

## WET CHEMISTRY TREATMENT AND SURFACE MODIFICATION OF RECYCLED GLASS PARTICLES FOR SUSTAINABLE CONSTRUCTION APPLICATIONS

<sup>1</sup>Oleg BABČENKO, <sup>1</sup>Klára BERANOVÁ, <sup>1</sup>Zdeněk REMEŠ, <sup>1</sup>Kateřina KOLÁŘOVÁ,  
<sup>1,2</sup>Jakub LÖRINC, <sup>1,3</sup>Jakub VOLF, <sup>2</sup>Zdeněk PROŠEK, <sup>2</sup>Pavel TESÁREK

<sup>1</sup>*Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, EU, [babcenko@fzu.cz](mailto:babcenko@fzu.cz)*

<sup>2</sup>*Faculty of Civil Engineering, Czech Technical University in Prague, Prague, Czech Republic, EU*

<sup>3</sup>*Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Czech Republic, EU*

<https://doi.org/10.37904/nanocon.2025.5016>

### Abstract

The surface contamination or bulk impurities in the matrix of soda-lime glass can significantly alter glass properties and via leaching influenced the alternative glass waste utilization as a partial replacement for sand or binder in concrete-based materials for sustainable construction applications. Therefore, in this work, we perform wet chemistry (different pH) treatment of the recycled glass particles obtained from the commercial source. The resulting changes in glass particle properties were analyzed using microscopic and spectroscopic techniques. Changes in the concentrations of Mg, Al, Ca and Na near the particle surfaces were detected, indicating potential elements release. For instance, treatment in HCl resulted in a decrease of all observed non-silica ions in the glass subsurface region while NaOH treatment resulted in a slight increase of Ca amount in the subsurface region which potentially can positively affect the calcium-silicate-hydrate formation in concrete-based constructions. The observed results can be helpful in the explanation of processes at interfacial transition zones in waste glass containing concrete-based materials.

**Keywords:** Soda-lime glass, wet chemistry, surface analysis, metal ions diffusion, civil engineering

### 1. INTRODUCTION

The natural resources exhausting, and issues of environmental pollution leads to increased demands for sustainable management and recyclable materials use. For instance, glass waste recycling in the glass industry, especially container glass, significantly reduces the need for raw materials and lowers energy consumption [1–3]. Moreover, since silica-based glass can be recycled many times retaining its properties it contributes positively to its overall environmental impact when considered in lifecycle assessments. On the other hand, the strict industry requirements for recycled glass quality/separation have resulted in large amounts of glass waste being dumped in landfills, creating environmental problems. With the aim of reducing glass waste landfilling, a variety of alternative recycling strategies was considered. It was proposed to use the waste glass for foam glass or glass wool fabrication, manufacturing of sandblasting media or filtration media for water treatment, road base material, partial replacement for sand or binder in concrete-based materials for sustainable construction applications [1]. Nevertheless, in many cases the contaminations or additives in waste glass that prohibit its recycling in glass industry may also limit the alternative recycling strategies.

Indeed, in the estimation of environmental pollution, glass is generally considered as non-biodegradable material with the landfilling as main environmental impact. However, the reaction of glass surface with water, especially if cracks in the glass are present, is known [4–6]. Therefore, diffusion of metal ions from glass waste, e.g. through reaction of glass in the form of shards or small fragments with rainwater, with leachate into the environment can be an important pollution issue as well [6–8]. Thus, the risk of pollutants release from the

waste glass via leaching must be taken into account as from the point of environmental pollution as from the point of alternative recycling strategies [8–11]. Moreover, glass treatment in alkaline or acidic liquids or melts can affect the composition of glass subsurface and thus its surface properties. In particular, the wet chemistry treatment of the waste glass and surface properties (chemistry or morphology) modification can be interesting for applications in the concrete-based materials and calcium-silicate-hydrate formation.

