materials proceedings

Proceeding Paper

CO_2-Mineralised Nesquehonite: A New "Green" Building Material †

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† Presented at International Conference on Raw Materials and Circular Economy, Athens, Greece, 5–9 September 2021.

Abstract: Synthetic nesquehonite with a $Mg(HCO_3)OH \cdot 2H_2O$ chemical formula is a solid product of CO_2 mineralization with cementitious properties. It constitutes an "MHCH" (magnesium hydroxy-carbonate hydrate) phase and, along with dypingite and hydromagnesite, is considered to be a promising permanent and safe solution for CO_2 storage with potential utilization as a supplementary material in "green" building materials. In this work, synthetic nesquehonite-based mortars were evaluated in terms of their compressive strengths. Nesquehonite was synthesized by CO_2 mineralization under ambient conditions (25 °C and 1 atm). A saturated Mg^{2+} solution was used at a pH of 9.3. The synthesized nesquehonite was subsequently studied by means of optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Impurity-free nesquehonite formed elongated fibers, often around a centerpiece, creating a rosette-like structure. The synthesized nesquehonite was mixed with reactive magnesia, natural pozzolan, standard aggregate sand and water to create a mortar. The mortar was cast into 5 × 5 × 5 silicone mold and cured in water for 28 days. A compressive strength of up to 22 MPa was achieved. An X-ray diffraction study of the cured mortars revealed the formation of brucite as the main hydration crystalline phase. Carbon dioxide mineralized nesquehonite is a very promising "green" building material with competitive properties that might prove to be an essential part of the circular economy industrial approach.

Keywords: CO_2 mineralization; nesquehonite; magnesium carbonates

Citation: Kastrinakis, A.; Skliros, V.; Tsakiridis, P.; Perraki, M. CO_2-Mineralised Nesquehonite: A New "Green" Building Material. *Mater. Proc.* **2021**, *5*, 60. https://doi.org/10.3390/materproc2021005060

Academic Editor: Konstantinos Simeonidis

Published: 8 December 2021

1. Introduction

Carbon emission reduction policies constitute a top priority, nowadays, to reduce the environmental impact of the greenhouse effect. During the 2000–2014 period, the USA had an 18% overall decline in carbon dioxide emissions, while many European countries experienced declines from 20% to over 30%. However, at the same time, China's CO_2 emissions increased by 50% and India's by 88%. For that reason, the development of effective carbon capture and storage (CCS) methods that exploit CO_2 emissions from industrial activities is of high interest [1–6].

As CCS becomes a key technology in the reduction in greenhouse gases, the utilization of CO_2 for the synthesis of market-usable products is considered attractive from the market point of view [7,8]. The most preferable option for Carbon Capture Utilization (CCU) is the synthesis of construction/building materials because of the increased need for concrete in the global market [8].

The synthesis of Mg-rich carbonate minerals is an effective method of CCS. It involves the interaction of Mg^{2+} ions with CO_2 in an aqueous solution, resulting in the rapid precipitation of hydrous Mg-carbonate minerals [9]. The source of this process could be several types of by-products, wastes, brines or even seawater. Nesquehonite ($MgCO_3 \cdot 3H_2O$) is the most energy-efficient product of CO_2 mineralization, because its synthesis requires earth's ambient conditions. Precipitation of nesquehonite takes place at temperatures lower than 50 °C and under alkaline conditions (pH ≈ 9), according to the following reaction:

$$Mg^{2+} + CO_2\ (g) + 4H_2O \text{ -> } Mg(OH)(HCO_3)\cdot 2H_2O \text{ or } MgCO_3\cdot 3H_2O\ (s) + 2H^+$$

Nesquehonite exhibits excellent engineering properties for making construction material [9–13] and can potentially be used for industrial purposes in acoustic or insulation panels [11]. The cementitious characteristics of nesquehonite are a relatively recent discovery [7,10].

