Bulletin No. 216

Acid Neutralization with Lime

- For Environmental Control and Manufacturing Processes

LIME
"THE"
VERSATILE
CHEMICAL

National Lime Association

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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 alkaline material 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 simple 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 raw materials (limestone) economically available. In spite of this, sources of limestone for the production of 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_2O_3	.10- .40	.05- .40
Al_2O_3	.10- .50	.05- .50
H_2O	.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:

$$CaCO_3 + \text{heat} = CaO + CO_2 \uparrow \text{ (gas)}$$
$$CaCO_3 \cdot MgCO_3 + \text{heat} = CaO \cdot MgO + 2\ CO_2 \uparrow \text{ (gas)}$$

About 80% of commercial 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.

$$CaO + H_2O = Ca(OH)_2 + \text{heat} \uparrow$$
$$CaO \cdot MgO + H_2O \text{ @ atm. pressure} = Ca(OH)_2 \cdot MgO + \text{heat} \uparrow$$

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:

$$CaO \cdot MgO + 2H_2O = Ca(OH)_2 \cdot Mg(OH)_2 + \text{heat} \uparrow$$

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 degree of the calcination (burning). The soft-burned limes are generally most reactive and will slake almost instantaneously 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 retention 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/1 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 strong alkalis such as sodium hydroxide (NaOH), which is a monoacid base, calcium hydroxide ($Ca(OH)_{2)}$ and Magnesium hydroxide ($Mg(OH)_{2)}$ are diacid bases. This means only one molecule of lime is needed to neutralize two molecules of monobasic acid, such as hydrochloride (HCl), whereas only one molecule of this type of acid is neutralized by one molecule of NaOH. With a dibasic acid, like sulfuric (H_2SO_4), still only one molecule of lime is needed to react with one molecule of sulfuric, but two molecules of sodium hydroxide 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 is neither acidic nor basic but has an equal molar content of hydrogen ions and hydroxyl ions. In other words, exhibits the pH of pure water, i.e., pH 7.0 at 25°C. 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, 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 12.454 is attained in a saturated solution at 25°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 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.

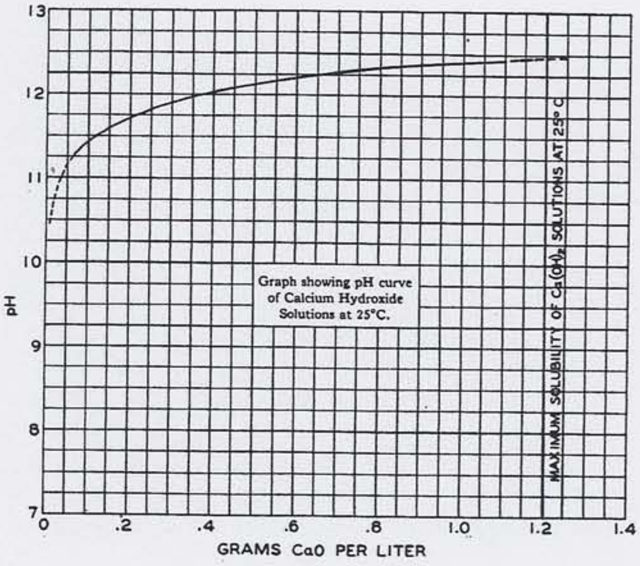

Figure 1 (2)

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,

$$\underset{\text{(80 wt. parts caustic soda)}}{2NaOH} + \underset{\text{(98 wt. parts sulfuric acid)}}{H_2SO_4} = Na_2SO_4 + 2H_2O$$

$$\underset{\text{(56 wt. pts. quicklime)}}{CaO + H_2O} + \underset{\text{(98 wt. pts. sulfuric acid)}}{H_2SO_4} = CaSO_4 + 2H_2O$$

