CEST 2021

17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

Performance evaluation of flue gas cured calcium rich fly ash based building blocks

USTA M.C.[1*], ADEGBILE A. M.[1], GREGOR A.[1], PAAVER P.[2], HAIN T.[3], YÖRÜK C.R. [1], UIBU M.[1] and TRIKKEL A.[1]

[1]Department of Materials and Environmental Technology, Tallinn University of Technology, 19086 Tallinn, Estonia
[2] Department of Geology, University of Tartu, 50411 Tartu, Estonia
[3] Department of Civil Engineering and Architecture, Tallinn University of Technology, 19086 Tallinn, Estonia

*corresponding author: Mustafa Cem Usta
e-mail: mustafa.usta@taltech.ee

Abstract This work focuses on the local alkaline wastes of Estonia where different waste streams were studied for the performance testing of the fly ash based building blocks. Fly ash from oil shale direct combustion and wood fly ash from district heating plant were considered in the applications for utilizing both CO_2 and combustion residues. These types of ashes contain Ca/Mg-oxides, silicates, or other metal oxides as candidate precursor materials for CO_2 mineralization. Based on the results obtained from the performance testing of all compacted and carbonated (both with model flue gas and 100%CO_2) samples, it can be concluded that flue gas curing can be an effective method for direct mineral carbonation of compacted fly ash blocks. The formation of carbonate phases in compact bodies lead to an increase in compressive strength. The rate limiting impact due to the low CO_2 concentration in flue gas curing was negligible on the CO_2 uptake level when elevated curing pressures were applied to the fly ash based compacts.

Keywords: Fly ash**,** accelerated carbonation, CO_2 mineralization.

1. Introduction

The chemical composition of solid fossil fuel combustion residues presents a wide range of opportunities for circularity in power production sectors by ash utilization applications. In principle, ashes containing a high amount of calcium could be useful for both capture and permanent sequestration of CO_2 through the formation of $CaCO_3$. Such types of ash are classified as class C type of ashes and originate from subbituminous and lignite coals. Other ashes containing high amounts of calcium are oil shale ash (OSA) and forestry wood ash (WA) which are also intensively used in power and heat production. The ash content of typical oil shale (OS) is much higher than the coals, although the ash content in solid biofuels is much smaller. Nevertheless, the processing of both OS and forestry fuels in power and heat production are well-established in Estonia and the generation of ashes on a large scale are becoming an important environmental problem. Huge quantities of CO_2 and alkaline solid wastes (ASW), mainly OSA and WA, are generated and disposed from energy sectors in Estonia [Uibu et al. 2009]. Fly ash (FA) as a mainly landfilled waste constitutes approximately 70% of total residues generated by power plants. FA can be found in small particle size and reactive nature (with respect to CO_2 mineralization and self-cementitious properties) [Usta et al. 2020]. As a result of long-term targets including 2050 climate goals of Estonia [Ministry of the Environment, 2019], there is a need to evaluate all mineral carbonation potential for local ASWs in order to lower the environmental burdens. Technologies including the utilization of both CO_2 and ASWs, mainly the applications for the production of building materials, enable easier and more feasible switch to the circular economy concepts. Therefore, twofold solution can be considered as a result of recent progresses made in accelerated carbonation technologies (ACT) [Tan et al. 2020, Chiang et al. 2017]; the first is CO_2 capture and storage from FG via CO_2 mineralization with FAs and the second is valorization of these FAs for the production of alternative hardened/building materials. In this respect, the use of FG and local available FAs was evaluated via direct gas-solid carbonation (form of mineral carbonation) at different curing pressures in order to investigate mechanical performance of FA based blocks and the effects on the final CO_2 uptake with related strength development of compacts.

2. Materials and methods

2.1. Selection and Characterization of fly ashes

Two different types of ash samples were selected from Estonia (OSA and WA). OSA was obtained from Auvere power plant which is operated by the direct combustion of OS in CFB boiler for power production, and ash was collected from the electrostatic precipitators. WA was obtained from Utilitas district heating plant which is operated by forestry wood (mix of pine chips and bark residues) and ash was collected from bag filters located in post-combustion zones of grate combustor.