High-energy consumption, costs and gas emissions (especially CO_2) are the main drawbacks of the production process of commercial cement. CO_2 emissions during the cement production process are primarily due to the decomposition of calcium carbonate (the basic reaction of the cement clinkerization), secondarily to the use of fuels for the required energy production and finally to the electricity consumption and transportation. Clinker's production line also possesses many disadvantages, such as increased energy requirements [14], costs and emissions of other gases (SO_2, NO_x), dust and particles [15]. It is imperative that a more environmentally friendly and less costly solution should be found for construction materials, while maintaining the same mechanical properties as common cements. Eco-cements based on reactive MgO and CO_2 mineralization are a promising solution with particular construction applications.

Reactive MgO Cements (RMCs) are alternative low-carbon cementing materials. The magnesium oxide used in eco-cements replaces the clinker used in common cements. Reactive magnesia can be produced synthetically from brine or seawater [16], or by calcination of magnesia-based minerals, such as magnesite ($MgCO_3$, cryptocrystalline or macrocrystalline) and dolomite [$(Ca,Mg)CO_3$]. Reactive MgO has high surface area and, thus, reactivity [17]. In reactive MgO cement production, the most commonly used firing apparatus is the vertical shaft kiln, in which preheating, calcination and cooling of materials all take place at the same time. The calcination of magnesite occurs at temperatures below 800 °C, which is significantly lower than that of cement clinkerization (1450 °C) [18] and, thus, less energy consuming. Nevertheless, reactive MgO gains its physical properties as a result of carbonation processes. During synthesis, CO_2 is chemically absorbed, creating carbonate phases [19]. The mineralization of CO_2 into thermodynamically stable carbonate phases such as nesquehonite (stable at 25–40 °C and 1 atm) leads to the sequestration of large amounts of carbon dioxide emitted at previous stages of production. Carbon capture and storage in such a way is both safe and sustainable, with the great advantage of complete carbon utilization. As a result, the production process of reactive MgO based eco-cements has a lower carbon footprint than the production of clinker.

Additionally, the high porosity of MgO cements is a crucial factor for the carbonation processes. CO_2 is diffused in the pores of the MgO cement mix and, after a chain of chemical reactions, amounts of hydrated magnesium carbonate, as brucite, nesquehonite, hydromagnesite, dypingite and artinite, are created. The carbonates' morphology also plays a significant role, as fibrous and needle-like crystals grown in hydrated magnesium carbonates are beneficial for the mechanical performance of reactive MgO cements [16]. With appropriate curing conditions, reactive magnesia-based cements demonstrate better mechanical properties than Portland Cements [20].

The advantages of eco-cements based on reactive MgO not only affect the production and mechanical properties of these cements, but also the potential of utilizing wastes and industrial by-products. Moreover, when the lifecycle of reactive MgO cement is completed, it may be recycled to produce magnesia for other uses [17].

The goal of this study was to investigate the mechanical and chemical characteristics of a new eco-cement building material produced by mixing nesquehonite with reactive magnesia. Through the synthesis of nesquehonite-based cements, we investigated the synthesis of a new "green" building material. A detailed microscopy study was carried out to fully characterize the new magnesium-hydroxy-carbonate-hydrate (MHCH) phases. Toward this goal, we synthesized multiple mortars and tested their compressive strength.

2. Materials and Methods

X-ray Diffraction patterns were obtained with a Bruker D8 Focus diffractometer in a θ-θ configuration employing CuKα radiation (λ = 1.5406 Å) with a fixed divergence slit size of 0.5° and a rotating sample stage. The samples were scanned between 4 and 70° 2θ. The step size and time per step were set to 0.017° 2θ and 80 s, respectively. Stereoscopic study was carried out under a Leica MZ8 binocular stereoscope. Scanning Electron Microscopy (SEM) was performed using a JEOL 6380LV-SEM equipped with an Oxford EDS-WDS. The thermal-gravimetric study of nesquehonite was carried out in a thermogravimetry instrument produced by Mettler under flowing nitrogen atmosphere with a heating rate of 10 °C/min in the temperature range of 25–1100 °C. STARSW software was used to evaluate the results. A static compression test was carried out using an MTS-E45.305 electronic universal testing machine with reference to the ASTM C109. The load–displacement (L–D) curve data were recorded in a computer using sensors installed at the load cell.

