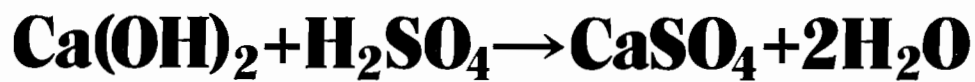


Acid Neutralization with Lime

for Environmental Control and Manufacturing Processes



**national
lime
association**



Acid Neutralization with Lime for Environmental Control and Manufacturing Processes

by Clifford J. Lewis and Robert S. Boynton



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Introduction

Even before the current federal and state drives for environmental cleanup, lime was the most widely used chemical for neutralizing acids. With the increasing pressure to treat mine and industrial trade wastes, many of which are acidic, the use of lime as an alkali for acid neutralization is increasing and its physical and chemical characteristics are being more fully utilized.

Although lime reacts readily with all types of acids, the strongest to the weakest of both inorganic and organic types, its well established neutralization function is not as uncomplicated as many chemists think—at least, if a high degree of efficiency is desired. (1) Thus, the prime objective of this bulletin is to provide a guide to the most effective ways of using lime to achieve the lowest possible capital and operating costs in neutralization operations. There are variations in purity of limes, their neutralizing power, reactivity, chemical reactions and sludge-forming characteristics. Also the preparation, concentration and transport of aqueous lime slurries have an important bearing on efficiency.

Lime Classification. Necessarily, commercial lime manufacturers, in order to meet the varied specifications of chemical and metallurgical process industries, must obtain the purest types of limestone economically available. In spite of this, sources of limestone for lime

will vary somewhat in the amount of impurities they possess, as illustrated in the following table. (2) These impurities are mainly silica, alumina, and iron oxide. A lime that contains less than 5% magnesium oxide, with most of the balance calcium oxide, is classified as *high calcium* lime. (3) (In the U.S. practically the MgO limit is 2.5% since very little lime contains between 2.5 to 5% MgO). A lime with a MgO content between 5 and 35% is characterized as *magnesian* lime. When the MgO content exceeds 35%, it is classed as *dolomitic* lime. Most of the latter class is made from dolomitic limestone that has a near equi-molar ratio of calcium and magnesium carbonate with a MgO con-

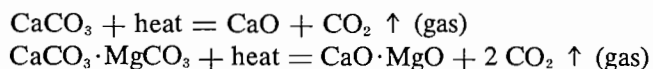
Typical Analyses of Commercial Quicklimes

Component	High Calcium Quicklimes Range* percent	Dolomitic Quicklimes Range* percent
CaO	93.25-98.00	55.50-57.50
MgO	.30- 2.50	37.60-40.80
SiO ₂	.20- 1.50	.10- 1.50
Fe ₂ O ₃	.10- .40	.05- .40
Al ₂ O ₃	.10- .50	.05- .50
H ₂ O	.10- .90	.10- .90
CO ₂	.40- 1.50	.40- 1.50

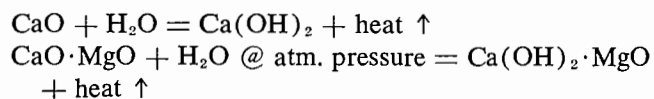
* The values given in this range do not necessarily represent minima and maxima percentages.

tent ranging between 35 to 42%, the remainder being chiefly calcium oxide (CaO).

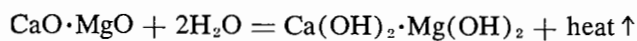
The first lime product, quicklime, (an oxide) is manufactured by calcining the limestone at about 2400°F. This drives off the chemically-bound carbon dioxide:



About 80% of the lime is sold as quicklime where neutralization users slake the lime into a hydroxide, in slurry form, called slaked lime. Slaking, a highly exothermic reaction, evolves considerable heat.



Note that the dolomitic lime does not completely hydrate, only the CaO component. About 20% of the quicklime, however, is hydrated by the lime manufacturer and is sold in bulk or in bags as a dry, ultra-fine white powder, called *hydrated lime*. Dolomitic lime producers, unlike the consumer who slakes dolomitic quicklime, make a highly hydrated dolomitic lime by hydrating under steam and pressure, as follows:



A lime slurry is easily made from hydrate by simply mixing it in water to the desired concentration. Generally, for economy, large consumers purchase quicklime, in spite of the extra step of slaking, since it is anhydrous, containing nearly 25% more lime than the hydrate. Small lime consumers generally find hydrate to be more convenient and economical, even though it is more expensive per unit in neutralizing power.

In addition to the varying concentrations and basicities of limes, another important variable is the degree of *reactivity* of the lime. This factor is influenced by the physical structure of the stone, the amount of impurities present, and the severity of the calcination (burning). The soft-burned limes are generally most reactive and will slake with explosive violence to yield a very reactive dry hydrate or a slaked lime slurry. Others are medium to hard-burned. The latter slake more slowly in varying degrees, producing a lime slurry that will not react with acids as rapidly as soft-burned lime.

Because of these differences, it is recommended that users slake the lime according to the manufacturer's recommendations. Usually this is a composite of the ratio of lime and water as fed into the slaker, optimum temperature of water and details on agitation and re-

tion time. Thus, before designing a treatment plant, it is judicious to study those limes economically available and determine which source to use. A highly reactive lime that requires little retention time for neutralization can be translated into a smaller and less costly plant than is required for a slow reacting lime.

Reaction Theory. Lime hydroxides, either from slaked quicklime or hydrated lime, are slightly soluble in water, although they are over 100 times more soluble than the limestone from which they are derived. Lime solubility declines as the temperature of the water rises, ranging from 1.4 g CaO/l at 0°C to about 0.5 g at 100°C in a straight line curve. The lime that goes into solution immediately ionizes into Ca^{++} , Mg^{++} and OH^- where these ions unite with the corresponding acid ions of opposite charge, forming calcium or calcium-magnesium salts and water as the reaction products. As the lime ions react, the excess lime in suspension continues to dissolve, ionize, and combine with the remaining acid ions until all acid is neutralized or all lime consumed.

Unlike other strong alkalis or bases, such as sodium hydroxide, both $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are diacid bases as opposed to NaOH which is a monoacid base. This means only one molecule of lime is needed to neutralize two molecules of monobasic acid, whereas only one molecule of this type of acid is neutralized by one molecule of NaOH. With a dibasic acid, like sulfuric, still only one molecule of lime is needed to react with one molecule of sulfuric, but two molecules of caustic soda are necessary.

Neutralization Defined. The term "neutralization" may have different meanings depending upon the neutralization requirements. From a strictly theoretical point of view, a "neutral" solution should be neither acidic nor basic but rather have an equal molar content of hydrogen ions and hydroxyl ions; in other words, exhibit the pH of pure water, i.e., pH 7.0. To this end, the pH scale ranging from 0 to 14 has been developed as a yardstick of acidity or basicity, values from pH 0 to 7 being acidic and values from pH 7 to 14 being alkaline (basic). However, it is frequently only necessary to neutralize an acid system to pH 5 or thereabouts to achieve a certain objective. Although neutralization is complete for practical purposes, technically this is *under-neutralization*. In contrast, it may be necessary to neutralize an acid to pH 9 or higher, well on the alkaline side as, for example, to precipitate metallic ions or to completely clarify a waste for acceptable disposal. This is an example of *over-neutralization*. Fortunately, lime products have the versatility for any desired degree of neutralization although some specific alkaline

reagents are either only or most effective in *under-neutralization* situations. Finally, lime and other alkaline materials and also acids are used for *pH control*. This consists of raising or lowering a particular pH by 1 or 2 pH points, thereby achieving a small amount of neutralization. However, this is not neutralization in the sense herein used.

Figure 1 shows the pH increase when lime is added to distilled water. The pH rises vertically from pH 7 to pH 10.5 when only a trace of lime is added. Maximum pH of nearly 13 is attained at maximum lime solubility (0 degrees C). The magnesium oxide component of dolomitic lime, however, is not capable of attaining this maximum pH, but rather the dolomitic material does so by virtue of the calcium oxide present.

The foregoing general comments will now be discussed in more detail, supported by numerous tables and graphs.

Reagents

Reagents most frequently considered for acid neutralization are listed in Table 1. Caustic soda and soda ash, being refined chemicals, are relatively pure and as commercial products approach their theoretical formulas. Limestones are naturally occurring minerals containing earthy impurities not indicated by their formulas. The quicklimes and hydrated limes contain most of the impurities occurring in the parent limestones.

