**Eion Corp Whitepaper** 

# **Engineering and Agronomy of CarbonLock as Aglime**

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Published: April 4, 2022 Revised: August 13, 2022



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## **Executive Summary**

We present legal and agronomic evidence demonstrating that silicate CarbonLock fulfills engineering requirements for commercial off-the-shelf carbonate aglime. In addition, we show that performance characteristics of CarbonLock show some advantages over aglime that have direct applicability for factor productivity on farmland. We show that CarbonLock is 20% more effective as an alkalizer than aglime, and achieves this performance in two years, whereas effectiveness of aglime in the final two years is only 25% that of the initial two years. Thus CarbonLock may help in maintaining a more consistent soil pH regime, without the wide swings between abundance and scarcity with infrequent aglime application.



# 1 Background

A central concern for Eion is to develop a pulverized silicate that performs consistently and predictably as a substitute for aglime. The expected characteristics of aglime are to some extent subject to state law. For example New York State Law agricultural liming material as:

"all materials and all calcium and magnesium products in the oxide, hydrate, carbonate or silicate form or combinations thereof and intended for use in the correction of soil acidity, including such forms of material designated as burned lime, hydrated lime, carbonate of lime, agricultural limestone, slag and marl" (§ 142-aa).

This places magnesium silicates such as CarbonLock squarely within the legal definition of aglime, although the popular conception of an aglime is a carbonate such as calcite or dolomite. In this document, we will use the term aglime to refer to carbonate-based aglimes.

The New York State Lime Law goes on to set guidelines for the particle size distribution of aglime. Sections 142-cc and 142-gg in Article 9-A state that for New York, a liming material must be properly labeled with guaranteed analyses and have a CCE of 60% or greater, at least 80% must pass a 20 mesh sieve, and 30% must pass a 100 mesh sieve. The context for this is a recognition that the rate of dissolution, and thus the rate of addition of alkalinity, is dependent on the particle size distribution (characterized by test mesh sizes). A clear interpretation is that to be accepted as an aglime substitute, CarbonLock must be engineered to provide alkalinity to the soil at a *rate* consistent with carbonate aglime, despite its being a crystalline silicate with considerably lower reactivity. This is in addition to providing a total *amount* of alkalinity with comparable calcium carbonate equivalence (CEE) to other materials on the market.

To achieve this rate performance expectation, we must:

- 1. Characterize the reactivity of aglimes generally, based on particle size distribution
- 2. Characterize the reactivity of a particular aglime as a reference case

- 3. Characterize the reactivity of silicates generally, based on particle size distribution
- 4. Characterize the reactivity of particular silicates
- 5. Compare the particular silicates relative to the reference aglime to predict how silicates would perform under similar field conditions
- 6. Apply the theory to derive an ideal particle size distribution for CarbonLock.

#### 1.1 Characterize the reactivity of aglimes generally

The University of Illinois Agronomy Handbook, Chapter 8 [1], presents simplified calculations for how to predict the dissolution rate of aglime based on mesh size:

Table 1: Aglime Size Guidelines

Mesh	μΜ	After 1 year	After 4 years	k <sub>1yr</sub>	k <sub>4yr</sub>	<i>k</i> <sub>avg</sub>
>8	>2380	5	15	0.051	0.041	0.046
8-30	2380-595	20	45	0.223	0.149	0.186
30-60	595-250	50	100	0.693	0.749	0.721
< 60	< 250	95	100	2.995		2.995

The percent of aglime that has completed its reaction after 1 year and after 4 years are used to compute a weighted average across all the size bins for the expected performance in bulk. The reference value for typical performance is 46.35% after 1 year and 67.5% after 4 years. Assuming that these follow first order kinetics, the expression that characterizes dissolution is:

$$\frac{N}{N_0} = 1 - e^{-kt} \tag{1}$$

This expression can be rearranged to estimate the rate coefficient for each size bin:

$$k = -\frac{\ln\left(1 - \frac{N}{N_0}\right)}{t} \tag{2}$$

Because the U IL handbook provides values for both 1 and 4 years, and these themselves are rounded to convenient multiples of 5, we compute the average across both time slices.

This plot represents the predicted dynamics for 155 individual pulverized lime products in the 2021 IL DOT voluntary limestone program [2]:

#### 1.2 Characterize the reactivity of a particular aglime

We purchased a commercially available dolomitic aglime from Tractor Supply as a reference case, and analyzed the particle size distribution in a Malvern laser particle size analyzer.

Table 2: Commercial Dolomite Example Kinetics

Mesh	$\mu M$	% Under	% Within
>8	>2380	100	0
8-30	2380-595	100	1
30-60	595-250	99	9
< 60	< 250	90	90

Using the coefficients in Table 1, The weighted average reactivity of the product in Table 2 is 2.762, which places it at the upper limit of the aglimes shown in Figure **??**.