2.1. Synthesis of Nesquehonite

Nesquehonite, a hydrous Mg-carbonate, is a thermodynamically and chemically stable solid product. A simple, fast and environmentally friendly synthesis of nesquehonite was achieved by reaction of gaseous CO_2 with a Mg-chloride solution under low pressure conditions, as follows:

$$MgCl_2 \cdot 3H_2O + CO_2(g) + H_2O \rightarrow MgCO_3 \cdot 3H_2O_{(s)} + 2HCl$$

A saturated Mg^{2+} solution was used for nesquehonite synthesis, at a temperature of 25 °C and pH 9.3. During the reaction, since the pH tended to reduce, a continuous input of high concentration (35%) NH_3 solution was required to keep the pH at alkaline values [9]. The NH_3 solution reacted with HCl to form NH_4Cl and was easily separated from the solid product (nesquehonite) using a vacuum pump.

2.2. Synthesis of the New "Green" Building Material

To synthesize the new "green" mortar, reactive magnesia with pozzolan was blended with nesquehonite, a carbon sequestration product that was formed in vitro herein. Standard aggregate sand and water were added together in the mix to cast a mortar. The new mortar was cast into a 5 × 5 × 5 silicone mold and cured in water for 28 days. The binder consisted of 40% MgO (reactive magnesia) + 50% Pozzolan + 10% nesquehonite. The binder was 40% mortar; the other 60% was standard aggregate sand.

3. Results

Synthesized nesquehonite was studied by means of X-ray Diffraction, optical microscopy (Figure 1) and scanning electron microscopy (Figure 1). Synthesized nesquehonite forms elongated fibers, exhibiting transparent to translucent diaphaneity and vitreous luster. Nesquehonite's chemical composition is characterized by the presence of OH- and CO_3^{2-} in the crystal structure (Mg $(HCO_3)(OH) \cdot 2H_2O$ describes it better [21]).

XRD analysis of the nesquehonite showed characteristic peaks at d = 6.52, 3.86, 3.04, 2.62, 2.51 and 1.92 Å, which correspond to Miller indices of $\{\bar{1}01\}$, {200}, $\{\bar{2}11\}$, {021}, $\{\bar{3}01\}$ and {400} [22].

Scanning Electron Microscopy (SEM) showed that the nesquehonite fibers were developed around a centerpiece, creating a structure called rosettes (Figure 1).

A typical compressive test was performed to study the engineering properties of the mortar. The sample achieved a compressive strength of 22 MPa after 28 days (Figure 2).

