

ALTERING OF THE GROUND SILICON-BASED WASTE SURFACE PROPERTIES AND COMPOSITION FOR USE IN CEMENTITIOUS COMPOSITES AS SECONDARY RAW MATERIALS

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Abstract

Due to increase of glass waste landfills, the alternative strategies of silicon-based glass waste disposal such as a partial replacement for cement and aggregates in concrete are investigated. However, the impurities and contaminants in glass waste complicates its direct use as efficient secondary raw material for sustainable construction applications and compel use of additives or glass surface modifications. Therefore, in this work the most common (dry and wet) surface modification strategies compatible with civil construction were used to alter the surface of ground glass from ordinary municipal glass waste. Different microscopy and spectroscopy methods were used to analyze the morphological and composition changes of modified ground soda-lime silica glass. The detected changes in glass surface composition were explained by etching, redistribution or polymerization of carbon-based surface contaminants or metal ions leaching. The observed findings indicate possibility of glass reactivity altering and will be helpful in the understanding and explanation of calcium-silicate-hydrate formation kinetic and early-age behavior of concrete with recycled glass admixture.

Keywords: Soda-lime silica glass, dry treatment, wet chemistry, composition analysis, civil engineering

1. INTRODUCTION

Silicon-based glass is a non-biodegradable material which can be effectively recycled many times without properties deterioration [1, 2]. However, despite certain impurities tolerance, contamination issues related the glass waste (GW) collection and sorting lead to problems with GW disposal. The huge amount of ordinary municipal GW, waste from foundries and end-of-life photovoltaic panels not suitable for glass industry end up in landfills causing environmental problems [1–3]. Indeed, besides territory occupation, dumped GW through reaction with rainwater and pollutants release (leaching) resulted in soil contamination with risk of further pollution. The increase in human population leads to increase in waste production and therefore increase in GW disposal importance which forces community to search for alternative strategies for GW utilization [3]. In particular, use of ground silicon-based glass as alternative fillers or partial replacement in concrete composites has been recognized as promising GW disposal strategy which additionally may save natural resources and positively contribute to carbon footprint reduction [4, 5].

However, variations of chemical composition and physical characteristics of glass particles' surface as well as its stability in aggressive media must be carefully considered since it can significantly affect interactions with the cement binder disrupting the concrete composites microstructure and deteriorating its mechanical strength or oppositely improving calcium-silicate-hydrate (CSH) formation kinetic [5, 6]. For instance, for soda-lime glass due to the higher alkali mobility than that of silicon and oxygen (network formers), Na or Ca content near the surface may differ from the bulk affecting glass reactivity at early hydration stage while reactive silica in content increase risk of deleterious alkali-silica-reaction [4–7]. Moreover, should be considered issue of

municipal GW organic contamination that can slow down the CSH formation [8]. Therefore, different bulk and surface modification strategies or use of additives are employed for improving glass reactivity and interaction with cement binder for GW utilization as secondary raw material in sustainable civil construction [7, 9].

In this work we realize recycled glass particles modification by dry (temperature and plasma) and wet (different chemicals) treatments. We investigate the decontamination efficiency of dry processing as well as effect of ground glass interaction with organic solvents, acidic or alkaline medium. The observed findings indicate possibilities for glass reactivity altering and modification of ground glass surface composition that created substantial background for experiments with recycled glass admixture containing concrete composites. These results will be helpful in the explanation of processes at interfacial transition zones during CSH formation.

2. EXPERIMENT

As material to study was used the ground waste glass (GWG) powder from packaging glass that has been discarded from the glass recycling loop, i.e. cannot be further used in the new glass production. The GWG with median particles size $36.0 \pm 0.2 \mu\text{m}$ was provided by company that deals with processing and alternative disposal of such municipal waste (Recifa a.s.). Obtained GWG powder was processed by dry and wet surface and/or bulk modification methods and analyzed by microscopy and spectroscopy techniques.

