1ST INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS
MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
M. Bogataj, Z. Kravanja & Z. Novak Pintarič (eds.)

University of Maribor Press

Upcycling with alkali activation technology

BARBARA HORVAT, MARK ČEŠNOVAR, ALENKA PAVLIN &
VILMA DUCMAN

Abstract In 2017 Termit and ZAG started a project where various waste materials containing enough SiO_2 and Al_2O_3 will be up-cycled into porous lightweight insulating alkali activated foams with potential to be used in the building industry. From several tested abundant waste materials from Termit focus in this article is on rock and glass wool. Glass wool had 2-times higher compressive strength from rock wool, which is due to its better dissolution in alkali media. However, both wools were selected for further experimental work.

Keywords: • alkali activated material • mineral wool • compressive strength • upcycling • circular economy •

CORRESPONDENCE ADDRESS: Barbara Horvat, Slovenian National Building And Civil Engineering Institute, Department for materials, Dimičeva ulica 12, 1000 Ljubljana, Slovenia, e-mail: barbara.horvat@zag.si. Mark Češnovar, Slovenian National Building And Civil Engineering Institute, Department for materials, Dimičeva ulica 12, 1000 Ljubljana, Slovenia, e-mail: mark.cesnovar@zag.si. Alenka Pavlin, TERMIT, Drtija 51, 1251 Moravče, Slovenia, e-mail: alenka.pavlin@termit.si. Vilma Ducman, Slovenian National Building And Civil Engineering Institute, Department for materials, Dimičeva ulica 12, 1000 Ljubljana, Slovenia, e-mail: vilma.ducman@zag.si.

DOI https://doi.org/10.18690/978-961-286-211-4.22 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

In 2017 Termit started circular economy project, where various waste materials were tested for the suitability for up-cycling into porous lightweight insulating alkali activated materials/foams that could be used in the building industry.

Focus was on the waste materials that are in abundance and showed high enough compressive strength after alkali activation. Among several tested waste materials from mixture of bottom and fly ash, raw material for ceramics, slag, foundry sand etc. both wools, i.e. rock and glass, were also examined. Both mineral wools represent health hazardous waste material (National Toxicology Program, Headquartered at the National Institute of Environmental Health Sciences NIH-HHS, 2017) in building industry after demolition of buildings. Since now the mineral wool waste material is discarded in municipal waste dumps (Väntsi, 2014) and using it back in the circular economy would not just benefit economy, but also nature with lowering the waste in municipal waste dumps, and animal and human health with complete incorporation of mineral wool fibres in alkali activated materials.

So far there were few researches done on mineral wool used in alkali activated synthesis (Yliniemi, 2016), in combination with fly ash (Kinnunen, 2016), in combination with metakaolin (Elijah, A. D., 2015, Master Theis).

The aim of the present study is thus the assessment of mineral wool for further (re-) use in construction sector.

1.1 Introduction into alkali activation technology (AAT)

Alkali-activated materials (AAM), often called geopolymers, are produced from precursors containing SiO_2 and Al_2O_3 in sufficient quantities and in reactive/glassy form (e.g. ashes, slags, metakaolin...), and alkaline activators, such as NaOH, KOH, Na-water glass, K-water glass). When precursors and activators are mixed, first dissolution and transport of the components (Al, Si) in the alkaline activators takes place, and then through poly-condensation of the Al and Si, an aluminosilicate network is formed. Many products can be obtained by the alkaline activation process which could replace traditional construction products (Provis et al., 2010, Zhang et al., 2014). They range from blocks, slabs, pavingstones, curbs, and partitions to refractory materials and materials for specific industrial applications (e.g. insulation plates).

And if waste material is used for their production, significant contribution to the reduction of the CO_2 footprint can be demonstrated comparing such material to cement, concrete or ceramic.