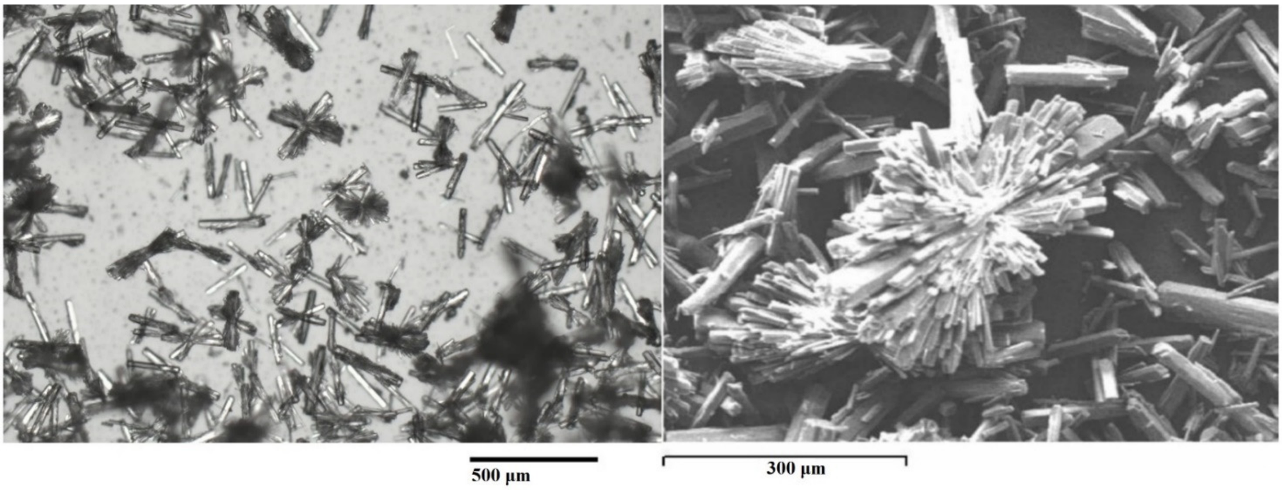

Figure 1. (**Left**) Stereoscopic view of the synthesized nesquehonite. (**Right**) Secondary electron (SE) image of nesquehonite showing prismatic crystals in the form of rosettes.

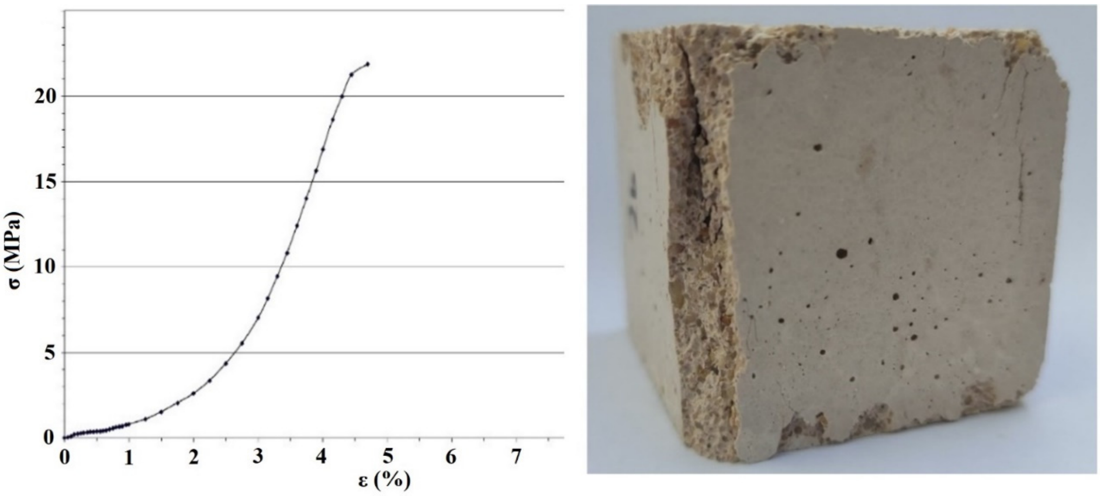

Figure 2. (**Left**) Comprehensive strength of the sample achieved herein. (**Right**) Photomacrograph of the mortar sample after the comprehensive strength test.

The sample's matrix broke into pieces after the loading reached the maximum value.

XRD analysis was only performed in the binder of the sample to identify the new phases formed after the 28 days of curing in water. According to the results, there was a high concentration of the magnesium hydrated phase, indicating that caustic magnesia reacted during the curing period. Mineralogical examination of the binder showed the existence of brucite, quartz, cristobalite, orthoclase, calcite, muscovite and stilbite.

In addition to the main crystalline phase, the binder also contained amorphous phases, as indicated by the characteristic hump between 15 and 35° degrees (Figure 3).

Thermal gravimetric analysis of the binder (Figure 4) showed a total mass loss on ignition of about 20%. The mass loss between 25 and 120 °C was 3%. In the DTA curve, two endothermic reactions above 200 °C were observed, of which one corresponded to the dehydroxylation and the other to decarbonation in the binder. The dehydroxylation of the sample started at about 300 °C and ended 460 °C. The sample lost about 10% of its total mass. Decarbonation occurred in two steps. The first decarbonation peak occurred between about 450 and 510 °C and corresponded to a mass loss of 1%. The second decarbonation peak occurred between about 630 and 680 °C and corresponded to a mass loss of 2%.

