DRAFT MEMORANDUM

To: Jon De'Ath, NLA

From: Wendy Merz and McKay Quinn, Trinity Consultants

cc: Hunter Prillaman, NLA

Date: May 16, 2024

RE: Lime Product Carbonation Potential in Various Applications

The National Lime Association (NLA) engaged Trinity to review available information regarding the reabsorption of carbon dioxide (i.e., carbonation) by lime during its product life under various applications. Trinity has completed a review of the latest information compiled in a literature review commissioned by the European Lime Association (EuLA). This information is used to calculate an overall average carbonation rate for the US Lime Market of 28% as outlined below.

Background

NLA, whose members are a key part of the US economy, is seeking to develop a low carbon transition strategy for the North American lime manufacturing industry. The industry's principal products include high calcium, dolomitic and hydrated lime with numerous outlets and uses for these products. A cornerstone tool for establishing a climate strategy is understanding a product's life cycle GHG emissions. In the case of lime, there is also the potential for a GHG sink during the product use phase which should be considered.

There are three main reactions that comprise the life cycle of lime:

1. **Calcination:** Lime is produced when limestone (calcium carbonate) is thermally decomposed in a lime kiln into quick lime (CaO) and carbon dioxide (CO_2) via the following reaction:

$$\text{Energy} + CaCO_3 \rightarrow CaO + CO_2$$

2. **Hydration:** Quick lime may be further processed by reaction with water to form hydrated lime via the following reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

3. **Carbonation:** During the use phase of a lime product, hydrated lime reacts with CO_2 in the atmosphere to regenerate calcium carbonate via the following reaction:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The carbonation rate of lime in a given product application is defined as the amount of atmospheric CO_2 absorbed (in Reaction #3) divided by the amount of CO_2 emitted during calcination. Carbonation is an exothermic reaction and therefore thermodynamically favorable, providing a permanent sink for atmospheric CO_2. For certain applications such as drinking water treatment, the carbonation reaction is complete (100%) and instantaneous. For other applications, carbonation occurs over time and to a limited extent. The timeframe for carbonation is shortened when conditions are enhanced to optimize process parameters such as temperature, relative humidity, contact surface area, pH and others. The timeframe for carbonation is an important consideration when accounting the impact of this carbon sink on annual GHG emissions as discussed below.

EuLA/Politecnico di Milano Literature Review Summary

There have been a number of scientific studies performed to quantify the uptake of CO_2 by lime used in various applications. The NLA commissioned a study by Franklin Associates in 2000 in which the carbonation rate in various lime product applications was estimated, however the results were provided as draft, and the study was never finalized or published. Additionally, the NLA completed other internal studies in the past which were not published. In 2018, the European Lime Association (EuLA) commissioned Politecnico di Milano (PoliMi) to conduct a literature review of peer-reviewed research on the carbonation rate of lime.[1] The resulting literature review considers the data quality associated with results of studies reviewed, categorizing the information by product type as "conclusive" (indicated by green highlighting), "less conclusive" (indicated by orange highlighting) or not available, as summarized in Table 1.

Based on the latest USGS data, lime production in the United States totaled 16.8 million metric tons in 2021 and 17.0 million metric tons in 2022.[2,3] The breakdown of the US lime market by product type is provided in Table 1 based on 2021 USGS data.

In instances where data was not available or where an application was not assessed through the EuLA PoliMi literature review, data from the NLA internal studies and Franklin Associates studies was included in Table 1 (indicated in pink highlighting) and used in calculating the revised US average carbonation rate with additional data available through unpublished studies shown in Table 2. This information acts to fill data gaps, however, since the NLA and Franklin studies were not peer-reviewed and published, they are used as a supplementary reference to demonstrate potential carbonation rates of the applications for which further research is necessary.

[1] https://eula.eu/wp-content/uploads/2023/11/LITERATURE-REVIEW-ON-THE-ASSESSMENT-OF-THE-CARBONATION-POTENTIAL-OF-LIME-IN-DIFFERENT-MARKETS-AND-BEYOND.pdf

[2] Source: https://pubs.usgs.gov/periodicals/mcs2023/mcs2023-lime.pdf

[3] Total production of quicklime, hydrated lime, and refractory dead-burned lime produced in the US (excludes quicklime purchased by independent commercial hydrators for hydration to avoid double counting).