Figure 2: Commercial Dolomite Particle Size Distribution.



#### **1.3** Characterize the reactivity of silicates generally

The dissolution rate of silicates is generally characterized as a function of surface area, that is:

$$k = \frac{moles}{m^2 \cdot s} \tag{3}$$

Brantley et al (2008) [3] provide kinetic coefficients for a wide variety of silicates under different acidity and temperature conditions (Figure 3a). It can be seen that the reactivity for different minerals varies widely, from  $10^{-8}$  to  $10^{-14}$ , or six orders of magnitude. Beerling et al (2020) [4] present fitted coefficients to the original data of individual minerals (e.g. Figure 3b) enabling calculation for any temperature or pH combination. Figure 5 presents these coefficients for forsterite, the mineral in CarbonLock, with numerator in grams and time in years.



Figure 3: Silicate Kinetics from Brantley (2008)

Figure 4: CarbonLock mineral kinetics.



Like aglimes, these reaction rates depend on the particle size of the material, by way of the surface area of the mineral. Navarre-Sitchler and Brantley (2007) [5] developed theory (NSB) to estimate reaction rates for varying particle sizes using a fractal concept – essentially conceptualizing particles as "rough spheres" (Eq 6) having higher surface area than would be expected from geometric spheres (Eq 5).

$$V_{indiv} = \rho \cdot \frac{4}{3} \cdot \pi r^3 \tag{4}$$

$$SA_{indiv} = 4 \cdot \pi r^2 \tag{5}$$

$$SA_{indiv} = 4 \cdot \pi r^2 \cdot \left(\frac{r}{\alpha}\right) \tag{6}$$

Figure 5 shows the surface area for rough spheres under the NSB model is approximately 20x higher than would be assumed from geometric spheres, using observed particle size distribution of a silicate measures as above with a laser particle size analyzer. Each sub figure shows observed PSD and surface area for one product with D50 of  $275\mu$ m (Fig 5a) and another product with D50 of  $25\mu$ m (Fig 5b), alongside modeled cumulative surface area using the spherical (Eq 5) and fractal (Eq 6) surface area models.

Figure 5: Particle size and surface area of two silicates





It is evident from figures that the NSB model fits the observed data fairly well for actual materials. This in turn enables prediction of surface area under a range of size distributions.

#### 1.4 Characterize the reactivity of particular silicates

As with aglime, the dissolution is acting on individual particles, which vary widely in their surface area to mass ratio. Beerling et al (2020) [4] presented a partial differential equation for estimating bulk dissolution rates using size-resolved population of particles that shrink as they dissolve. For simplicity we instead simulate the population as a set of ordinary differential equations, each size bin simulated individually, using the reaction coefficients from Figure 4. What can be seen in Figure 6 is that the dissolution rate computed on a bulk basis (whole population has a single surface area) produces faster reactivity than the size-resolved population, because the smallest particles with the highest reactivity disappear quickly, leaving larger particles with lower reactivity. The Beerling PDE would shift the reaction faster (particles shrink) although it could also be the case that the reaction rate could slow if particles become "smoother" as they react. The population of ODEs seems to balance the effect of these two potential conceptual models.





(a) Sibelco No 11

(b) Sibelco AFS120



For a product D50=275um, 31.5% has reacted by the end of year 1, resulting in a reaction coefficient of 0.378 (using the equations presented in Section 1). For a product of D50=25um, 77.6% has reacted by the end of year 1, resulting in a reaction coefficient of 1.496.

Thus, in reference to the aglime with k=2.762, we expect the 25um silicate to react approximately 50% as fast as the dolomite (1.496/2.762), and the 275um product to react approximately 25% as fast as the 25um product.

### **1.5** Compare the particular silicates relative to the reference aglime

We conducted a dissolution experiment under controlled conditions, adding mass of aglime and CarbonLock with constant CCE (expressed in meq/g). As above, the silicate products were the D50 of 275um and 25um. The materials were added to an acidic solution (initial pH 4.75), and stirred in a temperature controlled flask, periodically taking measurements of solution pH as a measure of dissolution. In considering the background presented in Section 3, it should be evident that the reaction rate is expected to slow as the reaction proceeds and solution pH approaches neutral. Thus, the initial slope of the reaction is the best indicator of fundamental kinetics of the mineral, ignoring the partial effect of pH on the kinetic coefficients. In addition, to fit kinetic parameters, pH was normalized to begin at 1 and progress towards zero; on a logarithmic plot the maximum is thus 0 at the initiation of the experiment and progresses increasingly negative.



