance. Volume fractions used can be grouped into three categories:

- Less than 1%: Where the primary purpose is to help with the plastic shrinkage.
- Between (1-2)%: Where the cost to effect is reasonable and can help in the improvement of concrete mechanical properties.
- More than 2%: the main advantage here will be the impact and blast resistance [12].

The higher the volume, the worse the workability of the concrete and the better the flexural performance [11]. The increase in the volume fraction of fibres will increase the peak load, deflection, and toughness of concrete [9] volume fraction and aspect ratio on the flexural and acoustic emission (AE). Higher than 2% can be used, but usually, due to cost, it is limited to specialised applications.

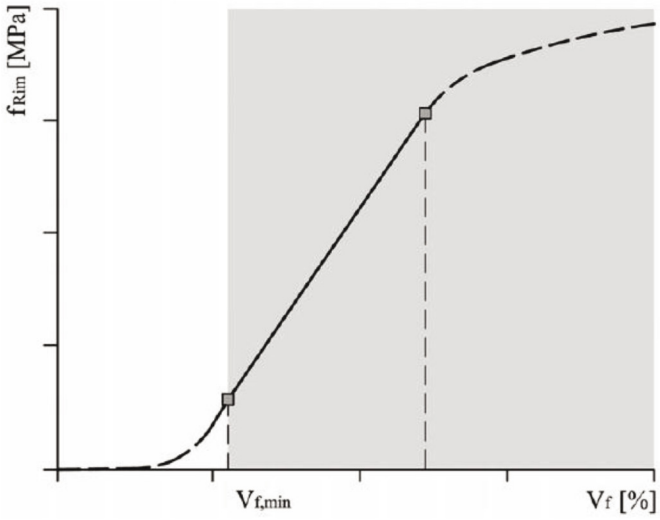

Fig. 4 The influence of fibre content on post-cracking steel fibre-reinforced concrete residual strength 2018 [13]
4. ábra A száltartalom hatása a repedés utáni acélszál-erősítésű beton maradószilárdságára, 2018 [13]

The maximum crack distance and the number of cracks have increased with the increasing fibre volume fraction. Deformed (hooked and twisted in the study) fibres showed more cracks than where undeformed (straight) fibres were used at a volume fraction between 1-2% [7].

Aspect ratio

Also called slenderness ratio (*l/d* ranges between 20-100), this parameter is also a measure of fibre stiffness and will affect mixing and placing. Fibres with relatively small equivalent diameters have low flexural stiffness, which helps to fit into the space they occupy in the concrete mixture. On the other hand, fibres with relatively large equivalent diameters have higher flexural stiffness and a higher effect on aggregates' consolidation during mixing and placement [14]. Fibre length affects the workability and aggregates' size to be used. Including the length and equivalent diameter effects into consideration, the aspect ratio showed effects on the flexural performance and workability, among others; if we took the case of straight fibres, the fibres with the highest aspect ratio were more effective in improving the flexural performance than those with lower aspect ratios [7]. On the other hand, the workability decreases with an increasing aspect ratio. Aspect ratios above 100 will be challenging to mix and achieve a uniform mix [15]. Combining various aspect ratios to improve the mechanical properties is more effective than a single aspect ratio [16].

3. Mix design

Fibres are added to improve the concrete, and the concrete mixture will vary significantly in many cases, including size graduation, binder type, admixtures, water/binder ratio, and additives. Fibres have no conditions for the type of cement and water to be used other than that for regular concrete. Fibres addition affects the physical characteristics of aggregates and their overall gradation. Such; lightweight and porous aggregates that should not be used due to their high absorption, enlarging the workability issue. Generally, the SFRC has higher cement, and fine-to-coarse ratio than regular concrete and the maximum coarse aggregate size affects the minimum cement dosage [17]. To avoid taking each part indivisibly, we try to look at the main parameters when using SFs. Workability is one of the critical issues that face the use of fibres, and bond strength is a very influencing parameter to the overall properties of SFRC.

Workability

Workability is the leading property of the fresh concrete we consider when dealing with SFRC. The addition of SFs reduces workability and accelerates the stiffening of fresh concrete. Both volume fraction and aspect ratio affects it. Some improvements to the concrete properties require a sufficient volume fraction to be used, which will result in a decrease in workability. Some adjustments are necessary when using a large volume fraction to maintain workability. Increasing the water volume to reach better workability will cause a reduction in mechanical strength and durability (larger porosity). The workability solution should not affect the water/cement ratio. It can be constant by increasing water and cement volume (reducing the fibres volume fraction) or adding additives that will increase the fine volume. Additives like pozzolans, fly ashes, calcium filler and micro silica. All with lower bulk specific gravity than cement. Fine volume has an optimum proportion to avoid segregation. If we exceed this portion, the amount absorbed by the fine will reduce the workability. If we are below the optimum, the internal friction between coarse aggregates and fibres will also lessen the workability. Fine-to-coarse aggregates ratios are obtained by adjusting the overall gradation to some gradation curve.

Another way is by adding water-reducing admixture (superplasticisers) to minimise the viscosity of the slurry [18]. New superplasticisers with the enhancement of workability can also maintain the plasticity of the mixture for a more extended period. The risk of "balling" should be kept in mind, as with the increase of the fibre volume fraction, the separation between the fibre is reduced.

Bond strength

Thinking of SFs as small, randomly distributed, non-continuous bars along with the mixture when considering the bond helps to understand the importance of the bond strength and how much it controls the effect of the reinforcements added.

The bond strength controls the tensile strength of the SFRC. If the bond strength is low, debonding (pull-out) failure is expected. Debonding failure makes the high strength of SFs go to waste, as the fibre cannot help resist the stresses. The bond can be strong till the failure is a rupture in the fibre, but it is unlikely to happen [2]. Between the two cases lies a bond strong enough to transmit stresses after matrix failure if the stresses have not exceeded the bond strength. This way, the fibres can bridge the cracks and help in post-cracking strength and resistance to crack propagation.

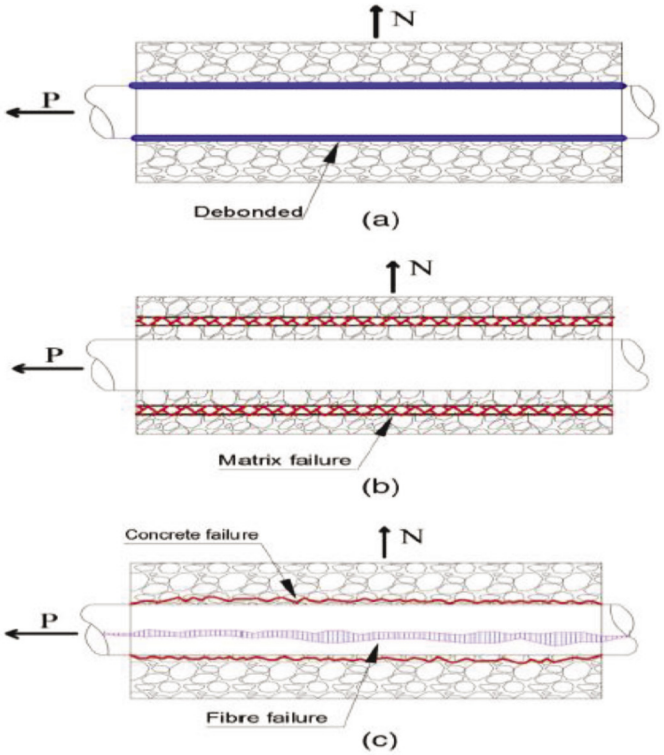

Fig. 5 Tensile failure modes under normal forces [2]
5. ábra Szakítósérülési módok normál erők mellett [2]

When designing the mixture, fibres length affects the maximum aggregate size; to ensure an efficient anchorage for the fibres, the maximum aggregate size should be less than (two-thirds/half) of the fibre length [18]. The increased size and volume of the aggregate particles greater than 5 mm will reduce the workability [15]. The shape and the properties of the fibres should be based on the bond strength that can be achieved, taking into consideration the mixture portions.

4. Mechanical properties

The fibres' role in the mixture should be cleared to understand the effect of SFs on the mechanical properties. Fibres improve the mechanical properties in concrete at different ratios. Flexural strength is more sensitive to the addition than compressive and tensile strength. Fibres help in the post-cracking strength, the toughness of the concrete, and the shear strength improvement.

Compressive strength

When it comes to compressive strength, the addition of fibre does not improve significantly. Still, as the fibres help bridge post-cracking stresses, the post-peak behaviour improves with the increased fibre volume fraction. The increase in fibre content improves the post-peak behaviour, and a more extended softening branch is observed [12], [15].

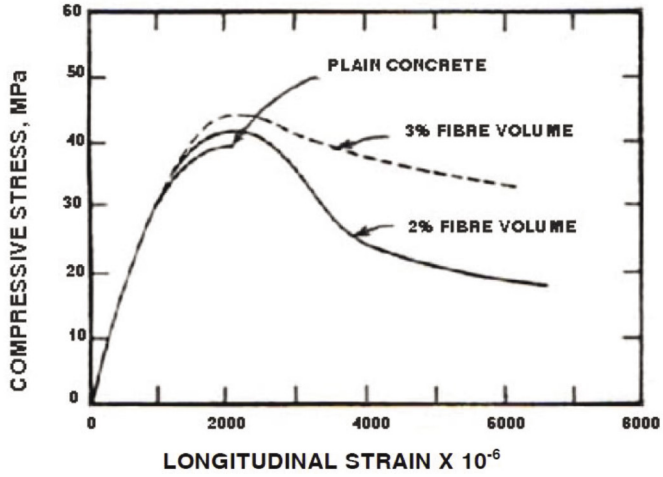

Fig. 6 Stress-strain for compression for SFRC [19]
6. ábra Acélszálerősítésű beton σ-ε diagramja [19]

Tensile strength

The tensile strength of the fibres is critical when choosing the fibre to use. The bond strength controls how much will be utilised from the fibres. Going back to the analogy of small randomly distributed non-continuous bars as a representation of SFs, the SFs' orientation to the tensile stresses significantly influences how much the fibres improve the direct tensile strength of the matrix. Fibres aligned with stress transformation increase the direct tensile strength.

At the first crack, the tensile strain can be increased as much as 100%, with 20-50 times the ultimate strain of plain concrete [12].

Flexural strength

Flexural strength is highly affected by adding fibres with high elastic modulus. Fibres with low elastic modulus improve the impact resistance and not much for the flexural [12]. The increase in flexural strength depends on the tensile strength of the fibres, orientation, volume fraction, shape, and aspect ratio. With a larger aspect ratio, the increase is better [7] three different types of steel fibers were considered, and three different aspect ratios were applied for the case of straight fibers. To quantitatively evaluate the cost effectiveness of reducing the fiber content of UHP-FRCC, cost analysis was also performed. Test results indicated that at low fiber volume

fractions (Vf ≤ 1.0%). The deformed bars have improved the flexural strength more by achieving a better bonding within the mixture. One of the very well-known applications of fibres is the pavement. The improvement in the flexural strength allows a decrease in the pavement's thickness required [15].

Other properties

The addition of steel fibre improves the toughness of the concrete; the concrete has better ductility, which means it can absorb higher energy prior to failure.

