

# Carbon Sequestration of Limestone Mine Waste through Mineral Carbonation and Utilization as Supplementary Cementitious Material

Verma Loretta M. Molahid<sup>1</sup>, Faradiella Mohd Kusun<sup>1,2\*</sup>, Nurfakhira Meor Ahmad Kamal<sup>1</sup>, Sharifah Nur Munirah Syed Hasan<sup>1</sup>, Noor Allesya Alis Ramli<sup>1</sup>, Ahmad Makmom Abdullah<sup>1</sup>, Zulfa Hanan Ashaari<sup>1</sup>

<sup>1</sup>Department of Environment, Faculty of Forestry and Environment, Universiti Putra Malaysia, 43400 Serdang, Selangor, MALAYSIA

<sup>2</sup>Institute of Tropical Forestry and Forest Product, Universiti Putra Malaysia, 43400 Serdang, Selangor, MALAYSIA

\*Corresponding Author

DOI: <https://doi.org/10.30880/ijie.2021.13.01.028>

Received 17 June 2020; Accepted 10 December 2020; Available online 25 February 2021

**Abstract:** This study highlights the potential of limestone mine waste for mineral carbonation and its potential as supplementary cementitious material. Mineralogical and chemical composition analysis of limestone mine waste sample were performed, and mineral carbonation experiment was conducted under ambient pressure and temperature. The effect of particle size and pH condition was investigated to observe the influence of the parameters on carbonation efficiency. The limestone mine wastes were identified to have potential for carbon sequestration due to its high calcium oxide content alongside magnesium oxide which are derived from Ca- and Mg-carbonate minerals. It can be seen from this study that smaller particle size and pH 10 condition were ideal for the carbonation process. The end product of calcium carbonate proved that mineral carbonation occurred during the reaction, indicating the potential of the mine waste as feedstock for mineral carbonation. Additionally, the use of limestone mine waste can also be regarded as supplementary cementitious material due to its chemical composition while at the same time serves as potential storage and sink for sequestered carbon dioxide.

**Keywords:** Limestone, mine waste, carbon sequestration, mineral carbonation, cementitious material, minerals

## 1. Introduction

Global warming has become the greatest concern on national level. It has been believed that the increase in greenhouse gas (GHG) emission in the atmosphere, mainly carbon dioxide (CO<sub>2</sub>) via fossil fuel consumption is the main source for the uncommon rise of the global temperature over the past several years [1], [2]. Global-scale climate modelling has predicted that the greenhouse gas concentration will continue to increase along with the earth's average surface temperature resulting in changes in weather, rise of sea levels, disturbed ecosystem, potential loss of life and property (caused by severe flooding, intense hurricane and rain, and sea level increase) and high risk of heat strokes and deaths from frequent fires and more hotter summer [3]. Furthermore, as reported by NOAA [4] and mentioned by Azdarpour et al. [5], carbon dioxide concentration has increased from 280 ppm in the 1970s to 402.9 ppm in 2016 mainly due to the increasing earth population and increasing activity of fossil fuel combustion. To date, carbon dioxide

concentration has reached 408 ppm which shows an increase of 6 ppm in just 1 year [6]. As a result, the earth has become warmer than before causing bad implication to the environment, human and other living things. Concern over the global warming issue on anthropogenic contribution (use of fossil fuel and CO<sub>2</sub> emission) gives rise to serious international demand on nation to lower their production of anthropogenic CO<sub>2</sub>.

Mining industries is considered as one of the activities that contribute to the increasing carbon dioxide level. Despite its role as one of the main industries in Malaysia, several other mining-related problems arise such as contamination of surface water with heavy metals originated from weathering of the mining materials and its abandoned waste, or also known as acid mine drainage [7], and decreasing of land caused by the accumulation of mining waste that have little to no market value. In an effort to overcome these issues, sequestration of carbon dioxide or also known as carbon capture and storage (CCS) has been proposed as the solution that can store carbon in a stable form and for a long period of time (i.e. mineral carbonation) by using carbon-intensive industrial waste such as mining waste as the feedstock for mineral carbonation [8], [9].

Mineral carbonation is the reaction of basic minerals with CO<sub>2</sub> to form non-toxic solid carbonate. It can occur naturally but a little modification to accelerate this natural process can contribute in reducing the level of excess CO<sub>2</sub> in the atmosphere, thus help reducing the global temperature. Reaction for mineral carbonation can be seen in Eq. (1) where CO<sub>2</sub> reacts with metal oxide bearing minerals forming insoluble carbon [10]. Examples of starting materials for mineral carbonation includes Mg-silicate minerals (e.g. Mg<sub>2</sub>SiO<sub>4</sub>, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and Fe- or Ca-rich silicates (e.g. Fe<sub>2</sub>SiO<sub>4</sub>, CaSiO<sub>3</sub>). Essentially, these minerals exist abundantly in various types of waste materials. Studies on mineral carbonation using steel slag (industrial waste) and minerals such as wollastonite and serpentinite (can be found in mine waste) is a widely discussed topic specifically on their high potential in capturing carbon dioxide. This is due to its high content of Mg- and Ca-rich silicate minerals and oxides. It has been proven that these feedstocks can capture carbon dioxide more efficiently in an optimized condition [11]-[20].