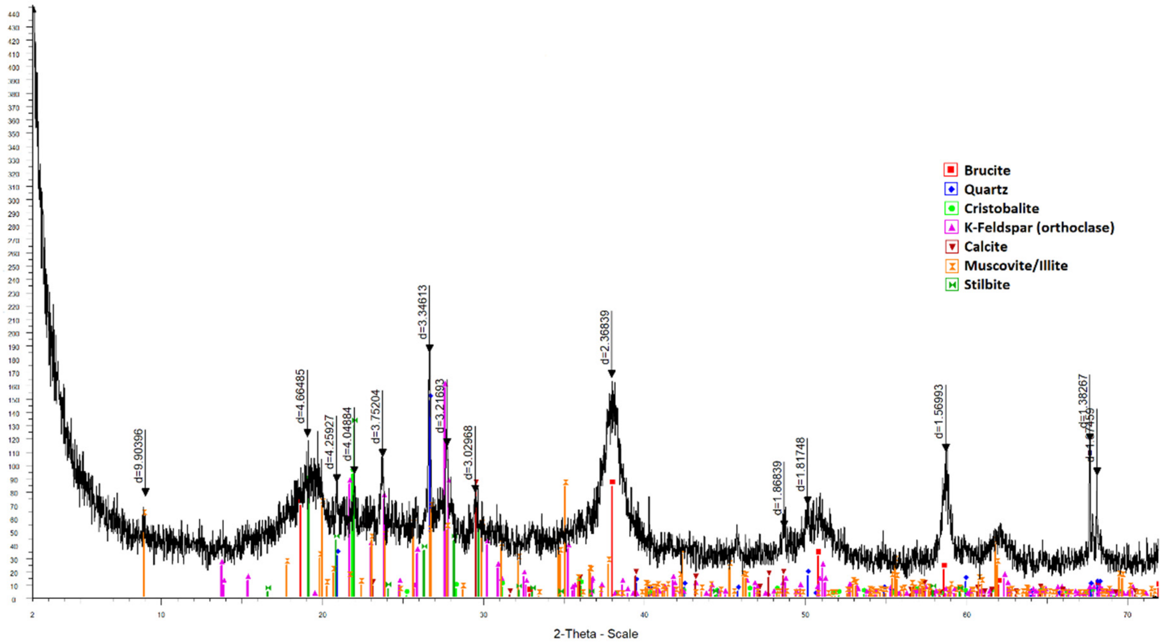

Figure 3. XRD pattern of the mortar's binder synthesized herein.