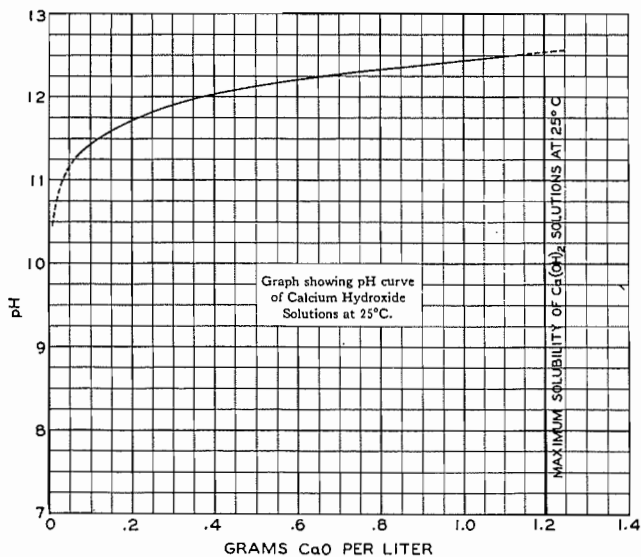
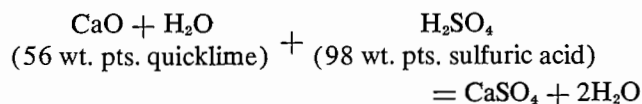
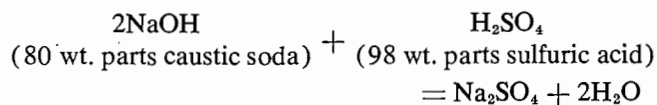


Figure 1 (2)

Basicity Factors. For acid neutralization, these reagents may be characterized by their ability to furnish alkalinity which combines with the hydrogen ion common to all acids, forming water. (The reaction chemistry of limestone is different from lime, carbon dioxide gas being first evolved. However, for comparison purposes, the concept of alkalinity is valid.) Since water (H_2O) represents one hydroxyl ion (OH^-) combined with one hydrogen ion (H^+), the theoretical neutralizing power of these reagents may be calculated from the weight of the *potential* hydroxyl ion in the reagent's theoretical formula. This neutralizing value is commonly referred to as the reagent's "Basicity Factor."

For example, using atomic weights and balanced chemical equations,



it is obvious that 80 pounds of caustic soda is theoretically required to equal the acid neutralizing value contained in 56 pounds of quicklime. If then, a unit neutralizing value of 1.00 is assigned to pure calcium oxide (CaO), the Basicity Factor (B.F.) of pure caustic soda may be calculated as $56/80 = 0.70$.

As previously stated, the limestones, quicklimes and hydrated limes contain impurities. With allowance for less than theoretical purity, the Basicity Factors of the commercial limestone and lime products vary downward slightly from their theoretical chemical formulas. For comparing relative acid neutralization potentials, typical Basicity Factors are presented in Table 2.

From the figures in Table 2, the greater acid neutralizing power of the lime products is apparent. Indeed, this is magnified when the price of a ton of neutralizing reagent delivered to point of use is divided by the reagent's Basicity Factor. (4) Only in situations involving nearby materials and/or fortuitous shipping charges will the quicklimes be at a disadvantage as representing the lowest cost alkalinity at point of use, except for limestone.

Reactions

Reactions of neutralizing reagents toward the more common acid systems will be discussed independently of their reaction rates. (As will be later pointed out,

Table 1 — Commercial Reagents for Acid Neutralization

Reagent	Theoretical Formula	Chemical Description
Caustic soda	NaOH	Sodium hydroxide
Soda ash	Na ₂ CO ₃	Sodium carbonate
High calcium limestone	CaCO ₃	Calcium carbonate
Dolomitic limestone	CaCO ₃ ·MgCO ₃	Calcium-magnesium carbonate
High calcium quicklime	CaO	Calcium oxide
High calcium hydrated lime	Ca(OH) ₂	Calcium hydroxide
Dolomitic quicklime	CaO·MgO	Calcium-magnesium oxide
Dolomitic hydrated lime	Ca(OH) ₂ ·MgO	Normal dolomitic hydrate
Highly hydrated dolomitic lime	Ca(OH) ₂ ·Mg(OH) ₂	Special dolomitic hydrate

Table 2 — Typical Basicity Factors of Acid Neutralizing Reagents
(In Decreasing Value Per Unit Weight)

Reagent	Descriptive Formula	Approx. B. F.*
Dolomitic quicklime	CaO·MgO	1.12
High calcium quicklime	CaO	0.96
Normal dolomitic hydrate	Ca(OH) ₂ ·MgO	0.88
Dolomitic pressure hydrate	Ca(OH) ₂ ·Mg(OH) ₂	0.83
High calcium hydrate	Ca(OH) ₂	0.73
Caustic soda	NaOH	0.70
Dolomitic limestone	CaCO ₃ ·MgCO ₃	0.58
High calcium limestone	CaCO ₃	0.54
Soda ash	Na ₂ CO ₃	0.52

* Basicity Factor

reaction rates weigh heavily in the economics of acid neutralization.)

Neutralization Limitations. Some generalizations can be made for reactions of all the neutralizing reagents cited. In the common acids or mixtures thereof, all will react in terms of the chemical equation on the *acid side* of the pH scale. Under-neutralization, involving pH end points on the acid side, enhances the efficiency of the least reactive reagents. This effect is often referred to as "driving force." Conversely, as the neutral point of pH 7.0 is approached or the area of over-neutralization above pH 7.0 is entered, some reactions may cease and new reactions begin. Some of the reactions are influenced by the presence of dissolved salts, particularly heavy metal salts, in the acid system and by the formation of insoluble precipitates. The dolomitic limes may be at a disadvantage in over-neutralization reactions

because the magnesium ion is precipitated by the calcium component of the dolomitic lime beginning at about pH 9.0. High calcium limestone (CaCO₃) requires under-neutralization for efficient reaction in any case. Finally, limestones containing much over 10% magnesium carbonate react so slowly in acid systems that their use for this purpose is rarely practical. (5)

Categories of Neutralizers and Reaction Products. It is beyond the scope of this bulletin to discuss all reactions involving acids and neutralizing reagents. Only major categories will be considered, namely:

1. Reactions in which all end products are soluble,
2. Reactions in which some end products are insoluble,
3. Reactions involving metals,
4. Reactions utilizing high magnesium reagents, and
5. Reactions involving high calcium limestone.

Table 3 summarizes reaction relationships illustrating each of these categories.

Major soluble and insoluble reaction products formed by the neutralizing reagents with acids may be summarized:

Solubles	Insolubles
All sodium salts	Calcium sulfate
All nitrate salts	Calcium sulfite
All chloride salts	Calcium fluoride
All chromate salts	Calcium phosphate
Magnesium sulfate	Magnesium fluoride
	Magnesium sulfite
	Magnesium phosphate

When metallic salts are present, these are precipitated as insoluble hydroxides over a broad pH range, depend-

Table 4 — Order of Precipitation of Typical Metals in Dilute Waste Acids with pH Increase

Metal	Metal Ion	pH
Ferric iron	Fe ⁺⁺⁺	2.0
Aluminum	Al ⁺⁺⁺	4.1
Chromium	Cr ⁺⁺⁺	5.3
Copper	Cu ⁺⁺	5.3
Ferrous iron	Fe ⁺⁺	5.5
Lead	Pb ⁺⁺	6.0
Nickel	Ni ⁺⁺	6.7
Cadmium	Cd ⁺⁺	6.7
Cobalt	Co ⁺⁺	6.9
Zinc	Zn ⁺⁺	7.0
Mercury	Hg ⁺⁺	7.3
Manganese	Mn ⁺⁺	8.5

The addition of the first two equations indicates that only the calcium component of the lime was fully effective at high pH.

Finally, in category 5 (limestone reactions), the limiting reaction factor is that limestone for all practical purposes is barely a *neutral reagent*. It is much slower in reactivity than dolomitic lime and will only neutralize to pH 6.5. Its reactions evolve carbon dioxide gas, some of which forms carbonic acid in the system. Only by aeration or aging, to remove this acid-forming gas, can values near pH 7 be achieved in limestone neutralization. The significance of this in systems where over-neutralization is necessary is obvious. It should also be borne in mind that copious evolution of the relatively heavy carbon dioxide gas, by the carbonates, can displace air. In confined areas this can result in suffocation. Somewhat the same situation applies to another carbonate, soda ash, although this sodium alkali will neutralize at a higher pH than limestone.

In summary, it can be said that while the neutralizing reagents react with acids in accordance with well-known chemical equations, reactions involving other substances and pH requirements strongly influence the choice of neutralizing reagents. This is especially pertinent when over-neutralization is necessary.

Reactivity

An understanding of the reactivity of an acid neutralization reagent is necessary for proper design of the system in which the reagent is to be used. Reactivity prescribes retention times which in turn dictate equip-

ment size, particularly tankage and space. Obviously this affects capital cost of the installation.

Neutralization Groupings. Reactivity is paramount in an assessment of the chemical reactions already discussed. For example, soda ash, although relatively soluble and reactive, is not an effective neutralizing reagent much above pH 7.0. Its reaction rate falls off sharply for lack of hydrogen ions necessary to drive the reaction sequences of the carbonate reagent. Caustic soda and limes, being "hydroxyl" compounds, are able to react with acids at much greater rapidity above pH 7. With dolomitic lime, however, the less basic magnesium component is not as effective as the calcium component above pH 9. In terms of acid neutralization reactivity, the reagents may therefore be arranged as follows:

Under-Neutralization	Over-Neutralization
Caustic soda	Caustic soda
Soda ash	High calcium lime products
High calcium lime products	ucts
Dolomitic lime products	Dolomitic lime products
High calcium limestone	(to about pH 9)

Limestone—Lime. Whether high calcium limestone is applied as a dry powder or a water slurry, the factor determining its reactivity is its particle size. This necessitates pulverization or fine grinding. This particle size consideration also applies to lime slurries. However, in this case, particle size is not only the result of slaking technique but also relates to the calcining technique used to produce the quicklime. Since for both limestones and limes, dissolution to produce ions for reaction occurs on the particle surface, surface area is of paramount importance. This is: the smallest particles are consumed first in the acid reaction, leaving the coarse particles with the least surface area to complete the reaction under conditions of least chemical driving force. In short, excess reagent is often necessary, with the coarser fraction wasted as a residue in order to complete the reactions within a practical retention time.