The durability of the concrete has improved with the addition of SFs. Corrosion is reduced in the SFRC as the fibres help to control the cracks. The SFRC have a better impact resistance of SFRC against dynamic loads. The higher the volume fraction of SFs, the higher the fatigue strength. SFs addition delays the onset of flexural cracking. Shear strength is significantly improved with the addition of SFs [16], [20], [21].

5. Conclusions

Steel fibre-reinforced concrete has the steel fibre as a new component in the material composition, which in order affects the material behaviour. The shape, aspect ratio, and volume fraction of SFs highly affects the degree of influence SFs have on the concrete. Shape of SFs controls the integration of the new material components and how well it will alternate the overall behaviour. Having deformations enhance the mechanical anchorage increasing the bond strength and the influence of the fibres. Aspect ratio of the SFs and volume fraction affect the workability and the mixing and placing of the concrete. Workability of fresh concrete decreases with the increase of SFs volume fraction and aspect ratio. Flexural performance is also improving with the increase of the aspect ratio and the volume fraction.

The bond strength between the fibres and the surrounding matrix is essential to improve the mechanical properties. If the bond is weak, debonding will happen, the fibre will not transfer stresses, and the tensile strength of the fibre will not be efficiently utilised.

Mechanical properties have seen improvement with the addition of SFs, and flexural strength is the most affected by the fibres' addition, and tensile, durability, toughness and shear strength are improved.

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Expansivity mitigation of black clay soil using agro-waste based inorganic polymer cement for flexible pavement subgrade

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Abstract

The use of cement for deficient black clay soil (BCS) improvement is a long time practice. But given the huge negative contribution of cement to carbon emission and climate change and its high demand by the construction industry that led to its scarcity and expensiveness, there is a need for an alternative binder to cement. The possible use of two biomass based inorganic polymer cements (IPC) was investigated herein. Rice husk ash (RHA) and sawdust ash (SDA) from biomass were used for this study. All experimental tests were carried out in accordance with British Standards. Soil samples were mixed with ash-IPC in steps of 0, 5, 10, 15 and 20% of the dry weight of the natural black clay soil. Results indicated significant improvement in all the geotechnical properties tested. The percentage passing the #200 sieve was reduced from 76.25% to 24.34% and 35.51% by RHA-IPC and SDA-IPC respectively at 20% treatment. Peak UCS values of 1123.56 and 954.28 kN/m^2 were respectively recorded for RHA-IPC and SDA-IPC treatments at 20% IPC content and at 28 days curing period. That represents an 813% increment in UCS value at 20% RHA-IPC content and 675% for SDA-IPC. The CBR value increased by 1500 and 1233% respectively for RHA-IPC and SDA-IPC treatments. The Scanning electron microscopy and energy dispersive X-Ray spectrometer EDS results indicated obvious improvement in the particle sizes in the microstructure of the treated BCS. The achieved improvements in all parameters tested are indications that the expansivity of the weak BCS has been reduced to acceptable levels and the effectiveness of using RHA-IPC and SDA-IPC for subgrade soils improvement.

Keywords: expansive clay, inorganic polymer cement, sawdust ash, rice husk ash, geopolymer cements, flexible pavements

Kulcsszavak: expanzív agyag, szervetlen polimer cement, fűrészpor hamu, rizshéj hamu, geopolimer cementek, rugalmas burkolatok

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1. Introduction

These days, suitable lands for engineering construction works in urban and metropolitan areas are scarce and expensive. The need for land for the purpose of housing and urban road networking has drastically increased due to the increase in population and migration to urban areas. This makes inevitable the utilization and construction on weak subgrades that are geologically characterized by poor geotechnical properties with low strength characteristics and high compressibility behavior. Improvement of these weak subgrade soils has proved to make more economic sense than replacing them with foreign competent materials [1]. This case becomes an issue of major concern when it comes to road networking around urban areas due to the high volume of materials required and haulage constraints, discomfort to the commuting vehicles and expensiveness. In the past, cement was the most commonly used soil improvement-agent. Cement has been used successfully to improve the strength and consistency properties of weak subgrade soils in both cold and hot climates [2-3]. However, due to the huge negative contribution of cement to climate change and emission of greenhouse gasses and its high demand in the construction industry that led to its scarcity and expensiveness, there is an emergency need for alternative binders to cement. A promising, efficient and eco friendly alternative to cement could possibly be agro-industrial waste ash inorganic polymer cements such as rice husk ash-inorganic polymer cement (RHA-IPC) and sawdust ash-inorganic polymer cement (SDA-IPC).

Black clay soils (BCS) are inorganic clays of high compressibility. BCS is very hard when dry but completely loses its strength when soaked in water. They are characterized by high shrinkage and swelling properties. According to Salahudeen and Akiije [4], the poor geotechnical properties of BCS have made construction on or with them an extreme challenge. Upon drying, cracks of varying widths and depths develop in black clays. Due to wetting and drying processes, heaving and shrinkage take place in the soil deposit. These vertical movements lead to failure of structures and flexible pavements built with or on them. These failures appear in the form of settlement, heavy depression, routing, cracking and unevenness. BCS are highly expansive with free swell index of over 50% and extremely weak when wet having a CBR value of less than 3% grossly leading to road network distortion as a result of seasonal variation in moisture condition [5-7]. In this study the improvement of BCS was undertaken using two agricultural waste materials: rice husk ash and sawdust ash with alkaline activators. Rice husk is a biomass

discharged from the milling of rice paddy. The total weight of RHA during the milling process of paddy is around 22% [8]. Koteswara-Rao et al. [9] discovered that RHA contains about 80-85% of silica by oxide composition. The chemical composition and reactivity of the amorphous or crystalline RHA depends largely on the burning duration, incineration temperature and grinding method of the ash.

The disposal of RHA in landfills constitutes serious environmental pollution. The incineration of rice husk results in a residual ash known as rice husk ash (RHA). Mboya et al. [10] observed that when rice husk is sufficiently burnt under a controlled incineration process, it becomes pozzolanic which is capable of replacing cement at an optimum amount of incorporation. Treatment of deficient soils with rice husk ash has been reported to improve the load bearing capacity of the soil to a good extent. Together with RHA, sawdust ash based inorganic polymer cement (IPC) was also investigated and compared in this research. Sawdust is biomass waste from the wood industry. The residue produced when the wood is sliced into timber of different sizes using saw-teeth is known as sawdust. The major chemical composition of sawdust is carbon (60.8%), oxygen (33.8%) and hydrogen (5.2%). Sawdust is highly combustible yet, the disposal of its residual ash is a very difficult challenge to the environmentalists [11]. Dumping of sawdust in the open environment causes aesthetic problems and air pollution which could lead to respiratory problems.

The BCS investigated in this study was treated with biomass based inorganic polymer cement (IPC) for the improvement of its geotechnical properties. Inorganic polymer cement (IPC), also known as geopolymer cement, is an alkali-activated aluminosilicate binder that is formed by reacting properly grinded ash that contains a sufficient amount of silica and alumina with a solution of alkali or alkali salts [12]. The mixture of silica and alumina materials results in crystalline-gels compounds forming a new matrix when hardened. Researchers [13] have reported the acceptability of IPC in improving the plasticity, shrinkage, bearing capacity, compressive strength, compressibility and durability characteristics of modified deficient soils. The geopolymerization process that determines the bonding strength soil properties improvement capability depends on the moisture/solid ratio, alkali concentration, heat energy, pH value, Al_2O_3/SiO_2 ratio, curing temperature and duration [14]. Two commonly used IPC of agro-industrial waste origin are RHA-IPC and SDA-IPC. The performance of these two polymer cements reported in the literature cannot be justifiably compared due to the varying properties and origins of the soils they were used to improve. This study investigated and compared the performance of the two biomass ashes in geopolymerisation process with the same soil. The study aimed at using RHA-IPC and SDA-IPC as BCS improvement admixtures in flexible pavement subgrade applications.

2. Materials and experimental procedures

This experimental design includes stepped addition of IPC to the soil in concentration of 0, 5, 10, 15 and 20% of the dry weight of the soil. A maximum amount of 20% of IPC was considered due to economic concern in higher amounts.

2.1 Materials

Black clay soil

The black clay soil used for this study was obtained from a borrow pit as disturbed sample at a location within Latitude $10^0$13'N and longitude $11^0$23'E. The location map is presented in *Fig. 1*. The oxide composition analysis of the BCS was carried out using X-ray fluorescence spectrometer as presented in *Table* 1.

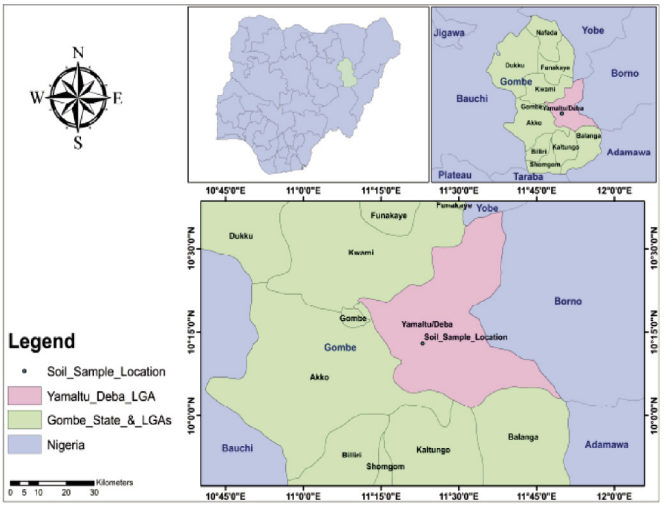

Fig. 1 Soil site location map
1. ábra: Talajtelephely térképe

Rice husk ash (RHA)

The rice husk used was locally obtained from a rice mill factory. RHA was produced by burning the dried rice husks in an open air. The burning process continued in an open air temperature for about a week. When the rice husk burnt to ash and cooled, the ash was sieved through sieve No. 200 (75 μm opening) to obtain the used component. The oxide composition analysis of RHA was carried out using X-ray fluorescence spectrometer as shown in *Table 1*. It was observed that the combined content of calcium oxide and silicon oxide for RHA and SDA are 67.94 and 69.51% respectively.

Oxide	SiO_2	Al_2O_3	SO_3	K2O	CaO	Fe_2O_3	MgO	P_2O_5	LOI *	Ag_2O	MnO	ZnO	PbO	TiO_2	NaO	MnO_2
RHA	64.2	6.4	0.91	4.68	3.74	6.42	4.8	3.6	4.65	-	0.43	0.2	0.06	0.64	-	0.35
SDA	65.3	6.09	3.12	9.1	4.21	3.63	3.39	-	12.8	-	0.69	2.52	9.1	0.4	1.00	-
BCS	49.4	15.1	-	2.25	3.58	14.2	-	-	11.1	2.17	0.23	-	-	2.09	-	-

**Loss on ignition*

Table 1 Oxide composition of materials (concentration in %)
1. táblázat Anyagok oxidos összetétele

Property	Value	Property	Value
% passing #200 sieve	76.25	**NBRRI Classification**	High swell potential
Liquid limit (%)	49	**NMC (%)**	22.8
Plastic limits (%)	25	**MDD (Mg/m³)**	1.65
Plasticity index (%)	24	**OMC (%)**	17
Linear Shrinkage (%)	22	**CBR (%)**	3
Free Swell (%)	82	**UCS (kN/m²)**	123.05
Specific gravity	2.41	**Colour**	Greyish black
ASHTO Classification	A-7-6 (28)	**Dominant clay mineral**	Montmorillonite
USCS	CL	-	-

Table 2 Properties of natural kaolin clay soil
2. táblázat Természetes kaolin agyag talaj tulajdonságai

Salahudeen et al. [7] reported that one of the compounds responsible for strength development in modified soils is calcium silicate hydrates. With the relatively high contents of these two oxides in the ashes used for this study, it is expected that IPC made of them will make significant improvement in the strength of the modified samples. However, the amount of loss on ignition content of an ash affects the strength yield of the sample since decreases with increase in loss on ignition content due to its increased content of volatile organic content.