In the current study we perform the wet chemistry treatment of the recycled waste glass (WG) in the form of glass powder from the commercial source. We investigate the effect of WG interaction with mild acidic and/or alkaline solutions and study WG powder properties before and after wet chemistry treatment by microscopy and spectroscopy techniques. The observed WG surface and subsurface composition changes can be helpful in the explanation of processes in high alkalinity mixtures for sustainable concrete-based constructions.

## 2. EXPERIMENT

Ground waste glass powder from ordinary, recycled municipal glass waste (Recifa a.s.) was used in the experiments [12]. The deionized (DI) water and three different solutions with 0.25 M concentration of NaOH, KOH, and HCl were used for wet chemistry treatment. The WG powder was placed in the amount of 10 g to 100 ml of each treatment medium/solution and mixed by magnetic stir for 1 h. It follows by the 24 h sedimentation of WG powder. After sedimentation treatment solutions were removed from vessels and each glass powder was washed by DI water (short mixing by glass stick) with following 24 h sedimentation. The washing cycle was repeated 5 times after which treated WG powders were dried by natural water evaporation.

The result of WG powder interaction with used solutions was studied using Zetasizer Nano ZS – ZEN3600 equipped with multi-purpose titrator MPT-2 (Malvern Panalytical). The pH measurements of the treatment solutions and washing media (all after sedimentation) were performed. The measurements were supported by the conductometry data obtained using PWT conductivity tester (Hanna instruments).

Dry powder microstructure analysis was realized by scanning electron microscopy (SEM) using TESCAN MAIA3 microscope (TESCAN GROUP, a.s.). Analyzed powders were spread in a dense layer on sticky copper tape on solid support. The size, shape, and surface morphology of WG particles were analyzed at acceleration voltage 10 kV with secondary electrons detector. Additionally, mounted to SEM setup the energy dispersive X-ray (EDX) detector with IDFix analytical software was used to perform the basic elemental analysis of WG.

Fourier Transform Infrared (FTIR) spectroscopy was realized using the dry-air ventilated commercial Nicolet IS50 FTIR Spectrometer (Nicolet CZ, Ltd.). The FTIR absorption spectra (64 scan/spectrum with 4 cm<sup>-1</sup> spectral resolution) were collected using a built-in attenuated total reflectance (ATR) accessory with a diamond ATR prism, DTGS detector and solid substrate beamsplitter in 200-1800 cm<sup>-1</sup> spectral range (SiO<sub>2</sub> fingerprint region). The spectra in 400-4000 cm<sup>-1</sup> spectral range were collected additionally using a KBr beamsplitter. The absorbance spectra were spectrally corrected using built-in software (OMNIC Spectra Software).

The X-ray photoelectron spectroscopy (XPS) characterization of dry WG powders was performed using the AxisSUPRA photoelectron spectrometer (Kratos Analytical). The monochromatized Al K $\alpha$  (1486.6 eV) with emission of 10 mA, activated charge-compensation and resolution 20 was used for all measurements. Regions of the survey spectra containing main peaks of all elements were measured with passing energy of 80 eV for purposes of quantitative analysis. The atomic concentrations were calculated using KoLXPD software. Correction was performed according to Smith et al. [13], while 3.5 nm was used for the electron attenuation length of C 1s photoelectrons.

The excitation-emission photoluminescence mapping of dried WG powder was performed using Agilent Cary Eclipse Fluorescence Spectrophotometer. Maps were measured in 300–800 nm excitation range with 10 nm step and 320–1100 nm emission range with 1 nm step. Measured spectra were processed using OriginPro 2016 software (OriginLab Corporation) under the academic license.

