Final report

M-Eranet2: Energy efficient nano-modified renders with CO2-storage potential

project no: NN 127023

Short summary of outcome and cooperation

The project was realised within the frame of EU funded M-Eranet project in cooperation with our Cypriot partners. It is necessary to note that due to the administrative differences between the two countries and thus the project had not started at the same time in Cyprus and Hungary. Hence there was a shift in time between the finalisation of the project. It has to be mentioned that Covid also hampered many activities, especially laboratory work and travel. It also caused a necessary readjustment of our activities. Nevertheless, the final report submitted to EU was accepted and it was awarded a 'success story by the evaluation board. The success story reports are available at the site:

https://m-era.net/success-stories/energy-efficient-nano-modified-renders-with-co2-storage-potential-ccsrender

The two project teams worked together and jointly on the research programme, which also meant that there were joint publications and also publications with authors from Cyprus and also only from Hungary.

Project aims

Anthropogenic activities over the past century have caused a dramatic increase of carbon dioxide (CO2) concentration in the atmosphere. A potential solution to this crucial problem is the storage of CO2 via mineral carbonation, which comprises one of the most promising carbon capture and storage (CCS) technologies.

The aim of the CCSRender project was the development of novel, environmentally-friendly lime-based renders with the ability to sequester CO2 directly from the atmosphere via in situ mineral carbonation. This was achieved through the addition of suitable mafic/ultramafic rocks (including quarry waste materials) in nanoscale to the aforementioned composites, following the application of the ball milling process. The latter has proved to be very efficient in increasing the CO2 uptake of mafic and ultramafic rocks.

The first stages of the project included field trips in the Troodos ophiolite complex, during which mafic/ultramafic rocks and quarry waste materials were sampled. Based on the mineralogical composition of these rock samples, the most promising ones were subjected to ball milling in order to create nanoscale rock powders with enhanced CO2 sequestration capacity. Mafic quarry wastes from Hungary were also used for the development of ultrafine powders. In order to determine the optimum milling parameters for each individual rock

sample, a significant number of ball milling experiments were performed in the framework of the project. The starting rock materials and the ball-milled samples were thoroughly characterised using a variety of experimental techniques. The research team focused on the development of sufficient quantities of the most promising nano-sized powders in order to be used as additives during the preparation of render mix designs.

Several lime-based render mixtures were designed and prepared in the lab through the addition of the new nanomaterials, at different quantities (weight by weight as a replacement to lime). The hardened end-products were characterised through a variety of laboratory tests. The results revealed that the nano-modified renders showed a significantly denser microstructure compared to the reference composites, due to the nano-filler effect, in combination with the enhancement of the carbonation reactions. This indicated that the use of the aforementioned nano-additives in renders can (i) accelerate the carbonation reactions, thus enhancing the early-age physico-mechanical properties of the end-products, and (ii) contribute to the reduction of atmospheric CO2 concentrations.

During the second half of the project, emphasis was also placed on the preparation of additional mix designs using different rocks/waste materials. The goal was to investigate the CO2-storage capacity of the new composites in relation to the type and percentage of nano-additives, the carbonation mechanism of the most promising mix designs, as well as the changes induced to the microstructure of the latter during carbonation. The experimental results clearly showed the positive effect of specific nano-sized rocks/waste materials on the carbonation mechanism and physico-mechanical properties of air lime renders. The new nano-modified composites compared favorably with composites containing well-known commercial nano-additives (i.e., nano-silica). Pilot applications performed before the end of the project further demonstrated the better performance of the nano-modified mixtures, compared to the unmodified ones, under real exposure conditions.

Materials and methods

Several fieldtrips were performed in Cyprus and Hungary before Covid to collect samples, which included identification and sampling of mafic/ultramafic rock samples, as well as of quarry waste materials. The ultimate goal was to find the most promising samples for CO2 sequestration. A total of more than 25 samples were collected and analysed using a variety of experimental techniques. Based on their detailed characterisation, the following rock samples were selected to be processed via ball milling, aiming to create nano-sized powders with enhanced CO2 storage capacity:

- Olivine basalt (Cyprus)
- Basalt quarry waste (Hungary)
- Dunite (Cyprus)
- Dolerite quarry waste (Cyprus)
- Dolerite quarry waste (Hungary)

A planetary ball mill was used and different milling parameters were applied. Subsequently, the ball-milled samples were characterised using the same techniques as the starting rock materials. The ultimate goal was to determine the optimum milling parameters for each rock type/waste material in terms of their CO2 storage capacity. The results revealed the following:

Ball milling substantially improves the ability of mafic/ultramafic rocks and quarry waste materials to sequester CO2.

