Periodica Polytechnica Civil Engineering, 67(1), pp. 298–307, 2023

Concrete Resistance Achieved with Subtly Ground Tube Glass of Cathode Ray as Supplementary Cementitious Material to Sulphate Attack

Zoran Grdić[1], Iva Despotović[2*], Dušan Grdić[1], Gordana Topličić-Ćurčić[1], Jelena Bijeljić[3], Nenad Ristić[1]

[1] Faculty of Civil Engineering and Architecture, University of Niš, Aleksandra Medvedeva 14, 18106 Niš, Serbia
[2] Faculty of Mechanical and Civil Engineering in Kraljevo, University of Kragujevac, Dositejeva 19, 36000 Kraljevo, Serbia
[3] College of Applied Technical Sciences Niš, Aleksandra Medvedeva 20, 18000 Niš, Serbia
[*] Corresponding author, e-mail: despotovic.i@mfkv.kg.ac.rs

Received: 29 August 2022, Accepted: 26 November 2022, Published online: 13 December 2022

Abstract

One of the essential requirements in modern civil engineering is a sustainable building, with the aim of reducing the harmful impact on the environment. Since the early XXI century, usage of recycled materials has been insisted on, which could, at least partly, substitute traditionally used materials. Although there is no serial manufacturing of TV sets with cathode ray tubes anymore, piles of cathode ray tube glass (CRT) at the waste disposal sites have still been on the increase. This experimental research was supposed to determine the potential for using subtly milled CRT glass as a supplementary cementitious material and to check the resistance of similar concretes to the sulphate action. Six testing concrete batches were made. The percentage of cement replacement percentage with CRT was: 5%, 10%, 15%, 20% and 35%, by mass. Durability assessment of concrete to sulphate action was done by visual estimation of concrete appearance as well as through testing the compressive strength variations of treated concrete specimens 3, 6, 12 and 36 months old. After soaking the specimens in a 5% solution of Na_2SO_4 for 36 months, concretes with 15% to 20% of replaced cement with finely ground CRT glass have simultaneously satisfactory compressive strength and resistance to sulfate attack. In this sense, this range of replacement of cement with finely ground CRT glass can be recommended for practical application.

Keywords

cathode ray tube glass, sustainable building, recycling; environment, sulphate action, durability

1 Introduction

The world is experiencing immense revolution in the electronic industry as in one of the most important and fastest - growing industries nowadays. Its development in the recent decades has created a huge number of jobs, accelerated technological development and simultaneously contributed to a generation of considerable e-waste as a consequence of electronic devices' phasing out. Cathode ray tubed computer screens and TV sets have not been sold in Europe for over a decade now. Yet, such devices still exist and are used in the households and there is a rough estimation that the European landfills annually receive 50000 to 150000 tons of obsolete CRT screens. It is anticipated that, annually, the amount of collected CRT glass will not be cut down in the near future [1, 2]. Speaking in environmental terms, the process of CRT waste recycling is very important. There can be two versions of cathode tube recycling: open and close loop recycling. The latter one consists of old screens recycling and new CRT devices production. Bearing that in mind, there are no factories in Europe any more manufacturing new screens with cathode tubes. In most of the cases, the CRT waste is delivered to the countries where such factories still exist. The open loop recycling version utilizes used up CRT screens to produce new and different products [3]. There is a large number of scientific papers studying the potential of application of CRT glass in production of: ceramic tiles, artificial marble, glass jewelry, decorative crystals, etc. The majority of researchers rely on the use of environmentally friendly binders that produce less carbon footprint in the production process. Geopolymer, and more

Cite this article as: Grdić, Z., Despotović, I., Grdić, D., Topličić-Ćurčić, G., Bijeljić, J., Ristić, N. "Concrete Resistance Achieved with Subtly Ground Tube Glass of Cathode Ray as Supplementary Cementitious Material to Sulphate Attack", Periodica Polytechnica Civil Engineering, 67(1), pp. 298–307, 2023. https://doi.org/10.3311/PPci.21086

generally Alkali-Activated Materials (AAMs) are among these binders which can potentially offer an efficient alternative to traditional binders. In the recent researches, waste glass was successfully used in alkali-activated materials. In the paper [4] the authors used the experimental and thermo-dynamic simulation to show that one can successfully replace even 50% of calcium sulfoaluminate cement (CSA) with glass powder. Civil engineering industry can be one of the possible directions of cathode glass usage. In that case, glass would be used for making cement composites in two different ways. The first would be using it as a fine aggregate, replacing a certain amount of natural aggregate. The second option would be using finely ground waste glass as a substitute for a part of cement while making concrete and mortar. The previous research pointed to the fact that milling the glass with amorphous silicon of high content into a fine dust (particles smaller than 100 μm in size) initiates its pozzolanic reactivity, that being the basic precondition for using it as a supplementary cementitious material [5–10]. Testing the durability of concrete with added CRT glass, be it used as a filler or as a replacement of a part of cement, is very topical. In this sense, the most frequent durability tests performed on cement composites modified in this way are: alkali-silicate reactivity, freeze-thaw resistance, freeze-thaw resistance with de-icing salts-scaling, sulfate attack resistance and chloride ion penetration. In the further text, the focus is on the testing of sulphate resistance of cement composites containing an addition of recycled waste glass.