Figure 7: Controlled dissolution experiments comparing aglime and CarbonLock

As expected, dolomite reacted most quickly, followed by the 25um and 275um material. It can be seen that the experimental data slow down considerably relative to the slopes of the initial change, satisfying our expectation that increasingly neutral conditions slow dissolution. The coefficient for dolomite was 0.0067. The coefficient for 25um material was 0.0032, or 47.8% that of dolomite, which is nearly identical to the 50% expected from theory developed in Section 4. The coefficient for the 275um material was 0.00087, or 27.2% as much as the 25um material, which is nearly identical to the 25% expected by theory. These experiments are continuing with greater fidelity, and with different materials, but overall suggest that our materials behave predictably under controlled conditions and can be engineered to reproduce the expected kinetics of aglime.

## **1.6** Apply the theory to derive an ideal particle size distribution for CarbonLock

Armed with the knowledge that the observed kinetics comparing silicates to carbonates are consistent with theoretical predictions, we can simulate a range of candidate particle size distributions, and compute their surface area (Figure 8), and examine whether their reaction arc is consistent with the aglime expectations laid out in Section 1.

Figure 8: D50 to surface area relationship



An inspection of Figure 6 suggests that an intermediate value of approximately 90  $\mu m$  would produce a reaction arc for an engineered silicate that meets the year 1 value expected of aglime (Figure 9). It can be seen that the size-discretized kinetics produce a product that is nearly the same as the benchmark product, and squarely within the expected performance for typical aglimes in Figure 1. Moreover, this reaction speed runs to completion after approximately two years, versus a long tail for aglimes with a residual pool of very slow to react coarse material. Thus, this product may also fit more squarely within two year crop rotations, while also meeting the demand for the carbon removal market.

Figure 9: Reaction arc of 90 µm silicate



While this paper is mostly concerned with engineering the particle size distribution to generate the required rate of reaction. It is helpful as well to contextualize the CCE of CarbonLock against not only the legal guidelines identified at top (CEE  $\geq 0.60$ ) but also norms in the industry. From the IL DOT survey identified earlier [2], we can see that the CEE of CarbonLock is far more effective than 155 aglimes evaluated in the survey (Figure 10)

Figure 10: Calcium Carbonate Equivalent of CarbonLock vs IL aglimes



This observation can be confirmed by a stoichiometric analysis of the silicate versus common carbonates used as aglimes (Table 3):

		-								
		C	Н	0	Si	Ca	Mg	CaO	MgO	CCE
Compound	MW	12	1	16	28	40	24	56	40	
g/mol		# of atoms					mass %			
CaCO <sub>3</sub>	100	1		3		1		56		1
$MgCO_3$	84	1		3			1		47	1.19
CaO	56			1		1		1		1.79
$Ca(OH)_2$	74		2	2		1		75		1.35
(CaxMg)CO3	, 92	1		3		0.5	0.5	30	22	1.09
CaSiO <sub>3</sub>	116			3	1	1		48		0.86
$Mg_2SiO_4$	140			4	1		2		46	1.14
Basalt								10	8	0.38

Table 3: Calcium Carbonate Equivalent of silicates in references to common aglimes.

In concluding, it may also be worthwhile to consider agronomic advantages of CarbonLock over aglime, both in its function as an alkalizer, as well as in its soil conditioning function. We choose for comparison the specific aglime from the IL DOT survey that has a particle size distribution that most closely approximates the "standard" reaction rates in the U IL Agronomy Handbook (Heartland Materials, Jackson MO, DOT producer number 77000-99).



Figure 11: Comparison of CarbonLock against a typical aglime

In a side by side comparison, in Figure 11, we can see that both products meet the year 1 expectation, but that CarbonLock continues its alkalizing function into the second year at approximately the same pace, while aglime levels off strongly as the fine materials are depleted, leaving considerably coarser materials. In fact, by the end of the fourth year, only 73% of the aglime has reacted, while 94% of CarbonLock has reacted, perhaps owing to its having an engineered size distribution that excludes the coarse fraction. The implications of this are several. First, approximately 25% of aglime is functionally inert, making its cost approximately 25% greater than is necessary. Second, in the last two years of a four year aglime application cycle, approximately 15% has reacted, which is itself 25% of the efficacy in the first two years, meaning that there are unrealized crop performance gains that can be captured.

Finally, experimental evidence has shown that the cations Mg and Ca in aglime are charge balanced by the nitrate anion  $(NO_3^-)$  in leachate from agricultural fields [6]. By contrast, silicate applications in similar crop systems have shown reduced leaching losses and greater nitrate uptake [7]. The implication here is that in addition to being a  $CO_2$  source, aglime enhances nitrate losses, while CarbonLock reduces them. Certainly this will vary with a number of factors, but the suggestion is that factor productivity of applied nitrogen would therefore increase, resulting in yield gains.

## References

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