Sawdust ash

The sawdust was obtained from a local registered sawmill. The same process performed on rice husk and RHA was also followed on sawdust and SDA. The X-ray fluorescence spectrometer results on sawdust ash are presented in *Table 1*.

Inorganic Polymer Cement

Two inorganic polymer cements were used in this study to modify black clay soil: rice husk ash-inorganic polymer cement (RHA-IPC) and sawdust ash-inorganic polymer cement (SDA-IPC). Preparation method of the ashes have been described above. The inorganic polymer cement (IPC) is a mixture of ash and alkaline activator. The alkaline activator used for this study is a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). NaOH and Na_2SiO_3 mixture was prepared in ratio of 1:1 which together formed 44% of the IPC. Meaning, the ash content of the IPC is 56%. The NaOH and Na_2SiO_3 solution was prepared by mixing water with NaOH and Na_2SiO_3 in a metal container. The RHA-IPC was prepared separately and used independently from SDA-IPC.

2.2 Experimental Procedures

All experimental tests were carried out in accordance with British Standards. BS 1377(1990) for natural BCS and BS 1924 (1990) for the ash-IPC modified BCS. Soil samples were mixed with ash-IPC in steps of 0, 5, 10, 15 and 20% of the dry weight of the natural black clay soil. The experimental tests conducted include sieve analysis, compaction characteristics, consistency limits, unconfined compressive strength (UCS) tests and California bearing ratio (CBR). The moisture-density test was carried out using the British Standard light compactive effort. The strength tests performed are the California bearing ratio (CBR) and unconfined compressive strength (UCS) tests. UCS samples were cured for 7, 14 and 28 days before the specimens were tested. The preparation and testing of CBR samples were carried out in accordance with the BS procedures and then based on the recommendation of the Nigerian General Specifications (1997) that required CBR specimens to be cured for six days in open air and then soaked for 24 hours before testing.

Scanning Electron Microscopy

The microstructure of the natural and ash-IPC modified BCS were studied after 28 days curing period. Two nanotechnological methods: Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectrometer (EDS) were used to study the microstructure of the specimens using a SEM model "Tecan Vega SEM". Some selected spots of the SEM were analyzed using the EDS. Surface roughness effect was prevented by polishing the specimens since the electron probe penetrates just to a shallow depth.

3. Results and analyses

3.1 Geotechnical Properties of the Untreated Black Clay Soil

The BCS used in this study was classified as A-7-6 soil according to AASHTO (1986) and CL using the ASTM (1992). The soil's properties are summarized in *Table 2*. It is obvious from *Table 2* that the soil will be unsuitable for road construction or any civil engineering application in its natural state. For any geotechnical applications, subgrade soil that has CBR value of 3%, plasticity index of 24%, free swell of 82% and having 76.25% of its portion passing #200 sieve has to be treated for property improvement before any application.

3.2 Expansivity mitigation by Particle Size and Consistency Improvement

The particle size distribution curves of the natural BCS and IPC treated soil samples are presented in *Fig. 2*. It is obvious that as the IPC content is increased, the curves shifted downward indicating a decrease in percentage fines content which is an appreciable improvement in the properties of the soil. The two IPC used (RHA-IPC and SDA-IPC) performed excellently at higher contents in improving the particle sizes of the soil. From the 76.25% passing the #200 sieve for the natural

BCS, 20% content RHA-IPC reduced it to 24.34% while it was reduced to 35.51% by SDA-IPC at 20% treatment. Soils having less than 50% of the portion passing the #200 sieve are classified as coarse by Unified Soil Classification System in ASTM (1992). In these results, there is an indication of cementation reaction between IPC and clay minerals of BCS which enhanced coagulation of the fine particles to form larger particles (Salahudeen et al, 2014). Expansivity of soils decreases with decrease in their fine content which has been reduced by 68.08% using the RHA-IPC and by 53.43% using the SDA-IPC.

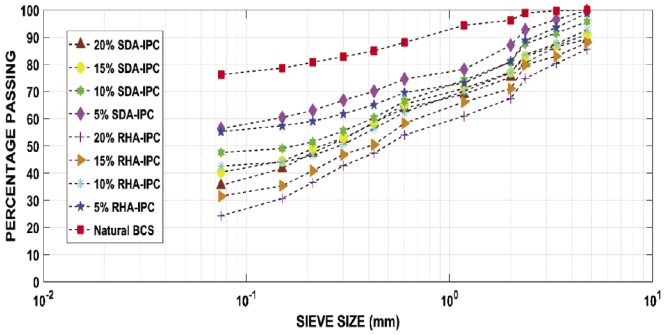

Fig. 2 Particle size distribution curves of natural and inorganic polymer cement modified black cotton soil
2. ábra Természetes és szervetlen polimercementtel módosított fekete pamuttalaj szemcseméret-eloszlási görbéi

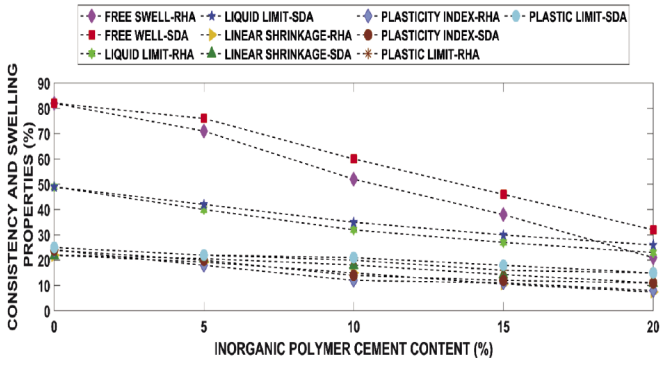

Fig. 3 Consistency limits and free swell of natural and inorganic polymer cement modified black cotton soil
3. ábra Természetes és szervetlen polimercementtel módosított fekete pamut talaj konzisztencia határai és szabad duzzadása

The consistency limits on the other hand, are important soil characterization and classification parameters. The lower the plasticity index of a soil, the lower is the clay content present in them and therefore the lower will be the expansivity potential of the soil. Clean sands are non-plastic because of the absence of clay content in them. The variation of Atterberg limits and free swell of treated and untreated BCS with IPC content are shown in *Fig. 3*. The treatment of the soil with both RHA and SDA IPC yielded a continuous decrease in the free swell and Atterberg limits. Suhail et al. [15] concluded that the decrease in free swell and plasticity of the soil admixed with chemical is as a result of the depressed double layer thickness due to introduced pozzolanic substances and cation exchange reaction by calcium, potassium and ferric ions. The plasticity index value of the natural BCS of 24% decreased to 12% at 10% RHA-IPC content and also to 12% at 15% SDA-IPC content. This result satisfied the recommendation of the Nigerian General Specifications (1997) that specified a maximum value of 12% plasticity index for materials to be used for road sub-base. It was observed that a lower amount of RHA-IPC is required for efficient improvement of BCS compared to SDA-IPC.

3.3 Moisture-Density Properties of IPC Treated BCS

The maximum dry density (MDD) and optimum moisture content (OMC) of a soil are respectively used to determine the amount of compaction densification and the required water content to achieve it both in the laboratory and on the field. It has a direct link with the strength potential of the soil. The variation of compaction characteristics of treated and untreated BCS is presented in *Fig. 4*. The MDD and OMC increased continuously with increased content of RHA-IPC and SDA-IPC. Soil stabilization scientists [16-17] are of the opinion that increase in MDD with chemical treatment could be as a result of the flocculation and agglomeration of clay particles due to exchange of ions at the clay surface. The increase in OMC may be due to additional water demands for the formation of $Ca(OH)_2$ compound and its dissolution into Ca^{2+} and OH^- ions which is required to release more Ca^{2+} ions for cation exchange reaction for strength gains. It could also be due to increased demand for moisture to balance up with the higher content of IPC needed for its hydration reaction. The MDD increased from 1.65 Mg/m^3 for the untreated soil to a peak value of 1.82 Mg/m^3 when treated with 20% RHA-IPC. For SDA-IPC treatment, the increment was from 1.65 Mg/m^3 for the untreated soil to a peak value of 1.78 Mg/m^3 at 20% treatment. These observations in the outcome of MDD and OMC are appreciable improvements on the natural weak BCS.

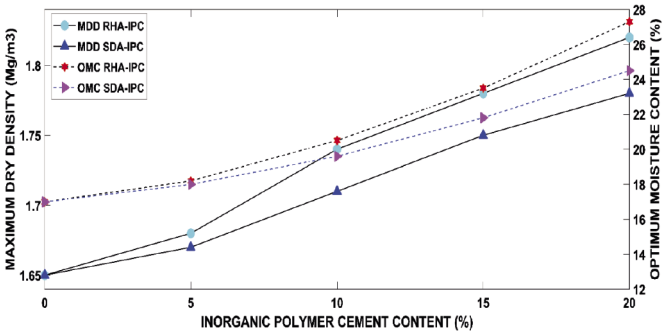

Fig. 4 Compaction characteristics of natural and inorganic polymer cement modified black cotton soil
4. ábra Természetes és szervetlen polimercementtel módosított fekete pamuttalaj tömörítési jellemzői

3.4 Strength Characteristics of IPC Treated BCS

Two strength tests for subgrade soils were considered in this study. They are the unconfined compressive strength (UCS) and California bearing ratio (CBR) tests. The UCS indicates the load bearing capacity of the soil under axial compression while the 6 days cured and 24 hours soaked CBR is used to determine the durability and resilience of the loaded subgrade soil in a harsh environment. The variation of UCS of BCS with IPC content for 7, 14 and 28 days curing periods are shown in *Fig. 5*. A general improvement was observed in the UCS values with both curing period and IPC content. Osinubi et al. [18] and Sadeeq and Salahudeen [19] opined that increase in UCS values could be as a

result of calcium aluminate hydrates and calcium silicate hydrates formations and improvements in the micro contents. When Ca^{2+} in IPC chemically reacted with the lower valence metallic ions in the BCS microstructure during ion exchange at the surface of clay particles which resulted in agglomeration of clay particles, the soil matrix gained more strength. Peak values of 1123.56 and 954.28 kN/m^2 were respectively recorded for RHA-IPC and SDA-IPC treatments at 20% IPC content and at 28 days curing period. That is, the RHA-IPC treatment caused an increment of 813% in UCS value at 20% IPC content while the SDA-IPC caused 675% increment also at 20% treatment after 28 days curing period. These improvement is significant to support the fact that the expansivity of the weak BCS has been reduced to acceptable levels.