### 3. RESULTS AND DISCUSSION

The measured pH values (within  $\pm 0.5$ ) and conductivity (2% accuracy) for WG powders (several minutes sedimentation after mixing) are summarized in **Table 1**. As it can be seen, adding WG powder to deionized water ( $H_2O$ ) resulted in an increase in pH and conductivity which indicates on induced exchange of sodium (mainly) and hydrogen ions in water [6, 9, 14]. A slight decrease of these values was observed after 24 h sedimentation, which continues with further washing. Nevertheless, the values remain high even after 5<sup>th</sup> water washing that indicates continued sodium and hydrogen ions exchange. Next, both alkaline solutions have comparable high pH values that are not changes after WG addition and even increase after 24 h sedimentation. With water washing pH and conductivity of solutions decreases till reach comparable values with water-treated WG. The 0.25 M HCl solution demonstrates low pH typical for acidic medium that again not changed after adding the WG powder or 24 h sedimentation. The following water washing purified the powder from acid rests, whilst the “final” pH value became as high as 8.4. The conductivity measurements of HCl treated WG after purification was also lower than for other solutions that probably can be related to decreased reactivity of HCl treated WG comparing to other (lower alkali-hydrogen ions exchange).

**Table 1** Measured pH and conductivity of treated WG powders

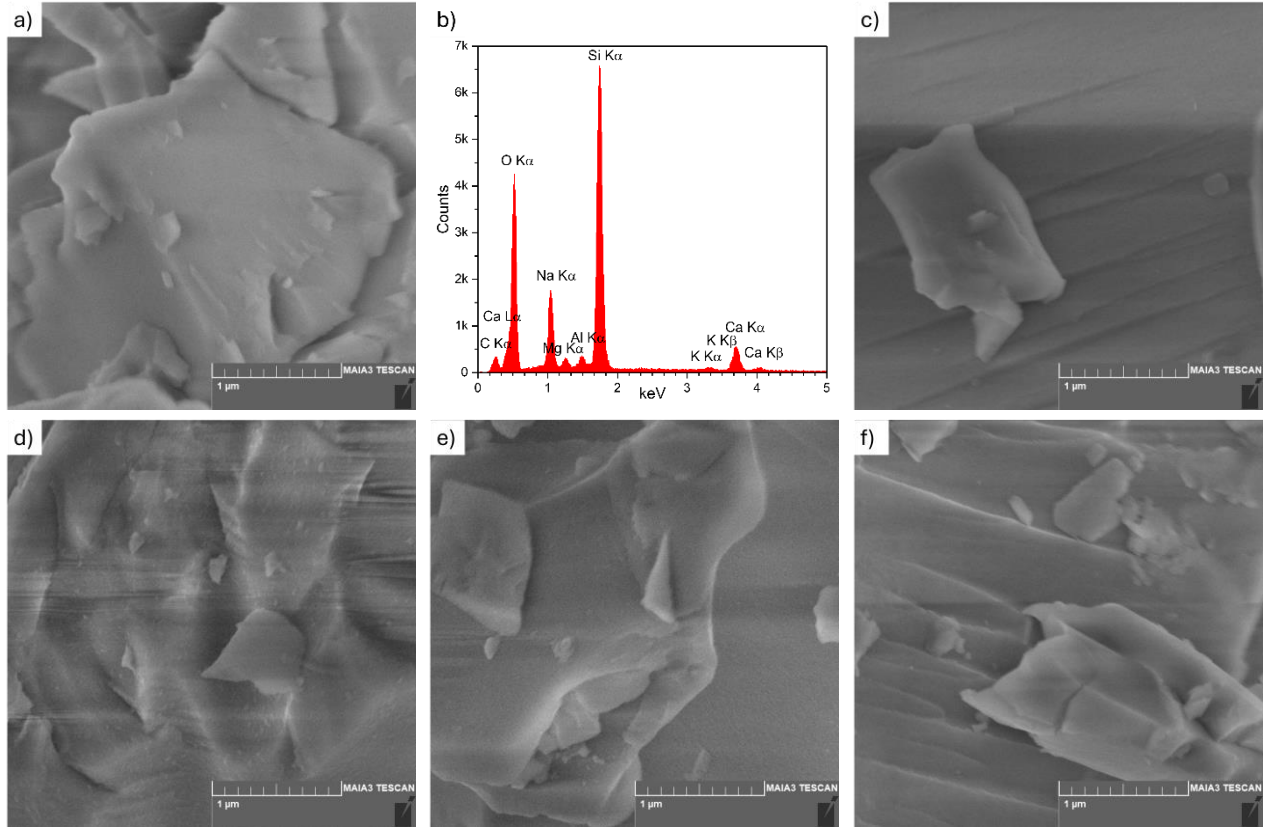
Liquid	$H_2O$		NaOH		KOH		HCl	
	pH	$\sigma$ ( $\mu S/cm$ )	pH	$\sigma$ ( $\mu S/cm$ )	pH	$\sigma$ ( $\mu S/cm$ )	pH	$\sigma$ ( $\mu S/cm$ )
Initial	5.3	4	13.3	165	13.4	160	1.6	155
WG add	10.5	155	13.3	165	13.4	160	1.6	155
1d stay	10.1	145	14.4	>200	14.4	>200	1.6	>200
1 <sup>st</sup> wash	9.8	115	13.2	145	13.0	145	1.8	130
5 <sup>th</sup> wash	9.2	80	9.8	85	9.6	80	8.4	70