The dry processing methods are represented by low pressure plasma treatment and annealing in controlled atmosphere. The GWG was exposed to radiofrequency plasma discharge in the large area low pressure system (AK 400, Roth&Rau) or treated via annealing in the cylindrical furnace (Clasic CZ s.r.o). The plasma treatment was realized for 4x5 min in oxygen at pressure 15 Pa and temperature $\leq 50^\circ\text{C}$ (marked as RT - room temperature) or at 500°C with resistive heating. The GWG annealing was realized at temperature 500°C in oxygen at atmospheric pressure for 12 h.

The wet chemistry processing was realized by GWG washing in deionized (DI) water, 0.25 M concentrated NaOH or HCl with subsequent purifying by DI water wash to remove residues and three different organic solvents (Acetone, Ethanol, Isopropanol). Each washing cycle with magnetic stir mix (200 rpm) lasts 1 h with 24 h GWG sedimentation. The washing procedure was followed by GWG drying via natural water evaporation.

GWG analysis first of all was performed using an Olympus BX53M optical microscope equipped with high-resolution camera which supports eye observation and digital photography. As standard characterization technique for surface microstructure analysis, the scanning electron microscopy (SEM) was employed. Prior to measurements, the examined GWG was spread in a dense layer on an adhesive copper tape on a solid substrate and smoothed out to form thin layer. The particle's surface was analyzed and images were captured using a secondary electrons detector of low voltage SEM MAIA3 (TESCAN, a.s.) at an acceleration voltage of 10 kV. Mounted to SEM setup an energy dispersive X-ray (EDX) detector with IDFix analytical software was used to perform the qualitative elemental analysis (depth of penetration of analysis is 1-2 μm) of GWG powder.

Next, GWG was analyzed using Fourier transform infrared spectroscopy (FTIR) method using Nicolet iS50 spectrometer in attenuated total reflectance (ATR) mode, where analyzed materials are pressed against surface of high-refractive-index prism (depth of penetration of analysis is in order of a few micrometers). Spectra measurements were performed in range $200\text{-}1800 \text{ cm}^{-1}$ (64 scans per spectrum with resolution 4 cm^{-1}) using diamond prism, cooled DTGS detector and solid-state beam-splitter.

The GWG surface composition changes were analyzed by means of X-ray photoelectron spectroscopy (XPS). GWG powder was fixed on Cu tape on solid holder and measured by AxisSUPRA photoelectron spectrometer (Kratos Analytical) collecting XPS signal from a 0.5 mm^2 area. Monochromatized Al K α with emission of 10 mA and activated charge-compensation were used for all measurements. The survey spectra were collected with low energy resolution of 80 eV and signal from C 1s, O 1s, Si 2p, Na 1s, Ca 2p, Al 2p, Mg 1s, K 2p, N 1s was detected. For quantitative analysis the survey spectra regions of mentioned core levels were measured with high energy resolution of 10 eV. Data were calibrated to SiO₂ peak binding energy of 103.7 eV.

3. RESULTS AND DISCUSSION

Ground waste glass appears as a white-grey powder due to strong light scattering and low optical absorption. However, by using the optical microscopy (**Figure 1a**), it can be seen that GWG is represented mostly by irregular transparent shards with inclusion of small amounts of colored shards or impurities. The analysis of as-received (i.e. untreated) GWG by SEM reveals that in spite of stated median particles size $36.0 \pm 0.2 \mu\text{m}$ the real particles' size distribution is more broad and larger (up to $50 \mu\text{m}$) particles decorated by the small fragments (tens of nanometers) can be found. Besides smaller fragments, on the surface of large GWG particles can be seen "scratches" or cracks related to grinding process (**Figure 1b**). According to observation, these cracks and scratches are not penetrated to GWG depth and thus should not be involved in deleterious alkali-silica reaction and concrete swelling [7, 10]. It also should be noted, that due to insulating nature of GWG the effect of charging was observed during the particles' surface analysis which complicates characterization while no clear evidence of non-GWG impurities was found.