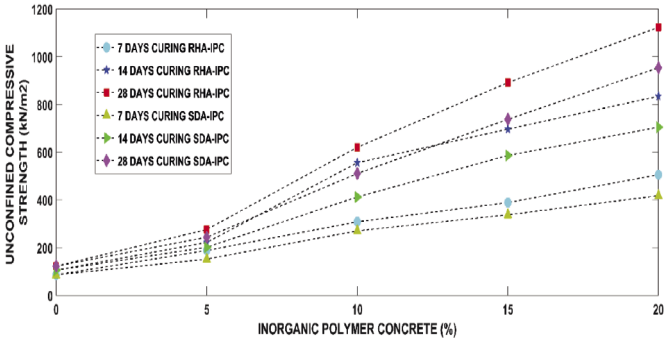

Fig. 5 UCS of natural and inorganic polymer cement modified black cotton soil
5. ábra Természetes és szervetlen polimer cementtel módosított fekete pamut talaj UCS

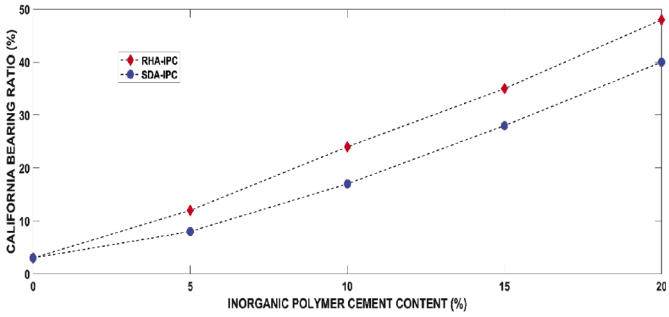

Fig. 6 CBR of natural and inorganic polymer cement modified black cotton soil
6. ábra Természetes és szervetlen polimer cementtel módosított fekete pamut talaj CBR

The variation of the 6 days cured and 24 hours soaked CBR values of the BCS with IPC content are presented in *Fig. 6*. The CBR values generally increased with increase in IPC content. This increase may be as a result of the abundant quantity of Ca needed for the formation of calcium aluminate hydrate and calcium silicate hydrate, the two major chemical compounds that bring about strength development in chemically treated soils. Peak CBR values of 48 and 40% were observed for the RHA-IPC and SDA-IPC treatments respectively at 20% IPC content from a value of 3% for the natural BCS. That represents 1500 and 1233% increments respectively for RHA-IPC and SDA-IPC treatments. It has been recommended [5] that CBR values of 20 – 30% for sub-base materials compacted at OMC is sufficient. The achieved UCS and CBR values are an indication of effectiveness of using biomass based inorganic polymer cements (IPC) for subgrade soils improvements with confirmation of rice husk ash (RHA) and sawdust ash (SDA) sources.

3.5 Microstructural Analyses of IPC Treated BCS

The results of scanning electron microscopy (SEM) together with the energy dispersive X-Ray spectrometer (EDS) analyses of 28 days cured samples of natural BCS, 10% IPC-RHA treated BCS and 10% IPC-SDA treated BCS are presented in *Fig. 7*, *8* and *9* respectively.

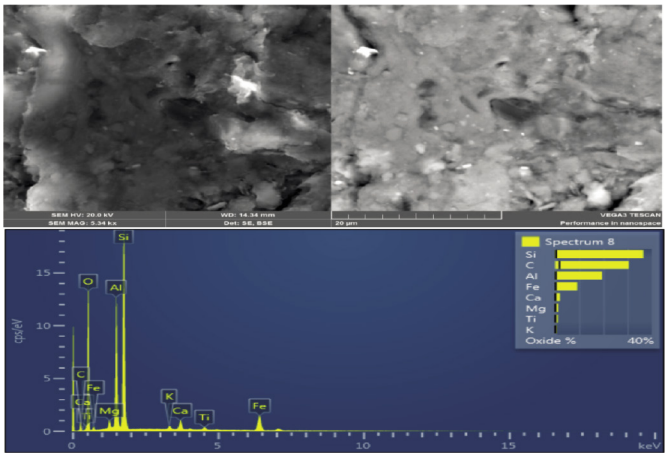

Fig. 7 SEM and EDS of natural BCS
7. ábra Természetes BCS SEM és EDS felvétele

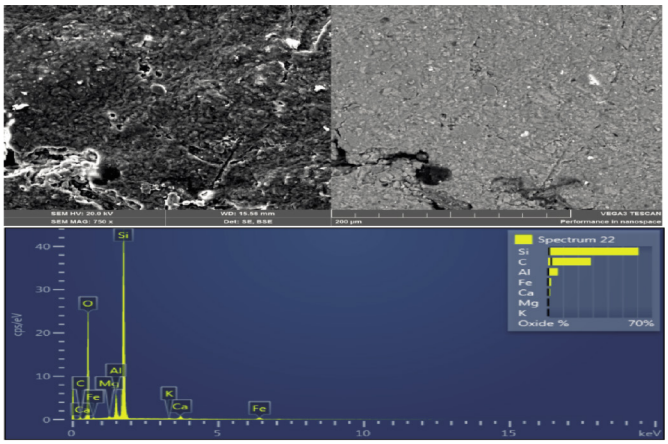

Fig. 8 SEM and EDS of 10% IPC-RHA treated BCS
8. ábra 10%-os IPC-RHA-val kezelt BCS SEM és EDS felvétele

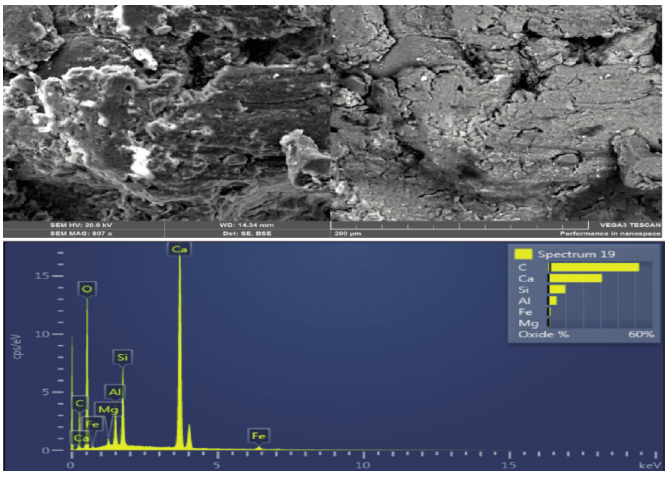

Fig. 9 SEM and EDS of 10% IPC-SDA treated BCS
9. ábra 10%-os IPC-SDA-val kezelt BCS SEM és EDS felvétele

The aluminosilicates mineral composition was observed in the EDS elemental analyses of the natural BCS. It consists majorly of Si, Al and Fe with some Ca content. The total oxide (%) as detected by the EDS for the natural soil is 40%. This value increased to 70% with 10% IPC-RHA content and 60% after IPC-SDA treatment. Reyes et al. [20] noted that the presence of elemental Carbon in the EDS is as a result of the carbon tape at the background of the sample holder attached to the machine. It was clear that the aggregate particles in the natural BCS SEM are smaller size distributions compared to those of IPC-RHA and IPC-SDA treated specimens. This could be due to the reactions of the higher valent cation, Ca^{2+}, which is also more active in the mixtures replaced the weakly bonded ions in the clay structure. Obviously, the higher strength values recorded at 28 days curing period could be as a result of the larger particle sizes formed in the BCS treated with 10% ash-IPC.

4. Conclusions

This study investigated the possible use of rice husk ash (RHA) and sawdust ash (SDA) admixed inorganic polymer cements (IPC) for improving black clay soils (BCS) in flexible pavement foundation application. The natural BCS was classified as A-7-6 and has CBR value of 3%, plasticity index of 24%, free swell of 82% and having 76.25% of its portion passing the number 200 sieve. This soil has geotechnical properties deficiency and was therefore improved to meet standard requirements. Following are conclusions drawn from this study results.

- Both RHA-IPC and SDA-IPC performed excellently in improving the particle sizes of the soil. From the 76.25% passing the #200 sieve for the natural BCS, 20% content RHA-IPC reduced it to 24.34% while it was reduced to 35.51% by SDA-IPC at 20% treatment. Likewise, the plasticity index value of the natural BCS of 24% decreased to 12% at 10% RHA-IPC content and to 12% at 15% SDA-IPC content. These are significant improvements in the expansivity properties of the soil.
- The MDD and OMC continuously increased RHA-IPC and SDA-IPC contents. The MDD increased from 1.65 Mg/m^3 for the untreated soil to a peak value of 1.82 Mg/m^3 when treated with 20% RHA-IPC. For SDA-IPC treatment, the increment was from 1.65 Mg/m^3 for the untreated soil to a peak value of 1.78 Mg/m^3 at 20% treatment.
- A general improvement was observed in the UCS and CBR values with IPC content. Peak UCS values of 1123.56 and 954.28 kN/m^2 were respectively recorded for RHA-IPC and SDA-IPC treatments at 20% IPC content and at 28 days curing period. That is, the RHA-IPC treatment caused an increment of 813% in UCS value at 20% IPC content while the SDA-IPC caused 675% increment. Peak CBR values of 48 and 40% were observed for the RHA-IPC and SDA-IPC treatments respectively at 20% IPC content from a value of 3% for the natural BCS. That represents 1500 and 1233% increments respectively for RHA-IPC and SDA-IPC treatments.
- The SEM and EDS results indicated improvement in the particle sizes in the microstructure of the treated BCS. These significant improvements support the fact that the expansivity of the weak BCS has been reduced to acceptable levels. The achieved improvements for all parameters tested are indication of effectiveness of using biomass based inorganic polymer cements (IPC) for subgrade soils improvements with confirmation of rice husk ash (RHA) and sawdust ash (SDA) sources.

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Some features of clay structure transformation in course of clayey swelling process

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Abstract
The original model of structural transformation in course of clay swelling, thermodynamical and physicochemical features of clayey swelling properties are examined. The model is based on the concept of mutual movement of clayey particles in aggregates of clayey rock at swelling with the formation of new pores between the clay particles that form the aggregates. The obvious mechanism of recycling of superfluous surface energy of clay particles is put in a basis of a model with modification of some parameters of the environment, for example, the concentration of a solution, through the change of relative orientation of clay particles, mainly, through turns from each other [1]. In the thermodynamic description, such a process will be shown in the change of a superficial tension on moistened sites of particles at movement during mutual turns. One of the major parameters of clay rock – micro-porosity in this case varies. In work [2] this phenomenon has been experimentally investigated with the use of methods of a static moisture capacity and Messbauer spectroscopy. The proposed model permits to explain the features of the clayey swelling process and to match the observed experimental data with the theoretical description of the clay swelling process.
Keywords: clay, moisture, swelling, Messbauer spectroscopy
Kulcsszavak: agyag, nedvesség, duzzadás, Messbauer-spektroszkópia

1. Introduction

It's well known [3], that the specific properties of clays are caused by the existence of clay minerals, structurally arranged like thin sheet particles (about 50 – 100 nm in diameter and about 1 nm in height, as it is shown on *Fig. 1*).