In our earlier studies [12], we demonstrate that used untreated WG powder consist of particles with large size distribution (mean values  $36.0 \pm 0.2 \mu m$ ) with its large (up to  $50 \mu m$ ), irregular pieces with sharp edges decorated by the small fragments (tens of nanometers). Therefore, in this study the shown SEM images (**Figure 1**) were taken with high magnification and are focused on the analysis of WG surface morphology changes. The detailed SEM of untreated WG powder (**Figure 1a**) agrees with previous observation [12] and demonstrates flat surfaces of large particles with “scratches” or cracks related to grinding process as well as smaller WG fragments on surfaces.

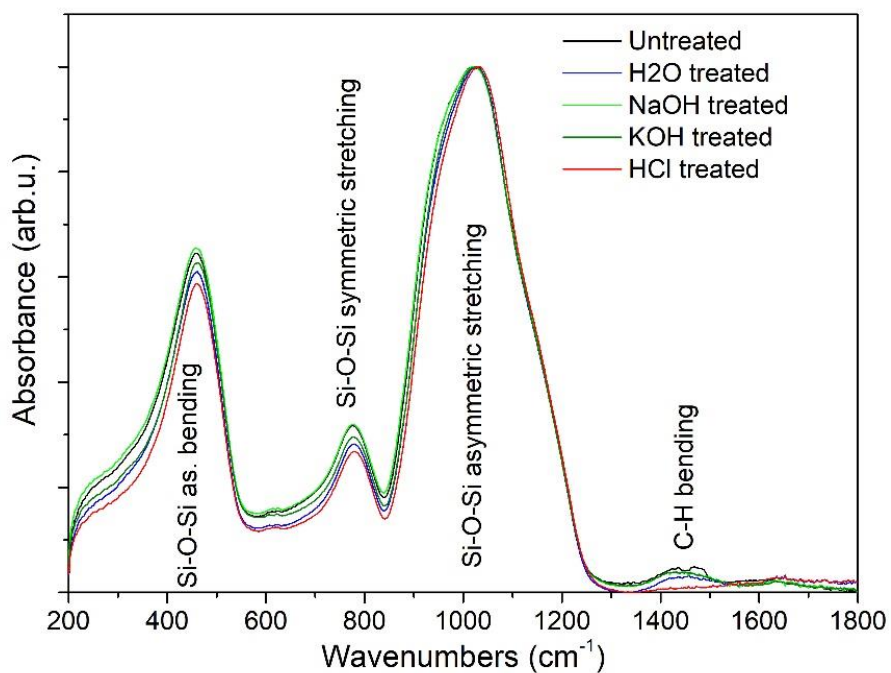
The performed EDX analysis of powders composition reveals expected high amount of Si and O elements (two of the strongest signal). Also, strong signal from Na and presence of Ca was observed, but also presence of Mg, Al, C and K were detected. However, since EDX depth resolution is in order of a few  $\mu m$  and the intensity of response signal from elements is energy sensitive and requires precise quantitative correction for estimation of samples composition, the observed data were taken as orientation for more surface precise analysis and here shown for the untreated sample only (**Figure 1b**). It must be added that presence of carbon has been directly or indirectly observed earlier [12, 15] and was related to WG surface contamination by organic residues which is not distinguishable by SEM.