Table 5 illustrates the neutralizing potential of a high calcium limestone in terms of screen size when boiled in excess sulfuric acid for the times indicated. (7)

Figure 2 illustrates the reactivity of high calcium lime during slaking. (8) This reactivity is related to the lime calcination. A soft-burned material having high porosity (minimum shrinkage) slakes rapidly, whereas low reactivity and a longer slaking time is associated with a hard-burned product and low porosity. This also applies to dolomitic quicklime. Lime slaking equipment should be designed to accommodate the slaking characteristics

Table 5 — Effect of Screen Size on Reactivity of a High Calcium Limestone

Boiling Time Hr.	Basicity Factor of Limestone as Grams Equivalent CaO per Gram Sample				
	Samples Ground to Pass Mesh No.:				
	30	65	80	100	200
½	0.4443	0.4572	0.4798	0.4874	0.5231
1	0.4571	0.4879	0.5030	0.5153	—
1½	0.4736	0.5088	0.5170	0.5244	—
2	0.4855	0.5211	0.5229	—	—
2½	—	0.5249	—	—	—
3	0.4958	—	—	—	—

of the lime of interest. Figure 3 shows reaction rates for the "lime" reagents over the pH scale, such data being necessary for retention time design. Magnesium oxide, rather than dolomitic lime, is used in this figure to better indicate the behavior of lime's magnesium oxide component. This data is approximate. It is prudent to more accurately determine the reaction rate range for the lime or limestone to be used. Table 6 provides reaction times for various alkalis in completing a typical neutralization reaction where all of the alkali is consumed. (3)

Dolomitic Lime Characteristics. Dolomitic lime is characterized by relatively slower reaction rates and more narrow pH ranges. (4) This is because of the lower

REACTIVITY	40° C TEMP. RISE	TO COMPLETE REACTION
HIGH	3 MIN. OR LESS	10 MIN. OR LESS
MEDIUM	3-6 MIN.	10-20 MIN.
LOW	> 6 MIN.	> 20 MIN.

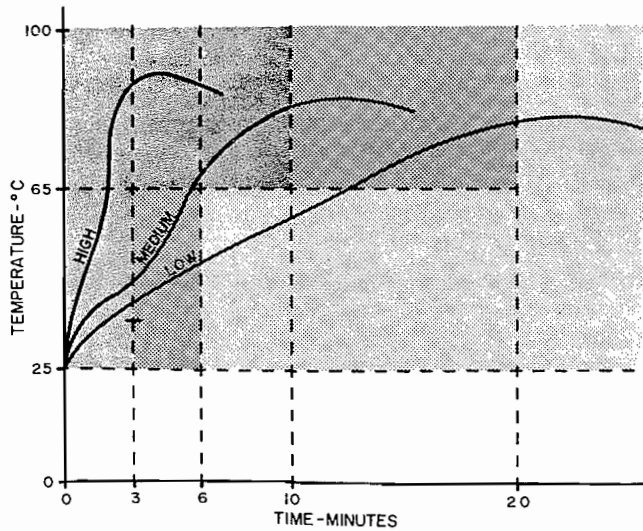


Figure 2 — Typical Lime (CaO) Reactivity Curves
Adapted from Slaking Rate Test-AWWA-B-202-65 (8)

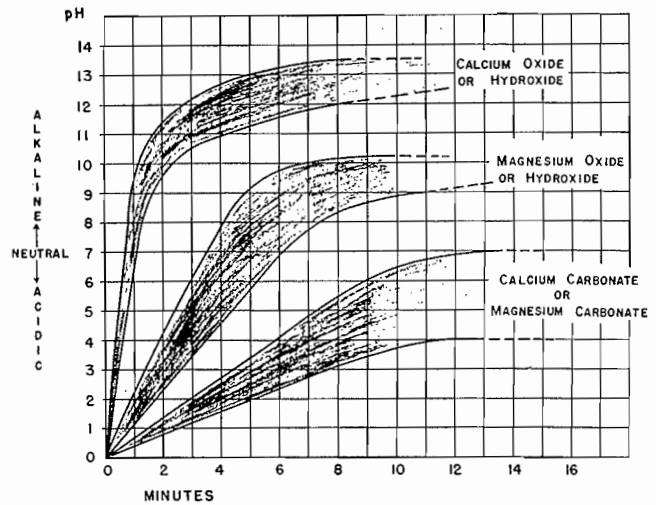


Figure 3 — Reaction Rate Ranges for Liming Material Constituents (4)

solubility of magnesium hydroxide as compared with calcium hydroxide. As pointed out, soluble magnesium salts are precipitated on the alkaline side of the pH scale (pH 9) and the magnesium component of the lime wasted. For over-neutralization with dolomitic lime, while maintaining practical retention times, a chemical excess of lime is necessary so that there is an excess of calcium to complete the work (Fig. 4). However, it is to be noted that generally the magnesia fraction of a dolomitic lime is much more reactive in *strong* acid solution than in *weak*.

By artificial methods, however, the reactivity rate of dolomitic limes can be markedly accelerated, although still falling short of the reaction time of 15 to 25 minutes, typical of high calcium quicklimes. These methods include increasing the temperature in the reaction

Table 6 — Reactivity of Alkaline Agents with Pickle Liquor (without Aeration) (3)

Agent	Room temperature	60° C
NaOH	a	a
Na ₂ CO ₃	0 in 0.75 hr.	0 in 0.75 hr.
MgO (reactive)	0 in 3 hr.	0.72
CaO	0 in 0.25 hr.	0 in 0.25 hr.
CaO·MgO	1.88	3.14
Ca(OH) ₂	0 in 0.5 hr.	0 in 0.5 hr.
Ca(OH) ₂ ·MgO	1.23	1.53
Cement dust (unreactive)	13.81	14.00
CaCO ₃ , precipitated	8.95	5.17
CaCO ₃ , limestone	20.40	18.80

a—Reaction practically instantaneous.

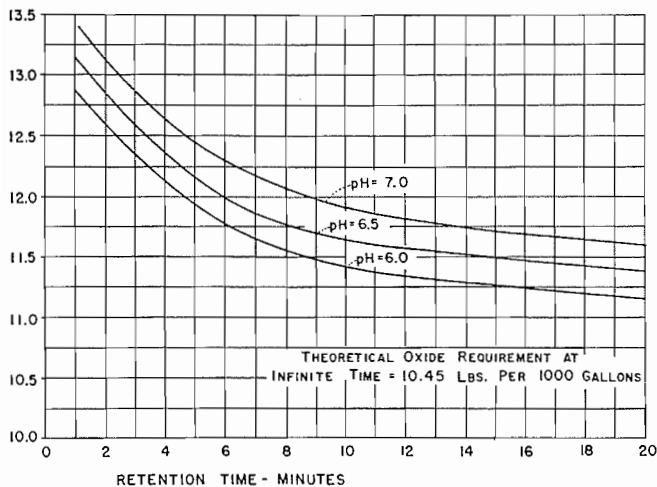


Figure 4 — Lime Requirement for Neutralizing ¼ Percent Sulfuric Acid Using a Dolomitic Pebble Quicklime Slaked and Slurried (4)

chamber to 170°F with applied heat, vigorous agitation, and using about 5% excess lime. This will accelerate the reaction to completion from 3 to 5 hours to 1 hour or slightly less. Still, with dolomitic lime's greater inherent basicity and less sulfate sludge weight, it can often prove to be the least costly alkali to use, mainly, of course, in neutralizing to pH 5.5 to 7.0. Most modern dolomitic limes are now produced in rotary kilns when the time-temperature conditions of calcination are closely controlled, resulting in dolomitic oxides that are softer burned and more reactive than from the older natural draft shaft kilns.

To summarize, high calcium limestones, dolomitic limes, and high calcium limes all exhibit a wide range of reactivity toward acids. Reaction rates are influenced primarily by chemical considerations (i.e., ion species), particle size and driving force. The greater the under-neutralization, the more these reaction rates draw together; while over-neutralization promotes wide divergence.

Preparation of Lime Slurry

Since this discussion is concerned primarily with acid neutralization using lime, only scant attention will be accorded the non-lime reagents. Caustic soda, being very soluble, is almost always applied as a solution. Soda ash and limestone may be applied dry. However, it is considered preferable to prepare a water solution of soda ash and a water slurry of insoluble limestone. In the case of lime, preparation of a water slurry is usually necessary for efficient utilization of the reagent.

Surface Area. Whether a water slurry of hydrated lime or "slaked" quicklime is applied for acid neutralization, the overriding factor for efficient utilization is the total surface area of the solid particles in the slurry. This surface area includes particle porosity and particle shape. High surface area is paramount because the particles must dissolve, that is, form hydroxyl ions before reaction with the hydrogen ion of the acid can occur. Such ionization takes place only at the solution interface on the particle.