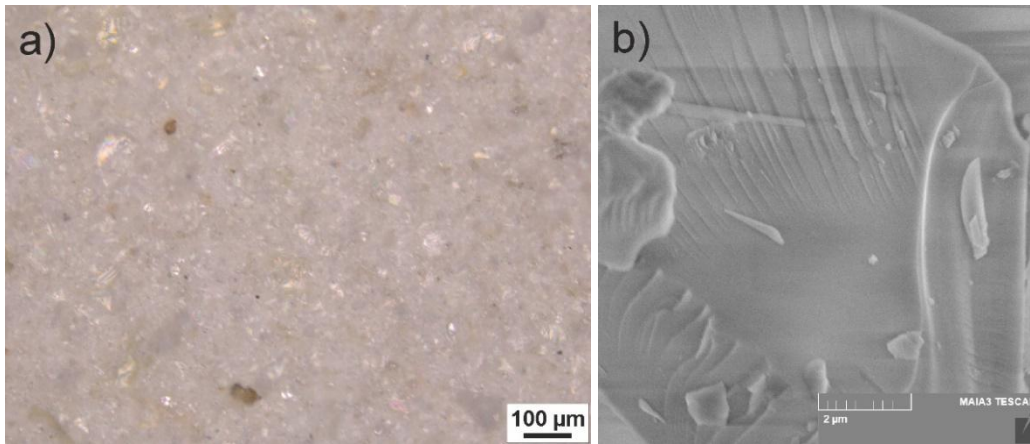


Figure 1 Optical microscopy image (a) and SEM microstructure image (b) of as-received GWG powder

The SEM analysis of plasma treated, annealed or wet chemistry treated GWG demonstrated morphology similar or identical to observed on the as-received GWG powder. This observation partially agrees with earlier revealed findings, which is taken as indication that no damage was caused to GWG surface by the performed treatments, i.e. changes will be only in the elemental composition.

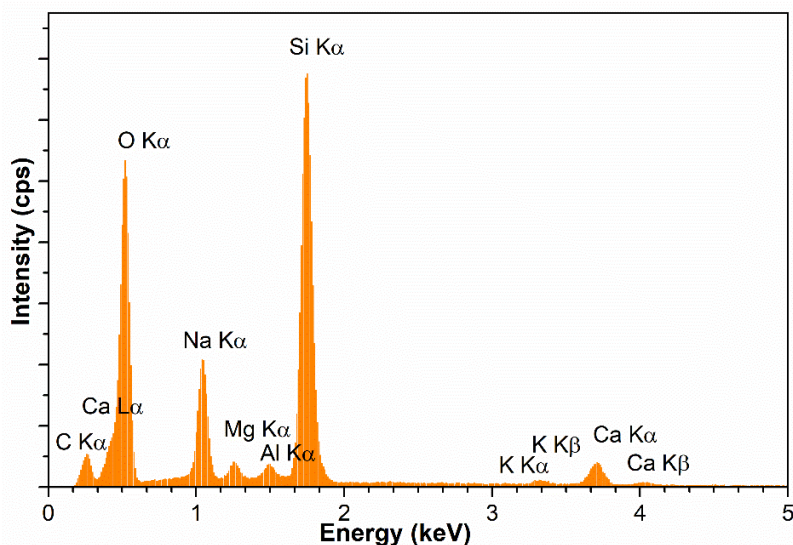


Figure 2 Typical EDX spectrum collected on the as-received GWG

The performed EDX analysis of as-received GWG powders composition reveals dominating amount of Si and O elements (two of the strongest signal) in it. Also, strong signal from Na and presence of C, Mg, Al, Ca and K were detected in studied sample (**Figure 2**). However, because of limited area (a few μm^2) from which the signal is collected and probably also insufficient EDX depth resolution (in order of a few μm) we observe the strong variation of signal intensities for different elements (especially sodium). This issue complicates the definite determination of the elemental composition of GWG powders. Moreover, it has to be considered that response signal from elements is energy sensitive varies for light and heavy elements and requires precise quantitative correction for estimation of samples composition. It again is complicated by detected carbon in material which is believed to be present mostly on GWG surface and earlier has been assigned to contamination by organic residues and/or absorbate from air [11, 12].

Therefore, the observed data were taken as orientation for more precise surface analysis and are shown for the untreated sample only. Nevertheless, via repeating measurements on different places (not shown here), no other elements than demonstrated were found in selected GWG. Thus, we make suggestion that although composition of the investigated GWG is acceptable for use in the experiments with cement-based materials, it is advisable to remove carbon-related impurities from the GWG surface to not spoil the experiments [8], while composition changes should be monitored by more surface sensitive technique.