Apart from this, limestone waste rocks have not yet been studied in depth on its potential for carbon sequestration. However, limestone was known as a material that contains high amount of calcium which shows a great potential for capturing carbon dioxide chemically in the form of carbonate mineral by means of mineral carbonation [21]. The high content of calcium oxide (CaO) in limestone waste can theoretically capture carbon dioxide, forming stable calcium carbonate. Furthermore, the use of limestone waste in capturing carbon dioxide can act as 'killing two birds with one stone' as this can help in solving the problem of increasing carbon dioxide emission from a carbon-intensive industry (i.e. limestone quarry) as well as the increasing of wasted land caused by the accumulated waste. By using limestone mine waste as the feedstock for mineral carbonation, the issue concerning wasteland can be resolved. This can lower the number of wastelands hence reducing the environmental footprint (reduced contamination of surface water caused by weathering of mining waste). The mining industries can also benefit from the utilization of limestone waste where it requires less expenditure for them to close the mine for rehabilitation, closure and long-term monitoring. In addition, mineral carbonation is considered as a permanent and safe method for carbon dioxide disposal because the reaction of carbon dioxide with the minerals form a carbonate product that does not hazardous to the environment, humans and other living things.

Likewise, there will be no risk of carbon dioxide leakage over time due to the lower energy state of solid carbonates compared to carbon dioxide gas [22], [23]. Moreover, the materials needed for mineral carbonation are abundant and it exists worldwide. These various types of feedstocks however are different in their characteristics (i.e. chemical, morphology and elemental composition), so the optimum condition for the mineral carbonation to occur cannot be assumed or determined with a certain fixed value as it is found to be greatly dependent on the experimental condition and material properties [11]. This highlights the importance of a laboratory scale experiment, so that the optimum condition can be determined specifically for the type of feedstock studied, and up-scaled in a pilot test and tested further for industrial application. In this study, sedimentary limestone waste rocks from a limestone mining site were studied and used to capture carbon dioxide. Thus, this study aims to evaluate the potential use of the limestone waste rocks to capture and store carbon dioxide by means of mineral carbonation and to investigate the influence of different pH condition and particle size fraction on carbonation process. Further utilization of the mine waste as supplementary cementitious material was also studied alongside its application for carbon capture and storage.

## 2. Methods

### 2.1 Materials

The limestone waste rock samples were collected from a limestone mining area operated by Imerys Sdn Bhd, located at Simpang Pulai, Perak. The samples were air-dried at room temperature (24 hours), grounded into small particles, and homogenized using a 1 mm sieve. Then, the pH was measured according to British Standard (BS) 1377, Part 3, Section 9 [24] to determine the natural pH of the limestone mine waste.

## 2.2 Mineralogical, Morphological and Chemical Analysis

Mineralogical analysis was carried out using X-ray diffraction (XRD) in a diffractometer (model Bruker-AXS D8 Advanced, USA). This analysis is required to obtain the mineral composition and crystalline phases of the samples [5]. The d-spacing was identified using OriginPro 9.55 software (Originlab Corporation, Northampton, UK). In addition, the morphological and chemical composition of the waste samples were characterized using scanning electron microscopy (SEM) (model Phillips XL30, Amsterdam, Netherlands) equipped with energy dispersive X-ray (EDX) to determine the elemental composition in percentage (%) and the morphological structure of the materials.

## 2.3 Experimental Method

The homogenized limestone waste was further sieved using 38  $\mu\text{m}$  and 75  $\mu\text{m}$  sieve for the carbonation experiment preparation. The experiment was carried out in a 250 mL round bottom flask under ambient temperature as well as ambient pressure (Fig. 1). 10 g of the sieved limestone waste sample (i.e. 38  $\mu\text{m}$  and 75  $\mu\text{m}$ ) were placed into the flask. 50 mL of 1M sodium chloride (NaCl) and another 50 mL of 0.64M sodium bicarbonate ( $\text{NaHCO}_3$ ) was then poured into the flask. The pH was then adjusted accordingly prior to the studied pH (i.e. pH 8, pH 10 and pH 12) using either 1M of sodium hydroxide (NaOH) or 1M of hydrochloric acid (HCl). Then dry ice was added into the slurry as a substitute for the carbon dioxide gas and the flask was sealed immediately to prevent the carbon dioxide from escaping. The flask was placed on the orbital shaker with 100 rpm shaking speed and was left overnight.

24 hours after the experiment, all samples were filtered using 0.45  $\mu\text{m}$  filter paper and air-dried for another night. Samples were then analyzed for their mineralogical, morphological and chemical composition using XRD and SEM-EDX analysis. Thermogravimetric analysis (TGA) was then carried out for the calculation of the carbonation conversion efficiencies and carbonation purity based on the weight loss in TGA using Eq. (2) and Eq. (3).