While manufacturing processes usually assure a dry hydrated lime product substantially passing a 200 mesh sieve, this may not always be so when quicklime is slaked to produce a water slurry. The dry hydrate can be readily mixed with water to form a slurry of finely divided, uniformly distributed particles exhibiting high surface area. However, to achieve a high surface area in a slurry of slaked lime, certain precautions must be observed. (9)

Slaking Water. First, advantage should be taken of the knowledge and experience of manufacturers of lime slakers. Depending on the type and quantity of quicklime and the acid system to be neutralized, a choice of slakers is possible. Generally, the technique is to feed the quicklime and water at controlled rates to produce a maximum slurry temperature and a desired slurry density. Since, during slaking, it is desirable that the quicklime literally "explodes" to produce a fine hydroxide particle with high surface area, proper slaking technique determines neutralization efficiency. Of equal importance is the quality of the water used for slaking. Recycled process water, or highly polluted water, may contain "accelerators" or "retarders" which affect lime slaking. Generally speaking, accelerators are ions which form soluble salts with calcium and magnesium such as chlorides. Retarders are those ions which form insoluble compounds, particularly with calcium. For example, water containing appreciable sulfite or sulfate ions may reduce slaking efficiency to the point of impracticality by forming calcium precipitates on the surface of the quicklime particles. (10) These precipitates "blind" the quicklime surfaces and prevent the water necessary for the slaking from penetrating the quicklime. This results in relatively coarse, incompletely slaked quicklime particles being wasted with grit and non-lime residue in the slaker rejects. To illustrate, the "control" curve in Figure 5 depicts the rate of heat development in a standard slaking rate test with high calcium lime. The other curves show the practical effect of some accelerators and retarders when slaking high calcium quicklime. Table 7 illustrates the effect of these retarders on the yield of available calcium hydroxide; and

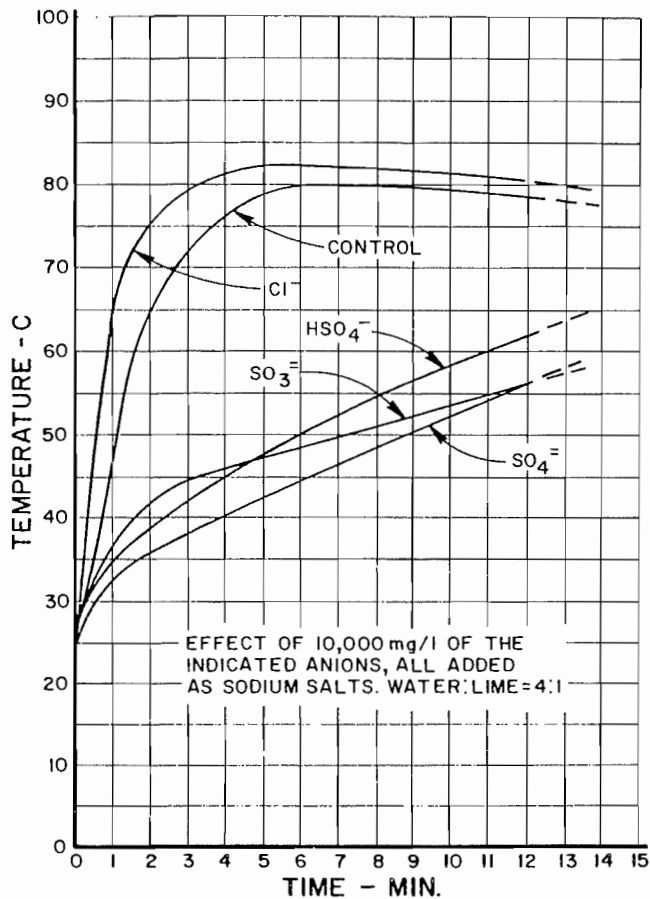


Figure 5 — Slaking Rate Test (10)

Table 8 translates this into lime slurry particle size. On the other hand, the adverse effect of these retarders on lime slurry quality *during* slaking is not evident when the retarders are present in the water used to dilute the lime slurry *after* slaking. Once optimum slaking has developed a maximum surface area of lime particles, the effect of retarders is minor or nil. This explains why the effect of retarders is negligible when present in water used to prepare a slurry from *dry* hydrated lime.

Lime Slurry Transport

Solutions and slurries of the reagents for acid neutralization are transported to point of application via pipelines. Such transportation of soluble caustic soda and relatively soluble soda ash is subject to no problem other than possible corrosion. Transporting a water suspension of pulverized limestone also presents no problem other than provision for the somewhat abrasive nature of limestone. But, in the pipeline transportation

Table 7 — Effect of Water Quality on Available Hydroxide (10)

Lime	Slaking Water	Dilution Water	% Yield
Commercial High Calcium Ohio Lime	Distilled	Tap	97
	Scrubber Feed T.D.S. 57,100 mg/l	Tap	73
	Distilled	Scrubber Feed T.D.S. 57,100 mg/l	96
Commercial 94% CaO Western Lime	Distilled	Tap	90
	Service Water T.D.S. 894 mg/l	Tap	85
	Service Water	Service Water	86
	Cooling Tower Blowdown T.D.S. 12,174 mg/l	Service Water	44
	Service Water	Cooling Tower Blowdown	85
	Thickener Overflow T.D.S. 73,100 mg/l	Tap	22
Technical Grade Calcium Oxide	Distilled	Tap	98
	Water 5400 mg/l SO ₄	Tap	50
	Water 6300 mg/l SO ₄	Tap	47

Table 8 — Particle Size Distribution as a Function of Concentration of Dissolved Solids (10)

Particle Size	Concentration of Sulfate (as Na ₂ SO ₄) in Slaking Water		
	None	2000 mg/l	10,000 mg/l
Retained on #10 Sieve	0	0	9.4%
" " #20 "	0	0.4%	17.0%
" " #40 "	0	13.4%	9.5%
" " #60 "	0	7.1%	3.3%
" " #100 "	0	1.2%	1.0%
Retained on Filter Paper	100%	77.8%	59.7%

of lime slurries, there is the persistent problem of scaling and plugging of pumps, valves and lines.

Scaling Problem and Cures. All causes for this are not understood. Lime has an inverse solubility, therefore, precipitating from solution if there is a temperature *increase* in the pipeline system from feed to discharge. Lime in solution reacts with carbon dioxide which may enter the transport system, resulting in the precipitation of lime carbonates. The water used to make the lime slurry may contain sulfate ions or other

ions which react with lime to form precipitates. Precipitation causes scaling. During the slaking operation, lime solutions tend to supersaturate, such supersaturation subsequently being relieved in the transport system with the formation of scale. This supersaturation is minimized in the case of slurries made from hydrated lime, but it can, nevertheless, occur. Also, because of the tendency of lime particles to settle, plugging may occur at valves, elbows and other "dead" areas of the system, especially if flow rates of the slurry vary widely or are intermittent. Increased pipeline velocities can minimize scaling but do not prevent it.

Over the years, during which lime has continued to be a major reagent for acid neutralization, many procedures and precautions have been developed to minimize and even prevent this problem. Among the more prevalent are:

1. Routine water flushing of the transport system.
2. Routine flushing of the transport system with dilute hydrochloric acid.
3. Cleaning the pipeline with a "pig" or other mechanical device.
4. Use of flexible piping from which scale can be broken by distortion.
5. Use of an "above-surface" trough (where climatic or indoor conditions permit), the trough thus being readily accessible for mechanical cleaning.
6. Holding the lime slurry in an "aging" vessel to relieve post precipitation of scale materials before the slurry is introduced into the transport system.
7. Introduction of 8-12 mg/l of sodium hexameta-phosphate upstream from the slaking or dilution tank. This phosphate softens the water so that the calcium carbonate that precipitates largely deflocculates instead of accumulates (scales).
8. Application of heat from an acetylene torch on dismantled sections of pipeline and accessories. The thermal shock causes the scale to defoliate.
9. Use of high-solids content lime slurry.

High Solids Lime Slurry. All of the foregoing have been employed with success. Of these, the use of high-solids content slurry may prove especially suitable for the larger neutralization installations. This concept is based on the premise that if the solids density is relatively high, in the range of 15% by weight, precipitation occurs on the particle surface (surface area effect) rather than on the inner walls of the system. Since quick-lime varies in its slaking properties, and slaking procedures likewise vary, both affecting surface area, the optimum slurry density to minimize or prevent scaling also varies. Thus, solids should be maintained as high

as possible consistent with the transport system limitations. Table 9 indicates the specific gravity of high calcium lime slurry over a range of solids. (2)

Slaking Design Pointers. As for plugging at valves or other "dead" areas, due to the settling and compacting characteristics of lime slurry, remedial measures such as water flushing or mechanical cleanout obviously apply. Squeeze valves or valves which operate either fully open or fully closed are desirable in the system. When the system contains a "loop" around which lime slurry is continuously flowing, take-off points should be as short and straight as possible. The monitoring system should be sensitive to lime slurry flow at point of addition to the acid.

Neutralization End Products

The end products of acid neutralization are sludge and effluent. Rarely does neutralization result in an effluent only. In times past, it was often expedient to impound the sludge in lagoons or settling basins and discharge the effluent to public waters. Such procedures focused attention on sludge volume and sludge settling rate. Frequently caustic soda was selected as the neutralizing reagent if for no other reason than the minimization or elimination of sludge due to the solubility of sodium salts. In contrast, the use of lime for sulfuric acid neutralization resulted in a gypsum sludge disposal problem. Today, these situations are pertinent. Because of the increasing tempo of the environmental clean-up in the U.S., with its attendant Environmental Protection Agency regulations for air and water pollution control, acid neutralization end products are undergoing a new evaluation.

It is beyond the scope of this bulletin to delve deeply into end-product factors which bear upon a choice of reagents for acid neutralization. Major areas to be considered include:

1. Sludge disposal,
2. Effluent disposal,
3. Effluent recycle, and
4. Air pollution

These considerations all influence the choice of neutralizing reagent and the degree of under- or over-neutralization permissible or required.

Sludge Problems and Disposal. Few, if any, sludges settle at a rate sufficient to utilize detention tanks for the accumulation of sludge for disposal on the land.

