materials proceedings

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Proceeding Paper

Feasibility Study of Waste Gypsum as a Full Replacement for Fine Aggregates of Controlled Low-Strength Material †

Wei-Ting Lin [1,*], Kinga Korniejenko [2], Dariusz Mierzwiński [2], Michał Łach [2], An Cheng [1] and Kae-Long Lin [3]

[1] Department of Civil Engineering, National Ilan University, Ilan 26047, Taiwan
[2] Institute of Material Engineering, Faculty of Material Engineering and Physics, Cracow University of Technology, 31-864 Cracow, Poland
[3] Department of Environmental Engineering, National Ilan University, Ilan 26047, Taiwan
* Correspondence: wtlin@niu.edu.tw; Tel.: +886-3-9317567, Fax: +886-3-9360125
† Presented at the 10th MATBUD'2023 Scientific-Technical Conference "Building Materials Engineering and Innovative Sustainable Materials", Cracow, Poland, 19–21 April 2023.

Abstract: The waste gypsum used in this study was a by-product of petroleum coke burning by petrochemical companies which has been treated with hydration. The waste gypsum has been stored in the atmosphere for over ten years and can be considered an inert filler. Its main chemical components were calcium sulfate dihydrate (47.90%), calcium hydroxide (21.64%) and calcium carbonate (14.80%). In this study, Portland cement and fly ash were used as cementitious materials, and waste gypsum of the particle size from 9.53 mm to 0.149 mm was selected as the fine aggregate to produce a controlled low-strength material (CLSM) and to verify the suitability of reusing waste gypsum. The water to binder ratio of 0.65 was used for the specimen. The test results showed that the CLSM specimen with a high amount of waste gypsum had air-hardening properties. The placement of the specimen in water caused abnormalities, such as cracking and disintegration of the specimens. The compressive strength of atmospherically maintained specimens increased with age, with 4.71 MPa and 6.08 MPa at 28 and 56 days, respectively. No significant changes in weight or volume were measured after the specimens had been left for 56 days and then immersed in seawater and water for 28 days. As specimens were immersed in seawater for up to 100 days, needle-shaped ettringite and C-S-H colloids filled the interface between the pores and the colloids. In accordance with the concept of eco-engineering, special consideration should be given to avoid long-term contact with water and to ensure the safety and durability of waste gypsum reuse through the design of multiple protective layers.

Keywords: air-hardening properties; microscopic analysis; waste reuse

Citation: Lin, W.-T.; Korniejenko, K.; Mierzwiński, D.; Łach, M.; Cheng, A.; Lin, K.-L. Feasibility Study of Waste Gypsum as a Full Replacement for Fine Aggregates of Controlled Low-Strength Material. *Mater. Proc.* **2023**, *13*, 19. https://doi.org/10.3390/materproc2023013019

Academic Editors: Katarzyna Mróz, Tomasz Tracz, Tomasz Zdeb and Izabela Hager

Published: 14 February 2023

1. Introduction

Climate change disasters have made reducing greenhouse gases more important than ever, and cutting CO_2 emissions from energy-intensive industries has become the main focus of net-zero carbon emissions. Among Taiwan's biggest energy consumers are thermal power generation, petrochemicals and cement manufacturing industries, including the second-largest petrochemical industrial zone in the world. Globally, it has been investing heavily in reducing this energy-intensive carbon emission problem in recent years, with the aim to achieve net zero carbon emissions eventually [1,2]. Petrochemical companies have used circular fluidized bed technology to reduce wastewater, reduce coal combustion, improve combustion efficiency and reduce carbon emissions. The derived wastes included fly ash (also known as mixed gypsum) and bottom ash (also known as by-product lime), which were then hydrated to produce hydrated by-product lime (also known as waste gypsum) for reuse to achieve the circular economy effect. The suitability of waste gypsum, which is

an industrial by-product of secondary treatment, as a component material for replacing construction concrete was also a subject worthy of in-depth study and research. Using such materials as replacement for construction materials would be the most promising solution for waste resource recovery and disposal on a large scale [3].