Table 1: US Market Share and Carbonation Rate of Lime Product Applications (1 of 3)

USGS Market Share Rank 2021	MARKET	World Lime Production (USGS 2021, thousand metric tons)[18]	% US Market Share	USE	% Carbonation Rate Summary: NLA (internal papers) [3,4]	NLA (internal paper) [17]	Franklin Associates	EuLA/ Politecnico di Milano (Natural)[1]	EuLA/ Politecnico di Milano (Enhanced)[1]	Carbonation Literature Assessment[2]	Data Quality Assessment (EuLA/ Politecnico di Milano)
					IRON						
					--	--	--	Negligible even after 100 years	7% direct route 31% indirect route	CONCLUSIVE	The literature review references a variety of conclusive sources and a robust sample size. Only two of the papers investigate natural carbonation, and therefore the natural carbonation process represents the most significant data gap. No real tests were performed in this industry, but both lab scale and pilot scale data is available.
					STEEL						
1	Iron and Steel	5,257	31.3%	Basic oxygen furnaces Electric arc furnaces Other Steel & Iron				5% (4 months) 28% (1 year)	39-56% (direct route). Fine particle slags, high contact with CO_2.	CONCLUSIVE	The literature review references a variety of conclusive sources and a robust sample size. No real tests were performed in this industry, but both lab scale and pilot scale data are available. If the data were to be improved, research should be focused on natural aging of the slag and additional studies on the promising results of enhanced carbonation processes.
2	Flue gas treatment	2,920	17.4%	S removal (utilities) HCl removal (municipal waste incinerators) Flue gas treatment for industrial boilers and other				32% instantaneous	9-66% (full scale	CONCLUSIVE	The literature review references a variety of conclusive sources and a robust sample size. The references literature includes ten real tests and eleven lab studies which investigate a range of temperatures and gas compositions. If any additional research were to be conducted, a focus on the age of air pollution control residues is the most significant data gap.
3	Soil Stabilization	1,640	9.8%	Modification, stabilization				37% (after 34 years - field research)	80%	LESS CONCLUSIVE	The literature review references a more limited number of available studies. Due to the unique nature of soil across climates and regions and how these differences affect carbonation, the data is less conclusive and additional studies should be completed.
4	Other chemical and industrial [8]	1,380	8.2%		5% [3]	--	--	--	--	NOT AVAILABLE	Carbonation in other processes not assessed due to a lack of available data.
					ALUMINUM						
								11.5% (no time information)	11.5%	CONCLUSIVE	The literature review references a variety of conclusive sources and a robust sample size. Data quality improvements could be made through a research focus on natural carbonation and age of red mud sample, however conclusive findings are possible with the available data.
					TITANIUM DIOXIDE						
5	Nonferrous metallurgy [9]				--	--	--	No information identified in literature	10-25% Direct Route 60% Indirect Route	NOT AVAILABLE	The literature review references limited studies which do not consider natural carbonation, differences in samples of red gypsum studied, or differences in operating conditions. Additional research in this industry would be necessary to make conclusive findings.
					OTHER NON-FERROUS METAL PRODUCTION						
		998	5.9%	Concentration of ores, Beneficiation (pH adjustment & enhance frothing)	25% [3]	6%	--	No information identified in literature	No information identified in literature	NOT AVAILABLE	Other non-ferrous metal production data, including data regarding carbonation as it relates to copper, nickel, zinc, lead, gold, platinum group metals, and lithium production, is limited or absent. Additional research in these industries would be necessary to make conclusive findings.

Table 1: US Market Share and Carbonation Rate of Lime Product Applications (2 of 3)