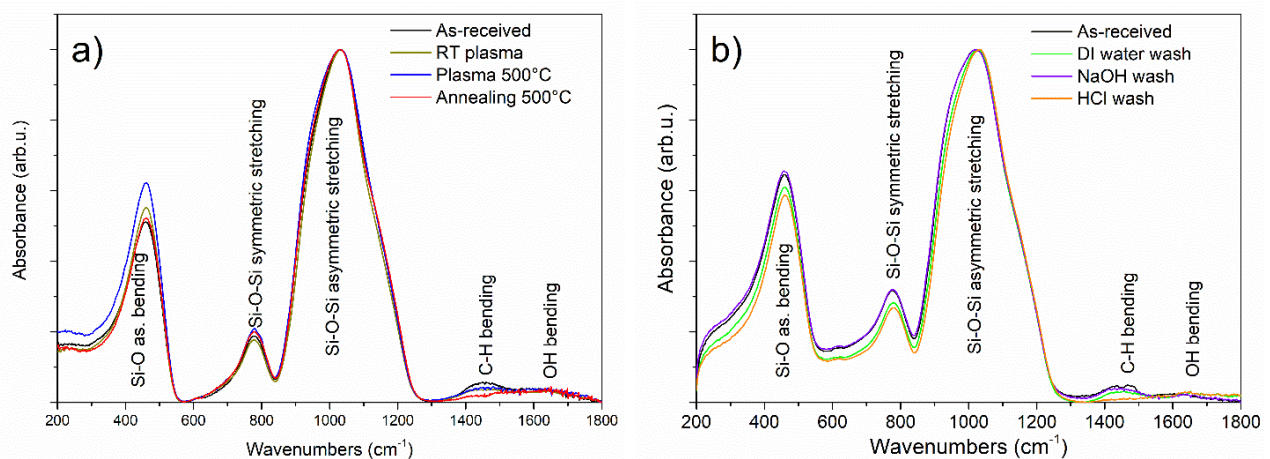


Figure 3 FTIR absorbance spectra of GWG powder treated by dry (a) and wet (b) process

The normalized ATR FTIR spectra of analyzed GWG powders are shown in **Figure 3**. As it can be seen, the measured IR absorbance spectra for as-received and treated GWG powders are quite similar. The broad bands found in the collected spectra were attributed to Si-O and Si-O-Si vibrations such as: asymmetrical bending at 463 cm^{-1} , symmetrical stretching at 788 cm^{-1} , and asymmetrical stretching at 1082 cm^{-1} characteristic for amorphous (non-crystalline) silica [13, 14]. In addition, were observed bands at 1450 cm^{-1} attributed to C-H bending vibration (assigned to organic contamination) and 1650 cm^{-1} attributed to OH bending vibration (assigned to hydroxyl groups or water on GWG surface) [13, 14].

The last two mentioned bands' intensity varies depending on the performed treatment procedure. Lowering of C-H bending vibration intensity which was the most evident for GWG annealed at 500°C for dry treatment and wash in HCl for wet treatment is taken as indication of possible removing of organic contaminates from the GWG particles surface. The slight variation of Si-O asymmetrical bending vibration intensity is related to imperfection of measuring setup which in case of GWG was sensitive to the size of the analyzed material. The similarities in the spectra indicate that amorphous nature of analyzed material is kept unchanged [11]. We propose that GWG with cleaner surface will better interact with cement in the experiments with concrete composites and promote calcium-silicate-hydrate formation.

The atomic concentrations of elements (regarding their core levels) derived from the XPS measurements for differently treated GWG are summarized in **Table 1**. Due to high surface sensitivity of XPS method and nature of investigated material the highest elements concentration was observed for oxygen (O 1s peak). All other detected materials such as silicon, sodium, calcium, magnesium, aluminum and potassium correspond to EDX measurements (**Figure 2**) and are found in amounts that can be expected for soda-lime silica glass [4, 7, 8]. High concentration of carbon at the surface of the raw GWG powder agrees with our previous observation and is explained by organic residues originally present in the glass waste and also to carbon precipitation on glass surfaces exposed to natural environment [9–13].