In recent years, researchers worldwide have focused on recycling and disposing of the ash generated by circulating fluidized beds. These studies covered the basic material properties, hydration mechanisms, activation methods and applications of circulating fluidized bed combustion ashes [4]. They also provided an overview of the prospects of applying it in cementitious composites, alkali-activated materials or geopolymers [5]. The application of civil construction materials also included soil conditioners, cement substitutes, lightweight aggregates, road construction materials, controlled low-strength material (CLSM), roller compacted concrete and other technologies [6–9].

In this study, the waste gypsum provided by the plastic chemical manufacturer has been exposed to the air for more than 5 years in an interior. This has been carried out to stabilize it so it can be used as a complete replacement for fine aggregates in cement mortar. Ordinary Portland cement was used as the cementitious material, fly ash as the supplementary cementitious material and waste gypsum as the inert filler (fine aggregates). Testing for compressive strength, volume stability, water/sea immersion and scanning electron microscope (SEM) observations were used to determine the feasibility of the CLSM application.

2. Experimental Details

2.1. Materials and Mix Proportions

The test materials in this study were ordinary Portland cement, fly ash, waste gypsum and water in cement mortar specimens, in which waste gypsum of different particle-size scales was used to completely replace the fine aggregates. The specific gravity of Portland cement is 3.15 and the fineness is 3690 cm^2/g; the specific gravity of fly ash is 2.25 and the fineness is 9100 cm^2/g. The main oxidation components of fly ash contained 54.98% of SiO_2, 29.23% of Al_2O_3 and 3.38% of CaO. Waste gypsum was sieved into the particle size ≦ 4.75 mm, and the particle size between 4.75 mm and 9.53 mm. The specific gravity of waste gypsum was 2.08 and the fineness modulus (less than 4.75 mm) was 3.58 in the oven-dried condition. The main chemical components of waste gypsum were calcium sulfate dihydrate (47.90%), calcium carbonate (14.80%), silicon dioxide (4.31%), calcium hydroxide (21.64%) and calcium oxide (5.82%). The external appearance of waste gypsum, as shown in Figure 1, reveals grayish-white multi-angular-shaped particles. The test mixture is presented in Table 1. The water/cementitious ratio was fixed at 0.65, the amount of fly ash instead of cement was 33%, and waste gypsum (fine aggregates) was 20% between 4.75 and 9.53 mm.

(**a**) Waste gypsum (large particles)

(**b**) Waste gypsum (small particles)

Figure 1. Appearance of waste gypsum.

Table 1. Mix proportions (kg/m^3).

Mix No.	Water	Cement	Fly Ash	Waste Gypsum (0.149–4.75 mm)	Waste Gypsum (4.75–9.53 mm)
A	225	200	100	896	224

2.2. Test Procedures

Following the ASTM C109 standard procedure, 5 × 5 × 5 cm cubic specimens were used for compressive strength tests. The specimens were kept in the atmosphere and were water-cured. The compressive strength tests were conducted at different ages (7, 14, 28 days), and the average values of the four specimens were taken. The volume stability test specimens were made according to ASTM C596 standard as 2.5 × 2.5 × 28.5 cm prismatic specimens, and the length was taken as the average of 10 specimens. The test specimens for the immersion and exposure tests were 5 × 5 × 5 cm cubic specimens. The evaluation indices included specimen scale, weight and strength, and the evaluation was based on the average of five measurements. The exposure environment included natural seawater immersion, tap water immersion and atmospheric exposure. For SEM observations, the crushed specimens (about 1 × 1 × 3mm) after the compressive strength test were selected and tested according to the test procedure of ASTM C1723, and the age of the observed specimens was 56 days.

3. Results and Discussion

3.1. Compressive Strength

After demolding, the waste gypsum mortar specimens were first maintained in water and air for comparison. When the age of curing reached 7 days, the appearance of the specimens in water curing was irregularly cracked (as shown in Figure 2), which revealed that during the hydration of the specimens, the calcium sulfate dihydrate, calcium hydroxide and calcium oxide of waste gypsum might still react with water to produce expansion, resulting in cracking of the specimen after water immersion. On the contrary, there was no significant difference in the appearance of the air-cured specimens. Obviously, the specimens with waste gypsum completely replacing the fine aggregates should be placed in the atmospheric condition so that the hydration reaction could grow continuously.