The technology of alkali-activated materials makes a promising alternative material production for civil engineering purposes because of the advantages such as low processing costs, satisfactory physical properties, high temperature stability, and fire and corrosion resistance in comparison with traditional construction materials. The properties of AAM are strongly affected by the content of reactive SiO_2 and Al_2O_3 in precursor, by the type and amount of alkali activator, and curing regime (Hajimohammadi et al., 2017). To achieve the synthesis of AAM with good mechanical properties, the right precursor to alkaline activator ratio needs to be determined. Different proportions of activator are added to precursor in order to study the alkali reaction products and characteristics such as mechanical properties of AAM. Chemical and mineralogical characterization (XRD, XRF, EDXS…) of precursor and viscosity measurement of mixtures can also be helpful tool for determination of influence of the alkali activator and its optimal amount for alkali activation reaction with precursor material. Properties of AAM are also affected by the curing regime, such as drying at room or elevated temperatures with different period of time.

2 Experimental

Sufficient amounts of rock and glass wool, presented in **Table 1** (with laboratory sample name, description of the sample and waste label from the Classification list of waste from Official Gazette of the Republic of Slovenia, no. 20/01 Annex 1) were collected from Termit's open waste dumps for research on a laboratory scale.

Table 1: Analysed Termit's samples collected from waste dump piles.

Laboratory sample label	Sample	Waste label
V-171/17	Glass wool	17 09 04
V-222/17	Rock wool	17 09 04

Source of labels: Official Gazette of the Republic of Slovenia, no. 20/01 Annex 1

Both collected samples were dried on 70 °C for 24 h in WTB Binder dryer. For X-ray fluorescence (XRF) and X-ray powder diffraction (XRD) analysis samples were further dried with measuring the moisture content with IR dryer at 105 °C to constant mass, and were afterwards grinded in vibrating disk mill (Siebtechnik) and sieved below 90 μm.

XRD analysis was performed (Empyrean PANalytical X-Ray Diffractometer, Cu X-Ray source) under same conditions for both samples: measuring in step 0.0263° from 4° to 70° angle, under cleanroom conditions, in powder sample holders with aperture diameter 27 mm. Mineral analysis, Scherrer size of crystallite domains, estimation of amount of amorphous phase and minerals with Rietveld refinement with external standard (pure Al_2O_3 crystal) were performed with X'Pert Highscore plus 4.1 on XRD data.

For XRF analysis (Thermo Scientific ARL Perform'X Sequential XRF) powder samples were first treated for 2 h at 950 °C in furnace (Nabertherm B 150) to remove organic compounds and CO_2, then mixed with Fluxana (FX-X50-2, Lithium tetraborate 50 % / Lithium metaborate 50 %) in ratio 1:10 for Fluxana to lower melting temperature. Mixture of Fluxana and glass wool was melted into discs at 1025 °C for 7 min, while mixture of Fluxana and rock wool was melted at 1075 °C for 9 min, both in furnace Claisse, The Bee Electric Fusion (few drops of LiBr were added to avoid gluing of melt in the platinum vessel). XRF analysis was performed with program OXAS on melted disks, while data were characterized with program UniQuant 5.

Loss of ignition at 950 °C was determined with gravimetric method from 2 parallel measurements and corrected with XRF analytical loss of ignition obtained on the fused basis.

For scanning electron microscopy (SEM; Jeol JSM-5500LV with tungsten filament cathode as electron source) and energy dispersive X-ray spectroscopy (EDXS; Oxford Instruments, Link Pentafet) investigation under low vacuum conditions both samples were dried, grinded and sieved below 90 μm.

On the fibers, dried and sieved below 250 μm (to add additional strength to final product with longer fibres no wool was sieved below 90 μm) mineral wools preliminary alkali activation test was performed. 10 M NaOH (Donau Chemie Ätznatron Schuppen, EINECS 215-785-5) was added to Na-glass (Geosil, 344/7, Woelner) in ratio 1:1, stirred until liquid became clear, poured into the sample under constant mixing. Ratio sample:NaOH:Na-glass was determined with viscometer (Haake PK 100, VT 500, PK2 1.0°), i.e. dry material was added into liquid mixture until viscometer could not measure the viscosity due to overload of torque, to maintain as uniform distribution of synthesized material as possible, and at the same time to have enough liquid phase for solid material to be in contact with alkali activator.