Mean sample was taken from each collected ash for material characterization. The physical material characterization was carried out with particle size distribution (PSD) and specific surface area (SSA) analyses. The particle size distribution of the initial samples was analyzed using laser scattering PSD Analyzer LA-950 (HORIBA). The BET-N_2 sorption method was used to measure the specific SSA with Kelvin 1042 sorptiometer. The chemical material characterization was carried out using the Bruker D8 Advanced X-ray Fluorescence (XRF) spectroscopy and X-ray Diffraction (XRD) at the department of Geology in Tartu University. The thermogravimetric analysis (TGA) was also carried out to obtain thermal characterization of both the initial and the carbonated samples by using the Setaram Labsys 2000 thermoanalyzer (20K/min, 21%O_2/79%Ar). The initial and carbonated samples were analyzed also with FT-IR spectrometer ALPHA to compare mineralogical changes. FT-IR measurements were recorded in the 400–4000 cm−1 region. The compressive strentgh measurements were performed with Toni TechnikD-13355.

Physical characterization

OSA and WA samples have relatively high BET SSA of 2.78 m^2/g and 3.23 m^2/g, respectively which can indicate higher carbonation ability since the carbonation reaction is promoted by the presence of a higher number of sites available in the initial material [Arandigoyen et al. 2006]. Although the SSA of WA was higher than OSA, due to its biomaterial nature as raw fuel it was revealed that the median particle diameter was 54,6µm for WA and 23.4µm for OSA.

Chemical characterization

Low-grade fossil fuels such as lignite coal and OS generate Ca-rich ash, that contains 5 – 25% free lime and can be suitable for mineral sequestration of CO_2 [Uibu et al. 2010, Bauer et al. 2011]. According to XRF analysis, the share of Ca- and Si-compounds in OSA and WA is higher than 60% (see Table 1). XRD analysis has shown that OSA and WA both have considerable content of lime, secondary Ca-silicates (a bit lacking for WA) and portlandite which are attributed as potential carbonation activated binders (see Table 2).

Table 1. Chemical Composition in percentile

Component	OSA	WA
SiO_2	29.38	18.08
Al_2O_3	9.58	2.73
TiO_2	0.578	0.19
Fe_2O_3	5.12	1.17
MnO	0.067	0.32
CaO	34.67	44.44
MgO	3.12	2.82
Na_2O	0.12	0.52
K_2O	3.91	7.69
P_2O_5	0.128	4.14
SO_3	4.96	4.35
L.O.I.	7.73	12.79

2.3. Preparation of compacts

In the first step the hydrated samples have been prepared with liquid to solid ratio of 0.25 w/v in a semi-batch Eirich EL1 type intensive mixer. The samples were homogeneously blended with water at the fixed rotation speed and time. Three sample batches were prepared without any additives: OSA (100%), WA (100%) and OSA/WA with mix-design ratio of 50/50. The samples were left to hydrate/cure in sealed bags overnight at room temperature and compacted on the following day using a hydraulic press into cylinders with diameter 20 mm and height 20 mm. Two different compaction pressures were applied to investigate the effect of compaction pressure on CO_2 uptake and strength of compacts. The compaction pressure of 150±10 kg/cm^2 was applied for samples cured at 5 and 10 bars and 300±10 kg/cm^2 for the samples cured at 15 bars. Carbonation experiments were performed in automated carbonation unit (stainless-steel chamber) consisting of temperature and gas controlling and monitoring apparatus (buchi pressflow gas controller-bpc). The gas mixture used for FG had a composition of $N_2/CO_2/O_2$-78/16/6% simulating the typical exhaust gas from a fossil fuel power generation plant. The carbonation tests were carried out at room temperature by applying 100% CO_2 and model FG (for comparison) at pressure levels of 5, 10 and 15 bar for curing time of 2 hours each. In order to maintain stable CO_2 concentration during FG curing, flushing and refilling steps were followed in every 20 min.