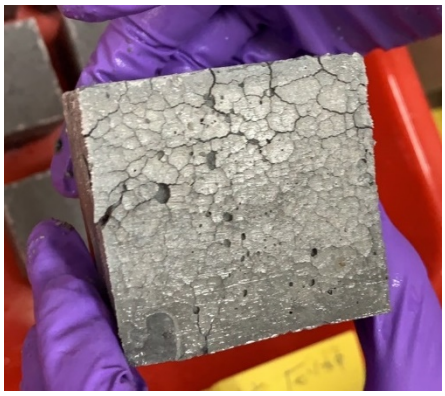


Figure 2. Appearance of the cracked specimen.

Figure 3 illustrates the compressive strength development of air-cured specimens at 7, 14, 28 and 56 days. The test results indicated a minimal difference between the four test values for each age, and the compressive strength of air-cured specimens increased with age, with compressive strengths of 4.71 MPa and 6.08 MPa at 28 days and 56 days, respectively. As waste gypsum, cement, and fly ash solidified in the specimen, a small number of components such as CaO and $Ca(OH)_2$ that might react with CO_2 were stabilized. C-S-H colloids continued to form more with age due to the solidification reaction with

cement and fly ash, resulting in higher compressive strengths in CLSM specimens. The strength results of specimens exposed to the atmosphere (by air curing) indicated that CO_2 in the atmosphere would not react continuously with the waste gypsum in CLSM specimens, causing harmful phenomena such as surface layer cracking.

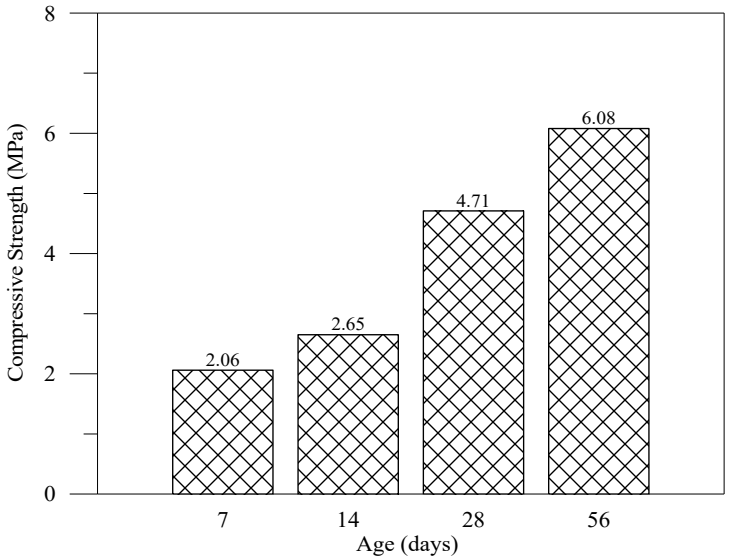


Figure 3. Compressive strength histograms.

3.2. Volume Stability

Among the tests measured at 28, 35, 42, 49 and 56 days, the length change curve along with age is shown in Figure 4. The length measurement value of the specimen at 28 days was used as the initial value for calculating the volume change. It was found that when exposed to an atmospheric CO_2 environment (atmospherically cured specimens), the length change of the specimens tended to be flat and did not change significantly. The average measured length change of the specimens was 0.0579% for 28 days of observation (age from 28 to 56 days). Based on the test results, it was assessed that CO_2 in the atmosphere would not react continuously with the waste gypsum in the specimens to compromise the volumetric stability of the CLSM specimens.