USGS Market Share Rank 2021	MARKET	World Lime Production (USGS 2021, thousand metric tons)(18)	% US Market Share	USE	% Carbonation Rate Summary					Carbonation Literature Assessment[2]	Data Quality Assessment (EuLA/ Politecnico di Milano)
					NLA (internal papers) (3,4)	NLA (internal paper) (17)	Franklin Associates	EuLA/ Politecnico di Milano (Natural)[1]	EuLA/ Politecnico di Milano (Enhanced)[1]		
6	Drinking Water Treatment	816	4.9%	Softening, corrosion control				100% instantanous	NOT ASSESSED	CONCLUSIVE	There are imited literature references regarding drinking water. However, of the two reliable and relevant studies, both were real tests which provided conclusive data.
7	Pulp & Paper (lime used in kraft pulping)	816	4.9%	Lime-based (Kraft) pulping only	--	13%	Lime in liquor cycle >14% (12)	NOT ASSESSED	NOT ASSESSED	NOT ASSESSED	Carbonation due to use of lime in the Kraft pulping process not assessed due to lack of available data.
8	Sugar Refining	566	3.4%	Purification step in the production of granulated sugar derived from sugar beets	90% (3)	11%	6-14% (13)	NOT ASSESSED	NOT ASSESSED	NOT ASSESSED	Carbonation in sugar production not assessed due to a lack of available data.
9	Miscellaneous and unspecified	613	3.6%	Includes glass production, other industrial and hazardous sludge treatment, and acid-mine drainage water treatment	--	--	--	--	--	--	Carbonation in glass production or other processes not assessed due to a lack of available data.
10	Paper - Precipitated Calcium Carbonate (paper filler)	444	2.6%	PCC production				PCC production: 85-93% instantaneous	No information identified in literature	CONCLUSIVE	Literature review references a robust sample size of relevant studies. Of the reliable and relevant studies, one is a real test. Therefore, the findings of the EuLA study are considered conclusive for carbonation applications to PCC production.
11	Wastewater Treatment	411	2.4%	neutralization precipitation				43-49% (reference time not reported)	NOT ASSESSED	LESS CONCLUSIVE	Literature review references limited studies. Of the studies available, the data is dated, based on only one source, and based on unclear methodologies.
12	Building Uses	244	1.5%	Sand lime brick (silica brick)				30% (reference time not reported)	No information identified in literature	LESS CONCLUSIVE	Sand lime brick data is available solely through a single pilot study. There is a general lack of data and therefore future research is necessary to further understand the carbonation process on sand lime bricks.
				Light-weight lime concrete - Autoclaved aerated concrete (AAC)				30% (10 years) - 60% (30 years)	No information identified in literature	LESS CONCLUSIVE	through six pilot studies . There is a general lack of data and therefore future research is necessary to further understand the carbonation process in this industry. In particular, the research should focus on natural carbonation and fly ash AAC.
				Pure air lime mortar				80-92% (after 100 years; depth 190 mm)	--	CONCLUSIVE	For both pure air lime mortar and mixed air lime mortar, the literature review references a variety of conclusive sources and a robust sample size. Of note, pure air lime mortars had nine lab scale studies and four real tests. No additional research is necessary at this time.
				Mixed air lime mortar				20-23% (after 100 years; depth 190 mm)	--	CONCLUSIVE	

Table 1: US Market Share and Carbonation Rate of Lime Product Applications (3 of 3)

USGS Market Share Rank 2021	MARKET	World Lime Production (USGS 2021, thousand metric tons)(18)	% US Market Share	USE	% Carbonation Rate Summary					Carbonation Literature Assessment[2]	Data Quality Assessment (EuLA/ Politecnico di Milano)
					NLA (internal papers) (3,4)	NLA (internal paper) (17)	Franklin Associates	EuLA/ Politecnico di Milano (Natural)[1]	EuLA/ Politecnico di Milano (Enhanced)[1]		
				Hemp lime				55% (after 91 days; depth 50mm)	65%	CONCLUSIVE	The literature review references a variety of conclusive sources and a robust sample size. Notably, the literature includes four lab scale studies and six real tests. No additional research is necessary at this time.
				Other (paints, natural fibers...)				--	--	NOT ASSESSED	Other building uses were not assessed due to a lack of available literature. Further research is necessary to evaluate these applications.
13	Refractories (dead-burned dolomite)	200	1.2%		--	--	--	--	--	--	--
14	Asphalt	141	0.8%	Anti-stripping agent	10% (3,4)	<1%	1-10%(15)	NOT ASSESSED	NOT ASSESSED	NOT AVAILABLE	Carbonation of asphalt not assessed due to a lack of available data.
15	Lime stabilization of sewage sludge	130	0.8%	Pathogen destruction & degradation of organic solids				43-49% (reference time not reported	NOT ASSESSED	LESS CONCLUSIVE	Sludge treatment data had limited literature review references. However, of the two reliable and relevant studies, both were real tests and therefore provided conclusive data.
16	Other environmental	112	0.7%		--	--	--	--	--	--	--
17	Fertilizer, including Aglime	67	0.4%		--	--	--	--	--	--	--
18	Other Construction	59	0.4%		--	--	--	--	--	--	--