Similar particles morphology (with “scratches” and cracks on large particles) as for untreated WG powder were found on water treated powder (**Figure 1c**). In the case of NaOH and KOH treated WG particles the high magnification SEM images (**Figure 1d, 1e**) demonstrate that the surface of particles is not smooth but slightly eroded (small cavities formed). These observations are in agreement with other works where alkaline solutions of high molarity decolorize or etch glass surfaces [14, 16]. This indicates the dissolving of WG matrix even in mild alkaline medium and its potential participation in calcium-silicate-hydrate formation in the concrete-based

materials. The last used solution was 0.25 M HCl with no evident changes of WG particles morphology comparing to untreated samples (**Figure 1f**).



**Figure 1** SEM image (a) and EDX spectrum (b) of untreated WG powder, and SEM images of WG powder treated in DI water (c), NaOH solution (d), KOH solution (e) and HCl solution (f).



**Figure 2** Infrared absorbance spectra of investigated dry WG powders

The normalized ATR FTIR spectra of analyzed powders are shown in **Figure 2**. As it can be seen, the measured IR absorbance spectra for untreated and wet chemistry treated WG powders are similar. The broad bands found in the spectra were attributed to Si-O-Si (in some cases noted just as Si-O) vibrations: asymmetrical bending at  $463\text{ cm}^{-1}$ , symmetrical stretching at  $788\text{ cm}^{-1}$ , and asymmetrical stretching at  $1082\text{ cm}^{-1}$  characteristic for amorphous (non-crystalline)  $\text{SiO}_2$  [5, 6]. The weak band at  $1450\text{ cm}^{-1}$  was attributed to C-H bending vibration that for HCl treated WG significantly decreases. This indicates possible removing of organic contaminates [15] from the WG particles surface.

The XPS analysis of WG powders was performed to investigate changes in WG subsurface composition and clarify the observations from other analytic methods. The calculated atomic concentration of chemical elements for studies samples is summarized in **Table 2**. Due to surface sensitivity of XPS method the highest elements concentration was observed for oxygen and carbon while all other elements (including Si) have lower signal. The treatment in DI water ( $\text{H}_2\text{O}$ ) or HCl resulted in a decrease of the carbon on WG surface (which corresponds to FTIR spectra shown in **Figure 2**) and increase of signal from oxygen. Contrariwise, treatment in KOH resulted in a higher percentage of carbon (probably adsorbed  $\text{CO}_2$  from air) and lower of oxygen in the total composition. The estimation of carbon layer thickness (d carbon in **Table 2**) as well as measured results correction can be performed according [13]. The calculations show that the estimated carbon layer thickness varies from 2.4 nm for KOH treated WG to 1.55 nm for HCl treated WG. As it was shown earlier, such layer can be efficiently detected by photoluminescence [15].