**Fig. 1 - Carbonation experiment carried out in a 250 mL round bottom flask placed on orbital shaker**

$$\text{Ca Carbonation efficiency (\%)} = \frac{\text{Ca mass in CaCO}_3}{\text{Ca total mass in feeding material}} \times 100 \quad (2)$$

$$\text{Ca mass in CaCO}_3 = \Delta w (\%) \times \frac{\text{MW Ca}}{\text{MW CO}_2} \times \text{mass of solid residue} \quad (3)$$

## 3. Results and Discussion

### 3.1 Physical Characteristics of Limestone Waste Rocks

The natural pH of the limestone waste was found to be 8.10, 8.26 and 8.27 for sample 1, 2 and 3, respectively (Fig. 2). This indicates that the materials are alkaline in nature [25]. It has been proved that precipitation is enhanced in a highly alkaline condition (pH 9.4) producing magnesium carbonate product with high purity [5]. Adding sodium hydroxide (NaOH) into solution can increase the pH and the precipitation rate. Based on the results and from previous studies, it can be seen that pH plays an important role in mineral carbonation process, suggesting that the natural pH of the limestone waste shows great potential for mineral carbonation process.

### 3.2 Mineralogical and Chemical Composition of Limestone Waste Rocks

In the raw limestone waste sample, it is obvious that calcite ( $\text{CaCO}_3$ ) is the most dominant mineral where the significant peak can be observed at 29.67° and 29.62° for sample 1, sample 2 and sample 3 respectively (Fig. 3). Other minor minerals were also observed in all three samples namely akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ), while bustamite ( $\text{MnCaSiO}_3$ ) was found in sample 3. Although only a few minerals can be observed through XRD analysis, there were probably other minor minerals present that have been 'masked' by the calcite mineral which has the strongest reflection at 29.67° and 29.62°. These peaks can overlap with other minerals, where its 'over-shadow' the characteristic and peak of other less abundant minerals [33]. Eventually, this is a common occurrence when dealing with carbonated samples where sequential extraction needs to be done to remove calcite, and for the minor phases was able to be identified. The chemical

composition from the EDX analysis (table 1) further support the mineralogical results which shows that raw limestone waste material was mainly composed of CaO with percentage range of 72.12% - 82.88%. In addition, carbon (C) was found to be the second highest components in limestone waste. Sample 3 with 24.03% has the highest amount of carbon, followed by sample 1 and sample 2 with percentage of 21.30% and 16.10% respectively. Small amount of MgO in sample 1 and sample 2 which come from akarmanite mineral, and some SiO<sub>2</sub> and MnO was also detected through the EDX analysis. SiO<sub>2</sub> probably come from both akarmanite and bustamite minerals, while MnO is from bustamite minerals.

The high percentage of CaO signifies the potential of limestone waste rocks to sequester carbon dioxide via mineral carbonation, producing calcium carbonate as the final product as the Ca<sup>2+</sup> ion reacts with carbon dioxide, converting it into CaCO<sub>3</sub> [10]. This implies that the high amount of metal oxides (i.e. CaO or MgO) contained in the limestone waste has the potential to store more carbon dioxide because of its high storage reserved for capturing and storing the carbon dioxide, despite being chemically in stable carbonate form.

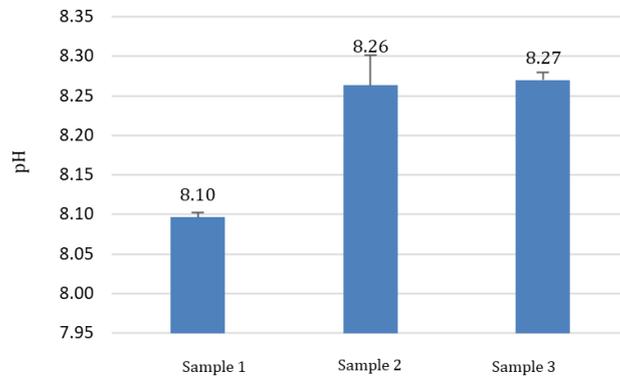


Fig. 2 - pH of limestone waste rock samples. Black bars indicate standard deviation from three replicates