Table 9 — Strength of Lime Suspensions (2)

Milk-of-lime Suspensions		Lime Content*			
Specific Gravity at 15° C.	Degrees Baumé (Bur. Stds. Scale)	Grams CaO per liter	Grams Ca(OH) ₂ per liter	Lbs. CaO per U.S. gal.	Lbs. CaO per cu. ft.
1.010	1.44	11.7	15.5	.097	0.7
1.020	2.84	24.4	32.2	.203	1.5
1.030	4.22	37.1	49.0	.309	2.3
1.040	5.58	49.8	65.8	.415	3.1
1.050	6.91	62.5	82.6	.520	3.9
1.060	8.21	75.2	99.4	.626	4.7
1.070	9.49	87.9	116	.732	5.5
1.080	10.74	100	132	.833	6.3
1.090	11.97	113	149	.941	7.1
1.100	13.18	126	166	1.05	7.9
1.110	14.37	138	182	1.15	8.7
1.120	15.54	152	201	1.27	9.5
1.130	16.68	164	217	1.37	10.3
1.140	17.81	177	234	1.47	11.1
1.150	18.91	190	251	1.58	11.9
1.160	20.00	203	268	1.69	12.7
1.170	21.07	216	285	1.80	13.5
1.180	22.12	229	303	1.91	14.3
1.190	23.15	242	320	2.02	15.1
1.200	24.17	255	337	2.12	15.9
1.210	25.16	268	354	2.23	16.7
1.220	26.15	281	371	2.34	17.6
1.230	27.11	294	388	2.45	18.4
1.240	28.06	307	406	2.56	19.2
1.250	29.00	321	424	2.67	20.0

* Data are based on a typical high calcium lime. In obtaining these data the milk of lime was placed in a wide cylinder, slowly rotating to permit agitation. The hydrometer was inserted and allowed to sink slowly; the reading taken when it stopped. In the case of a thin slurry, the reading must be taken quickly before the lime settles; while in the case of a thick cream of lime, duplicate readings should be taken to assure the correct hydrometer value.

This holds true for most sludge thickening procedures. To this end, sludge must be dewatered by filters, centrifuges or in evaporators to produce a material of sufficient density or stability for landfill. Chemical processes have been developed to expedite use of sludge for landfill. (11) Generally, caustic soda and soda ash yield by far the least weight of sludge and the highest dissolved solids content in the effluent. The use of limestone tends to enhance sludge settling rate and minimize sludge volume, particularly where sulfuric acid neutralization is concerned. Sludges resulting from the use of high calcium and dolomitic lime are generally noteworthy for slower settling rates and greater sludge volume (Fig. 6). Under-neutralization tends to minimize sludge volume, and over-neutralization increases it.

The leaching characteristics of sludges may far out-

weigh all other considerations in view of requirements involving the protection of both surface and underground water into which seepage from the sludge may enter. Total solubles in the sludge, including toxic substances, i.e., heavy metals, must be taken into account. Because of this, over-neutralization may be mandatory, thus requiring high calcium or dolomitic lime as the neutralizer. None of the reagents cited can achieve as low total dissolved solids content in the effluent and maximum metals precipitation as high calcium lime.

Effluents. The disposal of neutralization effluents involves the same, or even more stringent environmental regulations, as does the potential leachate from the sludge. After all, the leachate is essentially what remains of the effluent in the wet sludge. Caustic soda and

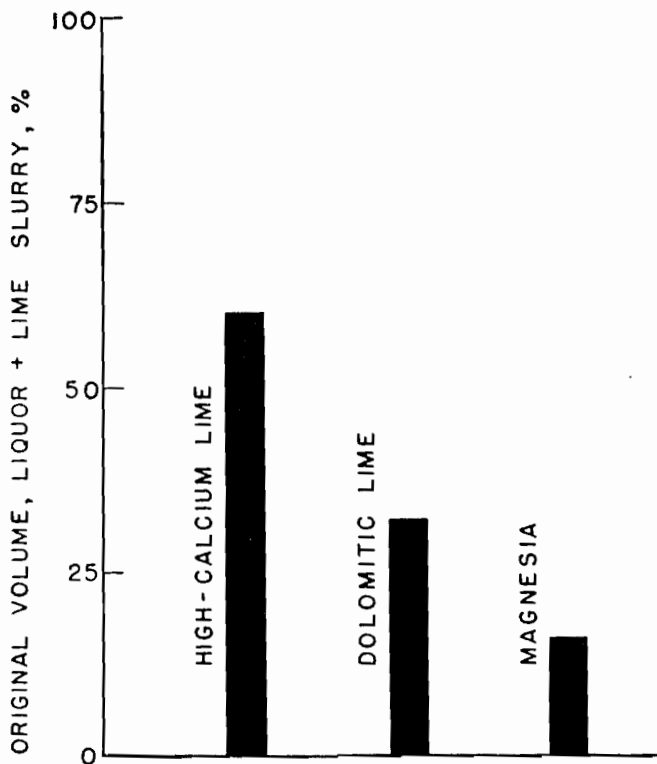


Figure 6 — Sludge from Neutralized Pickle Liquor (1)

soda ash appear to be at a disadvantage in view of the formation of so much soluble sodium salts, i.e., sulfates, sulfites, phosphates and fluorides. Again, if metals are present, high calcium lime offers the greatest assurance that the effluent will contain a minimum concentration of dissolved salts and objectionable metal ions. However, this is not to imply that dolomitic lime or even calcitic limestone will not find application in these systems. For example, effluents from gas scrubbers removing sulfur dioxide and containing but traces of dissolved metals may well produce sludges and under-neutralized effluents suitable for disposal and discharge to public domain.

As for effluent recycle, this consideration presents considerable appeal in view of plant water shortages in some localities and the increasing costs of plant water. As is well-known, high calcium lime, either quicklime or hydrated lime, plays an important role in domestic water treatment. Similarly, the use of high calcium lime in acid neutralization where the acid forms an insoluble precipitate with calcium can set the stage for recycle of the clarified effluent. Indeed, this is currently practiced in the case of municipal waste waters which, after clarifying with lime, are suitable for industrial processes. For systems containing sulfate or sulfite ions in poten-

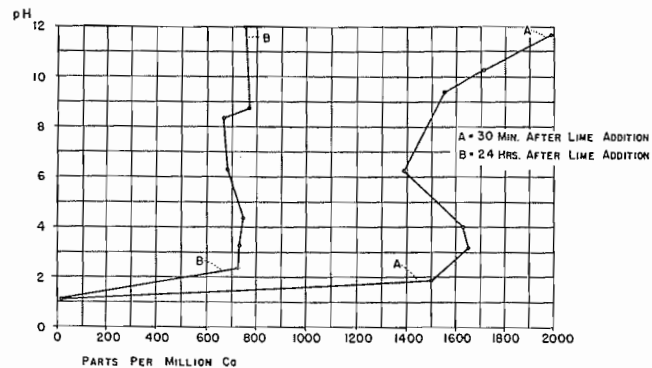


Figure 7 — Calcium in Effluent from Approx. 1/4 Percent H_2SO_4 -Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

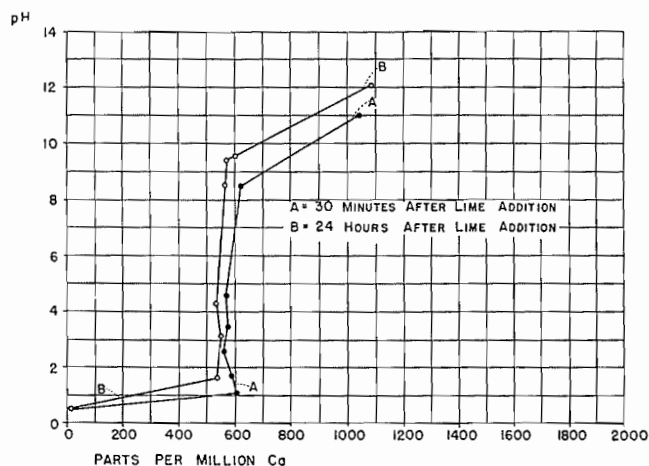


Figure 8 — Calcium in Effluent from Approx. 3 Percent H_2SO_4 -Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

tial recycle water, attention has already been called to the adverse effect of these ions in the lime slaker. In addition, the potential of the sulfate ion to scale and plug recycle lines should be analyzed. In sulfuric acid neutralization, the tendency of calcium sulfate to supersaturate the solution can cause severe scaling of transport equipment as this supersaturation is relieved. Figures 7 and 8 illustrate this situation. Although the use of dolomitic lime in the preparation of recycle water tends to minimize the formation of scale (Fig. 9), the formation of soluble magnesium sulfate might defeat the purpose of low solids content.

Summary

An earnest attempt has been made to bring into perspective the major considerations bearing on the neu-

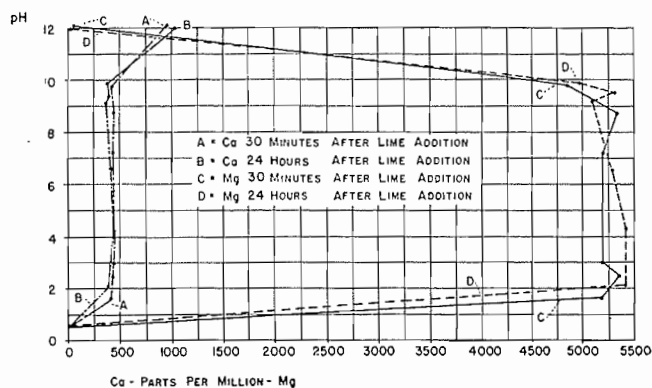


Figure 9 — Calcium and Magnesium in Effluent from Approx. 3 Percent H_2SO_4 -Water System Treated With Slaked and Slurried Dolomitic Quicklime (4)

tralization of acids with lime; also, to bring relationships into focus. However, it is not to be implied that the foregoing is the entire story. The ancient adage that "all rules have exceptions" has never been more meaningful as far as this presentation is concerned.