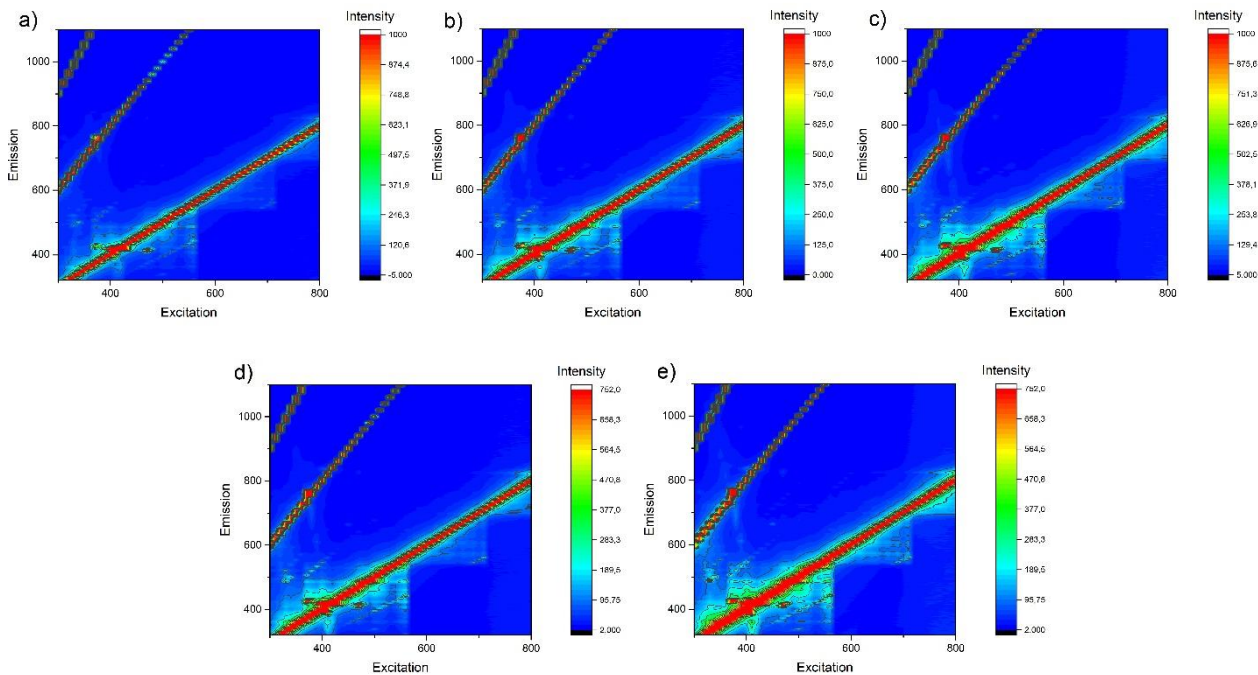
The significant change of chemical element amount after treatment was found for sodium that seems to be intensively washed out from the WG matrix (especially for HCl treated powder). These data correspond to pH and conductivity measurements that indicate a decrease of chemical reactivity of WG with treatment (especially in HCl case) and water washing (**Table 1**). The amount of Mg or Al in subsurface region slightly increases after DI water or alkaline solution treatment. Interestingly, that after NaOH treatment the amount of Ca on surface also slightly increases comparing to other treatment media, which can be beneficial for application in sustainable concrete-based constructions. Finally, it is important to note that potassium in the WG subsurface composition was below the detection limit of the spectrometer even after KOH treatment.

**Table 2** Atomic concentration of chemical elements derived from XPS and estimated carbon layer thickness.

WG treatment	Mg (at%)	Na (at%)	O (at%)	Ca (at%)	C (at%)	Si (at%)	Al (at%)	d carbon (nm)
Untreated	0.2	5.8	36.8	1.4	43.5	12	0.3	2.00
H <sub>2</sub> O	1	3.7	40.3	1.6	37.9	14.7	0.8	1.67
NaOH	0.7	3.6	36.4	2.4	44.2	12.2	0.4	2.04
KOH	0.6	3	32.8	1.6	49.7	11.6	0.6	2.41
HCl	0.1	2.5	42.9	0.8	35.8	17.6	0.2	1.55

Concerning the photoluminescence mapping, the lines related to first, second and third-order scattering maxima were clearly observed in the measured maps (**Figure 3**). The broadening of first order scattering line was observed in the region from 320 to 560nm excitation for wet chemistry treated samples. This broadening was stronger for NaOH and HCl pre-treated powder and probably should be related to eroded WG surface in the NaOH case (**Figure 1d**) and surface cleaned from carbon in the HCl case. The emission peaks around 414 nm at  $\lambda_{\text{ex}} = 470\text{ nm}$  and 426 nm at  $\lambda_{\text{ex}} = 370\text{ nm}$  were attributed to carbon layer of organic contaminants on the WG particles surface calculated from XPS measurement (**Table 2**) which is in agreement with [15].