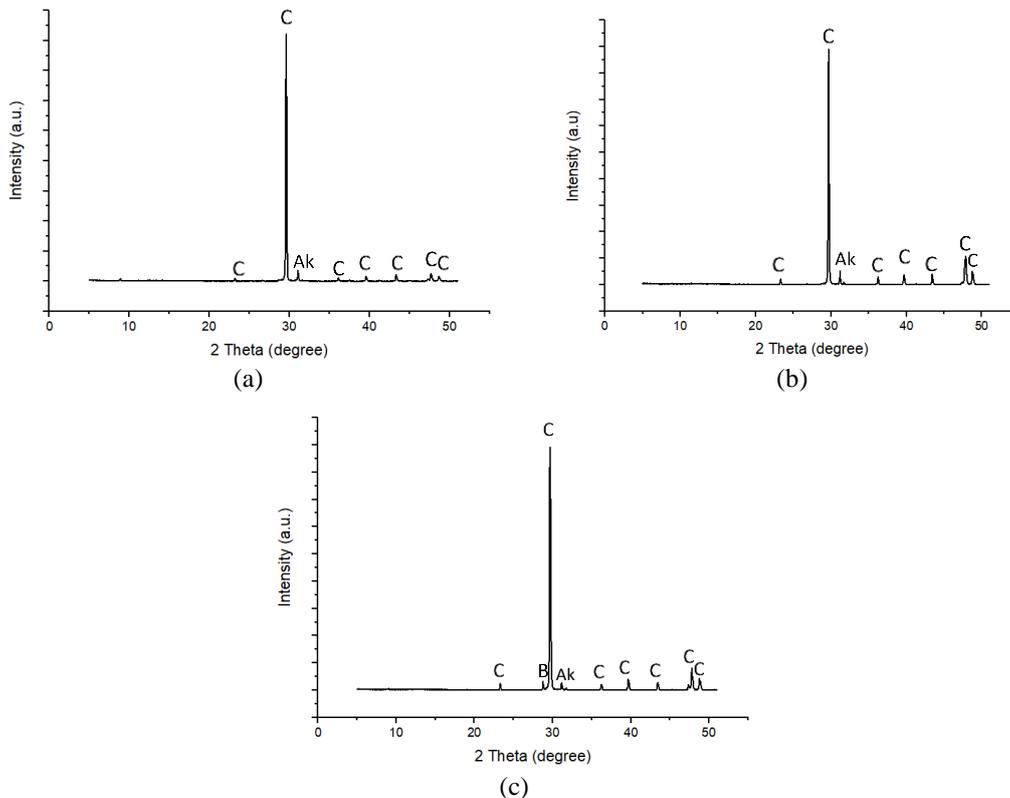


Fig. 3 - XRD pattern of raw limestone waste rock samples from three different point: (a) sample 1 (b) sample 2; and (c) sample 3. Labelled alphabet represents the minerals found in the waste: calcite (C); bustamite (B); and akarmanite (Ak)

**Table 1 - Chemical constituents of limestone waste rock sample 1 under different carbonation conditions**

Formula	Weight percent oxide %						
	Particle size ( $\mu\text{m}$ )		<38			<75	
	Untreated	pH 8	pH 10	pH 12	pH8	pH10	pH12
C	21.30	18.65	19.03	21.36	22.03	19.5	24.36
NaO <sub>2</sub>	-	-	-	-	-	-	2.52
MgO	4.36	3.51	2.64	6.41	4.92	2.11	2.22
Al <sub>2</sub> O <sub>6</sub>	1.00	-	-	-	-	-	2.33
SiO <sub>2</sub>	1.14	-	-	6.98	-	0.51	0.46
Cl	-	-	0.76	-	0.07	0.44	0.84
KO <sub>2</sub>	-	2.38	-	-	-	-	-
CaO	<b>72.12</b>	<b>75.45</b>	<b>77.58</b>	<b>65.25</b>	<b>72.98</b>	<b>77.45</b>	<b>67.27</b>

**Table 2 - Chemical constituents of limestone waste rock sample 2 under different carbonation conditions**

Formula	Weight percent oxide %						
	Particle size ( $\mu\text{m}$ )		<38			<75	
	Untreated	pH 8	pH 10	pH 12	pH8	pH10	pH12
C	16.1	25.37	12.25	20.01	18.70	16.87	16.95
NaO <sub>2</sub>	-	-	0.86	-	-	-	-
MgO	-	3.41	1.55	4.53	1.89	3.03	4.78
Al <sub>2</sub> O <sub>6</sub>	-	0.56	1.23	-	-	-	-
SiO <sub>2</sub>	1.02	-	0.68	-	-	-	-
Cl	-	0.38	0.11	-	-	-	-
KO <sub>2</sub>	-	-	-	-	-	-	-
CaO	<b>82.88</b>	<b>70.28</b>	<b>83.31</b>	<b>75.46</b>	<b>74.41</b>	<b>80.1</b>	<b>78.27</b>

**Table 3 - Chemical constituents of limestone waste rock sample 3 under different carbonation conditions**

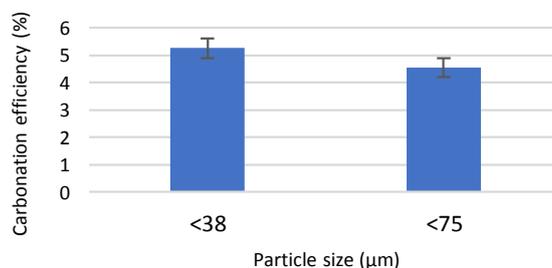
Formula	Weight percent oxide %						
	Particle size ( $\mu\text{m}$ )		<38			<75	
	Untreated	pH 8	pH 10	pH 12	pH8	pH10	pH12
C	24.03	20.65	16.08	17.62	20.95	14.70	19.44
NaO <sub>2</sub>	-	-	-	-	-	-	-
MgO	3.49	3.65	2.82	4.23	3.04	4.98	2.37
Al <sub>2</sub> O <sub>6</sub>	-	-	-	-	-	-	-
SiO <sub>2</sub>	-	-	-	-	-	-	-
Cl	-	-	0.27	-	-	-	-
KO <sub>2</sub>	-	-	-	-	-	-	-
CaO	<b>72.48</b>	<b>75.70</b>	<b>81.11</b>	<b>78.14</b>	<b>76.01</b>	<b>80.32</b>	<b>78.18</b>

### 3.2 Effect of Particle Size on Carbonation Efficiency

The influence of different particle on the carbonation efficiency was analysed by using the waste with two different particle size (i.e. less than 38  $\mu\text{m}$  and 75  $\mu\text{m}$ ). While particle size parameter was varied for the three samples, the pH condition was set at constant (i.e. pH 10). The reaction time for each experiment was 60 minutes. NaHCO<sub>3</sub> and NaCl were added to 10 g of limestone waste with specific particle size under ambient pressure as well as temperature. Carbonation reaction was left overnight and the samples were then collected for further analysis using TGA and SEM-EDX.