In the earlier period, different tests of sulfate resistance were conducted on concretes and mortars in which an amount of cement or fine aggregate was replaced by various versions of waste glass. For instance, Chen et al. [11] conducted comprehensive testing of concretes properties containing various waste glass particle contents. The size distribution of cylindrical glass particles, a by-product of IC – plate manufacturing plants, was from 38 to 300 μm and about 40% of particles were less than 150 μm. With reference to ASTM C267-01(2006) [12], a sulphate-immersion test was done. The chemical reaction expands in volume which induces internal stresses. That may generate internal cracks which can ultimately lead to failure. After five cycles of wet-and-dry exposures, it was recorded a significant weight loss and reduction in strength, all of which exhibited a strong sulphate attack on specimens. Weight and strength loss decreases to a high level as the waste glass content increases, especially of the samples with lower water/binder ratio. According to the properties of hardened concrete, optimum waste glass content is present in 40–50 wt.% in this research. The superficial defects of the tested samples show a qualitative proof of sulphate attack as well. Smashed windscreen waste glass and also commercial glass containers waste were the subject of research of Matos and Sousa-Coutinho [13]. Those researchers were testing the mechanical strength and durability of mortar with glass powder as a partial replacement for cement (0%, 10% and 20%). Portuguese standard E-462 [13] was used to evaluate the resistance to external sulphate attack. Blended Portland cement with 10% of waste glass replacement showed a high leveled resistance to sulphate attack, much higher than silica fume within the limit of 0.10%. The waste glass pozzolanic activity and silica fume bind portlandite (CH) which is released in the hydration of calcium silicates (C_3S and C_2S). Thus, CH can no longer react with sulphates, consequently preventing the formation of gypsum. Pozzolanic reaction creates a secondary calcium – silicate – hydrate (C–S–H) which decreases the capillary porosity of mortar and drastically enhances the paste - aggregate outlook. Özkan and Yüksel [14] performed an experiment on how compressive strength, chloride and sulphate resistance and expansion related to alkali – silica reaction (ASR) on cement - based mortars, made with cement consisting of waste glass and industrial by-products. Resistance to sulphates was tested by comparison of samples' compressive strength, exposed to 4% Na_2SO_4, with the strength of the reference samples. The findings proved that durability of mortars to sulphate attack was increased by replacing the cement with waste glass alone, whereas sulphate resistance is more increased if waste glass is used in combination with granulated blast-furnace slag or fly ash. The combination of waste glass and blast-furnace slag provides the best results. Analyzing the features of waste glass powders of different softness and comparing them with that of natural pozzolana, coal fly ash and silica fume was also done by Carsana et al. [15]. Glass was made using waste green bottles. Seven different mixtures of mortar were made with glass powders together with other mineral additions in which the part of cement replacement was 30%, with an exception of silica fume which was used with 10%. One durability test was an expansion due to sulphate attack, according to the ASTM C1012/C1012M-13 standard [16]. The mortars with milled glass exhibited a barely noticeable expansion (0.04%) even being of immersed in the sulphate solution over a year (when the tests were interrupted). Only the silica fumed mortar showed lower values. On the other side, mortars with ground quartz sand expanded 0.1% after only two months of testing, whereas the reference mortar made with ordinary portland cement (OPC) showed expansion after approximately eight months. Liu et al. [17] tested the sulphate attack durability of concrete where fine natural aggregate was partially or completely replaced with CRT funnel glass. The percentage of replacement of natural aggregate with CRT glass was 0%, 30%, 60% and 100%. The experimental concrete samples were cured in 5% and 10% solution of sodium sulphate. The authors monitored the compressive strength variation of the samples immersed in sulphate solution for 120 days. It is observed that the compressive strength of all different concrete mixes shows a similar trend. It increases in the initial stage, reaches a peak value, then tends to decrease. Authors concluded that this variation mainly depends on the continuous salt crystallization and generation of gypsum and ettringite in the pores or micro-cracks of concrete. The increase in sulfate ion concentration from 5% to 10% has a limited influence on the compressive strength.

When dissolved in water, sulphate salts can have deep adverse effects on concrete. Calcium, magnesium, potassium and sodium sulphates are the most common ones, present both in soil and in ground waters. Acidic rain and seawater contain dissolved sulphates as well creating an aggressive environment for structures made of concrete. Locations with significantly high sulphate concentration are industrial waste disposal sites. Sulphate corrosion is often first detected on the peripheral rims of concrete elements which, after a long exposure, causes cracks and strength decrease to occur. Explained in chemical terms, this type of corrosion is a very complex process [18–21].

According to the reviews of many study papers, with only a few being mentioned in the introduction, it is not hard to conclude that only a handful of researches of the concrete sulphate resistance were performed using finely milled CRT glass. One of this research objectives was to test sulphate resistance of concrete when a part of cement was substituted with subtly ground CRT glass. In Serbia, there is no national or European standard stipulating the testing procedure of sulphate resistance of concrete. In this respect, a custom testing plan and program were made, whose results are presented below. The basis for choosing the waste CRT glass fineness was the methodology of this research, with the purpose of its pozzolanic activity to be activated. The cited authors used two criteria to evaluate their own experimental research: visual inspection of the specimen surface and compressive strength variation. The primary motivation for conducting this study is solving the problem of disposal of CRT glass, which is a considerable environmental problem which can to a great extent be solved by proving that it is suitable to be used as a component of concrete. The significance of the study is reflected in the successfully proved potential of using CRT glass as a replacement for cement and even of making some economical gains.

2 Materials and methods

2.1 Cementitious materials

Ordinary Portland cement CEM I 52.5R manufactured by "CRH" Novi Popovac, according to the standards SRPS EN 196-1 [22], SRPS EN 196-3 [23], SRPS EN 196-6 [24] and SRPS EN 197-1 [25] was used in experiment. Large shards of CRT glass from the recycling center "Jugo - Impex E.E.R." d.o.o. Niš were milled using a laboratory ball mill so that glass could pass the sieve opening of 0.063 mm with no residue. Finely milled CRT glass had a density of 2.84 g/cm^3 and specific surface area by Blaine of 245 m^2/kg. The chemical composition of glass is presented in Table 1.