Table 1 Concentrations of chemical elements derived from the XPS measurements

GWG sample	O (wt%)	Si (wt%)	Na (wt%)	Ca (wt%)	Al (wt%)	Mg (wt%)	K (wt%)	N (wt%)	C (wt%)	O/Si
As-received	38.8	21.0	10.2	2.3	0.0	0.0	0.5	0.0	27.3	1.85
RT plasma	45.2	20.3	8.1	1.6	0.8	0.9	0.4	0.4	21.8	2.23
Annealing 500°C	43.8	23.1	6.6	2.1	0.0	0.9	0.3	0.2	23.0	1.90
Plasma 500°C	50.4	24.7	7.9	2.1	1.0	1.0	0.4	0.2	11.3	2.04
DI water wash	45.4	15.1	4.5	1.9	0.9	1.4	0.1	0.0	30.7	3.0
HCl wash	50.0	19.3	3.0	1.0	0.4	0.1	0.1	0.0	26.2	2.59
NaOH wash	42.5	12.8	4.6	2.9	0.4	1.0	0.1	0.0	35.7	3.32
Acetone wash	40.2	15.4	10.0	1.7	0.5	0.8	0.3	0.4	30.4	2.61
Ethanol wash	44.8	16.9	8.8	1.6	0.6	0.7	0.3	0.6	25.3	2.65
Isopropanol wash	44.2	15.4	11.2	2.0	0.5	0.7	0.2	0.5	24.9	2.87

Concerning the comparison of treatment methods we observe following. The dry surface treatment processes resulted to evident decreasing of carbon content on the GWG particles related to carbon oxidation which led to variation of all other detected elements [11]. The most efficient cleaning procedure in this case was plasma treatment at 500°C in air that resulted to the lowest carbon residues (partially agree with FTIR spectroscopy in **Figure 3a**) and O/Si ratio close to 2 (i.e. natural for SiO₂). However, it should be noted that the use of non-oxidative atmospheres for dry processing rather resulted to polymerization of organic contaminants [11].

On the contrast, washing in the water, organic solvents or other chemistries led to no change or increase in carbon content on GWG surface. The reason of this can be the nature of organic contaminants that not always are water soluble [8]. Surprisingly, washing in HCl, on contrast to FTIR observations (**Figure 3b**), led to similar carbon content as for as-received (untreated) GWG. The observed variation in other elements' concentration in this case can't be related only to carbon contaminants, but also to non-glass ions release to liquid media (i.e. leaching) [10, 13, 14]. In particular, washing in acid resulted to significant decrease of all metallic ions in the surface region leaving less impurities in SiO₂ shell over remaining GWG. Nevertheless, according to our findings, any employed treatment should not affect the crystallinity of GWG leaving the processed materials in the amorphous form suitable for use in cementitious composites.

4. CONCLUSION

The discarded from glass recycling ground soda-lime silica waste glass powder was modified by plasma treatment, high temperature annealing, washing in the organic solvents, acidic and alkaline media. The change in surface properties and composition of ground glass particles was investigated by electron microscopy, infrared and X-ray spectroscopies. We observe that all employed treatments preserve the surface microstructure of GWG and remain its amorphous nature suitable for use in cement-based composites. Dry

surface treatment methods, especially at elevated temperatures, were found as more suitable for decarbonization of GWG surface although they are more energetically demanding. The decarbonization efficiency of employed wet treatment method was lower, which can be related to need of higher washing media flow for organic residues removal and/or residues resistance to washing treatment. The significant decrease of metal ions from the surface region was observed for washing in acidic solution which leaves ion-depleted SiO₂ shell over remaining GWG. We propose that obtained findings will create a good basis for investigation and explanation of treated GWG particles interaction processes in cementitious composites used in civil engineering and will promote GWG use as secondary raw material.