Samples with pre-determined ratio (precursors to activators) were moulded into prisms of 80x20x20 mm^3, and after solidification characterized by XRD (synthesized material was grinded and sieved below 90 μm), SEM and EDXS. Compressive and bending strength were measured with compressive and bending strength testing machine (ToniTechnik ToniNORM) 3 months after synthesis.

3 Results and discussion

Moisture content after drying on 70 °C for 24 h and ignition losses at 950 °C are presented in Table 2.

Table 2: Moisture content after drying on 70 °C for 24 h and loss of ignition determined with gravimetric method and calculated from XRF data.

Laboratory sample label	Moisture [%]	LOI (950 °C)	LOI (XRF)
V-171/17	2,2	8,5	9,4
V-222/17	1,1	4,7	5,5

Ignition loss of rock wool is ca. 80 % higher compared to ignition loss of rock wool saying that glass wool has higher organic and carbonate content comparing to rock wool. (Heiri, 2001)

3.1 Chemical and mineralogical analysis

With XRF analysis amount of different oxides was followed. Results where mass percent of oxides is close or above 0,1 % are presented in **Table 3**.

Table 3: Mass percentage of oxides measured with XRF.

Laboratory sample label	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**BaO**
V-171/17	16,5	3,7	2,5	65,9	0,3	7,1	0,1		0,6	
V-222/17	2,1	9,8	17,3	43,5	0,8	16,8	1,3	0,3	6,7	0,07

Both samples had among detected oxides highest amount of SiO_2, glass wool even 50 % more than rock wool. Glass wool had more than 15 % of Na_2O, and more than 5 % of CaO. Rock wool had more than 15 % of Al_2O_3 and CaO, almost 10 % of MgO, and more than 5 % of Fe_2O_3. All other detected oxides were present in the samples in less than 5 %.

Minerals determined with XRD before and after alkali activation are presented in **Table 4**. Both precursors contained more than 90 % of amorphous phase, rock wool even more than 95 %, according to Rietveld refinement (pt), meaning most of SiO_2 detected with XRF in the initial materials was amorphous and easily available for reaction. Common mineral to both wool precursors is quartz, represented in glass wool in quantity of 5 mass %, and in rock wool in quantity of 3 mass %. Glass wool contains also small amount of calcite and dolomite.

After alkali activation of glass wool calcite dissolves completely, quartz crystallites start to dissolve according to Scherrer equation (crystallite domains shrink from 140 nm to 70 nm), dolomite breaks into smaller crystals or/and new smaller crystals form (there is 10-times more dolomite after alkali activation than before). Beside dolomite formation also thermonatrite forms and amount of amorphous phase lower significantly.

Alkali activation of rock wool leaves quartz intact and forms thermonatrite, almost 3-times bigger crystallites than in case of alkali activated glass wool, but 4-times less amount. Amount of amorphous phase stays high also after alkali activation.

Table 4: Percentage (pt) of minerals and amorphous phase in glass and rock wool and their alkali activated counterparts according to the Rietveld refinement; and size of crystallite domains estimated with Scherrer (S). Extra preparation of precursor is mentioned next to the sample's label.

Mineral		**Quartz**	**Calcite**	**Dolomite**	**Thermonatrite**	**Amorphous phase**
Chemical formula		SiO_2	$CaCO_3$	$CaMg(CO_3)_2$	$Na_2CO_3{\cdot}H_2O$	/
Mohs hardness scale [M]		7	3	3,5-4	1-1,5	/
V-171/17 Before AA	pt [%]	5,6	0,6	1,4		92,4
	S [nm]	140	60	90		
V-171/17, dried, milled, 250 µm After AA	pt [%]	4,6		15,5	10,7	69,2
	S [nm]	70		30	30	
V-222/17 Before AA	pt [%]	3,2				96,8
	S [nm]	130				
V-222/17, dried, milled, 250 µm After AA	pt [%]	2,3			2,5	95,2
	S [nm]	130			80	

3.2 Mechanical analysis

Compressive strength as one of the most important properties in building industry is presented in **Table 5**, with bending, shrinkage of width and length of optimally prepared prism, i.e. optimized value of ratio precursor vs. alkali vs. alkali glass according to viscosity measurements was for glass wool 1,5:1:1 and for rock wool 2:1:1.