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 (depending on the purity of the 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_2CO_3	Sodium carbonate
High calcium limestone	$CaCO_3$	Calcium carbonate
Dolomitic limestone	$CaCO_3 \cdot MgCO_3$	Calcium-magnesium carbonate
High calcium quicklime	CaO	Calcium oxide
High calcium hydrated lime	$Ca(OH)_2$	Calcium hydroxide
Dolomitic quicklime	$CaO \cdot MgO$	Calcium-magnesium oxide
Dolomitic hydrated lime	$Ca(OH)_2 \cdot MgO$	Normal dolomitic hydrate
Highly hydrated dolomitic lime	$Ca(OH)_2 \cdot Mg(OH)_2$	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	$CaO \cdot MgO$	1.12
High calcium quicklime	CaO	0.96
Normal dolomitic hydrate	$Ca(OH)_2 \cdot MgO$	0.88
Dolomitic pressure hydrate	$Ca(OH)_2 \cdot Mg(OH)_2$	0.83
High calcium hydrate	$Ca(OH)_2$	0.73
Caustic soda	$NaOH$	0.70
Dolomitic limestone	$CaCO_3 \cdot MgCO_3$	0.58
High calcium limestone	$CaCO_3$	0.54
Soda ash	Na_2CO_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 ($CaCO_3$) 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 3 — Reaction Relationships

High calcium lime + hydrochloric acid	$\xrightarrow{(1)}$	Calcium chloride (S)
Caustic soda + sulfuric acid	$\xrightarrow{(1)}$	Sodium sulfate (S)
Dolomitic lime + hydrochloric acid	$\xrightarrow{(2)}$	Calcium chloride (S) + magnesium chloride (S)
Dolomitic lime + hydrochloric acid	$\xrightarrow{(3)}$	Calcium chloride (S) + magnesium hydroxide (Ins)
Dolomitic lime + sulfuric acid	$\xrightarrow{(2)}$	Calcium sulfate (Ins) + magnesium sulfate (S)
Dolomitic lime + sulfuric acid	$\xrightarrow{(3)}$	Calcium sulfate (Ins) + magnesium hydroxide (Ins)
High calcium lime + sulfuric acid	$\xrightarrow{(1)}$	Calcium sulfate (Ins)
High calcium lime + ferric sulfate	$\xrightarrow{(1)}$	Calcium sulfate (Ins) + ferric hydroxide (Ins)
High calcium lime + ferrous sulfate	$\xrightarrow{(2)}$	Calcium sulfate (Ins) + unreacted ferrous sulfate (S)
High calcium lime + ferrous sulfate	$\xrightarrow{(3)}$	Calcium sulfate (Ins) + ferrous hydroxide (Ins)
Dolomitic lime + ferric chloride	$\xrightarrow{(2)}$	Mag. chloride (S) + calcium chloride (S) + ferric hydroxide (Ins)
Dolomitic lime + ferrous sulfate	$\xrightarrow{(3)}$	Mag. hydroxide (Ins) + calcium sulfate (Ins) + ferrous hydroxide (Ins)
Dolomitic lime + magnesium sulfate	$\xrightarrow{(2)}$	Mag. hydroxide (Ins) + calcium sulfate (Ins)
High calcium limestone + hydrochloric acid	$\xrightarrow{(2)}$	CO_2gas + calcium chloride (S)
High calcium limestone + sulfuric acid	$\xrightarrow{(2)}$	CO_2gas + calcium sulfate (Ins)
High calcium limestone + ferrous sulfate	$\xrightarrow{(2)}$	CO_2gas + calcium sulfate (Ins) + unreacted ferrous sulfate (S)
High calcium limestone + ferric sulfate	$\xrightarrow{(2)}$	CO_2gas + calcium sulfate (Ins) + ferric hydroxide (Ins)
S = Soluble		(1) Either over- or under-neutralization
Ins = Insoluble		(2) Under-neutralization
		(3) Over-neutralization (above pH 9.0)

ing on the metal ion. (6) A few metals, such as arsenic and chromium, may be present as anion complexes requiring special chemical treatment, such as reduction before neutralization. Table 4 illustrates the pH at which the more common metals begin to precipitate. These are presented as "guideline" material rather than for accuracy under all conditions. For example, in the case of waste sulfuric acid pickling liquor from the steel industry, the ferrous iron is not completely precipitated until about pH 9.2. Over-neutralization is therefore required. On the other hand, trivalent chromium can be precipitated at about pH 5.5 from a waste electroplating acid, an example of under-neutralization.