Each of the samples was analyzed using TGA to determine its carbonation efficiency. Fig. 5 shows the average carbonation efficiency (%) using different particle sizes, while Table 4 shows the specific carbonation efficiency of each

samples with different particle sizes. Based on the figure and table, the smaller particle size of  $<38 \mu\text{m}$  has a higher carbonation efficiency with an average value of 5.25% compared to 4.55% in sample with particle size of  $<75 \mu\text{m}$ . This is consistent with studies done by Yan et al. [20], in which the best results were achieved using the smallest particle size of  $45 \mu\text{m}$  and  $30 \mu\text{m}$ , respectively. This is due to the fact that the conversion rate involving solid carbonate production from calcium or iron is a function of the total specific surface area of the particle. The surface area is the place where the reaction occurs. Making the particle size smaller can increase the surface area thus increasing the reaction rate hence resulting in higher conversion rate. Rahmani et al. [26] proved that decreasing the particle size can also optimize leaching of  $\text{Mg}^{2+}$  ion to 99% and it is highly favorable for the production of carbonate product. This is because of the increase in the substrates surface area causing the reaction rate to escalate, resulting in an improvement that is favorable for the carbonation degree. In depth, the surface area can be increased by grinding or sieving, making the particle size smaller but with more available surface area for reaction to occur, this is also known as mechanical activation [8]. Hence, the limestone waste rock sample has shown that particle size can affect the carbonation reaction process.



**Fig. 5 – Average efficiency of carbonation in three samples for particle size of less than  $38 \mu\text{m}$  and  $75 \mu\text{m}$  at constant pH (i.e. pH 10)**

**Table 4 - Carbonation efficiency (%) of limestone waste rock using different particle sizes**

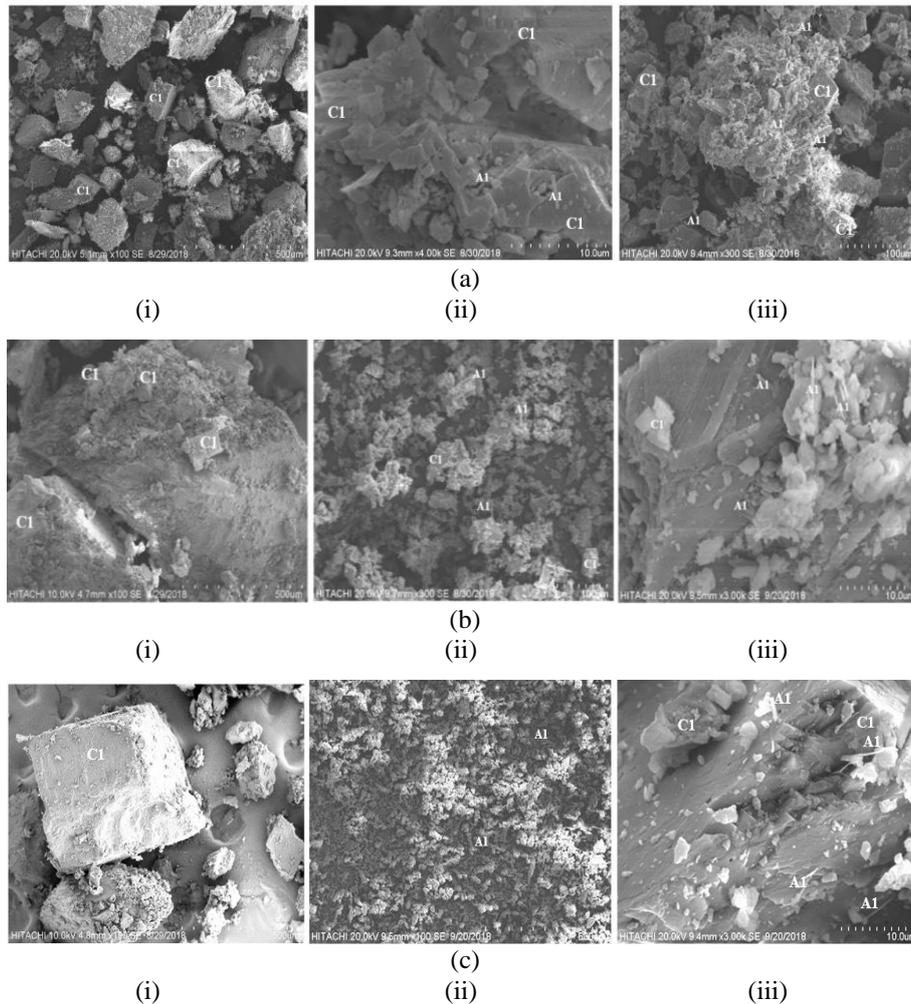
Sample	Particle size ( $\mu\text{m}$ )	Carbonation efficiency (%)
1	$< 38$	7.53
	$< 75$	3.77
2	$< 38$	3.34
	$< 75$	5.68
3	$< 38$	4.89
	$< 75$	4.20

### 3.3 Effect of pH on Carbonation Efficiency

Results from Table 1, Table 2 and Table 3 reveal that, at pH 10, the chemical constituent of CaO was relatively higher compared to pH 8 and pH 12. Meaning that in pH 10, more carbonate product was formed showing that pH 10 condition is more favorable for carbonation to occur. The fixation of carbon dioxide into limestone waste rock samples during carbonation test can be confirmed using microstructural analysis. Scanning electron microscopic imaging with energy dispersive X-ray (SEM-EDX) analysis was carried out to observe the occurrence of calcium carbonate ( $\text{CaCO}_3$ ) crystal after the carbonation reaction.