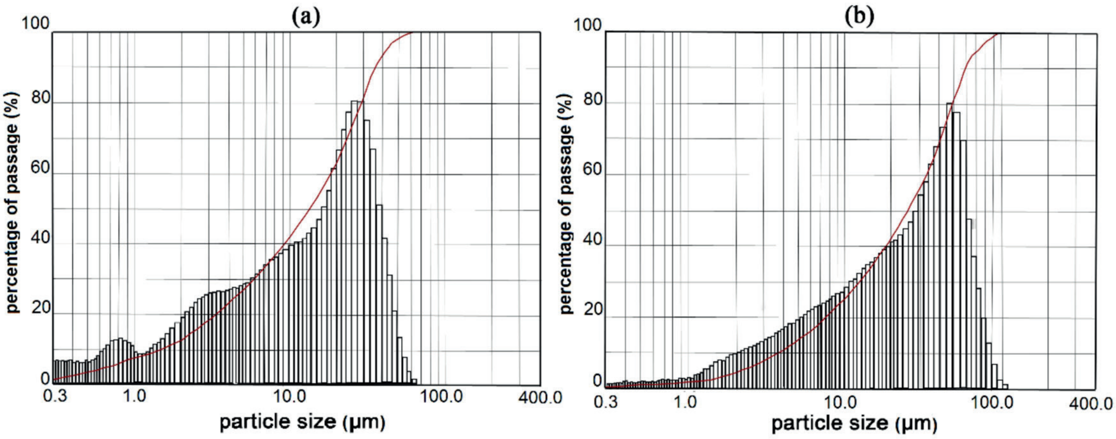
Although chemical compositions of typical soda-lime glass and used panel CRT glass appear similar, there are still some differences. In comparison with the typical chemical composition of soda-lime glass, panel CRT glass contains around 10% less SiO_2 and the same amount of CaO, around twice times less Na_2O, while the share of K_2O is 5% higher.

Fig. 1 (a) shows the particle size distribution of CEM I 52.5R and Fig. 1 (b) shows the particle size distribution of the examined glass. More than 63% of glass grains were finer than 36 μm, while 42% were finer than 20 μm. About 25% of cathode glass particles were smaller than 10 μm.

In this research, we tested the pozzolanic activity [26] of the glass using the SRPS B.C1.018 standard [27]. It classifies the pozzolanic material in three ways: based on the

Table 1 Compositions of panel CRT glass and soda-lime glass

Type of glass	Chemical Compound								
	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Na_2O (%)	SO_3 (%)	LOI (%)
CRT glass	60.61	2.88	0.58	1.31	0.53	6.45	7.61	0.09	1.04
Soda-lime glass	70.40	2.06	0.01	11.30	1.47	1.21	13.4	0.31	0.30



(a) (b)

Fig. 1 Particle size distribution of Portland cement CEM I 52.5R (a) and CRT glass (b)

content of reactive silica (SiO_2), based on the size distribution of particles and based on the mechanical properties. We examined the glass pozzolanic activity based on the mortar's tested mechanical properties according to which the glass must have grains finer than 0.063 mm and it needs to be dried at 98 °C. To prepare the mortar, we used 1350 g standard sand consisting of three fractions, 300 g of fine CRT glass, 150 g of standard hydrated lime and 270 cm^3 of water. We tested the mechanical strengths on test samples with dimensions 40 mm × 40 mm × 160 mm. They were hermetically enclosed in tin boxes. After the first 24 hours in laboratory conditions, we continued to cure them at 55 °C for additional six days. The results of the mortar mechanical properties we obtained are presented in Table 2.

The material is said to be pozzolanically active and ranked as having no less than class 5 if, at being seven days old, the minimum flexural strength is 2 MPa and compressive strength is 5 MPa, which we proved with this test.

2.2 Aggregate

The aggregate from the South Morava river were used, fractions 0/4 mm, 4/8 mm and 8/16 mm. The particle size distribution is determined using the dry sieving method according to SRPS EN 933-1 [28] and shown in Fig. 2.

Table 2 Results of mechanical properties of mortar

Test specimen	Flexural strength [MPa]	Compressive strength [MPa]
1	2.36	5.76
		5.82
2	2.28	5.76
		5.82
3	2.43	5.95
		5.82

2.3 Concrete mixtures composition

Reference concrete (E) is produced with 400 kg of cement and 1800 kg of three-fraction aggregate mix (Fig. 3): 43% fraction 0/4 mm, 23% fraction 4/8 mm and 34% fraction 8/16 mm. The water/binder ratio (w/b) is constant - 0.438. Superplasticizer Sika ViscoCrete 4000 BP on the basis of polycarboxylate is used for making the concrete mixes, which reduces the amount of water. The percent of replacement of cement with CRT glass was: 5, 10, 15, 20 and 35, in respect to the mass of cement. The highest percent of the share of mineral admixtures in CEM II (portland-composite cement) cement was chosen as the top limit of replacement of cement with glass. Designations of concrete mixes were made according to the share of replacement, whereby WG is an abbreviation for waste glass. For instance, in the case of 20% of replacement of cement with CRT glass, the batch mark is WG20. The composition of concrete mixes is presented in Table 3.

2.4 Test methods

2.4.1 Alkali-Silicate Reactivity (ASR)

Fine river aggregate and cement were used to make the reference mortar (E), with no added glass. In mortar WG1, we used CRT glass of 0.063/0.090 mm fineness to replace 35% of cement, whereas in mortar WG2, 35% of cement was replaced by ground CRT glass finer than 0.063 mm. The goal was to check the alkali-silicate reactivity of CRT glass in the mortar and to investigate the effect of the glass fineness on the ASR intensity. We chose this percentage of cement replaced by finely milled CRT glass because it was later found that it was the highest possible percentage of cement replacement in concrete. Another reason is an assumption that the potential ASR would be more strongly manifested if the cement replacement is 35% compared to the lower replacement ratio.