Table 5: Mechanical properties of alkali activated material prepared from mineral wools.

Laboratory sample label	Ratio P:NaOH:Na-glass	Shrinkage length [%]	Shrinkage width [%]	Bending strength [N/mm]	Compressive strength [N/mm^2]
V-171/17	1,5:1:1	0,7	1,4	7,2	18,4
V-222/17	2:1:1	2,3	3,9	1,7	10,1

Glass wool in comparison to rock wool had almost 3-times lower shrinkage, 4-times higher bending strength and almost 2-times higher compressive strength.

3.3 Microstructural analysis

SEM and EDXS of grinded and sieved below 90 µm glass wool is presented on **Figure 2**. It consists of cylindrical rods, fibres, of various diameters.

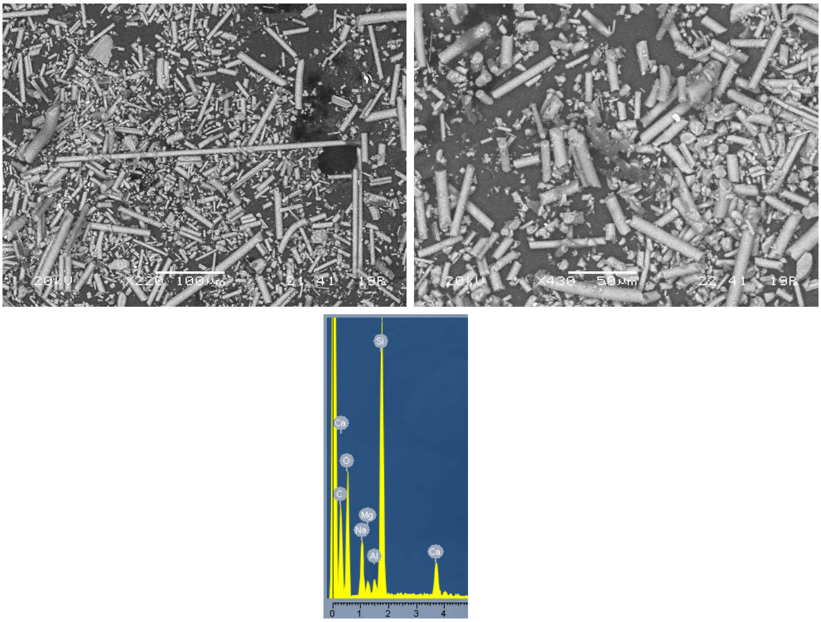

Figure 2: Left and middle: SEM micrographs of grinded and sieved below 90 µm glass wool showing elongated particles. Right: EDXS spectrogram of glass wool.

SEM and EDXS of grinded and sieved below 90 µm rock wool is presented on **Figure 3**. It consists of cylindrical rods, fibres, of various diameters and larger particles of various shapes used in mineral wool synthesis.

Also according to EDXS rock wool contains Fe, while glass wool does not. All other elements are present in both mineral wools. As expected, glass wool contains far more Si comparing to other elements, and very small amount of Al. Sum of Na and Ca is in the sample far greater than amount of Al, meaning that precursor has already enough ions with which inadequate coordination number of Al in the matrix is compensated, and from additional amount of Na crystals can form (thermonatrite).