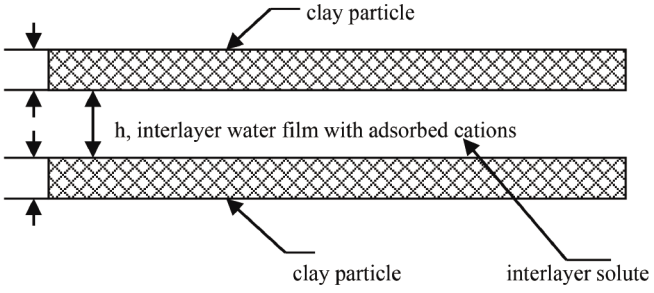

Fig. 1 Clay particles (aluminosilicate layers) and interlayer film between them
1. ábra Agyagszemcsék (alumínium-szilikát rétegek) és a köztük lévő rétegközi film

Also, it is common knowledge [4], that there are two main types of clay minerals – with mobile and fixed crystal lattices. Clay minerals of the first type (for example, montmorillonite) are able to swell. We dwell on this moment in more detail.

One of because the isomorphic substitutions in crystal lattice particles of clay minerals usually carry an electrical charge (usually negative), which is compensated by cations. These cations are called cations neutralizers. Cations-neutralizers are adsorbed onto the surface of particles and at hydration, they are able to dissociate (totally or partly) and make the double diffusion layer [3]. At this montmorillonite takes place, a certain amount of liquid enters between clay particles, and we can observe the swelling (*Fig. 1*).

From experimental data it follows, that isomorphic substitutions in aluminosilicate layers determine not only the presence of a certain amount of cations neutralizers but predetermine the possibility water molecule entry into the crystal structure of montmorillonite and the formation of so-called hydrate-ionic layers [5]. The specific course of the hydration process, cation displacement, and some elements of clay crystal lattice deformation and rotation, shows a competition between adsorbed cations and polar water molecules for neutralization of the negative valency charge on the corresponding sites in aluminosilicate layers. This specific community of adsorbed cations and polar water molecules is called hydrate-ionic layer.

Hydrate-ionic layers which give rise to the most important properties of montmorillonite, are also the most flowing link in the structure, since bonds between molecules and ions within these layers are much weaker than those in aluminosilicate layers. Thus, the condition necessary for forming the crystal structure, that is, the fixation of all particles, would be possible only over a some-what small range of hydrate-ionic layer size. This fact makes the crystal lattice of montmorillonite mobile and able to swell.

It is also significant that the hydrate-ionic layers while forming between aluminosilicate layers, not only separate silicate layers but also combine them into structures of secondary particles (crystallites). The main bonding elements in these structures are adsorbed cations. Sorption of cations of any type or size results from their ability to change position within the hydrate-ionic layers and is also due to the fact that multivalent cations simultaneously belong to two aluminosilicate layers (except the other surfaces of crystallites).

The number of interconnected hydrated aluminosilicate layers in the structure of crystallites along the crystalline axe "c" changes according to the composition of adsorbed cations and the ambient conditions (concentration of admixture in inter-particle solute or moisture). It's clear that mono-valence cations hydrate-ionic layers are the mostly weak links, bonding aluminosilicate layers. So, the difference between clay types in the ability to swell appears in competition between the areas of clay particle surfaces, where the hydrate-ionic layer was formed, and areas, where the hydrate-ionic layer was formed only partially or absent.

The original experimental results about features of interaction in a system "water – adsorbed cations – admixture of inter-layer solute" were obtained in [2]. These results permitted to formulate the model of structural change in course of clay swelling. The model is based on the concept of "fan" movement of clayey particles in aggregates of clay rock at swelling. It is best to use the swelling clay structure model proposed by [6] and shown in *Fig. 2*.

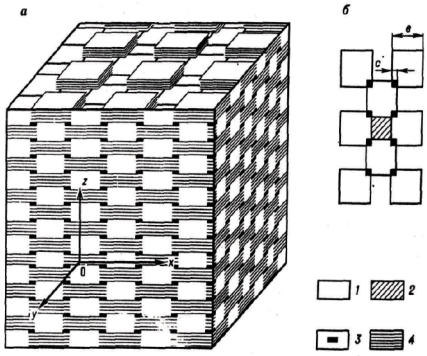

Fig. 2. Clayey rock aggregated structure. 1 – inter-aggregate (transport) pores, 2 – non-transport pores, 3 – intra-aggregate pores, 4 – aggregates
2. ábra Agyagos kőzet aggregált szerkezet. 1 – aggregátumok közötti (transzport) pórusok, 2 – nem transzport pórusok, 3 – aggregátumon belüli pórusok, 4 – aggregátumok

This model will be used by us as a basic one in further analysis of own experimental data. Comparison with other types of arrangement of clay particles in clay rock will be discussed below.

2. Experimental research

One of the major parameters of clay rock – micro-porosity in this case varies. In work [2] this phenomenon has been experimentally investigated with the use of methods of static moisture capacity and Messbauer spectroscopy.

The mechanism of this process is based on the obvious notion that clayey particles will primary move in a lateral direction then in normal (relatively basal surface of aluminosilicate layers) to utilize the superfluous surface energy of clay particles that is appeared in course of swelling. "Normal" movement is adjusted to changes in volume, and it is often limited or not possible in real underground conditions. "Lateral" movement is not connected with the volume change, but only with mutual clay particle displacement. It leads to a change of mutual orientation of clay particles, mainly, through turns from each other like elements of fan [2]. Such process has to be exhibited in change of such parameters of clay like its micro-porosity.

Moisture	43%	92%	93%
Sample 1	5,21	19,90	36,44
Sample 2	6,05	18,30	26,85
Sample 3	6,32	18,37	36,40
Initial	6,47	9,69	13,16

Table 1 The results of water content (in gramm on 100 gramm of dry sample) measurements in clay samples for differ meaning of moister
1. táblázat Az agyagminták víztartalmának mérési eredményei (grammban, 100 gramm száraz mintán) az eltérő nedvességtartalomra vonatkozóan

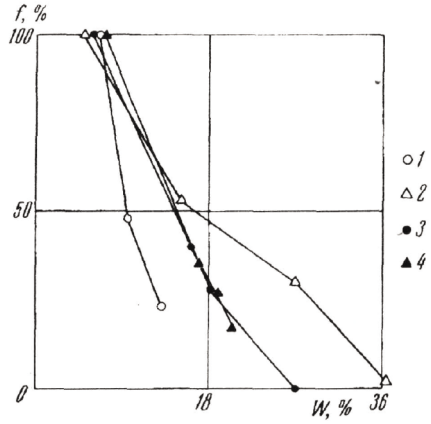

Fig. 3 Messbauer signal attenuation in clay samples for different moister 1 – initial sample, 2 – first sample, 3 – second sample, 4 – third sample
3. ábra Messbauer-jelek gyengülése agyagmintákban különböző nedvességtartalom esetén. 1 - kiindulási minta, 2 - első minta, 3 - második minta, 4 - harmadik minta.

Naturally, we obtained in course of experiments on the static moisture capacity of clayey samples, that when we change the inter-particle solute concentration, the quantity of adsorbed water for some fixed meanings of moister changes too (*Table 1*).

This was at once a measurement of Messbauer effect (Messbauer signal attenuation, *f*) in the same clay samples for same moister. Results are demonstrated in *Fig. 3*.

Good agreement between two series of experimental results can be seen in comparison of *Table 1* and *Fig. 3*.

Physically such a process appears in change of a superficial tension on moistened sites of particles at movement during mutual turns. It should be noted that no overall change in volume was observed during the experiments. Also, it should be noted that there are other ideas about the spatial distribution of clay particles during the formation of clay rocks. Using the concept of the interaction of clay particles according to the principle "basis - chip", it is possible to obtain structures that, when swelling, behave like a kind of "accordion": a change in the rock volume during swelling is caused by a change in the contact angle at the "basis - chip" node [8, 9]. There is another possible way of packing clay particles during the formation of clay rocks - according to the "basis - basis" principle, when the particles are located, similar to how it is shown in *Fig. 2*. Note that when such structures swell in both the first and second cases, there is a change in volume, and after the end of swelling, the structure should return to its original state. To verify this, we conducted an additional experiment on the

swelling of montmorillonite clays. Two samples of the same clay were taken. The first sample was at a fixed humidity, the second was subjected to swelling due to a change (growth) in the humidity in the desiccator. Then the second sample was brought to the same humidity value as the first one. At the end of the experiment, the specific surfaces of two initially identical samples were compared. For this, the method of adsorption-luminescence analysis (Airish et al.) was used, which makes it possible to fix the fraction of the particle surface available for swelling in montmorillonite. It was shown that the free specific surface of clay particles of montmorillonite clay in two samples after the experiment is different (*Table 2*). At the same time, no change in the total volume was also recorded. This can only mean one thing – when the clay swells, the clay particles move apart according to the mechanism of a fan or a deck of cards with the formation of new micropores, as in the first experiment. Thus, when clay rocks swell, the pore space is redistributed due to the formation of new pores that appear when clay particles move apart, forming clay micro aggregates and aggregates. On *Fig. 2*, this would look like the destruction of the original order in the arrangement of particles, accompanied by the transition of each neat stack of particles due to the rotation of each particle in its direction and the filling of transport pores with new micropores. Let us consider some thermodynamic features of the description of such a process.

It should be noted that no overall change in volume was observed during the experiments.

Also, it should be noted that the conclusion about the appearance of micropores due to the fan mechanism of the expansion of clay particles during ion exchange is not indisputable. Attention is drawn to the fact that during the ion exchange of calcium for sodium, the number of ions capable of being hydrated in water vapor doubles. At the same time, the hydration energy of calcium is 3.5 times higher than that of the sodium ion, the same applies to the size of stable aqua complexes of calcium and sodium [7], so that unambiguous conclusions can only be drawn from the change in the amount of water bound by sodium ions and the equivalent (by charge) the amount of calcium ions is difficult to do. It should also be emphasized that there are other ideas about the spatial distribution of clay particles during the formation of clay rocks. Using the concept of the interaction of clay particles according to the "basis–cleavage" principle, it is possible to obtain structures that, when swelling, behave like a kind of "accordion": the change in rock volume during swelling is caused by a change in the contact angle at the "basis–cleavage" node [8, 9]. There is another possible way of packing clay particles during the formation of clay rocks - according to the "basis - basis" principle when the particles are located and form an aggregate structure similar to the one shown in *Fig. 2*. Note that when such structures swell in both the first and the in second case, there should be a change in volume, and after the end of swelling, the structure should return to its original state. To verify this or to obtain experimental data refuting this fact, we carried out an additional experiment on the swelling of montmorillonite clays. Two samples of the same clay were taken. The first sample was at a fixed humidity, the second was subjected to swelling due to a change (growth) in the humidity in the desiccator. Then the second sample was brought to the same humidity value as the first one. At the end of the experiment, the specific surfaces of two initially identical samples were compared. For this, the method of adsorption-luminescence analysis [2, 5] was used, which makes it possible to fix the fraction of the particle surface available for swelling in montmorillonite. It was shown that the free specific surface of clay particles of montmorillonite clay in two samples after the experiment is different (*Table 2*). At the same time, no change in the total volume was also recorded. This can only mean one thing – when the clay swells, the clay particles move apart according to the mechanism of a fan or a deck of cards with the formation of new micropores, as in the first experiment. Thus, when clay rocks swell, the pore space is redistributed due to the formation of new pores that appear when clay particles move apart, forming clay micro aggregates and aggregates. In *Fig. 2*, this would look like the destruction of the initial order in the arrangement of particles, accompanied by the transition of each neat stack of particles due to the rotation of each particle in its direction and the filling of transport pores with new micropores.