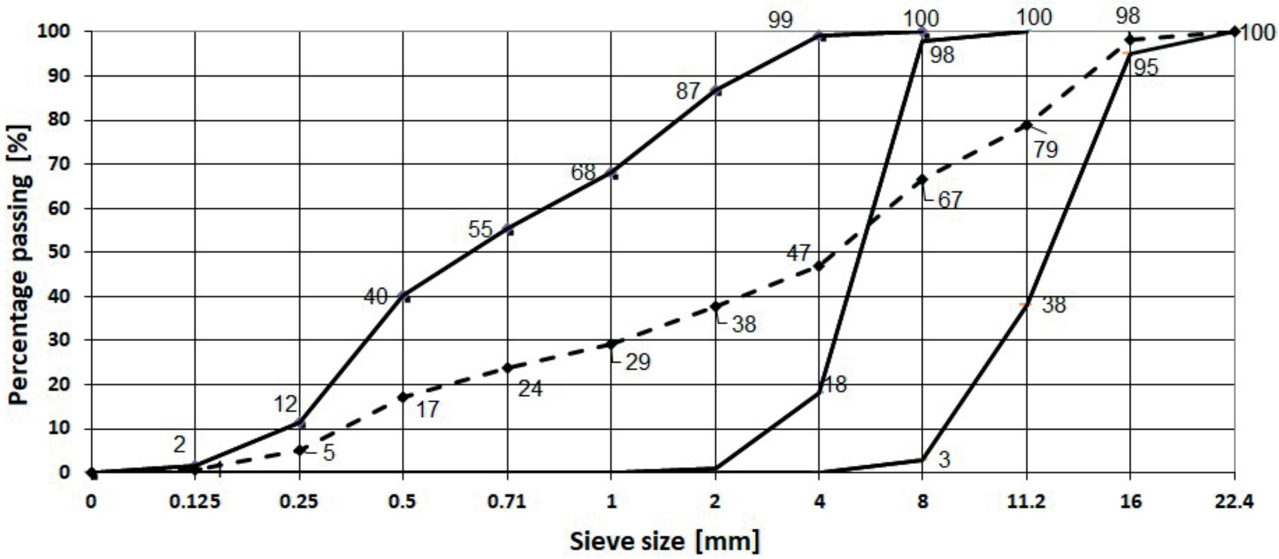


Fig. 2 Particle size distribution of fractions 0/4 mm, 4/8 mm, 8/16 mm and fractions mix of river aggregate

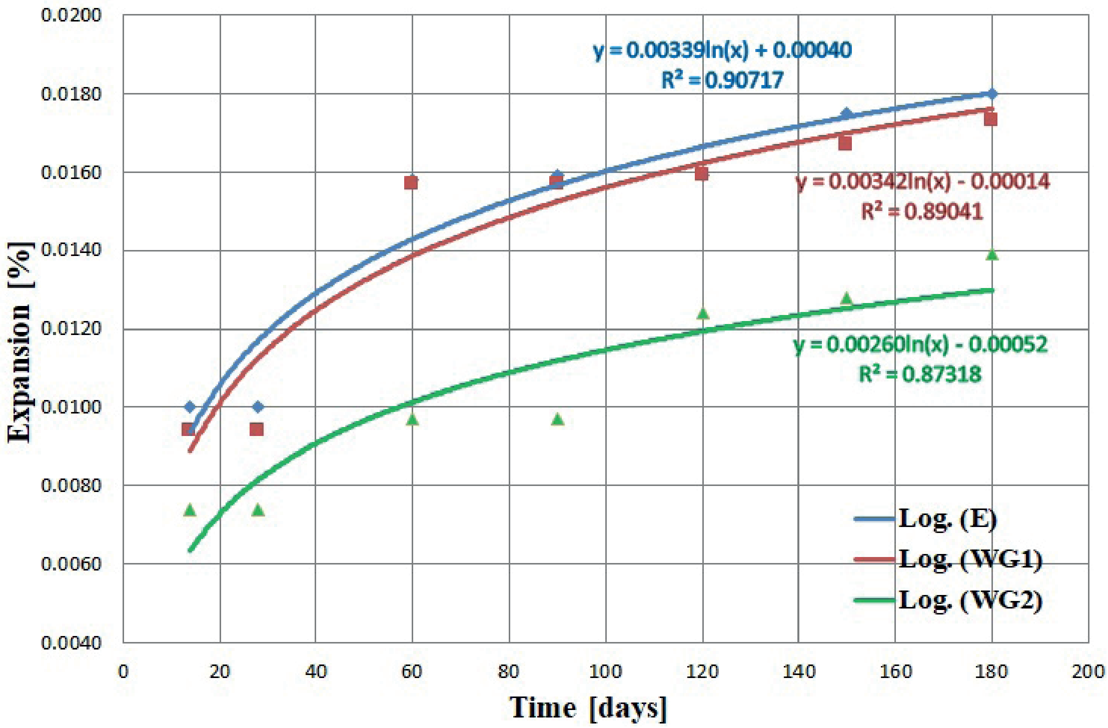


Fig. 3 Expansion of mortar prisms with the addition of CRT glass in the function of time

Table 3 Compositions of the concrete mixtures used in the experiment

Concrete	0/4 mm	Aggregate 4/8 mm	8/16 mm	Cement CEM I 52.5R	CRT < 0.063 mm	Water City Wat. Supply	*w/b*	Additive Superplasticizer
	kg/m³	kg/m³	kg/m³	kg/m³	kg/m³	kg/m³	–	kg/m³
E	774	414	612	400	-	175.3	0.438	2.40
WG5	774	414	612	380	20	175.3	0.438	2.40
WG10	774	414	612	360	40	175.3	0.438	2.40
WG15	774	414	612	340	60	175.3	0.438	2.40
WG20	774	414	612	320	80	175.3	0.438	2.40
WG35	774	414	612	260	140	175.3	0.438	2.40

2.4.2 Testing of concrete resistance to sulfate attack

Before we made each concrete batch, we thoroughly considered the cement homogenization with the appropriate quantity of milled CRT glass. For that purpose, we used a vessel of an adequate size with a lid and a mixer fitted with a convenient attachment. During the 5 minutes lasting mixing process, that special attachment revolved at 850 rev/min. We added three precisely measured segments of dried aggregate, from the coarsest to the finest, into the watered mixing drum. Afterwards, we added a half of the planned amount of water into the mixer, mixing it for 30 seconds to wet the aggregate grains evenly. Then, we poured the cement with milled CRT glass mixture into the mixer with the remaining water. From that moment, we measured the mixing time of these component materials using a calibrated stop-watch. After 60 seconds, we added the superplasticizer, with the total mixing time up to 5 minutes. In this research, each experimental concrete batch consisted of 24 cylinder shaped samples, 100 mm in diameter and 100 mm in height (a total of 144 samples). The concrete was cast into metal moulds and placed in using a vibrating table. A half of all the samples were composed of the "reference" ones soaked in saturated lime water until the testing. After 28 days and all the necessary preparations, the other half was immersed and cured in a 5% Na_2SO_4 solution until the testing. Comparative testing of the compressive strength of specimens cured in $Ca(OH)_2$ and Na_2SO_4 solutions was after 3, 6, 12 and 36 months.