In category number 4 (high magnesium reagents), this encompasses the decreasing solubility of the magnesium ion above pH 9.0. Magnesium begins to precipitate as the pH rises over 9 and at pH 10.2 is practically insoluble. To illustrate, using a waste sulfuric acid system requiring neutralization to pH 10.0 to substantially remove all ferrous iron,

$$Ca(OH)_2 \cdot Mg(OH)_2 + 2H_2SO_4 = \underset{\text{(insoluble)}}{CaSO_4} + 4H_2O + \underset{\text{(soluble pH 7.0)}}{MgSO_4}$$

$$Ca(OH)_2 \cdot Mg(OH)_2 + MgSO_4 = CaSO_4 + \underset{\text{(insoluble pH 10.2)}}{2Mg(OH)_2}$$

$$2Ca(OH)_2 \cdot Mg(OH)_2 + 2H_2SO_4 = 2CaSO_4 + \underset{\text{(insoluble pH 10.2)}}{2Mg(OH)_2} + 4H_2O$$

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 equipment 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	
Dolomitic lime products	Dolomitic lime products (to about pH 9)
High calcium limestone	

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 alkaline agents in completing a typical neutralization reaction where all of the alkaline materials are 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 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

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.

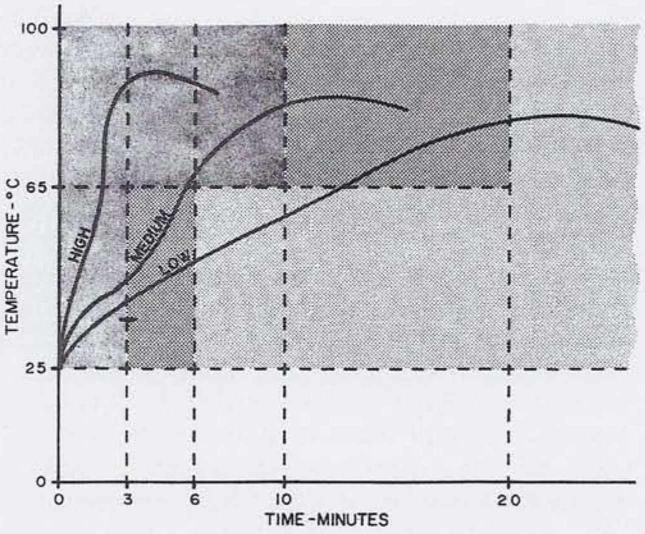

Figure 2 — Typical Lime (CaO) Reactivity Curves Adapted from Slaking Rate Test-AWWA-B-202-65 (8)

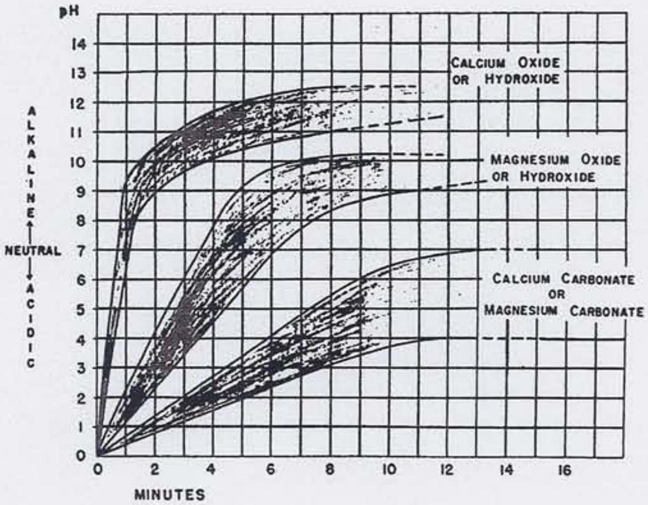

Figure 3 — Reaction Rate Ranges for Liming Material Constituents (4)

Table 6 — Reaction Time of Alkaline Agents with Pickle Liquor (without Aeration) (3) (Hours)

Agent	Room temperature	60°C
NaOH	a	a
Na_2CO_3	0.75	0.75
MgO (reactive)	3 hr.	0.72
CaO	0.25	0.25
$CaO \cdot MgO$	1.88	3.14
$Ca(OH)_2$	0.5	0.5
$Ca(OH)_2 \cdot MgO$	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.