Table 2. Phase Composition in percentile

Component	OSA	WA
Quartz	15	7.5
K-feldspar	14.2	3.2
Plagioclase	0.7	0
Mica	3.6	0
Calcite	9.8	27.7
Lime	17	20.3
Portlandite	1.4	3
Periclase	4.2	2.9
Anhydrite	9.3	0
C2S	13.9	4.1
Merwinite	3.2	4.3
Akermanite	4.5	3.8
Sylvite	0	1.7
Arcanite	0	8.6
Hematite	2.3	0
Apatite	0	12.6

3. Results and Discussions

The weight increase after carbonation takes place as a result of mineralized CO_2 in the form of $CaCO_3$. The thermal decomposition of $CaCO_3$ to calculate the net CO_2 uptake can be followed by TGA curves (600-800°C) in figure 2 (all results are also given in Table 3). It is important to point out that both ashes include $CaCO_3$ already in their initial forms. The full disappearance of portlandite (existing and formed after hydration) has not been achieved in two hours of FG curing especially at low curing pressures (5bar, see Fig. 2). It can clearly be seen from mass loss curves of both OSA and WA compacts cured at 5 bar that there is still small amount of portlandite left un-carbonated. With the increase of gas pressure (15 bar) in FG curing mass loss step regarding portlandite decomposition (400-500°C) disappears (Fig. 2) and final

CO_2 uptake increases (Table 3). However, comparison of different curing pressures under 100%CO_2 indicated that CO_2 uptake level is not strongly dependent on a curing pressure, especially for OSA as the CO_2 uptake values are around 9 to 10 kg/ton of block in all curing stages. The gas monitoring curves indicate similar trend for OSA cured at 5 and 10 bar. In general, carbonation reaction happens at two different rates being fast at the beginning and slowing down in the rest of the carbonation process (see Fig. 1). Most of the CO_2 uptake was achieved in first ten minutes for both of the FA compacts.

Table 3. CO_2 uptake (gr CO_2 per 100gr FA compact)

Sample name	5 bar		10 bar		15 bar	
	CO_2	**FG**	**CO_2**	**FG**	**CO_2**	**FG**
100%OSA	9.1	6.4	9.5	7.6	10.6	9.7
50%OSA/ 50%WA	6.9	4.9	7.7	6.2	8.4	7.4
100%WA	7.6	5.2	8.3	5.5	8.9	7.5

(CO_2-100%CO_2 cured, FG- flue gas cured)

Table 4. Compressive strength (MPa)

Sample name	5 bar		10 bar		15 bar	
	CO_2	**FG**	**CO_2**	**FG**	**CO_2**	**FG**
100%OSA	21.5	15.4	22.2	16.1	35.1	28.2
50%OSA/ 50%WA	15,6	10.9	16,4	12.7	27.5	21.3
100%WA	7.1	4.8	9.3	8.9	14.7	12,5

Measurements shown in table 4 are average number of each set of 4 samples with deviation of 3%. (CO_2-100%CO_2 cured, FG- flue gas cured)

The impact of compaction pressure was apparent as the compacts prepared with higher compaction pressure reached the highest compressive strength although the CO_2 uptake was not influenced by the possible low permeability of CO_2 gas (Tables 3-4). However, this effect could be more critical at lower curing pressures. The strength of samples cured in 100%CO_2 are slightly higher than the samples cured in FG. This could be somewhat linked to less CO_2 uptake levels as the the formation of carbonate phases in compact bodies can lead to increase in solid phase volume by reducing porosity and development of compressive strength [Praneeth et al. 2020, Ohenoja et al. 2020]. Due to the higher content Ca-Mg silicates which participate in hydraulic or pozzolanic reactions in OSA compacts the compressive strenght values were higher than WA compacts. Similar phenomenon also exists in mix design (OSA/WA) where there was no peculiar interaction between these two ashes as the results of both CO_2 uptake and compressive strength were proportional with single FA compact performances. According to FT-IR analysis (Fig. 3) of OSA and WA main reacting phases during the carbonation reaction are lime and portlandite in OSA and WA as the intensity of portlandite peaks (3636 cm-1) decreases and carbonates (876, 1421 cm-1) increases after both FG and 100 % CO_2 curing process respectively which confirms the carbonation trends obtained by the TGA measurements at 15 bar. Ca-bearing silicates (975 - 1115 cm^{-1}) play also a minor role in carbonation reactions as their intensities also slightly decrease.