The highest increase in CO2 uptake after ball milling was acquired for the dunite and olivine basalt collected from Cyprus, while smaller improvements were acquired for the other rocks/waste materials.

Regarding the optimum duration of ball milling, this was found to be different for each rock type; this is mainly attributed to the distinct mineralogical features of the studied samples.

Based on the thorough characterisation of the nano-sized powders, those with the highest CO2 storage capacity were selected for use as additives during the preparation of lime-based renders. A total of 20 mix designs (instead of the 10 initially planned) were prepared in the lab. These included reference mix designs (without nano-additives), as well as modified composites with unmilled or ball-milled rocks/waste materials (from both Cyprus and Hungary) as additives. It should be underlined that the new nano-materials were added to the composites in partial replacement to the lime binder. The mix designs prepared are summarised below:

- 8 Reference (without additives) mix designs with different types of aggregates and air/hydraulic lime as the binder (some of these mixtures were prepared using different mixing procedure)
- 4 Modified mix designs with 5% or 15% w/w unmilled dolerite or basalt quarry waste (from Cyprus and Hungary)
- 8 Nano-modified mix designs with 5% or 15% w/w nano-sized rocks/waste materials. Specifically, the following nano-additives were used: dolerite quarry waste from Cyprus, olivine basalt from Cyprus, dunite from Cyprus, and basalt quarry waste from Hungary. The dolerite quarry waste from Cyprus was added to the mixtures following different milling durations.

Results

The nano-modified lime-based renders showed a denser and more homogeneous microstructure, compared to the reference composites. This is attributed to the nano-filler effect, in combination with the enhancement of the carbonation reactions after the addition of the new nano-additives.

The composites containing 15% w/w nanomaterial showed a considerably higher degree of carbonation, compared to those with 5% w/w nanomaterial.

The composite containing 15% w/w dolerite waste nanomaterial showed a significant improvement of the compressive strength, compared to the composite with 5% w/w nano-sized waste dolerite and the reference one.

The addition of basaltic nanomaterial did not improve the compressive strength of lime-based renders, probably due to the abundance of chlorite in the basaltic sample hereby used.

A reduction of the flexural strength was observed in most of the nano-modified composites. This is likely related to the formation of microcracks in the latter, due to excess drying shrinkage induced by the increased water/binder ratios after the addition of nano-additives. The increased water demand of the nano-modified mixtures is also related to the presence of significant amounts of phyllosilicate minerals in the new nano-additives. Only the addition of nano-sized dunite resulted in an improvement of flexural strength, which is likely attributed to the relatively small amount of secondary phyllosilicate minerals in this specific rock sample. Nevertheless, additional experiments revealed that the negative effect of most of the studied nano-additives on the flexural strength of air lime renders could be eliminated through the use of superplasticisers.

Pilot applications revealed an enhanced degree of carbonation in the nano-modified renders, compared to the reference mixtures and the mixtures containing unmilled quarry wastes. Furthermore, the nano-modified renders showed the highest adhesion strength on substrates made of fired clay brick or porous limestone.

Nano-silica was used in complementary mix designs, aiming to compare the properties of the latter with those of the lime-based renders that contained nano-sized rocks/quarry waste materials. The main results and conclusions acquired are given below:

Thermal analyses indicated that the composite with 5% w/w nano-silica showed a more enhanced carbonation compared to the render with 5% w/w dolerite waste nano-additive. However, an increase of the quantity of the nano-sized waste from 5% to 15% w/w resulted in a considerable enhancement of the carbonation reactions at early curing times. Specifically, at 7 curing days, this increase in the degree of carbonation was more evident compared to that observed in the composite with 5% w/w nano-silica, thus indicating the positive effect of a higher quantity of nano-sized quarry waste on the carbonation process of air lime renders.

SEM observations revealed that both nano-silica and the new nano-additives contributed to the development of renders with a denser and more homogeneous microstructure, mainly due to the nano-filler effect, in combination with the enhancement of the carbonation and pozzolanic reactions. However, the nano-silica-bearing renders showed an even denser microstructure, compared to the specimens that contained the new nano-additives; this is attributed to the fact that nano-silica led to a more intense enhancement of the pozzolanic reaction compared to the new nano-additives, especially at early curing times.