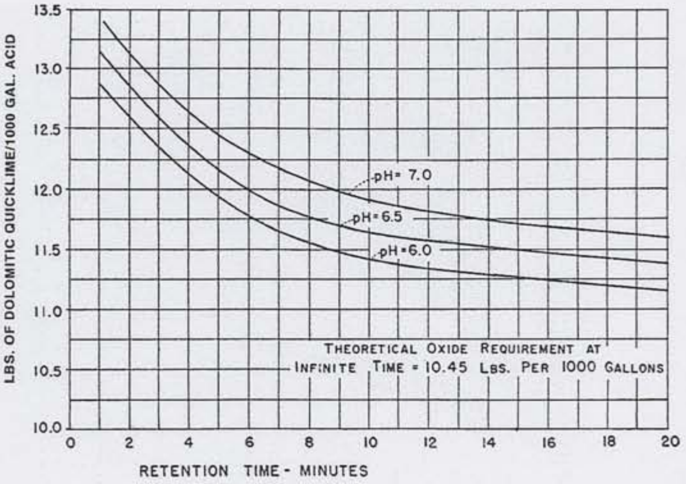

Figure 4 — Lime Requirement for Neutralizing ¼ Percent Sulfuric Acid Using a Dolomitic Pebble Quicklime Slaked and Slurried (4)

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 alkaline material 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 instantly reacts 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

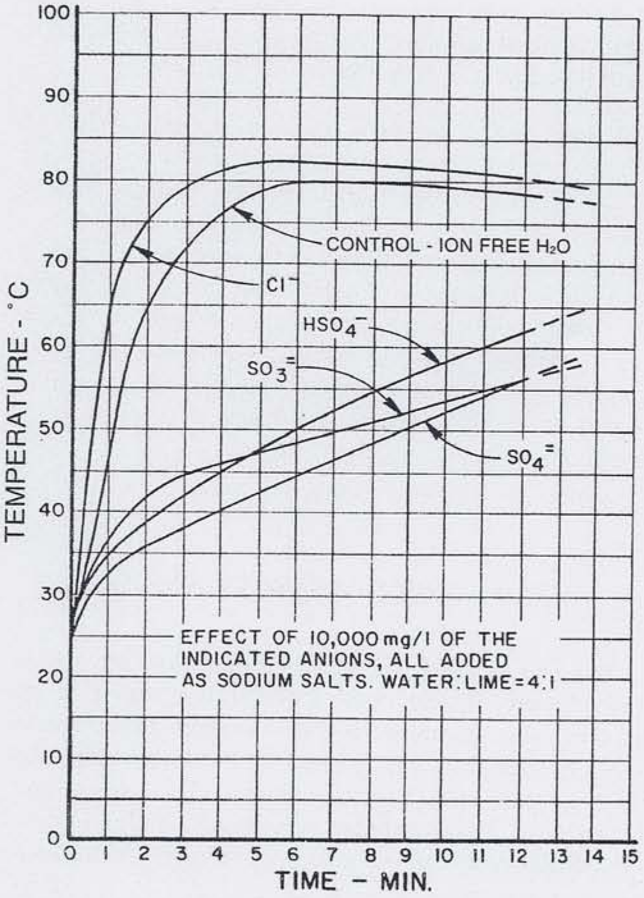

Figure 5 — Slaking Rate Test (10)

Table 8 translates this into lime slurry particle size. On the other hand, the adverse effect of these retarders on the 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.

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 of Lime Slurry as a Function of Concentration of Dissolved Solids (10)

	Concentration of Sulfate (as Na_2SO_4) in Slaking Water		
Particle Size	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%

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

Scaling Problem and Cures. 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 (Requires periodic clean-out).
7. Introduction of 8–12 mg/l of sodium hexametaphosphate 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 quicklime 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, or utilization,
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 outweigh 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**