Field	State	EC	CN
Oglanly	initial	67	291
Oglanly	final	62	242
Sarigyukh	initial	77	462
Sarigyukh	final	72	410
Berezovskoe	pnitial	47	43
Berezovskoe	final	52	78

Table 2 Changes in the exchange capacity and clay numbers of clay samples before (initial) and after (final) their moistening

2. táblázat Az agyagminták cserekapacitásának és agyagszámának változása a nedvesítés előtt (kezdeti) és után (végső)

However, the experiment also showed more interesting aspects of swelling. Samples from two deposits (Oglanlinskoe deposit (Turkmenistan) and Sarigyukhskoe deposit (Armenia), with a high content of the montmorillonite component. Experiments showed that their free surface decreased after the experiment. This can be explained by the fact that the process of turning particles due to the predominantly montmorillonite composition of the clayey the component went as deep as possible, with the destruction of the initial crystallites and the adhesion of the silicate layers that became completely free after the turns into new, larger micro aggregates, with a lower specific surface area of clay particles. surface (*Table 2*). This is evidenced by the change in such parameters as exchange capacity (EC) and clay number (CN). Let's consider some thermodynamic features of the description of such a process.

3. Thermodynamical aspects of clay swelling process

On the basis of the equations of balance for water and components of a solution (cations and anions of a solute), and also the first Lippmann equation, [3]

$$d\gamma / d\varphi = q \cdot \quad (1)$$

It is possible to receive a necessary ratio for interlayer distances between clay particles as a function of the concentration of a solution and the basic physical and chemical parameters of clay. As a condition of balance equality serves zero of a variation of free energy of Gibbs of all systems at constants pressure and temperature

$$\sum_{i=0,1,2} (\mu_i \delta_i + \overline{\mu}_i \delta_i^-) + \gamma\delta A + \mu_1^s \delta n_1^s = 0, \quad (2)$$

where μ_i – is the chemical potential of the correspondent component, index "0" – stands for water, index "1" – stands for cations, index "2" – stands for anions, index "s" means component, that is adsorbed on the surface, n_i – the number of moles of *i* - component in the system, symbol δ means variation (algebraic increment) of corresponding value, γ - modification of specific surface energy (surface tension) at the movement of clayey particles, φ - electrical potential, q – is the electrical charge of the unit of the surface of clay particles, A – square of moisture surface of clay particles. The consequence of *Eq. (1)* is the equality of chemical potentials of ions in an inter-aggregate and intra-aggregate solute

$$\mu_1 = \mu_1, \quad \mu_2 = \mu_2, \quad (3)$$

$$\mu_1 = \mu_1^0 + RT \ln C_1 + ez_1\varphi, \mu_2 = \mu_2^0 + RT \ln C_2 + ez_2\varphi,$$
$$\mu_1 = \mu_1^0 + RT \ln C_1 + ez_1\varphi, \mu_2 = \mu_2^0 + RT \ln C_2 + ez_2\varphi. \quad (4)$$

Here the index «0» remarks pure values of chemical potentials of cations and anions, z_1 and z_2 is a valency of cations and anions respectively, e is a charge of the electron, φ is an electrical potential of the solution, R – is a gas constant. We suppose that in the solution which is situated in transport pores $\varphi=0$ and in the solution between clay particles because it's determined by exchange cations of clay. Also suppose that $z_1=1$, $z_2=-1$ (binary 1-1 electrolyte). So, adding the first of *Eq. (4)* with the second we receive:

$$\overline{C}_2 \overline{C}_1 = C_2 C_1 = C_0^2 \cdot \quad 5)$$

Here C – is concentration, feature from above marks an accessory of the parameter to a pore solution, C_0- concentration of inter-aggregate solution. From condition for electrical neutrality of «particles – solute» system in general

$$\overline{C}_1 - \overline{C}_2 = 2q / H \quad (6)$$

we receive

$$\overline{C}_1 = (q/H) + \sqrt{(q^2/H^2) + C_0^2}, \quad \overline{C}_2 = -(q/H) + \sqrt{(q^2/H^2) + C_0^2} \quad . \quad (7)$$

Here H – is the interlayer distance (distance between two clayey particles). From a condition for the chemical potential of water we have, according to [1], the equation

$$2\gamma / H = RT(C_1 + C_2 - 2C_0) \cdot \quad (8)$$

The last with account (7), becomes

$$2\gamma / H = 2RT(\sqrt{q^2/H^2 + C_0^2} - C_0) \cdot \quad 9)$$

Equation (9) can be solved to find H:

$$H = A / C_0, \; A = [q^2 - \gamma^2/(R^2T^2)]/[2\gamma/(RT)] \cdot \quad (10)$$

It is possible to consider two limiting situations. When the concentration of an inter-aggregate solute is small, that, as is known from colloid chemistry, the charge of Stern layer behaves proportionally the square root from the concentration of a solution, and we receive from *Eq. (1)* and *Eq. (10)*

$$q \cong \sqrt{C_0} \Rightarrow H \cong 1/\sqrt{C_0} \cdot \quad (11)$$

When the concentration of an inter-aggregate solute is great, the charge of the Stern layer behaves proportionally to the first degree of concentration of a solution, and

$$q \cong C_0 \Rightarrow H \cong \text{const} \cdot \quad (13)$$

Such behavior is well coordinated with the results of well-known experiments on intra-crystal swelling of montmorillonite, [10].

The movement of clayey particles in course of swelling (change of chemical content of inter-particle solute) looks like the movement of fan in course of its opening, and it leads to a significant role of wetting effects in such process. Let's consider the dynamic scenario of this process. Physically, this scenario means that the swelling system, consisting of aggregates of clay particles, tends to absorb additional water and increase its volume, however, the system reacts differently: additional pores (micropores) are formed that absorb additional water from the interaggregate space, and, in general, volume changes system does not occur.

4. Physicochemical mechanics and features of clay swelling process

In [11], a model was proposed that well describes the process of clay rock swelling, when the volume of transport pores decreases due to the swelling of clay minerals without changing the total rock volume. The process is described by the next equation

$$\partial m / \partial t = -\beta \{ RTq / [V_0(1-m) - V_s] - \Gamma \} \quad (14)$$

Here m – the proportion of free water in the volume of clay soil water transport pores, V_0 - clay volume, R – gas constant, T – temperature, Γ - external load, β - swelling rate constant at the first stage. The minus sign on the right side of the equation emphasizes the fact that at this stage there is a decrease in the content of free water, and due to this, m decreases. The subscript "0" means the initial value of the corresponding value.

Obviously, in the resulting differential equation, the variables are separated, and it can be integrated:

$$\frac{RTq_0/V_0}{\Gamma} \ln \left[\frac{RTq_0/V_0 - \Gamma(1-m-V_s/V_0)}{RTq_0/V_0 - \Gamma(1-m_0-V_s/V_0)} \right] + (m-m_0) + \Gamma\beta t = 0 \quad (15)$$

The data of [12] were used to verify the obtained calculations.

In our case, it is necessary to modify *Eq. (14)* in such a way as to take into account the above experimentally observed phenomenon. During the process, the parameter q in *Eq. (14)* actually changes (increases), due to the fact that when the clay particles move apart, new surfaces of previously densely packed clay particles are released for complete hydration and the formation of a full-fledged diffusion layer. Therefore, we put instead of *Eq. (14)*

$$\partial m / \partial t = -\beta \left\{ RT \left[q_0 + \chi [V_0(1-m) - V_s]^{\delta} \right] / [V_0(1-m) - V_s] - \Gamma \right\} \quad (16)$$

Constant δ emphasizes the possibility of a nonlinear course of the swelling process. The physical meaning of the

modification of *Eq. (14)* made becomes transparent if we set δ=1. In this case, it can be seen that the load Γ, preventing swelling, will decrease by the amount χ, and the swelling process will go faster.

$$\frac{RTq_0/V_0}{\Gamma - RT\chi}\ln\left[\frac{RTq_0/V_0-(\Gamma-RT\chi)(1-m-V_s/V_0)}{RTq_0/V_0-(\Gamma-RT\chi)(1-m_0-V_s/V_0)}\right]+(m-m_0)+(\Gamma-RT\chi)\beta t=0 \quad (17)$$

The type of dependencies is shown in *Fig. 4*.

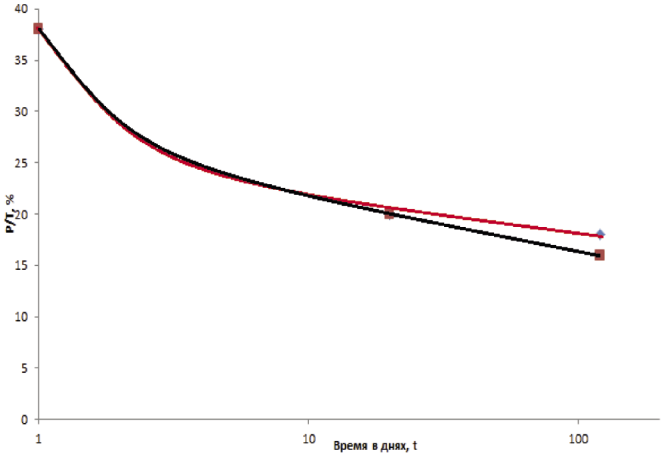

Fig. 4 Dependence of microstructural porosity of clays on time. Points correspond to experimental data from [12], solid lines are theoretical curves
4. ábra Az agyagok mikroszerkezeti porozitásának függése az időtől. A pontok a [12] kísérleti adatoknak felelnek meg, a folytonos vonalak az elméleti görbék

5. Conclusions

It was important for us to offer a model of coupled physical and chemical processes and their role in course of the swelling process and filtration of clays, which doesn't use a priori any suppositions about this rheology but uses only known facts about properties of components of clayey rocks.

The model is based on the concept of "fan" movement of clayey particles in aggregates of clayey rock at swelling. The obvious mechanism of recycling of superfluous surface energy of clay particles is put in a basis of a model with modification of some parameters of the environment, for example, the concentration of a solution, through the change of relative orientation of clay particles, mainly, through turns from each other [2]. Physically such process appears in a change of a superficial tension on moistened sites of particles at movement during mutual turns. One of the major parameters of clay rock – micro-porosity in this case varies. In [2] this phenomenon has been experimentally investigated with the use of methods of static moisture capacity and Messbauer spectroscopy.

The proposed model allows to give explanation of the main features of the relationship between interlayer distance (distance between two clayey particles) and concentration of interlayer solute. Also, it permits to obtain a suitable explanation of the change in microporosity and the type of packing of clay particles during the formation of the structure of clay rock.

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Using Hungarian andesite as a coarse aggregate for concrete

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Abstract

The study focuses on producing a new structural concrete utilising andesite aggregate as an igneous rock extracted from Hungary. Thus, the andesite coarse aggregates' physical properties, such as density, moisture content, water absorption and thermogravimetric properties, were tested. Two concrete mixtures were prepared, one using the quartz aggregate as a reference mix and one with 100% replacement of coarse aggregate by andesite aggregates for estimating the concrete proportions and the mechanical properties for long-term up to 240 days. Physical and mechanical tests showed that andesite extracted from Hungarian mountains could be a useful coarse aggregate for structural concrete with better behaviour than the normal quartz aggregate commonly used.