The results of the mechanical properties indicated the better performance of the specimens with nano-silica compared to those with the new nano-additives. However, this should not be considered a disadvantage for the new nano-modified composites, since lime renders are usually used in restoration/conservation projects whereby compatibility with weak traditional masonry materials is a prerequisite.

Regarding the flexural strength, the absence of any significant improvement in the nano-modified specimens that contained most of the new nano-additives or nano-silica is attributed to the fact that nanomaterials tend to increase the water demand of the mixture.

The overall results of the CCSRender project indicated that the proposed approach could provide an effective option for the sustainable management of rocks and/or waste materials generated from quarries. Furthermore, the results showed that the addition of nano-sized rocks as a replacement to the lime binder could notably contribute to the reduction of the CO2 emissions associated with the lime industry. At the same time, the new environmentally-friendly renders could sequester CO2 directly from the atmosphere and safely store it in the form of carbonate minerals.

The project results were presented to the scientific community through publications in peer-reviewed international scientific journals and peer-reviewed articles or abstracts in national and international conferences.

Selected journal publications

- RIGOPOULOS, I., TÖRÖK, Á., KYRATSI, TH., DELIMITIS, A., IOANNOU, I., 2018. Sustainable exploitation of mafic rock quarry waste for carbon sequestration following ball milling. ***Resources Policy*** 59, 24-32, https://doi.org/10.1016/j.resourpol.2018.08.002.
- RIGOPOULOS, I., IOANNOU, I., DELIMITIS, A., EFSTATHIOU, A.M., KYRATSI, TH., 2018. Ball milling effect on the CO_2 uptake of mafic and ultramafic rocks: a review. ***Geosciences,*** 8 (11), 406, https://doi.org/10.3390/geosciences8110406.
- KYRIAKOU, L., RIGOPOULOS, I., IOANNOU, I., 2019. Use of ultrafine mafic rocks for the enhancement of carbonation reaction in lime renders. ***International Journal of Architectural Heritage*** https://doi.org/10.1080/15583058.2019.1709583.
- KÓSA, ZS. TÖRÖK Á. 2020. Characterisation of Historic Binders and Stones of a Ruined Medieval Church (Hungary). ***Periodica Polytechnica- Civil Engineering***, 64,2, 597-604.
- KÓSA ZS., RIGOPOULOS, I., IOANNOU, I., KÁRPÁTI-PÁPAI Z., TÖRÖK, Á. (Submitted). Mechanical properties and workability of lime mortars with different binders and aggregates. **Minerals**

Selected conference presentations

- TÖRÖK, Á., KÓSA, Z., PÁPAY, Z., IOANNOU, I., RIGOPOULOS, I., 2019. Comparison of the physical properties of Hungarian and Cypriot lime mortars (oral presentation in Hungarian), *10th Hungarian Dimension Stone Congress*, Sept.19-20., Tata, Hungary / Magyarországi és ciprusi mészhabarcsok fizikai tulajdonságainak összehasonlítása. X. Díszítőkő Konferencia, 2019. szept. 19-20, Tata, Magyarország (előadás) (Abstract with Oral Presentation).
- TÖRÖK, Á., KÓSA, Z., PÁPAY, Z., IOANNOU, I., RIGOPOULOS, I., 2019. Comparative analysis of the mechanical properties and workability of lime mortars: examples from Hungary and Cyprus. *5th Historic Mortars Conference*, June 19-21, Pamplona, Spain (Abstract with Oral Presentation).
- RIGOPOULOS, I., KYRIAKOU, L., TÖRÖK, Á., KYRATSI, TH., IOANNOU, I., 2019. New generation of lime-based renders with the addition of ultrafine waste material from dolerite quarries. *RILEM International Conference on Sustainable Materials, Systems and Structures, Session: New generation of construction materials*, March 18-22, Rovinj, Croatia, (Full Paper with Oral Presentation).

- RIGOPOULOS, I., KYRIAKOU, L., TÖRÖK, Á., KYRATSI, TH., IOANNOU, I., 2018. Influence of mafic nano-additives on lime-based renders. *EGU 2018, Session: Geomaterials in construction: resources, properties, performance, environmental interactions, decay, and extractive industries waste management*, April 8-13, Vienna, Austria (Abstract with Poster Presentation).