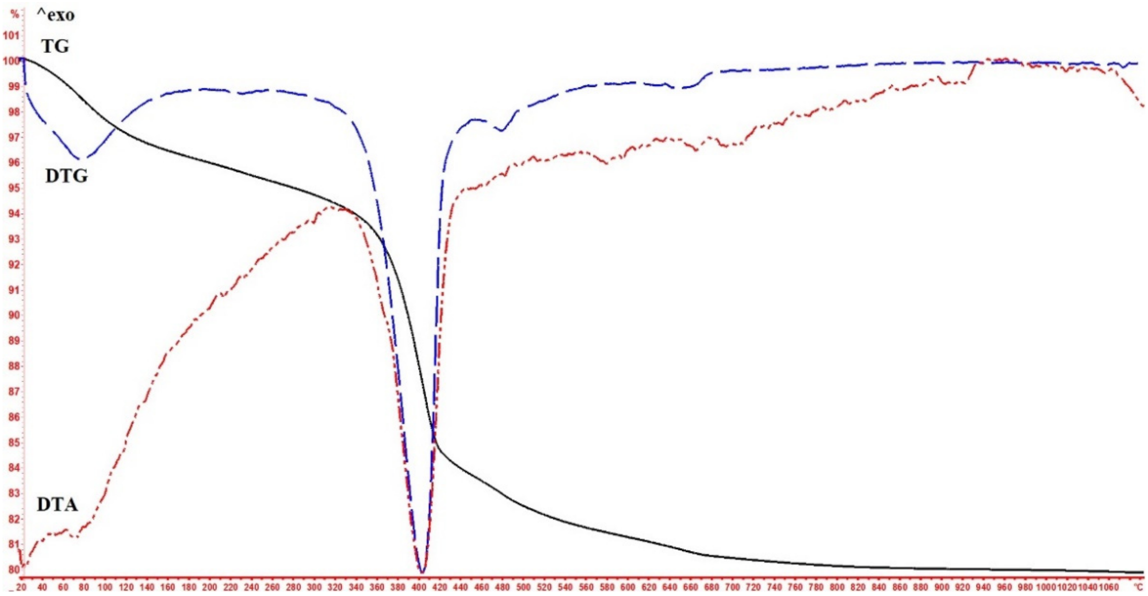

Figure 4. Thermogravimetry (TG)/differential thermal analysis (DTA)/derivative thermogravimetric (DTG) curves of the mortar's binder synthesized in this study.

SEM analysis indicated the presence of the $CO_3{}^{-2}$ in the amorphous phase formed during mortar curing (Figure 5) and showed that a reaction between nesquehonite, pozzolan and caustic magnesia took place.

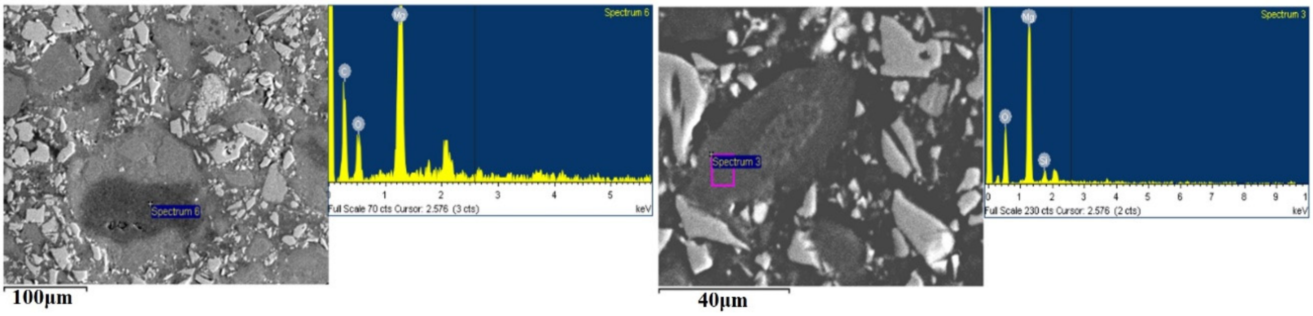

Figure 5. (**Left**) Amorphous Mg-phase containing $CO_3{}^{-2}$. (**Right**) Amorphous Mg-Si-phase [4].

4. Discussion

It was found that sequestering CO_2 through carbonization produces a solid material called nesquehonite that can be used for eco-friendly building materials. During the synthesis of nesquehonite, the carbon dioxide mineralization process left two moles of hydrochloric acid for every mole of carbon dioxide captured. Since ammonia aqueous solution (32% concentration) needed to be added to adjust the pH value of the solution, multiple circulation of the solution meant that the final by-product was a mixture of NH_4Cl-H_2O and $MgCO_3 \cdot 3H_2O$. The ammonium chloride was removed from the aqueous solutions following a filtration process with distilled water under vacuum conditions to separate the solid nesquehonite from the solution. The ammonium chloride could be then recycled to produce NH_4 and HCl [9].

The new eco-friendly mortar synthesized in this work proved to have competitive comprehensive strength in comparison with magnesium cements existing already in the market [23]. The new mortar achieved 22MPa, which shows its high potential.

The blended mix with Pozzolan and reactive magnesia achieved a compressive mortar strength of 22 MPa. The hydration of MgO in the presence of water produced a $Mg(OH)_2$ phase. The addition of nesquehonite increased the rate of MgO hydration and provided nucleation sites, resulting in higher strength. The material strengthened over time, under high humidity.

The addition of pozzolan, with high amounts of amorphous alumino-silicate compounds, can lead to the development of secondary magnesium and calcium alumino-silicate hydrate products (due to the reaction with the produced $Mg(OH)_2$ from magnesia hydration), with improved hydraulic properties. These compounds are responsible for hardening and development of higher strengths at later ages, simultaneously enchasing the microstructure (pore structure, paste-aggregates interface, etc) and durability of the final hardened mixture. It should be also noted that the presence of zeolite type phases in the raw pozzolan significantly improved the strength of the hardened mortar. The mortar presented a maximum compressive strength of 22 MPa.