References and Notes

1. PoliMI (2020). *Literature Review on the Assessment of Carbonation Potential of Lime in Different Markets and Beyond* , Table 1-2.
2. PoliMI (2020). *Literature Review on the Assessment of Carbonation Potential of Lime in Different Markets and Beyond* , Table 1-1. https://www.eula.eu/politecnico-di-milano-literature-review-on-the-assessment-of-the-carbonation-potential-of-lime-in-different-markets-and-beyond/
3. NLA "Confidential Draft" (8/19/1999) entitled Carbon Dioxide Reabsorption of Various uses of Lime.
4. NLA paper. Differences in CO2 Reabsorption Estimates. Trinity did not receive a copy of this document.
5. Franklin Associates (2000). *Greenhouse Gas Comparison of Lime and Limestone in Steelmaking in the United States and Canada.* Page 9. Trinity did not receive a copy of this document.
6. Franklin Associates (2000). *Greenhouse Gas Comparison between Lime and Other Absorbents for Flue Gas Scrubbing* . Page 6 & Page 13.
7. Franklin Associates (2000). *Greenhouse Gas Comparison of using Lime, Portland Cement, or Fly Ash in Soil Stabilization Applications.* Page 6. Trinity did not receive a copy of this document.
8. May include alkalis, calcium carbide and cyanamide, calcium hypochlorite, citric acid, food (animal or human), oil and grease, oil well drilling, petrochemicals, tanning, and other uses. Magnesia is included here to avoid disclosing proprietary data. Trinity did not receive a copy of this document.
9. Includes alumina and bauxite, magnesium, metals concentration (copper and gold), and other nonferrous uses.
10. Franklin Associates (2000). *Greenhouse Gas Comparison of using Lime or Caustic Soda in the Beneficiation of Non-Ferrous Ores.* Page 4. (note; report focuses on Copper)
11. Franklin Associates (2000). *Greenhouse Gas Comparison of using Lime or Caustic Soda for Drinking Water Treatment.* Page 6.
12. Franklin Associates (2000). *Greenhouse Gas Comparison of the use of Lime and Limestone in Paper Prodction and the use of Various Fillers in Fine Paper* . Page 7. Trinity did not receive a copy of this document.
13. Franklin Associates (2000). *Greenhouse Gas Comparison of using Lime or Limestone in the Manufacture of Granulated Sugar from Sugar Beets* . Page 5. Trinity did not receive a copy of this document.
14. Franklin Associates (2000). *Greenhouse Gas Comparison using Lime or Alum to Treat Wastewater.* Page 5. Trinity did not receive a copy of this document.
15. Franklin Associates (2000). *Greenhouse Gas Comparison using Lime or Synthetic Additives in Asphalt Paving Applications* . Page 4.
16. Franklin Associates (2000). *Greenhouse Gas Comparison of using Lime, Aerobic Digestion, or Anaerobic Digestion to Stabilize Sewage Sludge.* Page 4. Trinity did not receive a copy of this document.
17. NLA table entitled, "Key Lime Markets for Global Warming Analyses." (No date or background information provided)
18. U.S. Geological Survey, Mineral Commodity Summaries, January 2023

Average Lime Carbonation Rate in US Market

In order to calculate the average carbonation rate of lime products in the US market, the product's market share is multiplied by its average natural carbonation rate from the literature review for each application and then these values are summed to provide the overall US average carbonation rate of 28%. Applications for which data quality was deemed "conclusive" (applications highlighted in green) or "less conclusive" (applications highlighted in orange) are included in the first overall average as shown in Table 2. Applications for which there was no available data through the EuLA PoliMi literature review (applications highlighted in pink) are also included using average percent natural carbonation rates from internal NLA studies and Franklin Associates' commissioned study for NLA. The first overall average is supplemented with this additional data in the second overall average show in Table 2. It should be noted that for sugar refining, one of the NLA unpublished study references indicated a 90% based on the following justification:

> *In sugar refining, lime reacts with crude sugar juice to form insoluble calcium organic compounds. This solution is then carbonated with CO_2 to precipitate out $CaCO_3$ along with all other insoluble compounds. Analysis of the waste filter cake has revealed that 90% (by weight) of the filterable solids are $CaCO_3$ [MS Lime testing]. Because about one pound of filter cake is generated for each pound of lime used, our estimate of reabsorption is 90%.*

The other two unpublished studies indicated a carbonization rate of 11% and between 6 -14%. Due to these very different results, the 90% value was treated as an outlier and was not factored into the average carbonation rate calculated for sugar refining at this time.