The SEM images of raw limestone waste sample for sample 1, 2, and 3 was presented in Fig. 6 ((a)(i), (b)(i), (c)(i)) respectively. Breakage patterns, and a clear euhedral calcite grains can be observed in all of the three unreacted samples, consistent with findings by Lu et al. [27]. Evidently, the shape indicates calcium carbonate in its most stable form, namely calcite [28]. This is consistent with the mineralogical analysis where calcite was detected as the most dominant minerals found in the waste. In addition, the carbonated sample with pH 10 shows a hexagonal rod-shaped carbonated crystal in  $<38 \mu\text{m}$  and  $<75 \mu\text{m}$  particle size. This confirms the presence of calcium carbonate precipitate as reported by Azdarpour et al. [5], where rod or needle-shaped crystal is a common structure found for aragonite, which is one of the calcium carbonate mineral form besides calcite and vaterite. The low carbonation efficiency results showed that calcium carbonate with low purity was produced during the reaction, thus, implying that some of the limestone waste fraction remained unreacted throughout the reaction. Although it can be seen from these figures that during the experiments, most of the sample's surface is altered due to the reaction occurred, only small amount of the calcite and dolomite mineral reacted with carbon dioxide to produce carbonate product and in this case, aragonite was produced. This is most probably because limestone consists mainly of calcite; an anhydrous polymorph of  $\text{CaCO}_3$  and is thermodynamically the most stable at ambient conditions [29]. This explains the high carbonation efficiency found in sample 1 which is 7.53% (i.e. pH 10 with the particle size of  $<38 \mu\text{m}$ ) where the major mineral found was dolomite while the other sample with calcite as the major

mineral has a much lower carbonation efficiency (Table 4). Despite the low carbonation efficiency obtained, calcium carbonate in the form of aragonite is successfully precipitated at an ambient condition although it is generally formed at elevated temperature [29].



**Fig. 6 - SEM image of the three-limestone waste rock. (a)(b)(c) (i) Unreacted sample for sample 1, 2 and 3 respectively with a clear euhedral calcite grains (C1) with some breakage patterns. (a)(b)(c) (ii) and (iii) Carbonated sample for sample 1, 2 and 3 respectively showing hexagonal rod and needle-shaped of aragonite crystal (A1) with some unreacted calcite (C1)**

### 3.3 Potential Reutilization as Supplementary Cementitious Material

From another point of view, the use of limestone mine waste can be regarded as supplementary cementitious material (SCM) in the production of cement-based materials, in which the use of ordinary Portland cement can be reduced of its proportion. This is mainly due to the composition of minerals in the waste materials such as CaO and MgO that can help improve the structure of particles in the material. Based on its composition, the limestone mine waste has relatively lower pozzolanic behavior in which the pozzolanic oxides is estimated to be about 2.14%. It has been known that limestone has little reactivity and pozzolanic properties, which might indicate its potential for carbonated material sink [30]. The utilization of pozzolanic materials in SCM might reduce carbonation resistance of cement-based material [31]. From carbon sequestration perspective, carbonation reaction of components like CaO and MgO will produce carbonate minerals that can act as additional binder which can increase the strength of cement-based materials. It can be seen that characteristics of the cement-based material developed from the mine waste in this study which is in the form of brick are as presented in Table 5. Notably, all the bricks made of the limestone waste has surpassed the engineering specifications for load bearing bricks according to Malaysian Standards. Therefore, incorporation of mine waste has been useful in reducing the use of commercial ordinary Portland cement while at the same time securing its potential for carbon capture. Despite being in stable carbonate form, the availability of storage reserve in the mine waste material makes it potential for more carbon to be sequestered. It was found that limestone waste used as a SCM promotes further carbonation reaction thus increasing the strength of material and stimulates higher potential for CO<sub>2</sub> capture [32], [33].

The results are also comparable to some recent studies on the use of mine waste materials and its potential for CO<sub>2</sub> capture and storage [34]-[36].