2.4.3 SEM and EDS analyses

SEM (scanning electron microscope) and EDS (energy-dispersive spectroscopy) analyses are performed in order to acquire knowledge of the concrete microstructure and to check whether any gypsum and ettringite in the pores or micro-cracks of concrete. All concretes are observed and analyzed, but in this paper are shown only the samples representing the following concrete series: reference and WG15 ones.

3 Experimental results and discussion

3.1 Alkali-Silicate Reactivity (ASR)

According to the tests results presented in the diagram (Fig. 3), it can be concluded that mortars WG1 and WG2 had a lower value of expansion than reference concrete at all ages. At the ages of 180 days, the values of mortar prisms E, WG1, and WG2 expansions are +0.0180%, +0.0173%, and +0.0139%, respectively.

In accordance with the ASTM C33/C33M-13 [29] provisions, the expansion values after 6 months do not exceed the limit value of +0.10% in any of the three series of mortars. What is more, we concluded that the mortar with more finely milled glass WG2 has the lowest expansion value in comparison with the other two mortars. At the end of the test, WG2 exhibits 22.8% lower shrinkage than WG1 and the reference mortar. Consequently, the higher fineness of glass is, as in the case of the WG2 mortar, it contributes more to the expansion reduction. The literature review shows that an explanation of such a glass effect on the ASR occurrence is found in [14]. Free SiO_2 molecules in finely milled glass, that is an amorphous material, will be consumed during the pozzolanic reaction. It will also show reactions with other compounds forming a mineral phase. Dissolved silicon dioxide will be built into the crystal grid of the cement gel and will not be available for the process of the alkali-silicate reaction, which, as a rule, occurs much later than the pozzolanic reaction.

3.2 Resistance of concrete made with CRT glass on sulphate attack

After 3, 6, 12 and 36 months, visual inspections of the sample surface were performed and variations of compressive strength were calculated. The visual inspections of samples in the 12-month period did not establish emergence of any damage such as cracks and scaling. However, the visual inspection of the samples of reference concrete and concretes with 5% and 10% of added CRT glass after 36 months of curing in the sulphate solution identified clear changes on their surface (Fig. 4 (a)–(h). Those changes are most prominent in the places where there already were large pores on the concrete surface which were created as a consequence of water trapped near the mould walls. It is evident that those are locations where the sulphate solution could easily penetrate concrete.

The damage size was 3 to 12 mm, and depth 3 to 5 mm. In addition, in certain locations on the sample surface swelling was detected which rendered the concrete surface rough Swelling was caused by forming of ettringite in the concrete. On the other hand, the surface of the concrete samples with 15%, 20% and 35% of replacement of cement with glass, remained smooth and with no changes even after 36 months of curing in sulphate solution (Fig. 4 (g)). A higher substitution of cement with finely ground cathode ray tube glass helped reduce the presence of celite mineral which also contributed to a higher sulphate resistance of

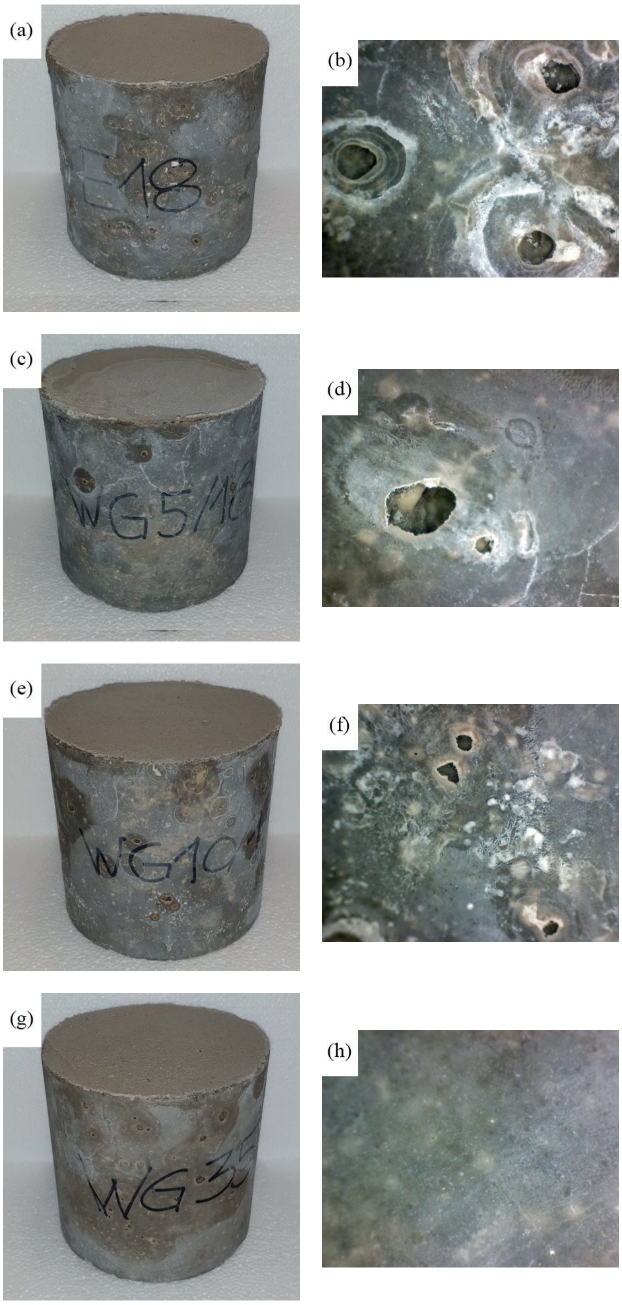


Fig. 4 Appearance of the sample surface after 36 months of curing in Na_2SO_4 – reference concrete E (a) and its magnification (b), WG5 (c) and its magnification (d), WG10 (e) and its magnification (f), WG35 (g) and its magnification (h)

concrete. We determined the sulphate resistance level of concrete batches with added CRT glass by comparing the compressive strength of reference samples for each batch and the samples exposed to sulphate attack (Table 4). After the concrete was exposed to sulphate solution for 3, 6, 12 and 36 months, we conducted a comparative testing of mechanical strengths by using the unbonded caps. It was done in accordance with the ASTM C1231/C1231/C1231M-15 standard [30].