**Figure 3** The excitation-emission photoluminescence maps of investigated WG powders: untreated (a), treated in DI water (b), NaOH solution (c), KOH solution (d) and HCl solution (e)

#### 4. CONCLUSION

Commercially available ground waste soda-lime glass powder was treated in different solutions. We observe that treatment in NaOH and KOH resulted in slight erosion of used non-crystalline WG particles due to surface etching that also affects the light scattering. Next, all treatment solutions resulted in a decrease of sodium amount in the WG subsurface region and thus decrease of sodium and hydrogen ions exchange in solutions. Treatment in DI water or 0.25 M HCl resulted in a decrease of organic residues (carbon) contamination of the WG surface. Moreover, treatment in HCl resulted in a decrease of all observed non-silica ions in the WG subsurface region reducing its reactivity while morphology of the WG particles is not changed. Treatment in KOH resulted in a higher amount of carbon on WG particles while no increase in potassium amount on the surface was observed. Treatment in NaOH, besides WG surface etching, resulted in a slight increase in amount of Ca in the subsurface region which potentially can positively affect the calcium-silicate-hydrate formation in concrete-based constructions. These findings create a good basis for investigation of treated WG particles interaction processes in cement-based mixtures used in civil engineering.

#### ACKNOWLEDGEMENTS

***The work was supported by the Czech Science Foundation project no 23-05500S. This work has used large research infrastructure CzechNanolab supported by the Ministry of Education, Youth and Sports of the Czech Republic through the project no. LM2023051.***

***The assistance of J. Libertínová with the SEM imaging is appreciated.***

#### REFERENCES

- [1] ADEKOMAYA, Oludaisi a Thokozani MAJOZI. Mitigating environmental impact of waste glass materials: review of the existing reclamation options and future outlook. *Environmental Science and Pollution Research* [online]. 2021, vol. 28, no. 9, pp. 10488–10502. ISSN 0944-1344, 1614-7499. Available from: <https://doi.org/10.1007/s11356-020-12263-0>

