Properties of Liming Materials

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Liming materials are used widely in aquaculture to neutralize acidity in pond soil and water, to increase alkalinity and hardness of water, to destroy disease carriers in soil, and for other purposes. Nevertheless, many who use these materials do not understand their properties.

There are several sources of liming materials. The most common source is limestone. Limestone is a rock with a relatively hard and massive structure. Chalk, marl, and seashells are similar to limestone in chemical composition and are sometimes used for liming materials. Chalk is much softer than limestone. Marl is a loose material that is deposited in lakes, and often is mixed with clay.

The main chemical components of limestone, chalk, marble, marl, and seashells are calcium and magnesium carbonates. Calcitic limestone is comprised almost entirely of calcium carbonate ($CaCO_3$) while dolomitic limestone is comprised of calcium and magnesium carbonate ($MgCO_3$) in a 1:1 ratio ($CaCO_3 \times MgCO_3$). Most limestone is neither calcitic nor dolomitic, but a mixture of calcium and magnesium carbonates in some proportion other than 1:1.

The most frequently used liming material in aquaculture, and in agriculture in general, is agricultural limestone. It is made by crushing limestone to a fine particle size. Materials similar to agricultural limestone may be made by crushing chalk, marl, and seashells.

A product called burnt lime is made by burning limestone or other sources of calcium and magnesium carbonate in kilns at high temperature. This may be done on an industrial scale, but in many nations, much of the burnt lime is made by small-scale producers using wood-fired kilns. The resulting reaction and product is illustrated below for calcitic limestone:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

Carbon dioxide is driven off, and the resulting product is calcium oxide (CaO). Usually, the product will be a mixture of calcium and magnesium oxides, for limestone or other carbonate-bearing source materials are a mixture of calcium and magnesium carbonates. The product made by burning limestone also may be called quick lime or unslaked lime, but it is most commonly called burnt lime.

Burnt lime may be treated with water to produce hydrated lime as illustrated below for the conversion of calcium oxide to calcium hydroxide [$Ca(OH)_2$]:

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

Hydration of burnt lime usually gives a mixture of calcium and magnesium hydroxides, because burnt lime usually is a mixture of calcium and magnesium oxides. The hydrated product is known as calcium hydroxide if made from pure calcium oxide. It is more commonly, and often more properly, referred to as hydrated lime. It also may be called slaked lime.

Burning of lime may not be complete, and the final product may be a mixture of oxides and carbonates. Likewise, if hydration of burnt lime is incomplete, the resulting product may be a mixture of carbonates, oxides, and hydroxides or of oxides and hydroxides.

In aquaculture, it is more practical to use the term agricultural limestone for the crushed, raw product just as done in other kinds of agriculture. It may be called calcitic agricultural limestone if it is nearly pure calcium carbonate or dolomitic agricultural limestone if it has calcium and magnesium carbonates in essentially 1:1 proportion. Most agricultural limestone is made from limestone rock, and the vendor should indicate if the source is marl, chalk, or seashells instead of limestone. The burnt and hydrated products can be referred to as lime.

All of the liming materials react with hydrogen ion (H^+) or acidity and carbon dioxide (CO_2) in basically the same way as illustrated below for calcium carbonate, calcium oxide, and calcium hydroxide.

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2 + H_2O$$
$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

$$CaO + 2H^+ = Ca^{2+} + H_2O$$
$$CaO + 2CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

$$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$$
$$Ca(OH)_2 + 2CO_2 = Ca^{2+} + 2HCO_3^-$$

If the carbonate, oxide, or hydroxide of magnesium are present, they react in the same manner as illustrated above for calcium compounds.

The ability of a liming material to react with acidity is the neutralizing value. Pure calcium carbonate is the standard for comparison with other compounds, and it is assigned a neutralizing value of 100%. One molecule of each of the liming compounds will react with two hydrogen ions (H^+), but the molecular weights of the compounds are different: CaO = 56, $Ca(OH)_2$ = 74; $CaCO_3$ = 100. Thus, CaO is 100/56 or 178.6% stronger than $CaCO_3$, and $Ca(OH)_2$ is 100/74 or 135% stronger than $CaCO_3$. Pure dolomite has the formula $CaCO_3 \times MgCO_3$, and one molecule will react with four hydrogen ions. It is 200/184.31 or 108.5% stronger than $CaCO_3$. Thus the neutralizing value of the products mentioned above are: $CaCO_3$, 100%; $CaCO_3 \times MgCO_3$, 108.5%; $Ca(OH)_2$, 135% ; CaO, 178.6%. Of course, products mixed with magnesium compounds will be stronger than pure calcium compounds because the atomic weight of magnesium (24.31) is less than for calcium (40.08). Also, agricultural limestone and lime seldom are made from pure compounds and lime may not be completely burned or hydrated. Thus, the neutralizing value must be determined by a laboratory test. Agricultural limestone should have a neutralizing value of 95% or more to be considered of good quality. High quality lime should have a neutralizing value of