It is again emphasized that each acid neutralization situation should be studied and evaluated on its own merits, not only in terms of today's effluent specifications but also realistically because of the obvious evolution of such specifications towards ever more stringent future pollution abatement requirements.

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About the publisher of this book

National Lime Association is the trade association for manufacturers of commercial quicklime and hydrated lime. Among its most important functions are the education of the consuming public as to the most efficient application of lime, as well as publishing general technical information in those fields where lime is used.

In addition to this book, National Lime Association has published the following literature applicable to the wastewater treatment field, which is available for a nominal cost:

1. "Water Supply & Treatment" (11th edition), 1976, by Merrill L. Riehl.
2. "A Study of the Reaction Between Calcium Oxide and Water," by T.C. Miller, Azbe Award No. 1, 1960.
3. "Chemical Lime Facts," Bull. 214, (5th edition), 1988.
4. "Lime Handling, Application and Storage," Bull. 213 (4th edition), 1982.
5. "Lime in Municipal Sludge Processing," Bull. 217, 1980.
6. "Lime—The Versatile Chemical" Brochure.

In addition, NLA has available two 16mm movies related to the treatment field:

1. "Lime—The Versatile Chemical," 30 min.
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Lime in Municipal Sludge Processing



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Lime in Municipal Sludge Processing

by Clifford J. Lewis and Kenneth A. Gutschick

Lime plays an important role as a conditioning reagent in the treatment and disposal of municipal waste sludge. Historically, lime has been used for hundreds, probably thousands of years to suppress odors and other nuisance value associated with the open disposal of human wastes. However, in recent years, particularly since the creation of the U.S. Environmental Protection Agency in 1970, the use of lime for conditioning municipal waste sludge has been receiving great attention at both operating and research levels.

From the standpoint of disposal, sludges from the treatment of municipal sewage are the most significant end products of the treatment process. Their volume, as related to burgeoning population, urban sprawl, the increasing value of land, and environmental protection requirements, have rendered the earlier procedures of disposal by lagooning or ocean dumping impractical and even prohibitive in some localities. Indeed, there is strong pressure to ban ocean dumping completely within the next few years. The EPA has indicated that municipal sludges must be disposed of on the land or by incineration, with the ash finding land disposal sites. The municipal waste treatment plant then has the following options for sludge disposal:

1. Land disposal
 - a. trenching (Fig. 1)
 - b. landfill
2. Agricultural utilization
 - a. liquid application
 - b. cake application
 - c. composting (Fig. 2)
3. Thermal approaches
 - a. incineration
 - b. pyrolysis
 - c. co-incineration



Fig. 1 — Trenching lime-treated dewatered primary sludge on Maryland farm site.



Fig. 2 — Windrow composting of lime-treated sewage sludge at Upper Occoquan Sewage Authority plant.

The sludges generated by municipal waste treatment plants may be primary, waste-activated, digester, thermally-conditioned, or combinations of all of the foregoing. Each of these sludges, depending upon the treatment process, must find a site for ultimate disposal. After thickening, these sludges contain about 3% to 5% solids by weight. It can be appreciated therefore why, without the benefit of ocean dumping or ability to lagoon this so-called "soup", direct application onto a land site must be near the sludge source because of the economics of transportation.

Furthermore, the problem of municipal waste sludge disposal is complicated by the presence of odors, heavy metals content and pathogens. Obviously, odors from lagooning or direct land application may beget adverse societal pressure. Likewise, the possibility of the uptake of heavy metals and even pathogens by plants or grazing animals or the likelihood of these dangerous, even hazardous substances leaching into the water table, is receiving serious attention from the regulatory agencies involved. Because of the above considerations, the role of lime in municipal waste sludge disposal has become most vital.

The addition of lime alone, or in conjunction with ferric chloride, conditions thickened sludges to enable dewatering at a practical rate on various types of filters to yield a filter cake with a sufficiently high solids content to economically permit long haul transportation prior to land disposal or which is dry enough to be incinerated. Of equal importance, this use of lime also destroys the sludge odors and pathogens and "fixes" heavy metals to minimize or prevent their leaching into surface or underground waters.

To achieve these benefits, there are few if any substitutes for lime where dewatering by filtration is required. This is generally not the case when dewatering is carried out with the centrifuge. In this case, polymers may be added to the thickened sludge prior to centrifuging. Even when lime or the combination of lime plus ferric chloride is not used for conditioning ahead of dewatering, it may be expedient to apply lime subsequently to minimize odors, fix heavy metals and destroy pathogens, depending upon the ultimate disposal of the sludge. Indeed, even in the case of sludge which has been thickened only, for direct application on the land, it may be necessary to periodically treat the land with lime or limestone to prevent the soil from becoming too acidic as a result of sludge decay.

Chemistry of Reactions

The chemistry of the reactions between high calcium lime and municipal waste sludge or between ferric chlo-

ride, lime and sludge for conditioning ahead of dewatering is complex and not very-well understood. Much research has been undertaken and is underway to define these reactions. The effort is further complicated in that municipal waste sludges differ widely in chemical composition. Such variations include the relative contents of phosphates, sulfates, heavy metals, oils and greases, industrial loadings, storm water run-off, type of solids concentration and probably other factors yet unknown. At this time, there appears to be reasonable agreement on the following:

1. Sludge alkalinity (bicarbonate) may be divided into alkalinity contained in the mobile sludge water and alkalinity contained in the bound water associated with the sludge solids.

2. The relative effectiveness of iron salts when used alone or in combination with lime for sludge conditioning ahead of dewatering is in the following order: ferric chloride (FeCl_3), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), ferrous chloride (FeCl_2) and ferrous sulfate (FeSO_4). The use of iron sulfates may cause problems when used with high lime doses.

3. When ferric chloride is used alone as a conditioning agent prior to dewatering, the ferric chloride is believed to form hydroxy-iron polymers which, through a bridging mechanism, cause flocculation of the sludge due to the action of the negatively-charged sludge particles with positively-charged iron polymers.

4. Ferric iron salts alone will not provide the most economical conditioning for all sludges. Often, a combination of ferric chloride and high calcium lime will provide more effective and/or more economical conditioning.

5. The effect of lime addition on ferric chloride-conditioned sludge has been explained in terms of a calcium link between negatively-charged ferric hydroxide precipitate and negatively-charged sludge colloids.

6. When lime alone is employed as the only conditioning agent, its effectiveness has been explained in terms of a calcium complex with functional groups on the sludge solids. The formation of this calcium complex with the lipids in primary sludge and with proteins and polysaccharides in waste-activated and digested sludges is believed to be the principal reason for improved sludge filterability.

7. The formation of calcium carbonate, calcium sulfate and calcium phosphate from these dissolved ions in the sludge-transported water has an adverse effect on sludge filtration rate because the fine precipitates impair cake permeability. This problem is magnified as the storage time for conditioned sludge is increased.

8. The alkalinity of raw secondary sludges and

mixed primary-secondary sludges is due principally to the presence of organic constituents.

9. The tendency of ferric iron to be reduced by sludges to ferrous iron increases as the pH is reduced from an upper limit of around 7 to some lower limit of around pH 3. Although ferrous iron provides little or no conditioning by itself, it does provide adequate conditioning in combination with lime. However, if the sludge conditioning is with ferric iron alone, some of the iron dosage would be lost due to the reduction process.

10. The positive effect of lime addition on iron-conditioned sludges is due to a combination of an increase in calcium ion concentration and a concomitant increase in pH. The increase in pH to the region around 12 produces sludge colloids and iron hydroxide precipitates with highly negative charges.

11. Operation and maintenance costs associated with iron or iron and lime sludge conditioning, i. e., chemicals, problems associated with calcium carbonate encrustation of filter media and piping, auxiliary fuel for cake incineration, etc., are a function of the chemical doses applied. Opportunities for reducing chemical doses are enhanced by a better understanding of the chemical reactions involved in sludge filterability.

It is beyond the scope of this bulletin to discuss in detail the development of the optimum lime dosage, whether lime should be used alone or in conjunction with ferric chloride, or to elaborate on the use of rotary vacuum filters, belt filters, filter presses and centrifuges for dewatering (Fig. 3). Suffice to say these reagents and the dewatering equipment mentioned all find their place

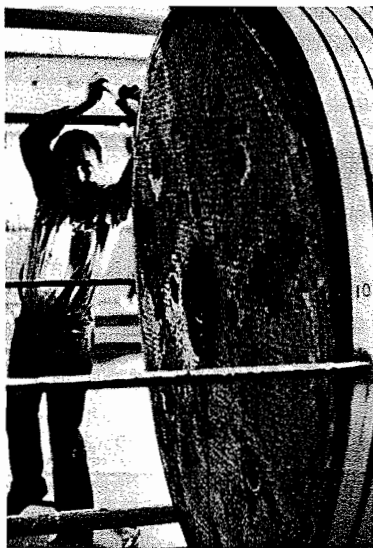


Fig. 3 — Removing lime-treated alum filter cake from pressure filter at Texas water treatment plant.

in the municipal waste treatment plant, depending upon local circumstances, sludge dewatering characteristics, and the ultimate land disposal of the sludge. At present, a combination of lime and ferric chloride for conditioning the sludge ahead of dewatering on rotary vacuum filters is the most common practice.