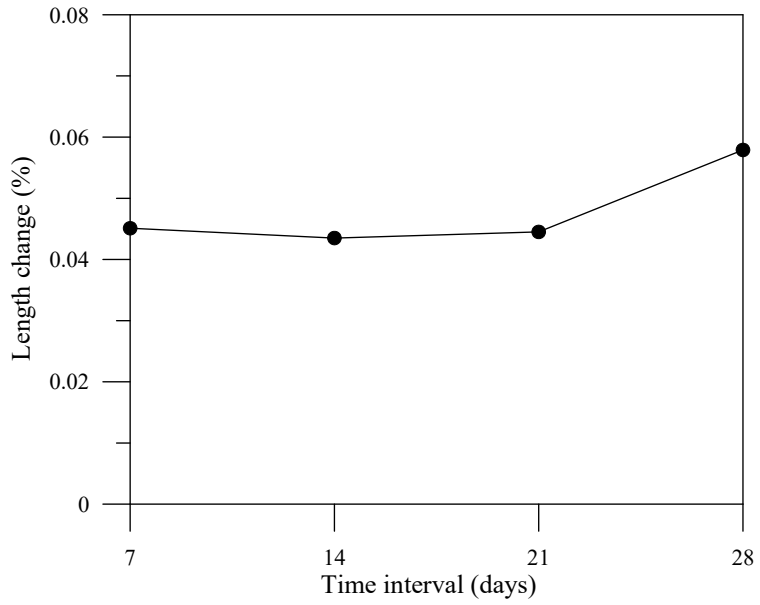


Figure 4. Length change curves.

After the specimen had been air-cured for 56 days, it was immersed in natural seawater, tap water and placed in the atmosphere. The length and weight variations at different ages of specimens immersed in tap water and seawater are shown in Figures 5 and 6, respectively. The results indicated that the average length variation of the specimens in seawater was 0.27%. In comparison, the length variation of the specimens before and after immersion in tap water was 1.00%. It can be deduced that there was no significant difference between the lengths of the specimens before and after immersion in seawater and tap water. After 28 days of immersion in seawater and tap water, the weight variations of the specimens were 3.20 and 2.93, respectively. Based on these results, it can be concluded that the weight fluctuations were insignificant. In addition, there was almost no change in the weight and volume of the specimens exposed to the atmosphere. Comparative appearances of the three immersed and exposed specimens are shown in Figure 7.

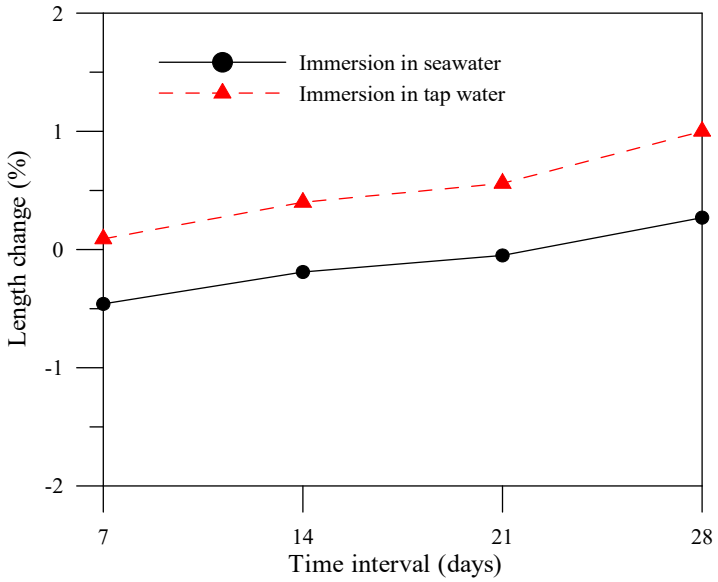


Figure 5. Trend of length change between seawater and tap water (black line: seawater).

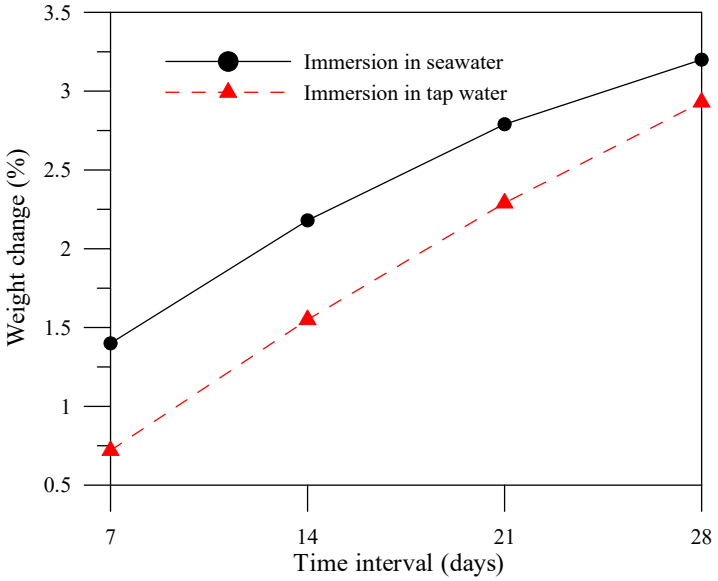


Figure 6. Trend of weight change between seawater and tap water (black line: seawater).