Keywords: andesite, coarse aggregate, compressive strength, concrete, flexural strength, quartz, shear strength

Kulcsszavak: adalékanyag, andezit, hajlítószilárdság, kvarckavics, nyomószilárdság, nyírás, szerkezeti beton

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1. Introduction

Millions of tons of aggregate are used each year in construction worldwide. The essential qualities of these aggregates are mechanical strength, service life, safety, and environmental aspects in construction; one of the most important places to provide these aggregates is natural stone products. Natural stones are essential building materials, as they are used as dimension stones and aggregates [1]. Their mechanical properties control their applicability. Volcanic rocks such as basalt and andesite are the most common types found in Hungary, and are utilised in the construction industry as aggregates [2-4], andesite, as one of the most common igneous rock types in Hungary, is often used as aggregate in road construction and railway constructions [2, 5, 6, 7]; or as armor stone in hydraulic engineering [8, 9]. In comparison, sedimentary rocks in Hungary are mainly used as building or decorative stones and sometimes as a concrete aggregate for small buildings [10].

Among the volcanic rocks, andesite is one of the most common volcanic rocks of the Carpathian Basin, which got its name from the American Andes mountains. Andesite, which comes in shades of brown, grey, and black, and their transitions, is typically composed of plagioclase feldspar and various coloured minerals. They show an extraordinary similarity with dacites, which is why in each case the site or the mixed analysis of the samples decides what their silicon content is and in which category they can be classified. Andesite is commonly found in Hungary, particularly in the Börzsöny, Cserhát, and Mátra mountain ranges and it is easily accessible due to its proximity to the surface. [10], the andesite used in this study was extracted from Kisnána (Mátra). However, different weathering categories ranging from fresh to residual soil can be observed within the andesite [11]. The favourable properties of andesite (high uniaxial compressive strength and resistance to abrasion) make it suitable for road and railway construction as pavement production. Andesite is a fine-grained volcanic rock with about (53–63%) silica-containing, grey-black colour. It has a porphyritic texture and is composed of plagioclase and pyroxene microliths (clinopyroxene and orthopyroxene), feldspar, pyroxene, and biotite phenocrysts in a glass matrix, and small amounts of magnetite minerals. Andesite's porosity ranges between 10% and 25%. Therefore, andesites used in indoor and outdoor spaces are exposed to a variety of physical and chemical factors, such as cold, heat, moisture, and household chemicals, as well as a number of impact-induced wear factors. Andesite materials show resistance to environmental factors to which they may be exposed [12, 13].

The andesite aggregate is nothing new. It has long been found to have favourable tensile and compressive strengths due to its higher modulus of elasticity and different shape [14]. However, the steady decrease in the water-cement ratio changes the saturation of concretes and is not typical when testing concretes older than three or six months. Transport is an important factor for economic and environmental reasons, and local materials should be known. Stone tests are available, but for structural concretes, there are often other considerations [10, 15], e.g. wear resistance is not important, and the conditions of placing are different.The purpose of this study was to investigate the potential use of andesite aggregate as a structural concrete aggregate. To accomplish this, laboratory experiments were conducted to evaluate the mechanical properties of andesite aggregate concrete and quartz aggregate concrete as a reference materials. Results showed that aggregate type significantly influences concrete properties, which is not always considered in conventional views and prediction models.

2. Experimental details

2.1 Materials

Two types of coarse aggregates with a particle size of 4-8 mm were utilised in the investigation mix designs. The coarse aggregate types used were normal quartz aggregate (*Fig. 1*) and crushed andesite aggregate (*Fig. 2*). The coarse aggregates accounted for 55% of the total aggregate content in the mixture. A fine aggregate, normal quartz sand with a particle size of 0-4 mm (*Fig. 3*), was also utilised and accounted for 45% of the total aggregate content. Ordinary Portland cement 42.5 N in accordance with EN 197-1, 2012 [16] was used as the binder and superplasticiser (Master Glenium C300) at a dosage of 0.7% by weight of cement used in the mixture.

Fig. 1 Used quartz gravel 4/8 mm particle size
1. ábra Az alkalmazott kvarckavics adalékanyag 4/8-as frakció

Fig. 2 Used crushed andesite aggregate 4/8 mm particle size
2. ábra Az alkalmazott andezitzúzalék 4/8-as frakció

Fig. 3 Used quartz sand 0-4 mm particle size
3. ábra Az alkalmazott kvarchomok 0/4-es frakció

2.2 Methodology

The physical properties of the aggregates were tested to determine the main aggregate characteristics as the particle size, density and water absorption to ensure proper mixes of the concrete, In order to determine the properties of concrete made by andesite aggregates, two concrete mixes were prepared. The volume content of the used materials in each mixture was kept the same, as shown in *Table 1*. To investigate the influence of aggregate types and determine the exact effect of this use, so volumes were included in each density, and the specimen's density was changed depending on the aggregate density.

After preparing the concrete mixtures, all specimens were cured for 7 days under water and then stored in the laboratory at ambient temperature until the age of 28, 120 and 240 days. Uniaxial compressive strength using 100 mm cubes, flexural tensile strength using 70 mm x 70 mm x 250 mm prismatic shapes, and Push off model with 100 mm diameter x 150 mm height cylinders specimens were used for shear strength tests made to determine the concrete characteristics and classification.

Material	Component materials in 1 m³ batch (kg/m³)	
	Mix Q	Mix An
Cement	450	450
Water (w/c: 0.38)	171	171
Fine aggregate (0/4)	799	799
Andesite aggregate (4/8)	-	962
Quartz aggregate (4/8)	958	-
Superplasticiser (0.75%)	3.37	3.37

Table 1 Concrete mix proportions
1. táblázat Az alkalmazott betonösszetételek

3. Physical properties testing

3.1 Particle size distribution

Andesite and quartz aggregates were sieved and divided into three fractions (0/4, 4/8, and 8/11) using a sieve series according to EN 933-1 [17]. The faction with a sieved size 4/8 mm is used as coarse aggregates in both andesite and quartz aggregates, and the sieved size of less than 4 mm is used as fine aggregate in the case of river quartz sand.

3.2 Particle density

The particle density of aggregates was determined with the Pycnometer device according to EN 1097–6:2013 [18], employing the water displacement method to measure volume accurately. Three consecutive volume measurements were performed for each type of aggregate to obtain an average particle density value; the value for each aggregate type are mentioned in *Table 2*.

Aggregate	Particle density kg/m³
Quartz aggregate 0/4	2640
Quartz aggregate 4/8	2590
Crushed andesite aggregate 4/8	2600

Table 2 Particle density test results of aggregates
2. táblázat Az adalékanyagok testsűrűsége

3.3 Moisture content and absorption

Aggregates (fine and coarse) were dried in an electric oven at 105 °C, to determine the moisture content value for each type of aggregate according to EN 1097–5:2008 [19]; the moisture content test for aggregates was carried out under the same environment and same conditions; moisture content results showed on *Table 3*.

Aggregate	Moisture content wt%	Water absorption wt%
Quartz aggregate 0/4	1.01	1.98
Quartz aggregate 4/8	1.52	1.10
Crushed andesite aggregate 4/8	3.53	1.27

Table 3 Moisture content and water absorption test results of aggregates
3. táblázat Az adalékanyagok nedveségtartalma és vízfelvétele

Water absorption of aggregates was determined as well, according to EN 1097–6:2013 [18], by measuring the quantity of water present in each aggregate at saturated surface dry state (SSD) and the results of water absorption shown in *Table 3*.

3.4 Derivatographic measurement

The derivatograph simultaneously produces a thermogravimetric (TG), derivative thermogravimetric (DTG) and a differential thermoanalytical (DTA) signal. A small sample was ground to powder and then heated in the device's furnace at a constant rate up to 1000 °C [20]. The test parameters used are: aluminium oxide as a reference substance, the test carried out with temperatures ranging from 20 to 1000 °C with 10 °C/min heating rate and 50 mg TG sensitivity with corundum crucible, under the atmospheric pressure, test results were analysed with the WINDER software. The derivatograms of the andesite and the quartz sample are shown in *Fig. 4* and *Fig. 5*. The study analysed the thermal behaviour of the quartz and andesite samples using a derivatograph. The quartz sample did not exhibit any changes during the test and was not analysed further. However, it was used as a reference for comparison with the andesite sample. The andesite sample showed a peak value (N) between 20 and 120°C, which is indicative of the evaporation of water from the pores. Based on the results, the andesite only loses water in the measured temperature range. Otherwise, its chemical composition is not affected by heat [21].

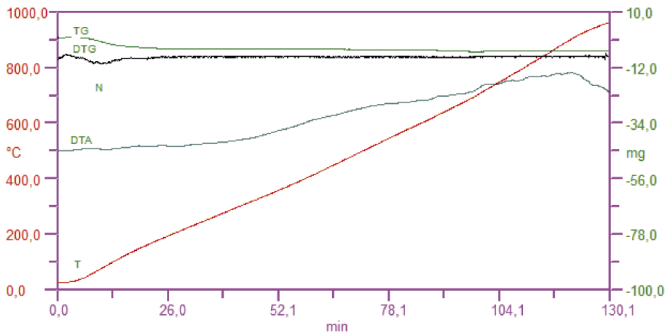

Fig. 4 Derivatogram of the andesite aggregate [18]
4. ábra Az andezit derivatogramja [18]

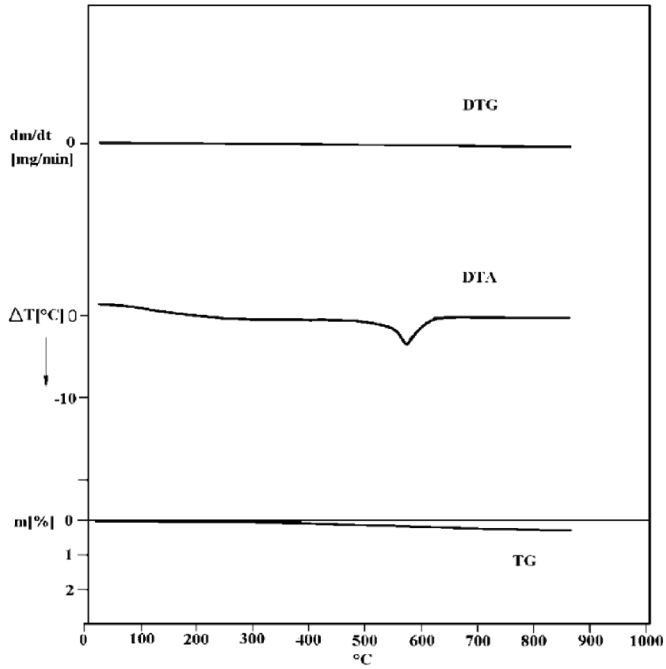

Fig. 5 Derivatogram of quartz aggregate [19]
5. ábra A kvarckavics derivatogramja [19]

4. Results and discussion

4.1 Compressive strength test

The uniaxial compressive strength test of concrete, according to EN 12390-3:2009 [22] for cubes with 100 mm x 100 mm x 100 mm, was carried out at 28 days, 120 days and 240 days age of the specimen, three cubes were tested at each time. *Table 4* and *Fig. 6* present the results of compressive strength tests on concrete made with quartz aggregate (Mix Q) and andesite aggregate (Mix An). The data shows that compressive strength increases with the age of the specimen. Notably, there was a significant increase in compressive strength from 120 to 240 days in the andesite aggregate concrete. On the other hand, the increase in compressive strength from 28 to 120 days in the quartz aggregate concrete was more significant. There can be several scientific reasons why the increase in compressive strength from 28 to 120 days in the quartz aggregate concrete (Mix Q) was more significant than the increase from 120 to 240 days in the andesite aggregate concrete (Mix An). One possible reason is that the increase in compressive strength from 28 to 120 days is more significant for the quartz aggregate concrete due to the rapid hydration of cement, which results in the formation of additional calcium-silicate-hydrate (C-S-H) gel and an increase in the density of the cement paste [26]. This effect is more pronounced at early ages when the hydration reactions are still active. Additionally, the specific properties of the quartz aggregate, such as its mineralogy, may also have played a role in the observed difference in the rate of increase of compressive strength with time. Quartz aggregate may have higher pozzolanic activity and react with the cement paste to form additional C-S-H gel and increase compressive strength at early ages [27, 28].