**Table 5 - Cement-based material (bricks) product and classification according to Malaysian Standard**

Brick type/ (This study)	Compressive Strength, N/mm <sup>2</sup>	Water absorption, %	Designation	Class	Average Compressive Strength, N/mm <sup>2</sup> (min)	Water absorption, % (max)
			Engineering Brick	A	69.0	4.5
				B	48.5	7.0
LMW40	34.3	1.2		15	103.5	
LMW50	29.7	0.5		10	69.0	
LMW60	40.2	1.4		7	48.5	
			Load Bearing Brick	5	34.5	No specific requirements
				4	27.5	
				3	20.5	
				2	14.0	
				1	7.0	
			Brick for Damp-proof Courses	DPC	As required	

LMW40-brick with 40% mine waste; LMW50-brick with 50% mine waste; LMW60-brick with 60% mine waste

#### 4. Conclusions

Carbon dioxide sequestration using limestone waste rock based on CaO with regard to effect of particle size and pH condition was studied with the aim of evaluating its potential in carbon capture and storage (CCS). Characteristic of limestone waste rock has been investigated using XRD and SEM-EDX analysis, and it was found that limestone waste rock contains high amount of CaO and was deemed favourable making it a suitable feedstock for the mineral carbonation reaction. Furthermore, carbonation results on the effect of particle shows that particle size reduction has shown great potential in improving the carbonation efficiency where smaller particle size (i.e. less than 38  $\mu\text{m}$ ) has achieved higher efficiency (5.25%) compared to using particle size of less than 75  $\mu\text{m}$  (4.55%). Results from the carbonation experiment indicate that particle size is one of the key factors in converting CaO to CaCO<sub>3</sub>. Moreover, carbonation results showed that CaCO<sub>3</sub> were produced during the mineral carbonation reaction. However, relatively lower carbonation efficiency obtained suggests that, further optimization of the operating parameters could help improve the carbonation reaction. Despite this, use of limestone mine waste is regarded as potential candidate for cement replacement alongside its carbon storage capacity.

#### Acknowledgement

This study was funded by Universiti Putra Malaysia and Ministry of Higher Education Malaysia under the grants FRGS 5540081 and GPIPS 9574900. The authors would like to acknowledge laboratory staffs of the Department of Physics, Faculty of Science, UPM and CRIM, Universiti Kebangsaan Malaysia for providing technical assistance for sample analysis.

#### References

- [1] Oalkers, E. H., & Cole, D. R. (2008). Carbon dioxide sequestration a solution to a global problem. *Elements*, 4, 305–310
- [2] Kusin, F. M., Akhir, N. I. M., Mohamat-Yusuff, F., Awang, M. (2016). Nitrous oxide emission from nitrogen fertiliser application in oil palm plantation of different stages. *International Journal of Global Warming*, 9(4), 529-541
- [3] Riebeek, H. (2010). Global Warming. <https://earthobservatory.nasa.gov/Features/GlobalWarming/page1.php>
- [4] NOAA Earth System Research Laboratory (2017). Trends in Atmospheric Carbon Dioxide. [www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)
- [5] Azdarpour, A., Asadullah, M., Junin, R., Manan, M., Hamidi, H., & Mohammadian, E. (2014). Direct carbonation of red gypsum to produce solid carbonates. *Fuel Processing Technology*, 126, 429–434.
- [6] NOAA Earth System Research Laboratory (2018). Trends in Atmospheric Carbon Dioxide. [www.esrl.noaa.gov/gmd/ccgg/trends/](http://www.esrl.noaa.gov/gmd/ccgg/trends/)