- [2] BERGER, Gregor, Zlatko RAONIC, Daniel FORTHUBER, Harald RAUPENSTRAUCH a Robert HERMANN. Energy and Material Flow Evaluation with CO<sub>2</sub> Emissions in the Glass Production Process. *Advances in Materials Physics and Chemistry* [online]. 2022, vol. 12, no. 05, pp. 82–105. ISSN 2162-531X, 2162-5328. Available from: <https://doi.org/10.4236/ampc.2022.125007>
- [3] BUTLER, John H. a Paul D. HOOPER. Glass Waste. In: *Waste* [online]. B.m.: Elsevier, 2019 [vid. 2023-08-18], pp. 307–322. ISBN 978-0-12-815060-3. Available from: <https://doi.org/10.1016/B978-0-12-815060-3.00015-3>
- [4] ZANINI, Roberta, Giulia FRANCESCHIN, Elti CATTARUZZA a Arianna TRAVIGLIA. A review of glass corrosion: the unique contribution of studying ancient glass to validate glass alteration models. *npj Materials Degradation* [online]. 2023, vol. 7, no. 1, 38. ISSN 2397-2106. Available from: <https://doi.org/10.1038/s41529-023-00355-4>
- [5] KIM, Jong Min, Sang Mok CHANG, Sung Min KONG, Kyo-Seon KIM, Jinsoo KIM a Woo-Sik KIM. Control of hydroxyl group content in silica particle synthesized by the sol-precipitation process. *Ceramics International* [online]. 2009, vol. 35, no. 3, pp. 1015–1019. ISSN 02728842. Available from: <https://doi.org/10.1016/j.ceramint.2008.04.011>
- [6] TORRES-CARRASCO, M., J. G. PALOMO a F. PUERTAS. Sodium silicate solutions from dissolution of glasswastes. Statistical analysis. *Materiales de Construcción* [online]. 2014, vol. 64, no. 314, e014. ISSN 1988-3226, 0465-2746. Available from: <https://doi.org/10.3989/mc.2014.05213>
- [7] TSAI, C.L., U. KROGMANN a P.F. STROM. Handling leachate from glass cullet stockpiles. *Waste Management* [online]. 2009, vol. 29, no. 4, pp. 1296–1305. ISSN 0956053X. Available from: <https://doi.org/10.1016/j.wasman.2008.10.013>
- [8] IMTEAZ, Monzur Alam, Mm Younus ALI a Arul ARULRAJAH. Possible environmental impacts of recycled glass used as a pavement base material. *Waste Management & Research: The Journal for a Sustainable Circular Economy* [online]. 2012, vol. 30, no. 9, pp. 917–921. ISSN 0734-242X, 1096-3669. Available from: <https://doi.org/10.1177/0734242X12448512>
- [9] BUNKER, B.C., G.W. ARNOLD, D.E. DAY a P.J. BRAY. The effect of molecular structure on borosilicate glass leaching. *Journal of Non-Crystalline Solids* [online]. 1986, vol. 87, no. 1–2, pp. 226–253. ISSN 00223093. Available from: [https://doi.org/10.1016/S0022-3093\(86\)80080-1](https://doi.org/10.1016/S0022-3093(86)80080-1)
- [10] TOGNONVI, Monique Tohoue, Arezki TAGNIT-HAMOU, Léon Koffi KONAN, Ablam ZIDOL a Wilfried Cyrille N'CHO. Reactivity of Recycled Glass Powder in a Cementitious Medium. *New Journal of Glass and Ceramics* [online]. 2020, vol. 10, no. 03, pp. 29–44. ISSN 2161-7554, 2161-7562. Available from: <https://doi.org/10.4236/njgc.2020.103003>
- [11] MARIÁKOVÁ, Diana, Klára Anna MOCO VÁ, Kristina FOŘTOVÁ, Tereza PAVLŮ a Petr HÁJEK. Waste Glass Powder Reusability in High-Performance Concrete: Leaching Behavior and Ecotoxicity. *Materials* [online]. 2021, vol. 14, no. 16, 4476. ISSN 1996-1944. Available from: <https://doi.org/10.3390/ma14164476>
- [12] BABČENKO, O, Z REMEŠ, K BERANOVÁ, K KOLÁŘOVÁ, J ČERMÁK, A KROMKA, Z PROŠEK a P TESÁREK. Characterization of different types of silica-based materials. *Journal of Physics: Conference Series* [online]. 2024, vol. 2712, no. 1, 012010. ISSN 1742-6588, 1742-6596. Available from: <https://doi.org/10.1088/1742-6596/2712/1/012010>
- [13] SMITH, Graham C. Evaluation of a simple correction for the hydrocarbon contamination layer in quantitative surface analysis by XPS. *Journal of Electron Spectroscopy and Related Phenomena* [online]. 2005, vol. 148, no. 1, pp. 21–28. ISSN 03682048. Available from: <https://doi.org/10.1016/j.elspec.2005.02.004>
- [14] MARAGHECHI, Hamed, Farshad RAJABIPOUR, Carlo G. PANTANO a William D. BURGOS. Effect of calcium on dissolution and precipitation reactions of amorphous silica at high alkalinity. *Cement and Concrete Research* [online]. 2016, vol. 87, 1–13. ISSN 00088846. Available from: <https://doi.org/10.1016/j.cemconres.2016.05.004>
- [15] REMEŠ, Zdeněk, Oleg BABČENKO, Vítězslav JARÝ a Klára BERANOVÁ. Enhanced Photoluminescence of Plasma-Treated Recycled Glass Particles. *Nanomaterials* [online]. 2024, vol. 14, no. 13, 1091. ISSN 2079-4991. Available from: <https://doi.org/10.3390/nano14131091>
- [16] SUN, Lianfang, Xingji ZHU, Minjae KIM a Goangseup ZI. Alkali-silica reaction and strength of concrete with pretreated glass particles as fine aggregates. *Construction and Building Materials* [online]. 2021, vol. 271, 121809. ISSN 09500618. Available from: <https://doi.org/10.1016/j.conbuildmat.2020.121809>