LIMESTONE SOURCES AND FACTORS AFFECTING THEIR QUALITY

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Addition of liming materials to correction soil acidity is an age old practice. According to Barber (1984), Cato and Varro used lime to correct soil acidity about 200 B.C. In America, benefits derived from liming acid soils were documented in the early 1800's (Ruffin, 1821). In a survey conducted in 1980, all but two of the North Central States (North Dakota and South Dakota) reported that research had shown a need for lime (Whitney, 1980). The need has not changed over the last 17 years, i.e. North and South Dakota still have little need for lime, but acid soils are a problem in the other states.

SOURCES OF LIMESTONE

Agricultural liming materials are defined as those products whose calcium and magnesium compounds neutralize soil acidity. While there are several materials that would satisfy this definition (Table 1), calcitic and dolomitic limestone constitute the majority of the tonnage used throughout the North Central area.

Calcitic and dolomitic limestone:

Calcitic and/or dolomitic limestone deposits are mined and ground to produce agricultural liming materials. In some states, these materials are mined to produce road rock, with the fines being screened for agricultural purposes. In other states, where sand and gravel deposits are readily available, limestone is ground specifically for the agricultural market. where by-product lime from the road rock business is the primary source of product, the best quality materials result from further grinding of the screenings to produce a product that will react relatively soon in the soil.

Limestone which contains less than 50% $MgCO_3$ is termed calcitic and that with over 50% $MgCO_3$ is referred to as dolomite rock. From a practical standpoint, materials that contain 5% Mg or more are often referred to as dolomitic. Since pure $MgCO_3$ has a lower molecular weight than $CaCO_3$ (84 versus 100), the neutralizing value of pure $MgCO_3$ will be 1.19 times greater for $MgCO_3$ than pure $CaCO_3$. Magnesium content tends to be higher in soils and limestone in the northern part of the region as compared to the southern areas.

While much to do has been made about Ca to Mg ratios in soils, there is little if any evidence to justify selecting liming sources on the basis of Mg concentration. In fact, work in Ohio by Eckert and McLean clearly demonstrated that Ca to Mg ratios in soil had no effect on crop yield. In low

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Mg areas, it would be wise to utilize dolomitic limestone if it were readily available. In areas of naturally occurring high soil Mg, use of calcitic limestone would only be justified if it could be purchased for equivalent cost to dolomitic limestone.

From an agronomic standpoint, the only differential between calcitic and dolomitic limestone might be in the degree of hardness of the rock. Even that is only of importance if the harder material dolomite is not ground as fine as the softer calcite. In some areas of the region. lime is yellow in color whereas in other areas it is more of a grayish color. The yellow color is the result of increased weathering and the presence of more iron oxides. While not absolute. yellow rock tend to be softer and thus easier to grind to a high quality product.

Burned Lime:

Burned lime. often referred to as quick lime is CaO. It is produced by driving the carbonate off of limestone with heat. Since it is often a fine material and is always quite caustic. it is often disagreeable to handle. Most of this material is used in the industrial market.

Cement kiln dust:

Cement is produced by heating lime and clay in a kiln and after cooling adding a small amount of gypsum. The by-product from this process has liming properties. but the quality varies depending on the lime used. It is a fine material, thus difficult to spread unless it is placed into a slurry or pelletized. The primary advantage of the product is that it contains from 1 to 4% potassium.

Coal ash:

Over 100 million tons of coal ash are generated by power plants in the United States annually. Approximately 30% of this is bottom ash. with the remainder being fly ash collected by precipitators in the flue gas stream. The relatively large particle size of the bottom ash does not lend itself to being a high quality liming material. On the other hand, the fineness of the fly ash makes it difficult to spread. Personal experience with one fly ash material would suggest that it is not a good candidate for slurring unless the application equipment has tremendous circulation capacity. In our experience, even with relatively good circulation. the material fill out of suspension and plugged 6 inch delivery hoses within 15 minutes.

The calcium content and consequently. the neutralizing value of coal ash varies with coal source. Sondreas et al. (1968) reported ranges of calcium concentrations for different coals: anthracite. 0.14 to 2.9%: bituminous. 0.5 to 26%: sub-bituminous. 1.6 to 37%; and lignite. 8.9 to 37%. Calcium carbonate equivalence of various fly ash materials ranged from 0 to 37% (Bidwell.1983). Coal ash materials must be used with caution as some of them contain potentially toxic levels of boron.

Marl:

Marl are soft, unconsolidated deposits of $CaCO_3$. They are usually mined, stockpiled and allowed to dry before being applied to land. Prior to the mid 1930's, marl was a major source of liming materials.