4. Conclusions

In this study, accelerated carbonation of FA based compacts at different gas pressures and CO_2 concentrations was investigated by evaluating the CO_2 uptake and strength performances of compacts for the production of carbonate-hardened/building materials. According to the results obtained from 100%CO_2 curing it can be concluded that it is possible to produce FA based compacts with 15-35 MPa compressive strength while binding 90-100 kgCO_2/ton of FA. Experiments with model FG have revealed that it is possible to achieve mineral sequestration of CO_2 in FA based blocks utilizing low concentration of CO_2. It was found that potential adverse low reaction rate effect due to the low CO_2 concentration in FG was negligible during the short curing process (2h) and this could further be eliminated by applying elevated gas pressures. Experimental results indicates that it is possible to achieve compressive strength values between 12-28 MPa while binding 75-90 kgCO_2/ton of FA compact with short FG curing times. The obtained results are promising for building material applications of FA in short curing time with FG utilization.

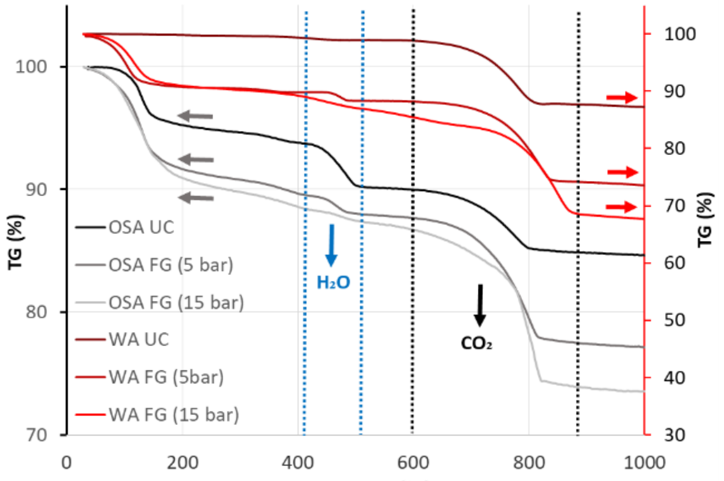

Figure 1. Mass loss curves of OSA and WA compacts (UC: Uncured, FG: Flue gas cured)

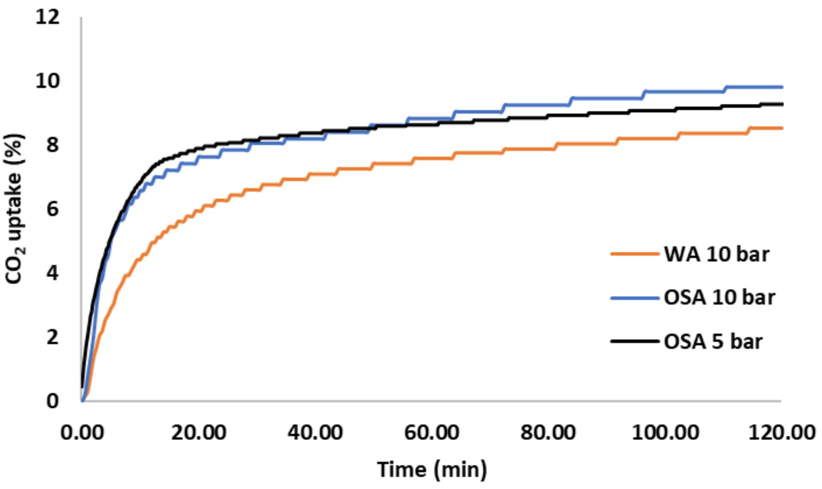

Figure 2. Gas consumption curves of OSA compacts in 5 and 10 bar and WA compacts in 10 bar