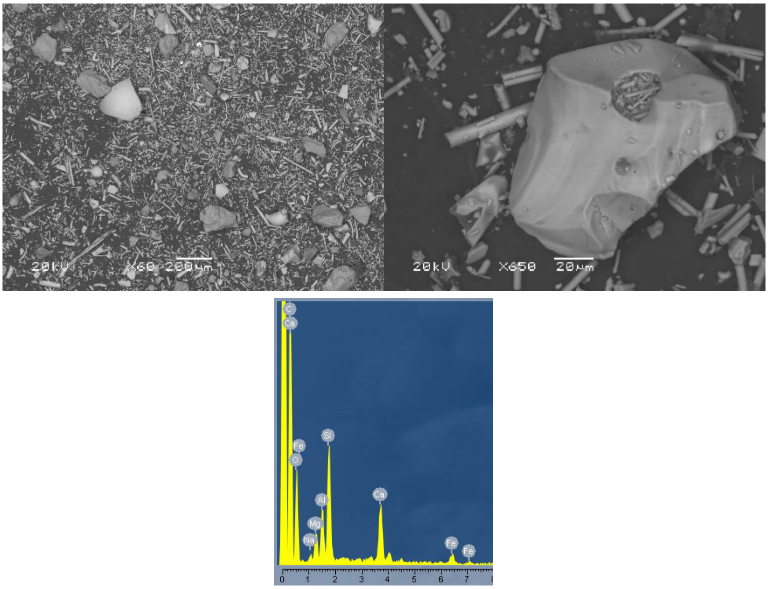

Figure 3: Left and middle: SEM micrographs of grinded and sieved below 90 µm rock wool showing elongated and random-shape particles. Right: EDXS spectrogram of rock wool.

On the other hand rock wool has significant amount of Al, which is far greater than amount of Na, meaning that addition of Na ions in alkali activated synthesis is required for compensation of Al extra bond in the alumo-silicate matrix. When using both mineral wools as precursors, thermonatrite crystals formed, but in case of glass wool the amount of thermonatrite was 4-times greater comparing to rock wool due to amount of initial Na comparing to Al, and due to added amount of Na that was bigger (molarity of alkali was constant) in case of glass wool (estimated surface for glass wool was 10-times higher to rock wool and therefore more liquid was required to wet the surface). Added Na could have been much smaller due to abundance of Na, meaning it is possible to lower molarity of alkali, which is beneficial for environment. The formation of thermonatrite would have been avoided or at least minimized, and it is to be expected that compressive strength due to thermonatrite's low Mohs hardness number would be greater.

SEM of alkali activated glass wool is presented on **Figure 4**. Initial fibres seem to be well incorporated in the matrix, giving it additional strength in all directions due to its random orientation because of low or no mechanics of continuum during alkali activated synthesis.

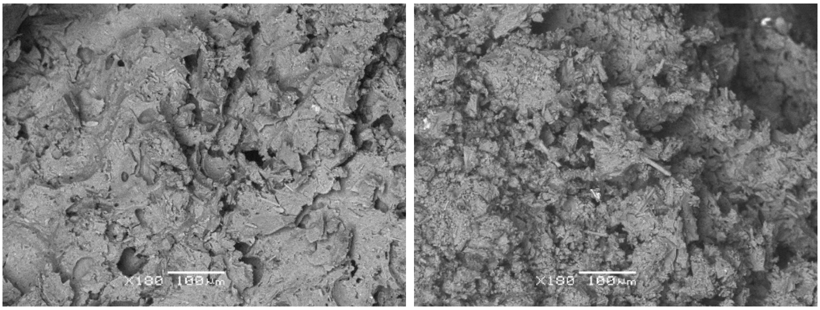

Figure 4: SEM micrographs of matrix from alkali activated glass wool.

SEM of alkali activated rock wool is presented on **Figure 5**. Initial fibres are less incorporated in the matrix when compared to alkali activated glass wool. Throughout the matrix larger particles, presented already in the precursor, did not react with alkali and its surface is not covered with matrix.