Adding to the strength variation, we also performed a visual inspection of a potential damage of the samples kept in the sulphate solution. If we firstly observe the results of compressive tests of the reference specimens soaked in calcium hydroxide solution for 3 months ($f_{E,3}$), we can conclude that as the part of finely ground CRT glass increases, the compressive strength decreases.

Concrete mixtures WG20 and WG35 have, respectively, 13.9% and 30.9% lower strength than the reference batch E.

With the tests made after 6 months ($f_{E,6}$), the initial difference in compressive strength is reduced between the reference batch and sample, when up to 15% of glass is replaced. With the test made after 12 months ($f_{E,12}$), the concrete mixture WG15 had 2.7% higher strength than E concrete. To sum up, after a year, WG20 and WG35 still had lower strengths than the reference batch, but the difference was respectively lower, 6.1% and 19.4%. Such trend was established by testing compressive strength even at the age of 36 months ($f_{E,36}$). Concretes WG20 and WG35 at the mentioned age had 4.3% and 17.8% lower value than the reference concrete. Such increased strength of concrete mixtures with an addition of CRT glass can be explained with the process of glass pozzolanic reaction. The CRT glass pozzolanic reaction occurs later than the cement hydration process and it is most intensive after 28 days. That explains the reduction of difference between the measured values of compressive strengths of the reference batch and the ones with added glass. After defining the impact of CRT glass presence on the compressive

Table 4 Mean results of sulphate resistance of concrete by measuring compressive strength of three specimens

Concrete	Reference specimens cured in solution of $Ca(OH)_2$				Specimens cured in 5% solution of Na_2SO_4				Strength variation $\Delta f_{p,n}$ [%]			
	$f_{E,3}$ [MPa]	$f_{E,6}$ [MPa]	$f_{E,12}$ [MPa]	$f_{E,36}$ [MPa]	$f_{NS,3}$ [MPa]	$f_{NS,6}$ [MPa]	$f_{NS,12}$ [MPa]	$f_{NS,36}$ [MPa]	$\Delta f_{p,3}$ [%]	$\Delta f_{p,6}$ [%]	$\Delta f_{p,12}$ [%]	$\Delta f_{p,36}$ [%]
E	67.76	71.14	72.71	73.55	66.33	69.07	71.27	59.24	2.16	2.92	1.98	19.46
WG5	63.83	67.02	71.54	71.92	58.95	62.64	67.22	57.21	7.64	6.54	6.04	20.45
WG10	62.30	69.27	73.51	74.26	61.57	63.72	66.15	60.69	1.17	8.01	10.01	18.27
WG15	65.08	71.83	74.70	75.28	60.71	64.96	68.59	65.24	6.72	9.56	8.18	13.34
WG20	58.37	62.96	68.26	70.40	57.54	60.33	64.38	63.72	1.42	4.18	5.69	9.49
WG35	46.81	52.98	58.58	60.48	44.75	50.02	56.60	55.89	4.39	5.59	3.39	7.59

strength of concrete, sulphate resistance of experimental concretes can be observed. After soaking the samples in 5% Na_2SO_4 solution for 12 months, there was no decrease of compressive strength higher than 10% compared to the samples soaked in calcium hydroxide. However, in the period from 12 to 36 months, due to the development of damage of concrete structure (which can be clearly seen on its surface) there was a considerable reduction of compressive strength in relation to the samples cured in the solution of $Ca(OH)_2$. The decline of strength is recorded for all the samples, but not in equal measure. In concretes E, WG5 and WG10 this decline is around 20%. On the other hand, in concretes WG15, WG20 and WG35 the strength decline is lower and amounts to 13.34%, 9.49% and 7.59% respectively. Therefore, it can be concluded that the reduction of compressive strength of concrete exposed to sulphate decreases with increase of percentage of replacement of cement with glass. This can be explained by the fact that finely ground CRT glass acts as a sealant (seals the pores), reduces penetration of fluids through concrete, and renders it more resistant to the sulphate solution attack. Regarding this effect of fine ground glass in cement matrix, further research can determine what effect the glass fineness has on the sulfate resistance of concrete. In the process, a compromise between the required compressive strength and required sulphate attack resistance should be found.

3.3 SEM and EDS analyses

Specimens of all experimental concrete series underwent SEM and EDS analyses. Further, only those analyses that are related to reference concrete and WG15 are presented. Fig. 5 (a) shows needle-like crystals of ettringite formed in the pores of cement paste. The sulfate ions penetrated into the microstructure because of the occurrence of microcracks in concrete. The air voids and the cracks allowed new crystals of ettringite to form in them because there was a reaction of incoming sulfate ions with interior hydration products and other suitable compounds. EDS analysis conducted on the ettringite crystals is shown in the Fig. 5 (b). Based on the EDS spectrum of WG15 concrete (Fig. 6 (a), (b)), one can observe that the marked location corresponds to the C-S-H gel. A considerable presence of silicon and calcium was detected. Also present are sodium, magnesium, potassium and iron. The mentioned elements have a ratio common for the cement hydrates.

On the observed concrete samples, SEM and EDS analyses do not indicate the presence of an undesirable alkali-silicate reaction, more precisely the A-S-R gel, which is in agreement with the results of the experimental tests of this phenomenon.

4 Conclusions

Many conclusions can be made based on the experimental results we obtained during this research. 35% of cement

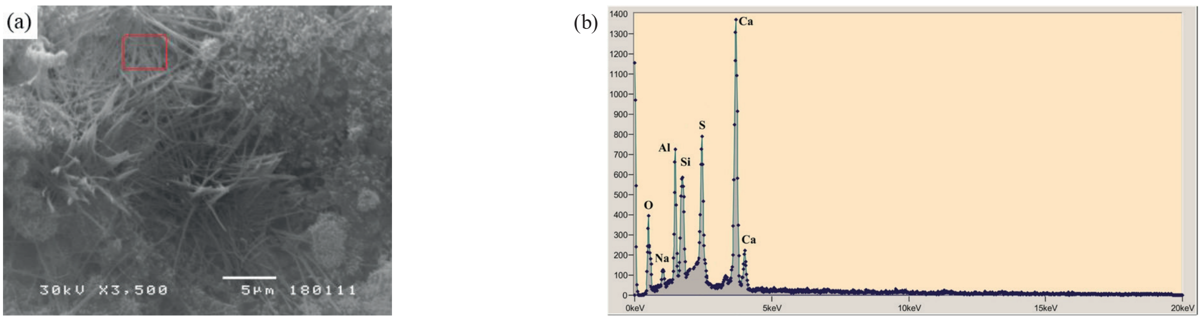


Fig. 5 Reference concrete 3500× magnification (a); EDS spectroscopy (b)