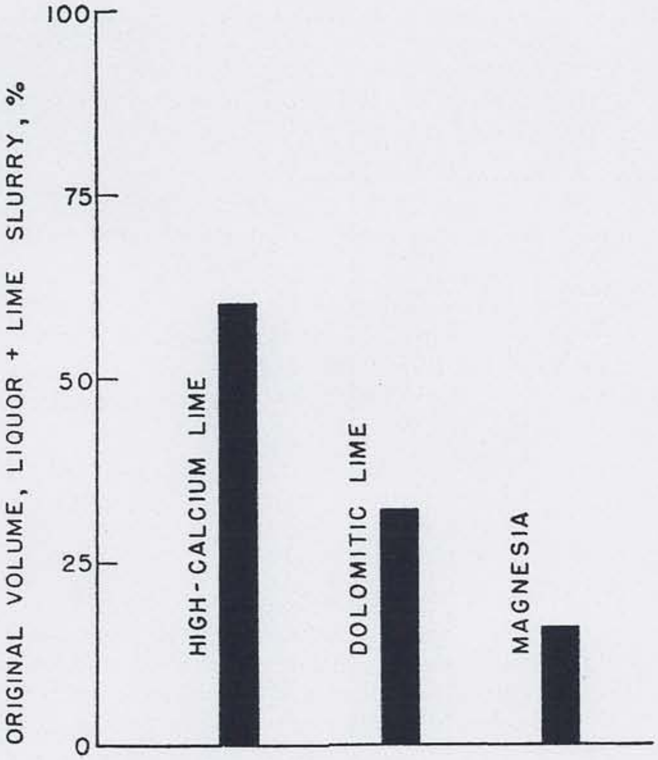

Figure 6 — Sludge from Neutralized Pickle Liquor (1)

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 metals 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 underneutralized 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 potential 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.

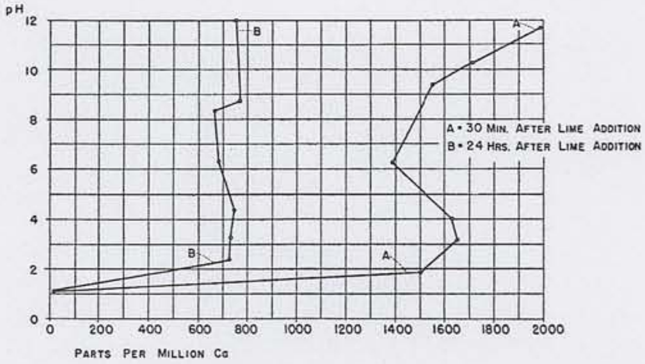

Figure 7 — Calcium in Effluent from Approx. ¼ Percent H_2SO_4-Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

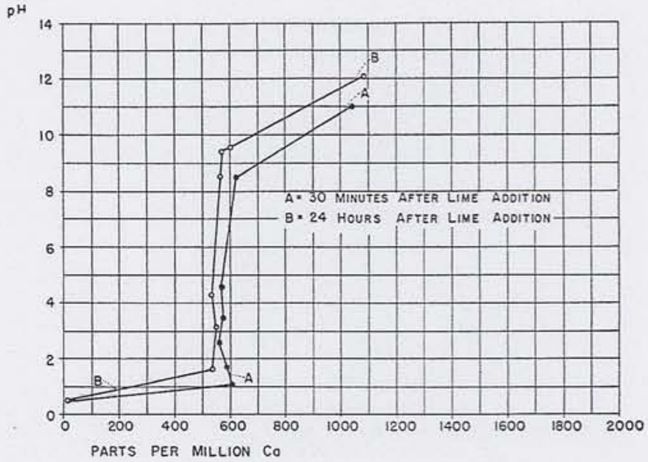

Figure 8 — Calcium in Effluent from Approx. 3 Percent H_2SO_4-Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

Summary

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

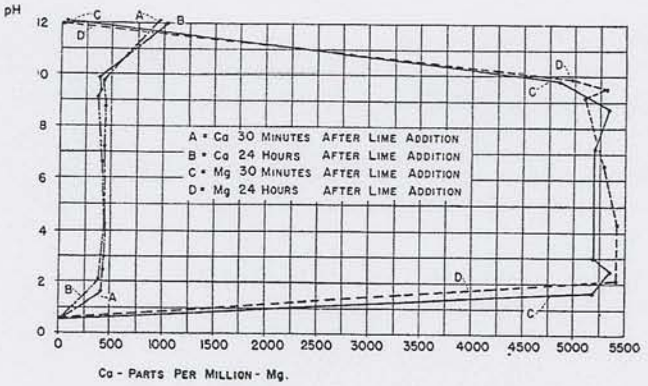

Figure 9 — Calcium and Magnesium in Effluent from Approx. 3 Percent H_2SO_4-Water System Treated With Slaked and Slurried Dolomitic Quicklime (4)

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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