For best reagent efficiency, a water slurry of hydrated lime or slaked quicklime should be mixed with the thickened municipal waste sludge ahead of dewatering so that the mix can enter the dewatering unit as homogeneously as possible. A good distribution of the lime permits a more accurate pH control of the mixture being fed to the dewatering unit, usually a rotary vacuum filter. When lime is used in conjunction with ferric chloride, or other iron salt, it is desirable that the iron salt be added to the thickened sludge ahead of lime so that it is well-distributed before lime addition. This minimizes the precipitation of iron hydroxides (which are not too effective as dewatering reagents) and promotes the formation of the desired iron-lime polymers. However, it is not unusual in actual practice to find that the iron salt and lime are flash-mixed ahead of the introduction of this mixture to the thickened sludge.

When used alone, the dosage of lime slurry may be controlled entirely by the pH of the system being fed to the dewatering unit. However, when used in conjunction with an iron salt, particularly ferric chloride, the dosage of the iron salt, after being determined by experimentation, is usually set and the lime slurry then added in an amount which maintains the desired pH of the system being dewatered. As already indicated, reagent dosage will vary depending upon the characteristics of the thickened sludge and the extent to which the total system can be thoroughly mixed ahead of dewatering. It is not desirable that the dosages of iron salt and lime be varied simultaneously. This is because the iron salt is acidic whereas the lime is alkaline. Thus, these reagents neutralize each other. Consequently, their respective dosages can be simultaneously increased to a point of impracticability without greatly affecting the final pH of the system.

The U.S. Environmental Protection Agency has issued, under date of September, 1979, a most authoritative and comprehensive publication entitled, "Process Design Manual for Sludge Treatment and Disposal", (EPA 625/1-79-011). Chapter 8, pages 8-6 to 8-14, contains highly useful information concerning the use of lime and ferric chloride for conditioning municipal wastewater sludges. Table 1 reproduces a portion of page 8-7 from this publication. One of the largest municipal waste treatment plants now operating in the

Table 1 — Typical Conditioning Dosages of Ferric Chloride (FeCl₃) and Lime (CaO) for Municipal Wastewater Sludges *

Sludge Type	Vacuum filter		Recessed plate pressure filters	
	FeCl ₃	CaO	FeCl ₃	CaO
Raw primary	40-80	160-200	80-120	220-280
Raw waste-activated sludge (WAS)-air	120-200	0-320	140-200	400-500
Raw (primary + trickling filter)	40-80	180-140		
Raw (primary + WAS)	50-120	180-320		
Raw (primary + WAS + septic)	50-80	240-300		
Raw (primary + WAS + lime)	30-50	none		
Elutriated anaerobically digested				
primary	50-80	0-100		
primary + WAS (air)	60-120	0-150		
Thermal-conditioned sludges	none	none	none	none
Anaerobically digested sludges				
primary	60-120	200-260		
primary + trickling filter	80-120	250-350		
primary + WAS (air)	60-120	300-420	80-200	220-600

* All values shown are for pounds of either FeCl₃ or CaO per ton of dry solids pumped to the dewatering unit.
1 lb/ton = 0.5 kg/t

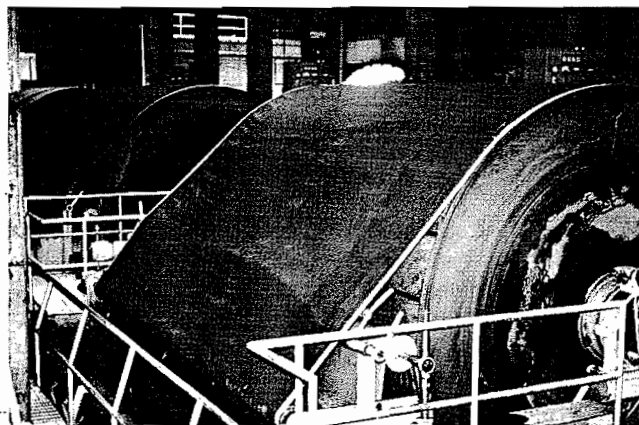


Fig. 4 — Rotary vacuum filters for sewage sludge dewatering at Blue Plains plant, Washington, D.C.

United States—Blue Plains in Washington, D.C., employs a lime-ferric chloride system for sludge dewatering on rotary vacuum filters (Fig. 4). The Upper Occoquan plant, located in Centreville, Va., southwest of Washington, D.C., conditions sludge with lime and ferric chloride for dewatering via filter presses (Fig. 5a, b, & c).

As has already been pointed out, after the sludge is dewatered, it may be incinerated or disposed of on the land. The choice of these procedures will finally be resolved by local circumstances. Incinerators require auxiliary fuel and may produce off-gases which require scrubbing. Land disposal requires both available land and societal acceptance. Major considerations pertain-

ing to land disposal involve odors, the leachability of heavy metals if not “fixed” by lime and the pathogen content of the sludge if pathogen content has not been destroyed by lime addition. Such considerations may require that the dewatered sludge be further limed at point of land disposal, especially if the receiving soil is naturally acidic in the first place. In the case of composting, the presence of lime in the sludge not only reduces odors but can enhance the composting reaction if the pH is not too high. As has been pointed out, lime destroys pathogens in the range of pH 12, but at this pH, the composting environment may not be suitable for microbial growth. If this situation occurs, it may be desirable to age the lime-conditioned sludge in order to allow the pH to drop by virtue of the lime reacting with carbon dioxide or other acid formers.

Background on Lime

Lime is one of the world’s most versatile chemicals. In 1979 the tonnage of lime marketed in the United States was surpassed only by that of sulfuric acid, the leading chemical. Lime is considered to be an energy-intensive chemical product because it is produced by heating naturally-occurring limestone to about 2400°F in order to drive off the carbon dioxide from the limestone to yield the quicklime product. Fortunately for this chemical, which has so many vital uses in our complex technical structure, lime can be produced in huge tonnages via rotary kilns burning coal fired directly into

the kiln. This affords lime an almost endless supply of a least-expensive and most-abundant fuel.

There are various forms of commercial lime and limestone ranging from high calcium pebble quicklimes and dolomitic quicklimes through the hydrated counterparts of these materials. Table 2 illustrates these forms with their chemical compositions.

When lime is used for municipal waste sludge conditioning, whether for dewatering or subsequent control of odors, pathogens or alkalinity (pH), high calcium lime products are generally used, almost without exception. This is because the high calcium materials are reactive at much higher pH than their high magnesium

counterparts. Table 3 illustrates the relative alkalinity (basicity) of commercial lime products and sodium alkalis using pure calcium oxide (CaO) equivalent to 1.00.

Because of the lower chemical equivalency of magnesium as compared with calcium, the dolomitic materials should yield the greater alkalinity. However, this is not the case because the magnesium component cannot develop pH values much in excess of pH 9.0, and indeed any magnesium which may have been solubilized at lower pH values is reprecipitated by the calcium component of the lime system at pH values much above 9.0. However, this is not to imply that dolomitic liming

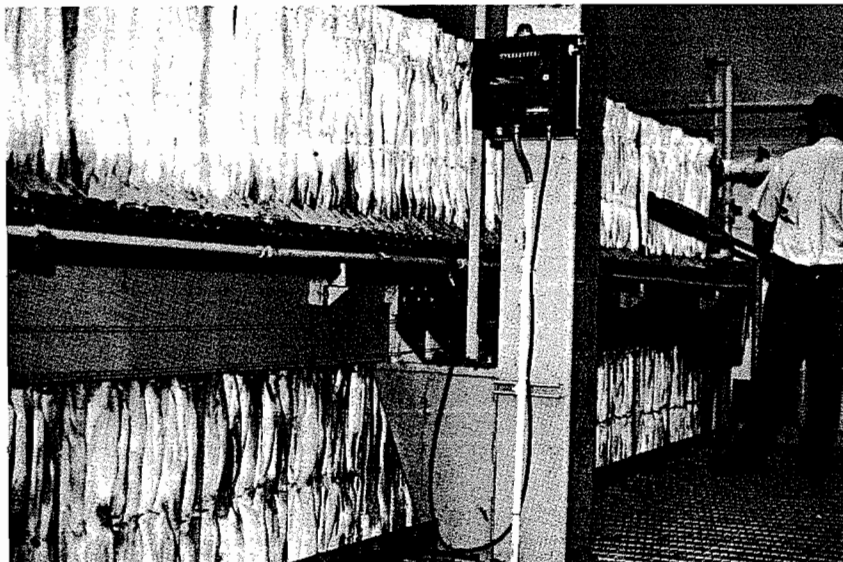


Fig. 5a



Fig. 5b

Fig. 5 — Filter press operation at Upper Occoquan Sewage Authority plant, Centreville, Va., where sludge is conditioned with 20% lime plus 2% ferric chloride to produce good filter cake.

- (a) One of filter presses in operation.
- (b) Removing filter cake containing 40-45% solids.
- (c) Close-up of sludge cake; outer white bands represent chemical pre-coat sludge obtained from tertiary treatment section.