Papermill sludge:

As its name implies, papermill sludge is a by-product of the paper industry. They utilize CaO to recover spent pulp liquor and in the process, produce $CaCO_3$. Since they are wet materials that must be dried, they do not have the best spreading qualities.

Pelleted lime:

Pelleted lime is very finely ground limestone that is aggregated into granules with a binding agent. Although the initial material is very fine, once granulated it behaves as a somewhat larger particle. Since the particles break apart more readily than limestone, it likely is more effective than would be lime of the same larger particle size, but not as effective as would lime of the finer particle size from which it was made. The apparent reason that they are not as effective as the initial sized material is that even though they break apart easily, the material is surrounded by soil and thus cannot move even when dispersed. The advantage of this type of material is that it can be blended with fertilizers and broadcast with a spinner spreader.

Slag:

Blast furnace slag is a by-product of the pig-iron industry. It is the result of mixing iron ore, coke, and limestone at high temperatures. The liming value of this process is the formation of a by-product that contains silicates of Ca, Mg, and Al.

Slaked lime:

Slaked lime is the result of adding water to burned lime to form $Ca(OH)_2$ or $Mg(OH)_2$. Like burned lime it is a fine, caustic material that is difficult to handle.

Sugar beet sludge:

As the name implies, this is a by-product of the sugar beet industry. The quality will vary depending on the input lime and on water content.

Water treatment sludge:

Many municipalities and water companies utilize very finely ground calcitic limestone to soften water. After use, a high percentage of the lime is reclaimed and placed into lagoons for partial dewatering. Some companies then market the material as a liquid lime while others dry the material and market it as a dry material. The softening process determines how much dewatering will occur. Those systems that utilize alum in the process generally are not able to obtain more than 30% solids, whereas those with very low or no alum generally can obtain a 50% solids material. When properly slurried. these materials can be accurately applied to farm land. The quality of the product will depend on the CCE of the initial liming material and on final water content.

Wood ash:

The liming value of this product stems from the Ca, Mg, and K carbonates. While CCE is relatively high, about 78%, these materials should be applied on the basis of their K content rather than liming value. Repeated applications of these materials as a liming source may result in excess application of K, P, Zn, and B.

To be a good liming material, the products must meet several requirements:

1. It should have a mild alkalizing (pH increasing) effect. The intent is to raise the pH to near neutral. The ideal material should have an action mild enough to cause no harm where an overdose is applied.

2. It should result in a desirable proportion of cations adsorbed on the cation-exchange sites. The added cations should be mostly calcium, although some magnesium is good. Little or no sodium should be included.

3. It should have a favorable effect on soil structure. The most favorable base for good soil structure is calcium.

4. It should not be too expensive.

These characteristics exclude materials such as sodium carbonate because it has too strong an alkalizing effect and supplies the wrong cation. Gypsum is also excluded as it is a neutral salt and has no alkalizing effect.

LIMESTONE QUALITY

Limestone quality is determined by the ability of the rock to neutralize acidity, often referred to as calcium carbonate equivalence, fineness of grind, and with some products moisture content. The ability to neutralize acid was determined at the time the rock was laid down. Therefore, there is not much one can do about it, one simply needs to know what it is. Fineness of grind is controlled by the quarry operator and/or the quality of equipment being used for grinding. In some cases, disinterest in producing quality liming materials; lack of time to adequately grind the material to meet demand: or poor equipment results in poor quality product. Moisture content is not of significance on dry products, but is of major importance in determining quality of slurried materials.

Experience has shown that delivery of poor quality lime to the field may not always be the fault of the quarry. Quarries that are not just in the ag-lime business, i.e. those that produce road rock and ag-lime, often maintain an ag-lime pile and a "screenings" pile. During the busy part of the season, there is often a line at the ag-lime pile and no line at the screenings pile. Those truckers with a self centered objective, i.e. get loaded and back on the road as fast as possible, are tempted and often do load from the screenings pile as it looks nearly as good to the untrained eye as the ag-lime.

Calcium carbonate equivalence, the term used to define limestone purity, is defined as the acid-neutralizing capacity of the material expressed as weight percent of calcium carbonate. Thus pure calcium carbonate, calcite, has a calcium carbonate equivalence of 100, whereas, pure magnesium carbonate has an equivalence of 109 because magnesium has a lower atomic weight. Values lower than 100 indicate the degree of impurities in the material. Calcium carbonate values for several liming materials are shown in Table 2.

Several studies have shown the importance of fineness of lime on change in soil pH. Meyer and Volk (1952) concluded that calcitic material should be 40 mesh or finer, dolomitic limestone should be in the 60- to 80- mesh range, and that 4- to 8- mesh material had little value as a liming material (Table 3). Love et al. (1960) concluded that the relative efficiency of various particle sizes was related to the time of incubation and to the relative acidity of the soil. They found that the longer the incubation, the more effective the coarser materials became (Table 4). Similarly, the lower the initial soil pH, the more effective the coarser materials. Barber (1967) summarized the results of several field experiments relating crop yield to particle size fraction (Table 5). While the results were quite variable, they reflect the general relationship.