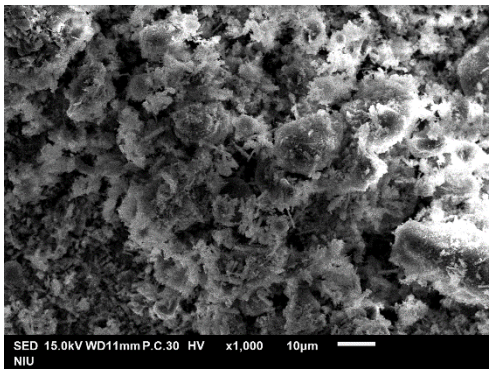
(**a**) atmosphere (**b**) seawater (**c**) tap water

Figure 7. Appearance of the three immersed and exposed specimens.

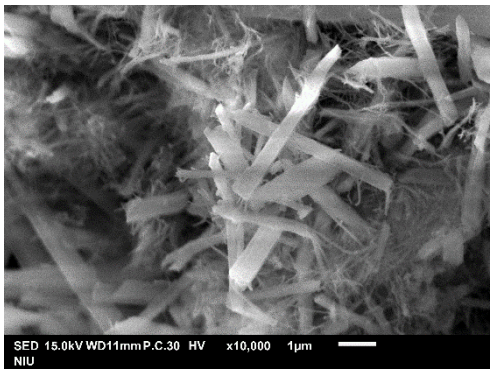
3.3. SEM Observations

Scanning electron microscopy photographs and corresponding energy dispersive X-ray (EDX) analyses are shown in Figure 8. Figure 8a,b show the surface microstructure of the waste gypsum specimens. It can be found in Figure 8a that hexagonal calcium hydroxide accounted for the majority of hydrates. In contrast, the larger particles of calcium hydroxide produced finer hydrates on the surface, and some areas of hydrates showed needle-like or column-like hydrates. Unhydrated fly ash particles were also observed on the surface of the microstructure. By magnifying the SEM photograph up to 10,000× (Figure 8b), it can be clearly observed that the interstices were filled with needle-shaped hydrides, which were presumed to be C-S-H and ettringite. The long needle-like crystals indicated the formation of large amounts of calcium–alumina hydrates (ettringite) in the waste gypsum specimens. In addition, since gypsum was the main component of the specimens, dispersed fibrous structures of the C-S-H gels were also observed, which is consistent with previous literature results [10,11]. The results of EDX in Figure 8c confirmed that the hydrates were primarily composed of Ca, Si and Al and that the hydrates were C-S-H or ettringite.

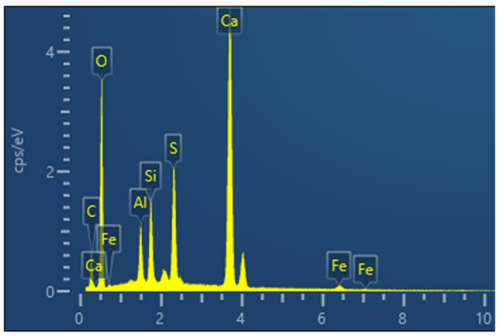
Figure 8d,e illustrate SEM images of the specimens after 56 days of curing, followed by 100 days of immersion in tap water and seawater. The specimen in Figure 8d revealed a large area of sodium hydroxide and needle-shaped hydrates (ettringite), and the water immersion facilitated the continued hydration of the specimens. In contrast, the unreacted fly ash particles continued to react to form C-S-H colloids, which filled the interface between the pores and the waste gypsum. Sodium hydroxide was observed in the specimen in Figure 8f; the specimen was immersed in seawater and the sulfide in the seawater was favorable for the growth of needle-like hydrates (ettringite). Dense ettringite could be seen filling the pores and interfaces on the surface of the specimens. From the EDX analysis results (Figure 8f), it can be verified that most of the hydrated reactants were ettringite (Ca-Si-Al crystals).