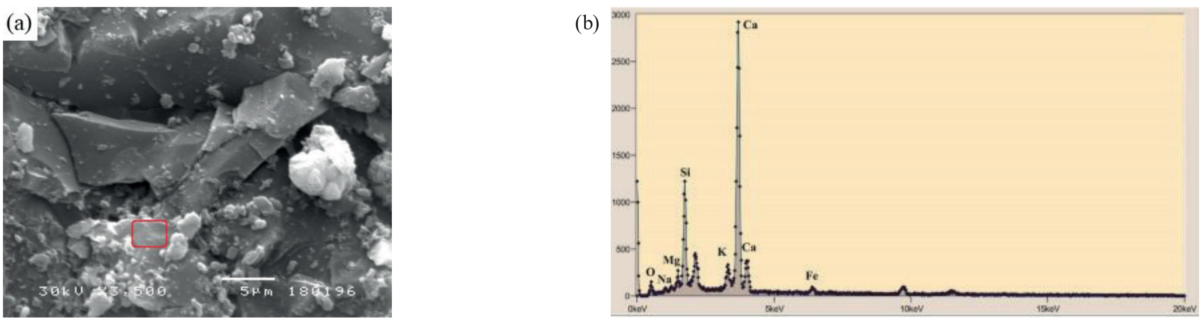


Fig. 6 WG15 concrete 3500× magnification (a); EDS spectroscopy (b)

mass replacement with CRT glass finer than 63 µm does not cause the appearance of alkali - silicate reaction. Free silicon in glass powder, being an amorphous material, is consumed during the pozzolanic reaction. It reacts with other ingredients forming a mineral phase. Thus, the dissolved silicon dioxide is included in the cement gel crystal grid and it is not included in the process of alkali-silicate reaction which would normally appear later than the pozzolanic reaction. By measuring the compressive strength of concrete samples in which a part of cement was substituted by CRT glass and soaked in calcium hydroxide, we found that, through time, the difference of compressive strengths, compared to the reference batch E, declines. With the tests performed after 36 months, the batches in which cement was substituted with up to 15% of CRT glass have the same or slightly higher compressive strengths than the reference batch.

After soaking the samples in 5% Na_2SO_4 solution for 12 months, there was no decrease of compressive strength higher than 10% compared to the samples soaked in calcium hydroxide. However, in the period between 12 and 36 months, due to the development of damage of the concrete structure there was a considerable reduction of compressive strength in relation to the samples cured in the solution of $Ca(OH)_2$. It is obvious that the generation and accumulation of sulfate corrosion products in the cracks and pores influenced the reduction of compressive strength of concrete. In the beginning, the cracks and pores are not fully filled with corrosion products and do not significantly affect the strength of concrete. In the later period, the excessive filling of corrosion products generates pressure on the walls of internal cracks. In this way, new cracks are formed, while the existing ones wide. The created microdamage in the structure directly caused the reduction of compressive strength of concrete. Based on the results obtained by SEM and EDS analyses of the reference concrete and the concrete with the replacement of up to 10% of cement with glass, it is evident that ettringite emerges as a product of sulfate action caused by the reaction of incoming sulfate ions with interior hydration products. Evidently, buildup of ettringite in the transit zone leads to the reduction of the bond strength between the cement paste and aggregate. It is another reason why there is a certain reduction of compressive strength of these concretes. In concretes where a higher percentage of cement was replaced with glass, no emergence of ettringite was observed, which is in agreement with the previous conclusion. It can be stated that the reduction of compressive strength of concrete exposed to sulphate attack decreases with the increase of the replacement of cement with glass. Finely ground CRT glass functions as a sealant, reduces the penetration of fluid through concrete and makes it resistant to the sulphate solution attack. Based on the obtained results, concretes with 15% to 20% of replacement of cement with finely ground CRT glass would be optimal for practical application.

Acknowledgments

The work reported in this paper is part of the investigation within the research project TR-36017 "Utilization of by-products and recycled waste materials in concrete composites in the scope of sustainable construction development in Serbia: investigation and environmental assessment of possible applications" supported by the Ministry for Science and Technology, Republic of Serbia. This support is gratefully acknowledged.

References

[1] Grdic, D. Z., Ristic, N. S., Toplicic - Curcic, G. A., Bijeljić, J., Grdić, Z. J. "Resistance of concrete made with finely milled cathode ray tube glass as a supplementary cementitious materials to sulphate attack", In: Šajna, A., Legat, A., Jordan, S., Horvat, P., Kemperle, E., Dolenec, S., Ljubešek, M., Michelizza, M. (eds.) Construction Materials for a Sustaniable Future: Proceedings of the 2nd International Conference CoMS 2020/21, vol. 1, Slovenian National Building and Civil Engineering Institute (ZAG), 2020, pp. 96–105. ISBN 978-961-94071-8-9

[2] Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I. "CRT glass state of the art: A case study: Recycling in ceramic glazes", Journal of the European Ceramic Society, 27(2–3), pp. 1623–1629, 2007. https://doi.org/10.1016/j.jeurceramsoc.2006.05.009

[3] Singh, N., Li, J., Zeng, X. "Global responses for recycling waste CRTs in e- waste", Waste Management, 57, pp. 187–197, 2016. https://doi.org/10.1016/j.wasman.2016.03.013

[4] Idir, R., Cyr, M., Tagnit-Hamou, A. "Pozzolanic properties of fine and coarse color-mixed glass cullet", Cement and Concrete Composites, 33(1), pp. 19–29, 2011. https://doi.org/10.1016/j.cemconcomp.2010.09.013

[5] Shi, C., Wu, Y., Riefler, C., Wang, H. "Characteristics and pozzolanic reactivity of glass powder", Cement and Concrete Research, 35(5), pp. 987–993, 2005. https://doi.org/10.1016/j.cemconres.2004.05.015