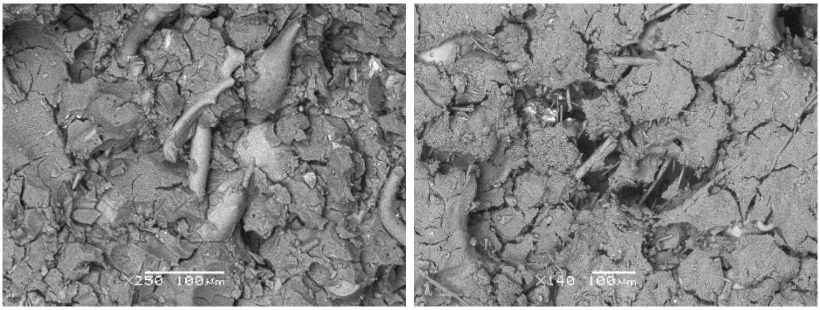

Figure 5: SEM micrographs of matrix from alkali activated rock wool.

4 Conclusion

Alkali activation of both rock and glass wool showed promising results for further research due to high enough compressive strength, i.e. alkali activated glass wool had compressive strength 18 MPa and rock wool 10 MPa (in agreement with (Kinnunen, 2016)) with optimizing only viscosity of alkali activated material at the beginning of reaction. According to (Yliniemi, 2016) glass wool had higher maximal reached compressive and bending strength comparing to rock wool, which is in agreement with our research. Glass wool had approximately 2-times higher compressive strength comparing to the rock wool due to the better dissolution of glass wool's components in alkali media and better embedment of not completely dissolved remainings in the matrix.

With up-cycling waste mineral wools not only that those health dangerous fibres are well incorporated in the matrix, which does not enable inhaling them, but also waste material becomes source material again and gets back into economy circle, which is aim of Termit's research in project with ZAG.

Acknowledgments

Project No. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" was granted by Ministry of Education, Science and Sport of Republic of Slovenia. The investment is co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport and the European Regional Development Fund.

The Metrology Institute of the Republic of Slovenia is acknowledged for the use of XRF.

References

National Toxicology Program, Headquartered at the National Institute of Environmental Health Sciences NIH-HHS (2017). Certain Glass Wool Fibers (Inhalable)

Väntsi, O., Kärki, T. (2014). Mineral wool waste in Europe: a review of mineral wool waste quantity, quality, and current recycling methods. *Journal of Mater Cycles Waste Management, 16*, 62-72. doi: 10.1007/s10163-013-0170-5

Yliniemi, J., Kinnunen, P., Karinkanta, P., Illikainen, M. (2016). Utilization of Mineral Wools as Alkali-Activated Material Precursor. *Materials, 9*, 312. doi:10.3390/ma9050312

Elijah, A. D. (2015). Fibre-reinforced mineral wool geopolymer composites. Master Thesis, Faculty of Technology, University of Oulu

Heiri, O., Lotter, A. F., Lemcke, G. (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments - reproducibility and comparability of results. *Journal of Paleolimnology, 25*, 101-110. doi:10.1023/A:1008119611481

Kinnunen, P., Yiniemi, J., Talling, B., Illikainen, M. (2016). Rockwool waste in fly ash geopolymer composites. *Journal of Material Cycles Waste Management, 19*, 1220-1227. doi: 10.1007/s10163-016-0514-z

Provis, J.L., Duxon, P., van Deventer, J.S.J. (2010). The role of particle technology in developing sustainable construction materials. *Advanced Powder Technology, 21*, 2-7. doi: 10.1016/j.apt.2009.10.006

Zhang, Z., Provis, J.L., Rei,d A., Wang, H. (2014). Geopolymer foam concrete: An emerging material for sustainable construction. *Construction and Building Materials, 56*, 113–127. doi: 10.1016/j.conbuildmat.2014.01.081

Hajimohammadi, A., Ngo, T., Mendis, P., Kashani, A., S.J. van Deventer, J. (2017). Alkali activated slag foams: The effect of the alkali reaction on foam characteristics. *Journal of Cleaner Production 147,* 330-339.