Combined XRD, SEM and DTA analysis showed that the amorphous phase in the binder contained $CO_3{}^{2-}$ in its structure since none of the magnesium hydrate carbonate minerals were detected. The SEM study also revealed the existence of $CO_3{}^{2-}$ in the binder of the mortar.

5. Conclusions

The synthesis of a nesquehonite-based eco-friendly mortar proved to be a relatively low energy process. Nesquehonite, as a CO_2 sequestration product, required low pressure conditions, meaning that it is an energy-efficient product. The synthesis of nesquehonite described herein is a simple, fast and environmentally friendly process and constitutes a potential long-term CO_2 storage method. It could also be applied at larger/industrial scales with the aim of capturing and permanently storing CO_2 emissions.

The "green" mortar synthesized from nesquehonite reactive magnesia and pozzolan exhibits competitive strengths in comparison with existing products.

Author Contributions: A.K. carried out the laboratory experiments and the writing of the manuscript as part of the work related to his Diploma Thesis; V.S. carried out the laboratory experiments and the interpretation of the results, and coordinated the research and the writing of the manuscript; P.T. participated in the laboratory tests and the interpretation of the results, and contributed to the manuscript writing; M.P. coordinated the research and contributed to the manuscript writing. All authors have read and agreed to the published version of the manuscript.