The applications with conclusive carbonation data have an average carbonation rate of 22% and account for a 60% share of the US lime market. The applications with less conclusive carbonation data have an average carbonation rate of 5% and account for a 13% share of the US lime market. The applications with carbonation data only available through unpublished studies have an average carbonation rate of 2% and account for 20% share of the US lime market.

Table 2: US Average Lime Carbonation Rate

Application	Market Share (%)	Average % Natural Carbonation[3]	Amount of CO2 captured[1,2] (MT CO_2e)	Carbonation Timeframe (years)
Iron and Steel	31.27%	28%	1,324,191	1
Flue gas treatment	17.37%	32%	840,596	<1
Soil Stabilization	9.75%	37%	545,884	34
Nonferrous metallurgy - Aluminum Only[5]	2.97%	12%	51,624	NA
Drinking Water Treatment	4.85%	100%	734,082	<1
Paper - PCC	2.64%	89%	355,490	<1
Wastewater Treatment	2.44%	46%	170,080	NA
Sand lime brick[4]	0.24%	30%	10,975	NA
Light-weight lime concrete - AAC[4]	0.24%	45%	16,463	0 to 30
Pure air lime mortar[4]	0.24%	87%	31,645	100
Mixed air lime mortar[4]	0.24%	22%	7,866	100
Hemp lime[4]	0.24%	55%	20,121	<1
Lime stabilization of sewage sludge	0.77%	46%	53,797	NA
Other chemical and industrial	8.21%	5%	62,073	NA
Nonferrous metallurgy other than Aluminum[5]	2.97%	16%	69,580	NA
Pulp & Paper (lime used in kraft pulping)	4.85%	14%	99,101	NA
Sugar Refining	3.37%	10%	52,615	NA
Asphalt	0.84%	5%	6,342	NA
US Average Carbonation Rate Based on Published Studies			**28%**	
Revised US Average Carbonation Rate - With Additional Data Available through Unpublished Studies			**29%**	

[1] Carbon dioxide emissions from 2021 lime production extracted from EPA's FLIGHT Tool (http://ghgdata.epa.gov/ghgp)
All emissions data is presented in units of metric tons of carbon dioxide equivalent using GWP's from IPCC's AR4
Total lime process emissions (MT CO2e) 15,126,053

[2] Where a range for carbonation rate was provided in the literature, an average is calculated. Where carbonation rate was not available, the amount of CO_2 captured isconservatively assumed to be zero.

[3] For the purposes of this table, the enhanced carbonation rates were not considered. Only natural carbonation rates, as specified in the reviewed studies, were considered in the average values.

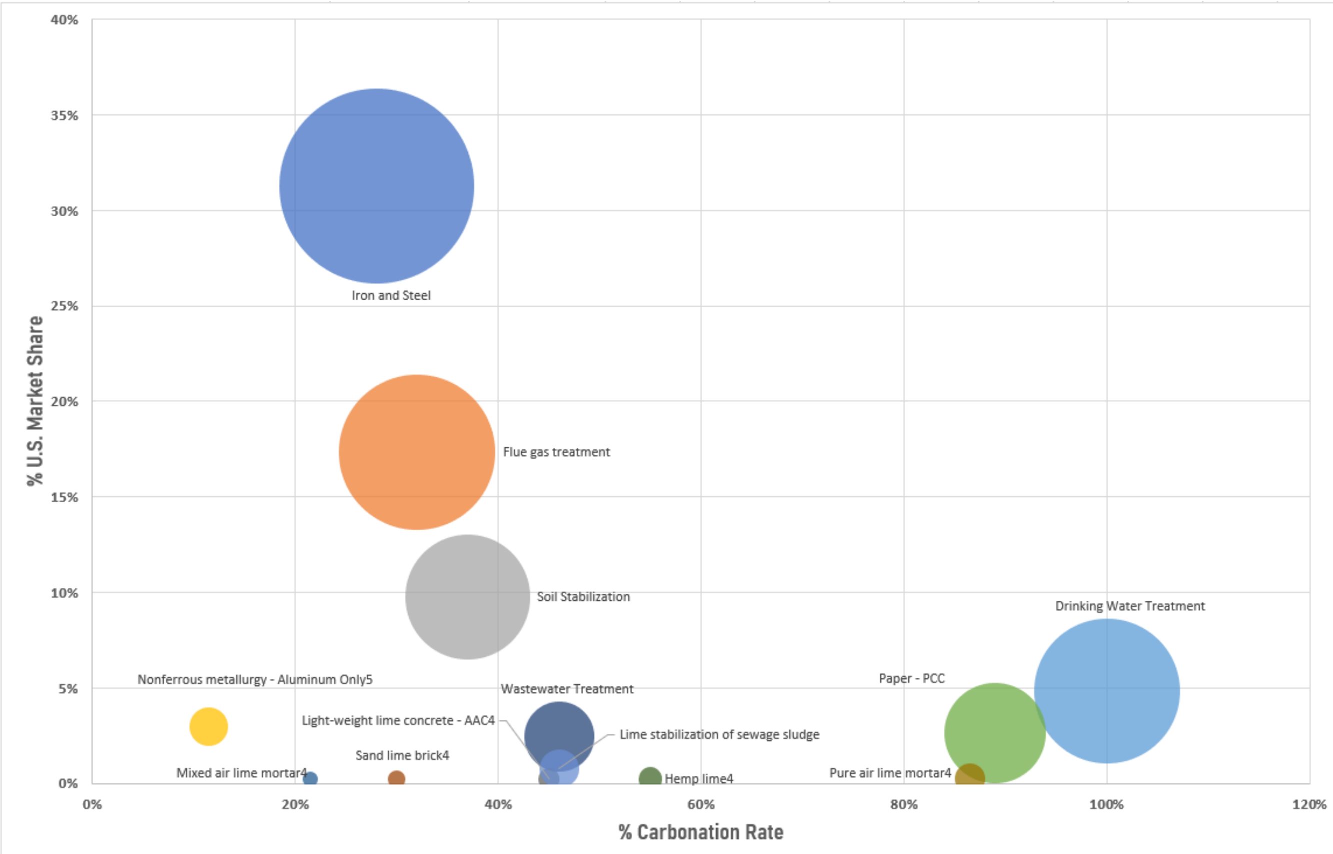
[4] Assumes that 1.5% market share for building uses is equally apportioned to each of the six categories shown in Table 1.