130%, and if it is sold specifically as burnt lime (unhydrated), the neutralizing value should be no less than 160%.

Fig. 1. A finely-ground agricultural limestone (right) versus a coarsely-ground one (left).

The fineness rating also is important in determining the quality of agricultural limestone. Limestone and other sources of calcium and magnesium carbonates are highly insoluble, and they must be crushed to fine particle size (0.25 mm or less; 60 mesh or less) to make them reactive. Material passing a 60 mesh (0.25 mm. opening) screen is given a fineness rating of 100%. The fineness rating declines as the proportion of coarse particles increases, and a laboratory procedure based on sieve analysis of agricultural limestone is used to assign a fineness rating. A good quality agricultural limestone must have a neutralizing value of 95% or more and a fineness rating of 95% or greater. A finely-ground and a coarsely-ground agricultural limestone are shown in Fig. 1. The fineness rating usually is not applied to lime, for the burning process converts limestone to a fine powder.

Liming materials tend to have a similar appearance. It usually is impossible to visually distinguish differences among samples of them (Fig. 2). A quick test of the pH of a slurry of 1 part liming material and 5 parts distilled water can reveal if a material has been burned. Burned materials, either hydrated or not, will have a pH of 11 or above.

Fig. 2. Samples of six different samples of liming materials including calcitic agricultural limestone, dolomitic agricultural limestone, marl, and burnt lime. They are visually indistinguishable

It is possible to identify liming materials by calcium and magnesium content. The percentages of calcium and magnesium in pure samples of agricultural limestone and lime are provided in Table 1. The ratio of calcium: magnesium in products made from pure dolomite is 1.65.

"...these products vary greatly in quality in most nations..."

Most countries do not require vendors to label liming products according to composition, neutralizing value, or fineness rating. Experience indicates that these products vary greatly in quality in most nations, and some products are not labeled even as to the correct compound. For example, a recent study of the properties of 49 brands of liming products in Thailand revealed that only about one half of them were of high quality and labeled as to the correct compound. Shrimp and fish farmers should acquaint themselves with the properties of liming materials and insist that vendors provide data regarding product quality. Vendors providing this information would have a competitive advantage, and other vendors would be forced to follow their lead. This would greatly reduce the possibility of inferior products remaining in the market for long.

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Application rates for liming materials given in pond management manuals and reported by testing laboratories are given in terms of pure calcium carbonate with neutralizing value and fineness rating of 100%. Most commercially available liming products will not have neutralizing values and fineness ratings of 100%, but their equivalent dose may be calculated as follows:

$$\text{Dose} = \frac{\text{Recommended dose (kg/ha)}}{\text{NV}/100 \times \text{FR}/100}$$

Where:

- Dose = liming rate for available product (kg/ha)
- NV = neutralizing value of available product (%)
- FR = fineness rating of available product (%)

For example, suppose that the recommend liming dose is 1,000 kg/ha, and the product available for use has a neutralizing value of 90% and a fineness rating of 82%. The dose is calculated below:

$$\frac{1{,}000 \text{ kg/ha}}{90\%/100 \times 82\%/100}$$

Table 1. Percentages of calcium and magnesium in samples of agricultural limestoneand lime made from pure calcitic or dolomitic limestone.

Product		% Ca	% Mg
Agricultual limestone			
Calcitic	$CaCO_3$	40.08	0.00
Dolomitic	$CaCO_3 \cdot MgCO_3$	21.74	13.18
Burnt lime			
Calcitic	CaO	71.47	0.00
Dolomitic	CaO·MgO	41.58	25.22
Hydrated lime			
Calcitic	$Ca(OH)_2$	54.10	0.00
Dolomitic	$Ca(OH)_2 \cdot Mg(OH)_2$	30.27	18.36