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REFERENCES

- [1] BRISTOGIANNI, T., OIKONOMOPOULOU, F. Glass up-casting: a review on the current challenges in glass recycling and a novel approach for recycling “as-is” glass waste into volumetric glass components. *Glass Structures & Engineering* 2023, vol. 8, pp. 255-302. Available from: <https://doi.org/10.1007/s40940-022-00206-9>
- [2] BAEK, C.R., KIM, D.H., JANG, Y.-C. Exploring glass recycling: Trends, technologies, and future trajectories. *Environmental Engineering Research* 2024, vol. 30, no. 3, 240241. Available from: <https://doi.org/10.4491/eer.2024.241>
- [3] ADEKOMAYA, O., MAJOZI, T. Mitigating environmental impact of waste glass materials: review of the existing reclamation options and future outlook. *Environmental Science and Pollution Research* 2021, vol. 28, no. 9, pp. 10488–10502. Available from: <https://doi.org/10.1007/s11356-020-12263-0>
- [4] MOHAJERANI, A., et al. Practical recycling applications of crushed waste glass in construction materials: A review. *Construction and Building Materials*. 2017, vol. 156, pp. 443–467. Available from: <https://doi.org/10.1016/j.conbuildmat.2017.09.005>
- [5] BUENO, E.T., et al. A review of ground waste glass as a supplementary cementitious material: A focus on alkali-silica reaction. *Journal of Cleaner Production*. 2020, vol. 257, 120180. Available from: <https://doi.org/10.1016/j.jclepro.2020.120180>
- [6] TOGNONVI, M.T., et al. Reactivity of Recycled Glass Powder in a Cementitious Medium. *New Journal of Glass and Ceramics*. 2020, vol. 10, no. 03, pp. 29–44. Available from: <https://doi.org/10.4236/njgc.2020.103003>
- [7] MARAGHECHI, H., SHAFATIAN, S.-M.-H., FISCHER, G., RAJABIPOUR, F. The role of residual cracks on alkali silica reactivity of recycled glass aggregates. *Cement and Concrete Composites*. 2012, vol. 34, no. 1, pp. 41–47. Available from: <https://doi.org/10.1016/j.cemconcomp.2011.07.004>
- [8] LIU, G., FLOREA, M.V.A., BROUWERS, H.J.H. The hydration and microstructure characteristics of cement pastes with high volume organic-contaminated waste glass powder. *Construction and Building Materials*. 2018, vol. 187, pp. 1177–1189. Available from: <https://doi.org/10.1016/j.conbuildmat.2018.07.162>
- [9] PROŠEK, Z., et al. Surface modification of waste glass powder by plasma treatment: Impact on cement paste microstructure and strength development. *Construction and Building Materials*. 2025, vol. 485, 141693. Available from: <https://doi.org/10.1016/j.conbuildmat.2025.141693>
- [10] SUN, L., ZHU, X., KIM, M., ZI, G. Alkali-silica reaction and strength of concrete with pretreated glass particles as fine aggregates. *Construction and Building Materials*. 2021, vol. 271, 121809. Available from: <https://doi.org/10.1016/j.conbuildmat.2020.121809>
- [11] REMEŠ, Z., BABČENKO, O., JARÝ, V., BERANOVÁ, K. Enhanced Photoluminescence of Plasma-Treated Recycled Glass Particles. *Nanomaterials*. 2024, vol. 14, no. 13, 1091. Available from: <https://doi.org/10.3390/nano14131091>

- [12] THOMPSON, J.B., WASHBURN, E.R., GUILDNER, L. A. Adsorption of Carbon Dioxide by Glass. *The Journal of Physical Chemistry*. 1952, vol. 56, no. 8, pp. 979–981. Available from: <https://doi.org/10.1021/j150500a012>
- [13] KIM, J.M., et al. Control of hydroxyl group content in silica particle synthesized by the sol-precipitation process. *Ceramics International*. 2009, vol. 35, no. 3, pp. 1015–1019. Available from: <https://doi.org/10.1016/j.ceramint.2008.04.011>
- [14] TORRES-CARRASCO, M., PALOMO, J.G., PUERTAS, F. Sodium silicate solutions from dissolution of glasswastes. Statistical analysis. *Materiales de Construcción*. 2014, vol. 64, no. 314, e014. Available from: <https://doi.org/10.3989/mc.2014.05213>