Age (day)	Concrete type	Average compressive strength (MPa)	Standard deviation (σ)	COV%
28	Mix Q	67.56	2.62	4
28	Mix An	85.81	3.82	4
120	Mix Q	79.12	1.43	2
120	Mix An	86.82	2.67	3
240	Mix Q	80.60	1.41	2
240	Mix An	93.80	0.17	0

Table 4 Compressive strength test results
4. táblázat Nyomószilárdság vizsgálati eredmények

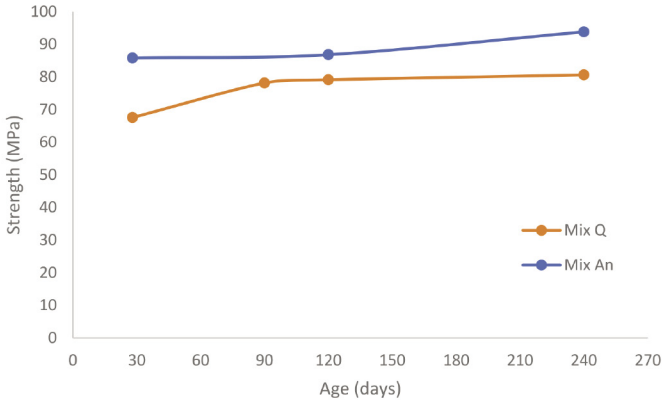

Fig. 6 Compressive strength results
6. ábra Nyomószilárdsági eredmények

4.2 Flexural strength test

The flexural tensile strength test was performed according to EN 12390-5 [23] using 3-point loading bending flexure machine *Fig. 7*, with a constant loading rate 80 N/s, for prisms with 70 mm x 70 mm x 250 mm, at ages 28 days, 120 days and 240 days for three specimens each time.

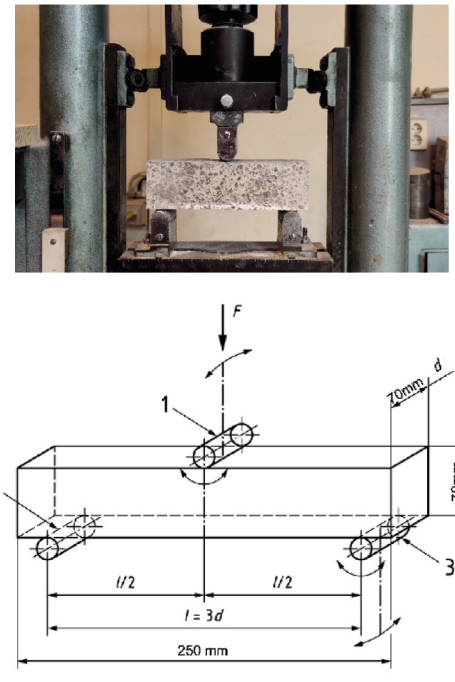

Fig. 7 Three-point bending test [22]
7. ábra A központos hajlító vizsgálat elrendezése [22]

The results of flexural tensile strength tests showed almost similar behaviour between the specimen made by quartz aggregates and the andesite aggregate with a difference of about 20% higher for concrete (Mix An) as shown in *Table 5* and *Fig. 8*. The change in tensile strength for both (Mix-Q) and (Mix-An) with the specimen age are not noticeable.

Age (day)	Concrete type	Average tensile strength (MPa)	Standard deviation (σ)	COV%
28	Mix Q	8.4	0.06	1
28	Mix An	10.2	0.17	2
120	Mix Q	8.8	0.15	2
120	Mix An	10.9	0.29	3
240	Mix Q	8.8	0.20	2
240	Mix An	11.0	0.06	1

Table 5 Flexural tensile strength test results
5. táblázat Hajlítószilárdság vizsgálati eredmények

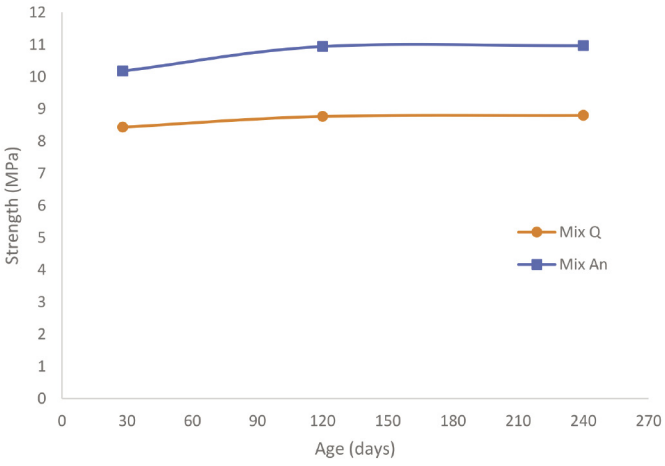

Fig. 8 Flexural tensile strength results
8. ábra Hajlító-húzó szilárdsági eredmények

The andesite aggregate's lower porosity than the quartz aggregate resulted in a higher modulus of elasticity and compressive strength of the concrete, which translates to a higher flexural tensile strength. Moreover, andesite aggregate contains high amounts of silica, alumina, and iron oxide [29]; these elements may react with the cement paste and form additional C-S-H gel, which can increase the flexural tensile strength.

4.3 Shear strength test

The shear strength test was performed using the push-off model. The cylindrical concrete specimens with 100 mm diameter and 200 mm height, the detailed dimension and loading arrangement of the loading specimens were drawn in *Fig. 9*, tested in compression with a loading rate 10 kN/minute. Shear strength test results (*Table 6* and *Fig. 10*) showes that in case of andesite concrete (Mix An) the strength is linearly increased with the concrete age increase, while in case of quartz concrete (Mix Q) the strength increased up to 120 days age, then it does not change until 240 days.

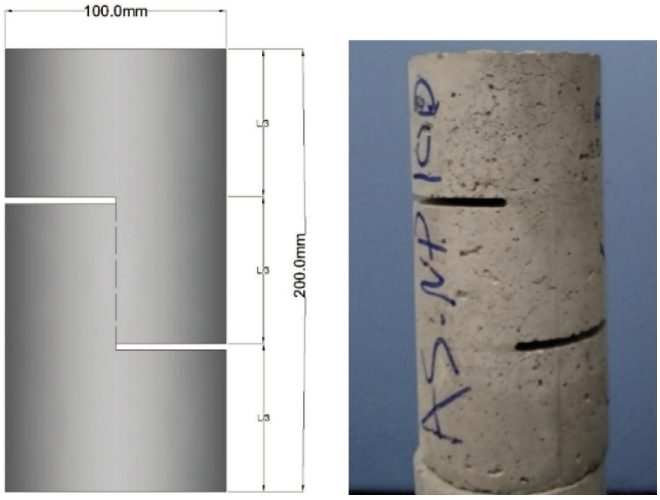

Fig. 9 Push-off specimen dimensions [23]
9. ábra Nyíró (push-off) vizsgálati elrendezés [23]

Age (days)	Concrete type	Average shear strength (MPa)	Standard deviation (σ)	COV%
28	Mix Q	10.3	0.47	5
28	Mix An	10.4	0.41	4
120	Mix Q	10.9	0.60	6
120	Mix An	11.3	0.31	3
240	Mix Q	10.9	0.12	1
240	Mix An	12.2	0.31	2

Table 6 Shear strength results
6. táblázat Nyírószilárdság vizsgálati eredmények

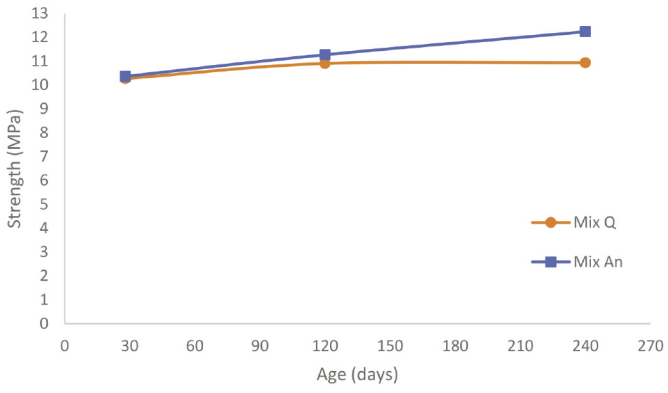

Fig. 10 Shear strength results
10. ábra Nyírószilárdsági eredmények

5. Conclusions

The objective of this study was to evaluate the potential of andesite aggregate as a structural concrete aggregate by examining its mechanical properties over a period of 240 days. The following conclusions are drawn based on the test results and the analysis:

Andesite as one of the most common volcanic rocks used in road construction, and it would be a good aggregate to use as an aggregate for structural concrete.

The particle density results showed almost similar densities for both quartz and andesite aggregates. It does not change the density of concrete to such an extent that it needs to be taken in case of static calculation.

Quartz aggregates were not shown any change during the derivatograph test, but in the case of andesite aggregates, the peak value (N) can be seen from 20 °C and 120 °C, according to the evaporation of water from the pores.

The results of the study indicate that andesite aggregate can be used as a structural concrete aggregate, as it demonstrated similar or better mechanical properties compared to concrete made with quartz aggregate.

Even though both particle densities were the same, the concrete made with andesite aggregates showed higher characteristic compressive strength by about 27% at age 28 days, 10% at age 120 days and 16% at age 240 days.

The compressive strength of concrete made with andesite aggregate showed a significant increase from 120 to 240 days, while the increase in compressive strength for concrete made with quartz aggregate was more significant at early ages.

The flexural tensile strength for concrete (Mix Q) and (Mix An) showed almost similar behaviour by specimen age, with about 20 to 24% increase in strength for concrete made with andesite aggregate (Mix An) compared with (Mix Q) made with quartz aggregate.

Shear strength behaviour in case of (Mix An) concrete increased linearly with the age , while in case of quartz concrete (Mix Q) the strength increase only noticed up to 120 days age.

The pozzolanic activity and mineralogy of the aggregate played an important role in the mechanical properties of the concrete, and further research is needed to investigate these aspects.

Our tests showed that the replacement of quartz gravel with the tested andesite in building construction structures improves the concrete mechanical properties.

This can already be seen in the standard 28 days test, but the trend is the same or improving up to 240 days age.

This is the basis for the fact that it is worth carrying out detailed durability and fire resistance tests, which is important in the case of high-rise buildings and rarely tested for andesite, because the traffic construction does not required it.

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Books:

[6] Mehta, P. K. – Monteiro, P. J. M.: Concrete. Microstructure, properties, and materials. *McGraw-Hill*, 2006, 659 p.

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