[6] Schwarz, N., Cam, H., Neithalath, N. "Influence of a fine glass powder on the durability characteristics of concrete and its comparison to fly ash", Cement and Concrete Composites, 30(6), pp. 486–496, 2008. https://doi.org/10.1016/j.cemconcomp.2008.02.001

[7] Khmiri, A., Chaabouni, M., Samet, B. "Chemical behaviour of ground waste glass when used as partial cement replacement in mortars", Construction and Building Materials, 44, pp. 74–80, 2013. https://doi.org/10.1016/j.conbuildmat.2013.02.040

[8] Grinys, A., Balamurugan, M., Augonis, A., Ivanauskas, E. "Mechanical Properties and Durability of Rubberized and Glass Powder Modified Rubberized Concrete for Whitetopping Structures", Materials, 14(9), 2321, 2021. https://doi.org/10.3390/ma14092321

[9] Gimenez-Carbo, E., Soriano, L., Roig-Flores, M., Serna, P. "Characterization of Glass Powder from Glass Recycling Process Waste and Preliminary Testing", Materials, 14(11), 2971, 2021. https://doi.org/10.3390/ma14112971

[10] Belebchouche, C., Moussaceb, K., Bensebti, S.-E., Aït-Mokhtar, A., Hammoudi, A., Czarnecki, S. "Mechanical and Microstructural Properties of Ordinary Concrete with High Additions of Crushed Glass", Materials, 14(8), 1872, 2021. https://doi.org/10.3390/ma14081872

[11] Chen, C. H., Huang, R., Wu, J. K., Yang, C. C. "Waste E-glass particles used in cementitious mixtures", Cement and Concrete Research, 36(3), pp. 449–456, 2006. https://doi.org/10.1016/j.cemconres.2005.12.010

[12] ASTM "ASTM C267-01(2006) Standard Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes", American Society for Testing and Materials, West Conshohocken, PA, USA, 2006. https://doi.org/10.1520/C0267-01R06

[13] Matos, A. M., Sousa-Coutinho, J. "Durability of mortar using waste glass powder as cement replacement", Construction and Building Materials, 36, pp. 205–215, 2012. https://doi.org/10.1016/j.conbuildmat.2012.04.027

[14] Özkan, Ö., Yüksel, İ. "Studies on mortars containing waste bottle glass and industrial by-products", Construction and Building Materials, 22(6), pp. 1288–1298, 2008. https://doi.org/10.1016/j.conbuildmat.2007.01.015

[15] Carsana, M., Frassoni, M., Bertolini, L. "Comparison of ground waste glass with other supplementary cementitious materials", Cement and Concrete Composites, 45, pp. 39–45, 2014. https://doi.org/10.1016/j.cemconcomp.2013.09.005

[16] ASTM "ASTM C1012/C1012M-13 Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution", American Society for Testing and Materials, West Conshohocken, PA, USA, 2013. https://doi.org/10.1520/C1012_C1012M-13

[17] Liu, T., Qin, S., Zou, D., Song, W. "Experimental investigation on the durability performances of concrete using cathode ray tube glass as fine aggregate under chloride ion penetration or sulfate attack", Construction and Building Materials, 163, pp. 634–642, 2018. https://doi.org/10.1016/j.conbuildmat.2017.12.135

[18] Bjegović, D., Štirmer, N. "Theory and concrete technology", Faculty of Civil Engineering, University of Zagreb, Zagreb, Croatia, 2015. ISBN 978-953-6272-77-8

[19] Bulatović, V. "Sulphate resistance of concrete with recycled aggregate concrete", Doctoral Thesis, University of Novi Sad, 2017.

[20] Neville, A. M., Brooks, J. J. "Concrete Technology", Pearson Education Ltd., 2001. ISBN 9780582988590

[21] Grdić, Z. "Concrete Technology", Faculty of Civil Engineering and Architecture, University of Niš, Niš, Serbia, 2011.

[22] ISS "SRPS EN 196-1 Methods of testing cement - Part 1: Determination of strength", Institute for Standardization of Serbia, Belgrade, Serbia, 2017.

[23] ISS "SRPS EN 196-3 Methods of testing cement - Part 3: Determination of setting times and soundness", Institute for Standardization of Serbia, Belgrade, Serbia, 2017.

[24] ISS "SRPS EN 196-6 Methods of testing cement - Part 6: Determination of fineness", Institute for Standardization of Serbia, Belgrade, Serbia, 2019.

[25] ISS "SRPS EN 197-1 Cement - Part 1: Composition, specifications and conformity criteria for common cements", Institute for Standardization of Serbia, Belgrade, Serbia, 2013.

[26] Radhi, M. S., Rasoul, Z. M. R. A., Alsaad, A. J. "Mechanical Behavior of Modified Reactive Powder Concrete with Waste Materials Powder Replacement", Periodica Polytechnica Civil Engineering, 65(2), pp. 649–655, 2021. https://doi.org/10.3311/PPci.17298

[27] ISS "SRPS B.C1.018:2015 Nemetalne mineralne sirovine - Pucolanski materijali - sastojci za proizvodnju cementa - Klasifikacija, tehnički uslovi i metode ispitivanja (SRPS B.C1.018 Non-metallic mineral raws - Puzzolanic materials - constituents for cement production - Classification, technical conditions and test methods), Institute for Standardization of Serbia, Belgrade, Serbia, 2001. (withdrawn 2015) (in Serbian)

[28] ISS "SRPS EN 933-1 Tests for geometrical properties of aggregates - Part 1: Determination of particle size distribution - Sieving method", Institute for Standardization of Serbia, Belgrade, Serbia, 2013.

[29] ASTM "ASTM C33/C33M-13 Standard Specification for Concrete Aggregates", American Society for Testing and Materials, West Conshohocken, PA, USA, 2013. https://doi.org/10.1520/C0033_C0033M-13

[30] ASTM "ASTM C1231/C1231M-15 Standard Practice for Use of Unbonded Caps in Determination of Compressive Strength of Hardened Cylindrical Concrete Specimens", American Society for Testing and Materials, West Conshohocken, PA, USA, 2016. https://doi.org/10.1520/C1231_C1231M-15