[5] Assumes that 5.9% market share for nonferrous metallurgy is equally apportioned to aluminum and other non-ferrous metal production including titanium dioxide.

It should be noted that the carbonation timeframe is also a consideration should the NLA or its members wish to account for carbonation as a carbon sink when quantifying the industry's greenhouse gas (GHG) emissions and overall impact on climate change. As indicated in Table 2, the carbonation timeframe for lime used for iron and steel manufacturing, flue gas treatment, drinking water treatment, precipitated calcium carbonate manufacturing, and for hemp lime used in construction is a year or less. These five applications account for over 57% of the US lime market. However, the carbonation timeframe for the applications with less conclusive published studies representing the 13% of the US market (for which the carbonation data is available through EuLA PoliMi's literature review) is either unknown or 30 years or more. Hence, the overall reduction to annual GHG emissions due to carbonation is less than 28%.

Figure 1 below shows the amount of carbon dioxide captured by natural carbonation across the applications listed in Table 2 with "conclusive" or "less conclusive" data. Applications with no available data through EuLA PoliMi's literature review are not included in Figure 1. The area of each circle represents the amount of carbon dioxide captured by the application as a percentage of the total process carbon dioxide emitted during commercial production of lime for the US market.

Figure 1: US Lime Carbonation by Product Type



Additional Considerations

The information in the EuLA/Politecnico di Milano Literature Review provides a comprehensive overview of the quality and current availability of carbonation data for various lime products/applications. As a next step, NLA may want to consider commissioning additional studies to close the data gaps, especially for applications that account for larger portions of the US market that currently have less conclusive data or no data at all. For example, soil stabilization applications account for almost 10% of the US market, however the data is less conclusive due to regional variations in soil and climate. Hence, additional studies across US regions would provide more conclusive information regarding the carbonation rate of lime used for soil stabilization.

There are also three lime applications, each of which account for 5% or more of the US market, that have no carbonation data available aside from unpublished studies which are not available to the public:

- Other chemical and industrial applications,
- Nonferrous metallurgy except for aluminum, and
- Lime used in pulp and paper manufacturing.

Should the NLA or any of its members wish to take carbonation rate into consideration when quantifying lifecycle GHG emissions, peer-reviewed published data would be advised. In order to prioritize the need for additional carbonation studies, the application should be considered in addition to market share. For example, assuming the carbonation data would be used to account for use phase emissions in a life cycle assessment (LCA), there may be more of a demand for carbonation information related to the industrial uses listed above than for soil stabilization due to market and regulatory drivers for LCA and Scope 3 quantification.