References

1. Gerdemann, S.J.; O'Connor, W.K.; Dahlin, D.C.; Penner, L.R.; Rush, H. Ex Situ Aqueous Mineral Carbonation. *Environ. Sci. Technol.* **2007**, *41*, 2587–2593. [CrossRef] [PubMed]
2. Gislason, S.R.; Oelkers, E.H. Carbon Storage in Basalt. *Science* **2014**, *344*, 373–374. [CrossRef] [PubMed]
3. Lackner, K.S.; Wendt, C.; Butts, D.P.; Joyce, E.L.; Sharps, D.H. Carbon Dioxide Disposal in Carbonate Mineral. *Energy* **1995**, *20*, 1153–1170. [CrossRef]
4. Matter, J.M.; Kelemen, P.B. Permanent Storage of Carbon Dioxide in Geological Reservoirs by Mineral Carbonation. *Nat. Geosci.* **2009**, *2*, 837–841. [CrossRef]
5. Matter, J.M.; Stute, M.; Snaebjornsdottir, S.O.; Oelkers, E.H.; Gislason, S.R.; Aradottir, E.S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardottir, H.; Gunnlaugsson, E.; et al. Rapid Carbon Mineralization for Permanent Disposal of Anthropogenic Carbon Dioxide Emissions. *Science* **2016**, *352*, 1312–1314. [CrossRef] [PubMed]
6. Michael, K.; Neal, P.R.; Allinson, G.; Ennis-King, J.; Hou, W.; Paterson, L.; Sharma, S.; Aiken, T. Injection Strategies for Large-Scale CO2 Storage Sites. *Energy Procedia* **2011**, *4*, 4267–4274. [CrossRef]
7. Galvez-Martos, J.L.; Morrison, J.; Jauffret, G.; Elsarrag, E.; AlHorr, Y.; Imbabi, M.S.; Glasser, F.P. Environmental Assessment of Aqueous Alkaline Absorption of Carbon Dioxide and Its Use to Produce a Construction Material. *Resour. Conserv. Recycl.* **2016**, *107*, 129–141. [CrossRef]
8. Zevenhoven, R.; Fagerlund, J.; Björklöf, T.; Mäkelä, M.; Eklund, O. Carbon Dioxide Mineralisation and Integration with Flue Gas Desulphurisation Applied to a Modern Coal-Fired Power Plant. In Proceedings of the ECOS2012, Perugia, Italy, 26–29 June 2012.
9. Ferrini, V.; De Vito, C.; Mignardi, S. Synthesis of Nesquehonite by Reaction of Gaseous CO2 with Mg Chloride Solution: Its Potential Role in the Sequestration of Carbon Dioxide. *J. Hazard. Mater.* **2009**, *168*, 832–837. [CrossRef] [PubMed]
10. Glasser, F.P.; Jauffret, G.; Morrison, J.; Galvez-Martos, J.-L.; Patterson, N.; Imbabi, M.S.-E. Sequestering CO2 by Mineralization into Useful Nesquehonite-Based Products. *Front. Energy Res.* **2016**, *4*, 3. [CrossRef]
11. Vito, C.D.; Ferrini, V.; Mignardi, S.; Cagnetti, M.; Leccese, F. Ex Situ CO_2 Mineralization via Nesquehonite: A First Attempt for an Industrial Application. In Proceedings of the 2012 11th International Conference on Environment and Electrical Engineering, Venice, Italy, 18–25 May 2012; pp. 323–327.
12. Ballirano, P.; De Vito, C.; Ferrini, V.; Mignardi, S. The Thermal Behaviour and Structural Stability of Nesquehonite, MgCO3·3H2O, Evaluated by in Situ Laboratory Parallel-Beam X-ray Powder Diffraction: New Constraints on CO2 Sequestration within Minerals. *J. Hazard. Mater.* **2010**, *178*, 522–528. [CrossRef] [PubMed]
13. Ballirano, P.; De Vito, C.; Mignardi, S.; Ferrini, V. Phase Transitions in the MgCO2H2O System and the Thermal Decomposition of Dypingite, Mg5(CO3)4(OH)2·5H2O: Implications for Geosequestration of Carbon Dioxide. *Chem. Geol.* **2013**, *340*, 59–67. [CrossRef]
14. Madlool, N.A.; Saidur, R.; Hossain, M.S.; Rahim, N.A. A Critical Review on Energy Use and Savings in the Cement Industries. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2042–2060. [CrossRef]
15. Chatterjee, A.K. Chemistry and Engineering of the Clinkerization Process—Incremental Advances and Lack of Breakthroughs. *Cem. Concr. Res.* **2011**, *41*, 624–641. [CrossRef]
16. Ruan, S.; Unluer, C. Comparative Life Cycle Assessment of Reactive MgO and Portland Cement Production. *J. Clean. Prod.* **2016**, *137*, 258–273. [CrossRef]
17. Unluer, C.; Al-Tabbaa, A. Impact of Hydrated Magnesium Carbonate Additives on the Carbonation of Reactive MgO Cements. *Cem. Concr. Res.* **2013**, *54*, 87–97. [CrossRef]
18. Vandeperre, L.J.; Al-Tabbaa, A. Accelerated Carbonation of Reactive MgO Cements. *Adv. Cem. Res.* **2007**, *19*, 67–79. [CrossRef]
19. Panesar, D.K.; Mo, L. Properties of Binary and Ternary Reactive MgO Mortar Blends Subjected to CO_2 Curing. *Cem. Concr. Compos.* **2013**, *38*, 40–49. [CrossRef]
20. Liska, M.; Al-Tabbaa, A. Performance of Magnesia Cements in Porous Blocks in Acid and Magnesium Environments. *Adv. Cem. Res.* **2012**, *24*, 221–232. [CrossRef]
21. Skliros, V.; Tsakiridis, P.; Perraki, M. A Combined Raman, Fourier Transform Infrared, and X-ray Diffraction Study of Thermally Treated Nesquehonite. *J. Raman Spectrosc.* **2020**, *51*, 1445–1453. [CrossRef]
22. Stephan, G.W.; MacGillavry, C.H. The Crystal Structure of Nesquehonite, $MgCO_3$. $3H_2O$. *Acta Crystallogr. B Struct. Sci.* **1972**, *28*, 1031–1033. [CrossRef]
23. Yang, N.; Tran, M.H.; Scott, A.; Dhakal, R.P.; Watson, M.; Shi, C.J. Properties of Magnesium Based Cements. In Proceedings of the Wellington: New Zealand Concrete Industry Conference, Wellington, New Zealand, 12–14 October 2017.