Fig. 5c

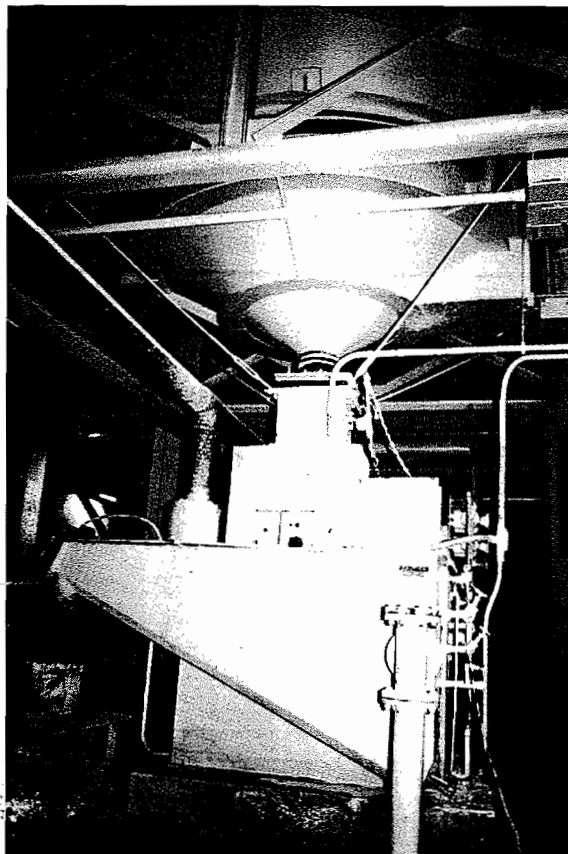


Fig. 6a

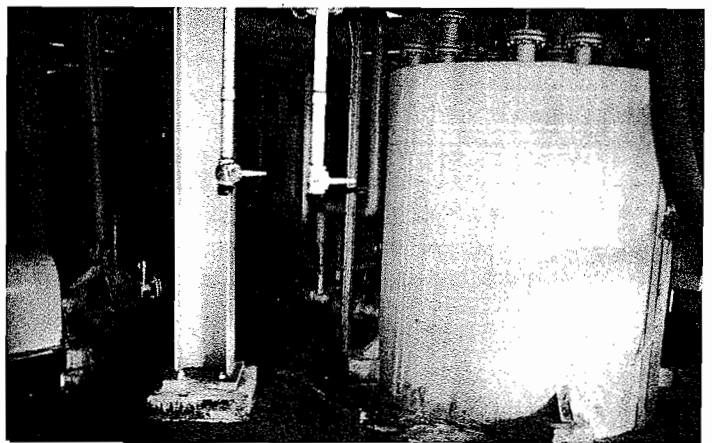


Fig. 6b

Fig. 6a—Modern lime handling facility at Upper Occoquan plant; quicklime from silo is fed to detention-type slaker.

Fig. 6b — Lime slurry from holding tank is pumped to filter presses or to tertiary treatment.

Table 2

Reagent	Theoretical Formula	Chemical Description
High calcium limestone	CaCO_3	Calcium carbonate
Dolomitic limestone	$\text{CaCO}_3 \cdot \text{MgCO}_3$	Calcium magnesium carbonate
High calcium quicklime	CaO	Calcium oxide
High calcium hydrated lime	$\text{Ca}(\text{OH})_2$	Calcium hydroxide
Dolomitic quicklime	$\text{CaO} \cdot \text{MgO}$	Calcium-magnesium oxide
Dolomitic hydrated lime	$\text{Ca}(\text{OH})_2 \cdot \text{MgO}$	Normal dolomitic hydrate
Highly hydrated dolomitic lime	$\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2$	Special dolomitic hydrate

materials could not be used for some applications in municipal sludge disposal where local circumstances are favorable.

Important Considerations On Lime's Use

As in the case with most chemical systems requiring informed design and controlled reagent dosage, lime systems for municipal waste treatment plants can beget operating problems. Because of the relatively rapid injection of lime systems into the environmental cleanup program during the last 10 years, the National Lime Association has undertaken an educational program in this area through publications and presentations.

Based on the available literature and field experience, the following is a recapitulation of the more important considerations relative to the use of lime in municipal waste sludge conditioning for disposal:

- A. The relative cost of a unit of calcium oxide (quicklime) as contrasted with calcium hydroxide (hydrated lime) must be taken into account. Commercial quicklimes will range from 90-95% available calcium oxide, whereas commercial hydrated limes will yield from 70-73% calcium oxide. This will vary with the purity of the parent limestone, the lime calcining and hydrating opera-

tions, and shipping procedures. These figures are presented only to indicate that the purchaser of hydrated lime obtains a product which contains chemically-combined water and, of course, freight is also paid on this water content. However, where the quantity of lime required is not sufficient to justify the investment in, and operation of, a lime-slaking system, commercial hydrated lime may be the preferred reagent.

- B. Lime-handling, lime-slaking, lime-slurrying and lime-transporting systems can be designed to avoid spillage and when properly designed are quite compatible with, even contributory to, all aesthetic values which may be required in a municipal waste treatment plant. Figure 6 illustrates lime-storage, lime-slaking and lime-slurry transport systems in a modern municipal waste treatment plant.

Table 3 — Typical Basicity Factors of Acid Neutralizing Reagents

(In Decreasing Value per Unit Weight)

Reagent	Descriptive Formula	Approx. B. F.*
Dolomitic quicklime	CaO · MgO	1.12
High calcium quicklime	CaO	0.96
Normal dolomitic hydrate	Ca(OH) ₂ · MgO	0.88
Dolomitic pressure hydrate	Ca(OH) ₂ · Mg(OH) ₂	0.83
High calcium hydrate	Ca(OH) ₂	0.73
Caustic soda	NaOH	0.70
Dolomitic limestone	CaCO ₃ · MgCO ₃	0.58
High calcium limestone	CaCO ₃	0.54
Soda ash	Na ₂ CO ₃	0.52

* Basicity Factor

- C. Lime slurries have a tendency to chemically scale their transport systems. This is chiefly due to entrained carbon dioxide gas, which precipitates calcium carbonate, but it can also be caused by the inverse solubility of calcium hydroxide. However, if the lime slurry in transport is maintained above 12% solids density, preferably around 15%, such scaling is usually eliminated.
- D. When a lime slurry is handled in a recycling loop, take-off points should be as close to the loop as possible and control valves preferably should be the flexible squeeze type. It is best to operate slurry take-off valves in the fully-opened position. The more coarse lime solids in a loop tend to deposit behind closed or constricted valves. Pro-

vision should be made for back-flushing the take-off assembly and for physically cleaning it by means of a tee when back-flushing procedures are ineffective.

- E. Properly slaked lime slurries are not unusually abrasive and are transported in pipelines at velocities of from 5-10 ft. per second without important erosion to the transport system. However, if a pulverized quicklime is used, the normal core and inert material, which is rejected by a lime-slaker operating on pebble quicklime, may not be so rejected by the slaker and instead report as finely-ground abrasive material in the lime-slurry transport system. Under this circumstance, excessive erosion to pumps and pipeline may occur.
- F. Control of pH of the sludge-lime-iron salt system being fed to a vacuum or pressurized filtering device is very important. Because lime and ferric chloride are such excellent aids in municipal sludge dewatering, there is frequently a tendency to over-lime this system. However, because of the wide variation in sludge characteristics, depending upon the locale and the municipal waste treatment process, the optimum pH can best be developed by trial and error. This may range from pH 9 to in excess of pH 12. A pH of 9 is usually adequate to destroy odors and fix heavy metals, but in this range, the pH is not sufficiently high to destroy all pathogens. At the higher pH value, the excess calcium ions in solution react with carbon dioxide in the air of the filter system or with bicarbonate, if present in the filter wash water. This causes the formation of calcium carbonate precipitate which may lead to scaling and plugging in the filter system. Even the use of domestic water for washing the filter may cause this precipitation, if the water contains bicarbonate ion which may be present to inhibit corrosion of the domestic water system. Some installations provide means for washing the filter systems with dilute inhibited hydrochloric acid. This treatment removes incipient scale before plugging can become serious. If, in the sludge dewatering system, a pH sufficiently high to satisfactorily destroy pathogens cannot be maintained without scaling, it is then best to add some additional lime to the dewatered filter cake in the cake transport system.

The National Lime Association hopes the information in this bulletin will prove useful and solicits contacts from those desiring any further information we may have on the role of lime in municipal sludge conditioning and disposal.

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About the publisher of this book

National Lime Association is the trade association for manufacturers of commercial quicklime and hydrated lime. Among its most important functions are the education of the consuming public as to the most efficient application of lime, as well as publishing general technical information in those fields where lime is used.

In addition to this book, National Lime Association has published the following literature that is applicable to the wastewater treatment field:

1. "Chemical Treatment of Sewage and Industrial Wastes," by Dr. Wm. A. Parsons, 1965 (under revision).
2. "Water Supply & Treatment" (11th edition), 1976, by Merrill L. Riehl, \$5.00 plus 35¢ postage.
3. "A Study of the Reaction Between Calcium Oxide and Water," by T. C. Miller, Azbe Award No. 1, 1960, \$1.00 plus 39¢ postage.
4. "Chemical Lime Facts," \$1.50 plus 25¢ postage.
5. "Lime Handling, Application and Storage" (3rd edition), 1976, \$2.00 plus 25¢ postage.
6. "Lime, The Versatile Chemical," Brochure, Free, 1980.
7. "Lime, The Versatile Chemical," 16 mm. sound-color movie, available on free loan basis, 30 minutes.
8. "Acid Neutralization with Lime", 1976, \$1.00 plus 25¢ postage.