- [7] Affandi, F. N. A., Kusin, F. M., Sulong, N. A., & Madzin, Z. (2018). Hydrogeochemical assessment of mine-impacted water and sediment of iron ore mining. *IOP Conference Series Earth and Environmental Science*, 140, 012-023
- [8] Jacobs, A. D., & Hitch, M. (2011). Experimental mineral carbonation: approaches to accelerate CO<sub>2</sub> sequestration in mine waste materials. *International Journal of Mining, Reclamation and Environment*, 25, 321–331.
- [9] Hitch, M., Ballantyne, S. M., & Hindle, S. R. (2010). Revaluing mine waste rock for carbon capture and storage. *International Journal of Mining, Reclamation and Environment*, 24, 64–79.
- [10] Sanna, A., Uibu, M., Caramanna, G., Kuusik, R., & Maroto-Valer, M. M. (2014). A review of mineral carbonation technologies to sequester CO<sub>2</sub>. *Chemical Society Reviews*, 43(23), 8049–8080.
- [11] Ukwattage, N. L., Ranjith, P. G., & Li, X. (2017). Steel-making slag for mineral sequestration of carbon dioxide by accelerated carbonation. *Journal of the International Measurement Confederation*, 97, 15–22.
- [12] Selamat, S. N., Nor, N. H. M., Rashid, M. H. A., Ahmad, M. F., Mohamad, F., Ismail, A. E., & Seiji, Y. (2017). Review of CO<sub>2</sub> Reduction Technologies using Mineral Carbonation of Iron and Steel Making Slag in Malaysia. *Journal of Physics: Conference Series*, 914(1)
- [13] Said, A., Laukkanen, T., & Järvinen, M. (2016). Pilot-scale experimental work on carbon dioxide sequestration using steelmaking slag. *Applied Energy*, 177, 602–611
- [14] Revathy, T. D. R., Palanivelu, K., & Ramachandran, A. (2016). Direct mineral carbonation of steelmaking slag for CO<sub>2</sub> sequestration at room temperature. *Environmental Science and Pollution Research*, 23(8), 7349–7359
- [15] Ghacham, A. B., Pasquier, L. C., Cecchi, E., Blais, J. F., & Mercier, G. (2016). CO<sub>2</sub> sequestration by mineral carbonation of steel slags under ambient temperature: parameters influence, and optimization. *Environmental Science and Pollution Research*, 23, 17635–17646
- [16] Ding, W., Fu, L., Ouyang, J., & Yang, H. (2014). CO<sub>2</sub> mineral sequestration by wollastonite carbonation. *Physics and Chemistry of Minerals*, 41, 489–496
- [17] Pan, S. Y., Chiang, P. C., Chen, Y. H., Chen, C. D., Lin, H. Y., & Chang, E. E. (2013). Performance evaluation of aqueous carbonation for steelmaking slag: Process chemistry. *Energy Procedia*, 37, 115–121
- [18] Baciocchi, R., Costa, G., Poletini, A., & Pomi, R. (2009). Influence of particle size on the carbonation of stainless steel slag for CO<sub>2</sub> storage. *Energy Procedia*, 1, 4859–4866
- [19] Romao, I. S., Gando-Ferreira, L. M., Da Silva, M. M. V. G., & Zevenhoven, R. (2016). CO<sub>2</sub> sequestration with serpentinite and metaperidotite from Northeast Portugal. *Minerals Engineering*, 94, 104–114
- [20] Yan, H., Zhang, J., Zhao, Y., Liu, R., & Zheng, C. (2015). CO<sub>2</sub> Sequestration by direct aqueous mineral carbonation under low-medium pressure conditions. *Journal of Chemical Engineering of Japan*, 48(11), 937–946
- [21] Han, D., Namkung, H., Lee, H., Huh, D., & Kim, H. (2015). Journal of Industrial and Engineering Chemistry CO<sub>2</sub> sequestration by aqueous mineral carbonation of limestone in a supercritical reactor. *Journal of Industrial and Engineering Chemistry*, 21, 792–796
- [22] Lackner, K. S., Wendt, C. H., Butt, D. P., Joyce, E. L., & Sharp, D. H. (1995). Carbon dioxide disposal in carbonate minerals. *Energy*, 20, 1153–1170.
- [23] Chae, S. C., Jang, Y. N., & Ryu, K. W. (2009). Mineral carbonation as a sequestration method of CO<sub>2</sub>. *Journal of the Geological Society of Korea*, 45, 527-555.
- [24] BS 1377-3. (1990). Method of Test for Soils for Civil Engineering Purposes - Part 3: Chemical and Electro-chemical Test. British Standards. London, UK
- [25] Hasan, S. N. M., Kusin, F., Jusop, S., & Yusuff, F. (2018). Potential of Soil, Sludge and Sediment for Mineral Carbonation Process in Selinsing Gold Mine, Malaysia. *Minerals*, 8(6), 257
- [26] Rahmani, O., Highfield, J., Junin, R., Tyrer, M., & Azdarpour, A.B. (2016). Experimental investigation and simplistic geochemical modeling of CO<sub>2</sub> mineral carbonation using the mount tawai peridotite. *Molecules*, 21(353), 1–19
- [27] Lu, J., Mickler, P. J., & Nicot, J. (2014). Geochemical impact of oxygen impurity on siliciclastic and carbonate reservoir rocks for carbon storage. *Energy Procedia*, 63, 4782–4798
- [28] De Yoreo, J. J., & Vekilov P. G. (2003). Principles of crystal nucleation and growth. *Reviews in Mineralogy and Geochemistry*, 54, 57-93.
- [29] Chang, R., Kim, S., Lee, S., Choi, S., Kim, M., & Park, Y. (2017). Calcium Carbonate Precipitation for CO<sub>2</sub> Storage and Utilization: A Review of the Carbonate Crystallization and Polymorphism. *Frontier in Energy Research*, 5, 1–12
- [30] Kusin, F. M., Hasan, S. N. M. S., Hassim, M. A., & Molahid, V. L. M. (2020). Mineral carbonation of sedimentary mine waste for carbon sequestration and potential reutilization as cementitious material. *Environmental Science and Pollution Research*, 27 12767-12780
- [31] Ashraf, W. (2016). Carbonation of cement-based materials: Challenges and opportunities. *Construction Building Materials*, 120, 558–570
- [32] Qin, L., Gao, X., & Chen, T. (2019). Influence of mineral admixtures on carbonation curing of cement paste. *Construction Building Materials*, 212, 653–662
- [33] Milinovic, J., Dias, Á.A., Janeiro, A.I., Pereira, M.F.C., Martins, S., Petersen, S., & Barriga, F.J.A.S. (2020). XRD

identification of ore minerals during cruises: Refinement of extraction procedure with sodium acetate buffer. *Minerals*, 10(160), 1–19

- [34] Hasan, S. N. M. S., & Kusin, F. M. (2018). Potential of mining waste from metallic mineral industry for carbon sequestration. *IOP Conference Series: Materials Science and Engineering*, 458, 012013
- [35] Hasan, S. N. M. S., Kusin, F. M., Jusop, S., & Mohamat-Yusuff, F. (2019). The mineralogy and chemical properties of sedimentary waste rocks with carbon sequestration potential at Selinsing Gold Mine, Pahang. *Pertanika Journal of Science and Technology*, 27(2), 1005-1012
- [36] Hasan, S. N. M. S., Kusin, F. M., Hasim M. A., & Molahid V. L. M. (2020). Potential of mining waste from metallic mineral industry for carbon sequestration. *IOP Conference Series: Materials Science and Engineering*, 736(2), 022046