States within the North Central region have utilized data similar to this to arrive at efficiency factors for various particle sizes (Table 6). They then use these factors to calculate the relative fineness efficiency of liming materials by summing the result of multiplying the factor times the percentage of product within each category. Most states then utilize the fineness efficiency factor and calcium carbonate equivalence to calculate a relative efficiency factor for the material. Terms used to define this include effective neutralizing value, neutralizing index, or effective calcium carbonate equivalence.

Illinois research has shown that the effective neutralizing value of liquid lime is related to calcium carbonate equivalence and moisture. Since these materials are all very fine, fineness efficiency is not of concern. The equation used in Illinois to determine effective neutralizing value is

$$(\% \text{ CCE} \times \% \text{ dry matter})/100$$

An ENV for typical ag-lime in Illinois is 46.35. Therefore, a material that has a CCE of 90% and dry matter of 50% is 97% as effective as typical lime [(.90 x .50)/46.35 = .97)] on a wet ton basis.

LIME LAWS

Several states within the North Central Region have laws that govern the sale and distribution of agricultural limestone. These include Ohio, Wisconsin, Iowa, Minnesota, Kansas, Nebraska, Kentucky and Ontario, Canada. Illinois, Indiana, North Dakota, and South Dakota do not have lime laws. Both Illinois and Indiana have a voluntary limestone quality program. The laws and voluntary programs utilize calcium carbonate equivalence and fineness efficiency to determine limestone quality.

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Table 1. Sources of liming materials in the North Central Region.

Burned lime
Calcitic limestone
Cement kiln dust
Coal Ash
Dolomitic limestone
Marl
Papermill sludge
Pelleted lime
Slag
Slaked lime
Sugar beet sludge
Water treatment sludge
Wood ash

Table 2. Calcium carbonate equivalence values for some common liming materials.

Material	Composition	Neutralizing value
Calcitic limestone	$CaCO_3$	100
Dolomitic limestone	$MgCO_3$	109
Burned lime	CaO	150-179
Hydrated lime	$Ca(OH)_2$	120-136
Marl	$CaCO_3$	70-90
Slags	$CaSiO_3$	60-90
Burned oyster shells	CaO	90-110

Table 3. Influence of lime fineness on soil pH in a one-year period for limestone fractions applied at rate of 3 tons per acre, and the average relative effectiveness for alfalfa yield.

Particle Size	Soil pH		Relative effectiveness	
Mesh	Calcitic	Dolomitic	Calcitic	Dolomitic
No lime	4.96	4.96	0	0
4-8	4.92	5.04	5	8
20-30	5.62	5.52	54	39
40-50	5.88	5.81	74	65
60-80	6.32	6.24	96	84
<100	6.45	6.56	100	100

Table 4. Relative efficiency of various dolomitic limestone fractions as affected by reference pH and time of equilibration under field conditions.

Fraction	pH 5.5				pH 6.0			pH 6.5	
Mesh	1mo.	1yr.	2 yr.	3 yr.	1 yr.	2 yr.	3 yr.	2 yr.	3 yr.
	(Where < 100 fraction at 3 years equilibration for each pH level = 100)								
8-20	3	9	27	-	-	21	54	13	24
20-40	5	29	77	100	11	50	80	28	55
40-60	8	53	83	100	16	72	100	53	73
60-100	14	67	100	100	2	85	100	67	92
<100	40	67	100	100	48	93	100	90	100

Table 5. Relationship between limestone fineness and crop yield based on averaged data from field experiments.

Particle size (mesh)	Relative yield	Limestone required for equal crop response (80%) relative yield
20-30	71	3.9
31-40	75	3.0
41-50	83	2.7
51-60	89	2.3
61-80	94	2.1
80	100	1.8

Table 6. Fineness efficiency values by particle size used by selected states within the North Central Region.

State	Particle Size	Eff. Factor	State	Particle Size	Eff. Factor
Illinois	>8	.05	Kentucky	>8	.05
	8- 30	.20		8-30	.20
	30-60	.50		30-60	.50
	<60	1.00		<60	1.00
			Minnesota	8-20	.20
Iowa	4-8	.10		20-60	.60
	8-60	.30		<	1.00
	<60	.60	Nebraska	4-8	.10
Kansas	>8	.00		8-60	.30
	8-60	.50		<60	.60
	<60	1.00	Wisconsin	8-20	.20
				20-60	.60
				<60	1.00

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