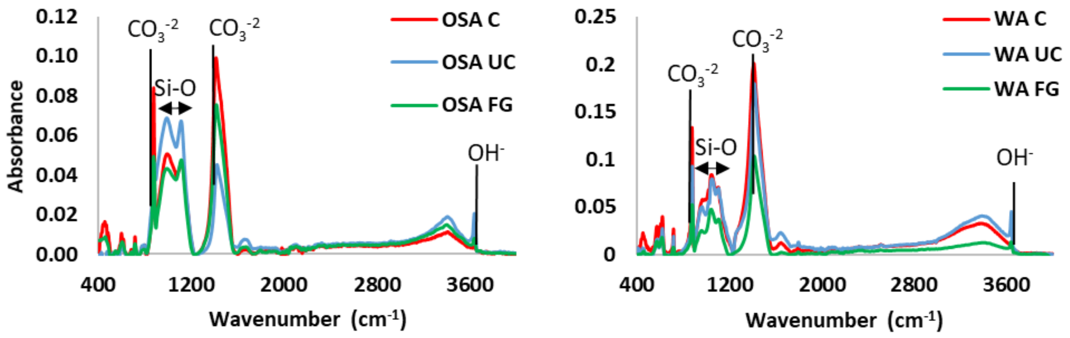

Figure 3. FT-IR analysis of OSA and WA compacts cured at 15 bar in FG and 100%CO_2 (C: 100% CO_2 cured, UC: Uncured, FG: Flue gas cured)

Acknowledgement

This work is partly supported by the CLEANKER project which has received funding from the European Union's Horizon 2020 Framework Program under Grant Agreement No. 764816. This work has been partially supported by ASTRA "TUT Institutional Development Program for 2016-2022" Graduate school of Functional Materials and Technologies.

References

Tan, W., Ahmad, A., Leo, C., & Lam, S. (2020). A critical review to bridge the gaps between carbon capture, storage and use of CaCO3. *Journal of CO_2 Utilization, 42*, 101333.

Chiang, P., & Pan, S. (2017). Carbon dioxide mineralization and utilization. SINGAPORE: SPRINGER Verlag, SINGAPORE.

Usta, M. C., Yörük, C. R., Hain, T., Paaver, P., Snellings, R., Rozov, E., . . . Uibu, M. (2020). Evaluation of new applications of oil shale ashes in building materials. *Minerals, 10*(9), 765.

Praneeth, S., Guo, R., Wang, T., Dubey, B. K., & Sarmah, A. K. (2020). Accelerated carbonation of biochar reinforced cement-fly ash composites: Enhancing and sequestering CO2 in building materials. *Construction and Building Materials, 244*, 118363.

Ohenoja, K., Rissanen, J., Kinnunen, P., & Illikainen, M. (2020). Direct carbonation of peat-wood fly ash for carbon capture and utilization in construction application. *Journal of CO2 Utilization, 40*, 101203.

Arandigoyen, M., Bicer-Simsir, B., Alvarez, J., & Lange, D. (2006). Variation of microstructure with carbonation in lime and blended pastes. *Applied Surface Science, 252*(20), 7562-7571.

Uibu, M; Velts, O; Kuusik, R. (2010). Developments in CO_2 mineral carbonation of oil shale ash. *Journal of Hazardous Materials*, 174, 209−214.

Bauer, M., Gassen, N., Stanjek, H., & Peiffer, S. (2011). Carbonation of lignite fly ash at ambient t and p in a semi-dry reaction system for CO_2 sequestration. *Applied Geochemistry, 26*(8), 1502-1512.

Uibu, M., Uus, M., & Kuusik, R. (2009). CO_2 mineral sequestration in oil-shale wastes from Estonian power production. *Journal of Environmental Management, 90*(2), 1253-1260.

Kliimapoliitika põhialused aastani 2050. (2019, February 5). Retrieved April 21, 2021, from https://www.envir.ee/sites/default/files/low_carbon_strategy_until_2050.pdf