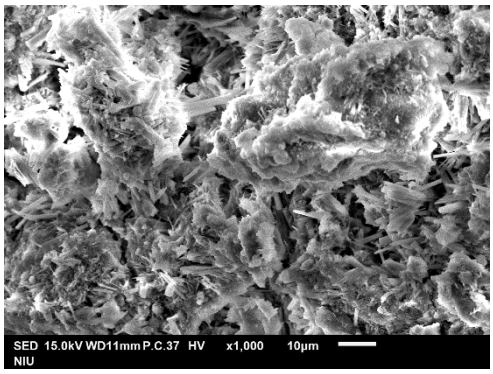
(**a**) Air-cured specimen at 56 days (×1000)



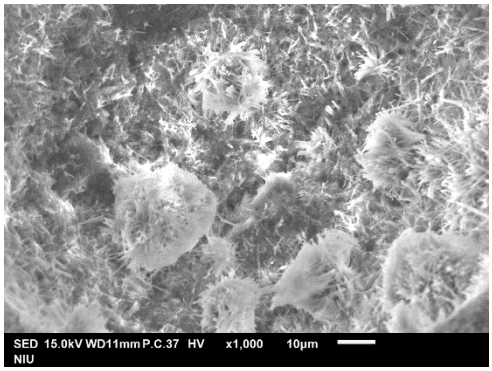
(**b**) Air-cured specimen at 56 days (×10,000)



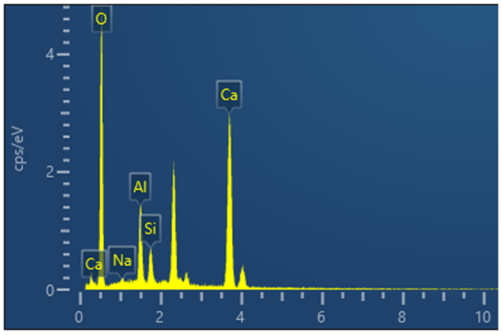
(**c**) EDX for ai-cured specimen at 56 days



(**d**) Immersion in tap water for 100 days



(**e**) Immersion in seawater for 100 days



(**f**) EDX for specimen in seawater

Figure 8. SEM photos (×3000).

4. Conclusions

In this study, cement and fly ash were used as cementitious materials and waste gypsum was used as the fine aggregates, which were suitable for CLSM. The compressive strengths at 28 and 56 days were 4.71 and 6.08 MPa, respectively. The air-curing method should be applied to avoid abnormalities such as volume expansion after curing the specimen in water. With the hydrated blending reaction, the waste gypsum in the CLSM specimen continued to react with cement and fly ash. The reaction produced more ettringite, C-S-H colloids and other hydrates with age, increasing the compressive strength. In waste gypsum, some components react with CO_2 in the air, such as CaO and $Ca(OH)_2$, but they have become stable, allowing for the specimen to maintain a reasonable volume. In addition, the volume and weight of the specimen did not change significantly after being immersed in seawater and tap water, and the appearance of the specimen was intact.

Additionally, it was determined that waste gypsum can entirely replace fine aggregates in construction and can significantly increase the amount of reuse, thus achieving the effect of the green circular economy.

Author Contributions: Conceptualization, W.-T.L., A.C. and K.K.; methodology, K.K.; validation, W.-T.L., D.M. and M.Ł.; investigation, A.C.; resources, K.-L.L.; data curation, W.-T.L. and D.M.; writing—original draft preparation, W.-T.L. and K.K.; writing—review and editing, W.-T.L. and M.Ł.; visualization, A.C. and K.-L.L.; supervision, W.-T.L. and K.-L.L.; project administration, W.-T.L. and D.M. All authors have read and agreed to the published version of the manuscript.

Funding: The National Science and Technology Council (NSTC) in Taiwan supported this research with grant NSTC 111-2923-E-197-003-MY3 and the Polish National Centre for Research and Development in Poland, under the M-ERA.NET 3 program, grant number M-ERA.NET3/2021/144/3D-FOAM/2022.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Publication cost of this paper was covered with founds of the Polish National Agency for Academic Exchange (NAWA): "MATBUD'2023—Developing international scientific cooperation in the field of building materials engineering" BPI/WTP/2021/1/00002, MATBUD'2023.

Conflicts of Interest: The authors declare no conflict of interest.

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