

Acid

Neutralization

with Lime

- **For Environmental Control and Manufacturing Processes**



National Lime Association

Acid Neutralization with Lime for Environmental Control and Manufacturing Processes

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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 lime-

stone 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-

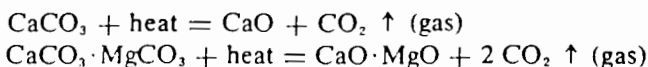
Typical Analyses of Commercial Quicklimes

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 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

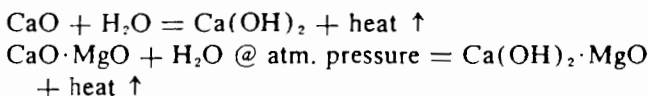
* The values given in this range do not necessarily represent minima and maxima percentages.

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

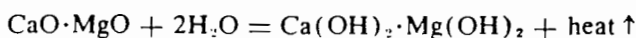
The first lime product, quicklime, (an oxide) is manufactured by calcining the limestone at about 2400°F. This drives off the chemically-bound carbon dioxide:



About 80% of 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.



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 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 re-

tention 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 strong alkalis such as sodium hydroxide (NaOH), which is a monoacid base, calcium hydroxide ($\text{Ca}(\text{OH})_2$), and Magnesium hydroxide ($\text{Mg}(\text{OH})_2$), 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.

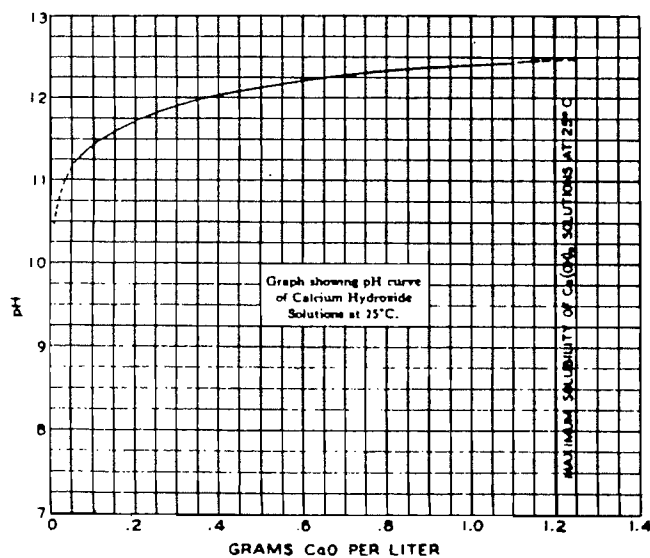
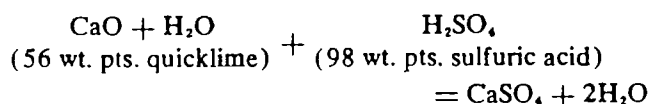
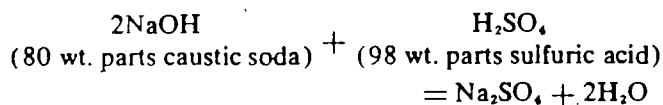


Figure 1 (2)

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,



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 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 3 — Reaction Relationships

High calcium lime + hydrochloric acid	<u>(1)</u> →	Calcium chloride (S)
Caustic soda + sulfuric acid	<u>(1)</u> →	Sodium sulfate (S)
Dolomitic lime + hydrochloric acid	<u>(2)</u> →	Calcium chloride (S) + magnesium chloride (S)
Dolomitic lime + hydrochloric acid	<u>(3)</u> →	Calcium chloride (S) + magnesium hydroxide (Ins)
Dolomitic lime + sulfuric acid	<u>(2)</u> →	Calcium sulfate (Ins) + magnesium sulfate (S)
Dolomitic lime + sulfuric acid	<u>(3)</u> →	Calcium sulfate (Ins) + magnesium hydroxide (Ins)
High calcium lime + sulfuric acid	<u>(1)</u> →	Calcium sulfate (Ins)
High calcium lime + ferric sulfate	<u>(1)</u> →	Calcium sulfate (Ins) + ferric hydroxide (Ins)
High calcium lime + ferrous sulfate	<u>(2)</u> →	Calcium sulfate (Ins) + unreacted ferrous sulfate (S)
High calcium lime + ferrous sulfate	<u>(3)</u> →	Calcium sulfate (Ins) + ferrous hydroxide (Ins)
Dolomitic lime + ferric chloride	<u>(2)</u> →	Mag. chloride (S) + calcium chloride (S) + ferric hydroxide (Ins)
Dolomitic lime + ferrous sulfate	<u>(3)</u> →	Mag. hydroxide (Ins) + calcium sulfate (Ins) + ferrous hydroxide (Ins)
Dolomitic lime + magnesium sulfate	<u>(2)</u> →	Mag. hydroxide (Ins) + calcium sulfate (Ins)
High calcium limestone + hydrochloric acid	<u>(2)</u> →	CO ₂ gas + calcium chloride (S)
High calcium limestone + sulfuric acid	<u>(2)</u> →	CO ₂ gas + calcium sulfate (Ins)
High calcium limestone + ferrous sulfate	<u>(2)</u> →	CO ₂ gas + calcium sulfate (Ins) + unreacted ferrous sulfate (S)
High calcium limestone + ferric sulfate	<u>(2)</u> →	CO ₂ gas + 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 pre-

cipitate 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,

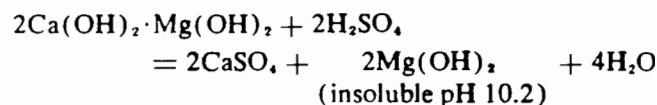
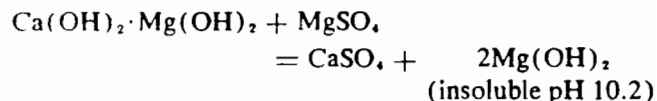
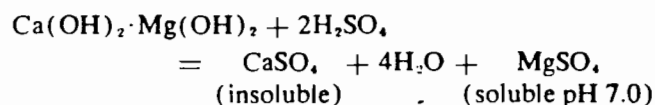


Table 4 — Order of Precipitation of Typical Metals in Dilute Waste Acids with pH Increase

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 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

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.

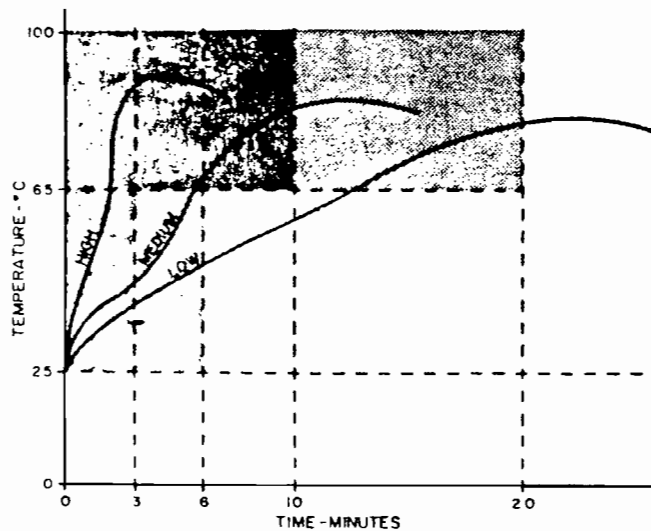


Figure 2 — Typical Lime (CaO) Reactivity Curves Adapted from Slaking Rate Test-AWWA-B-202-65 (8)

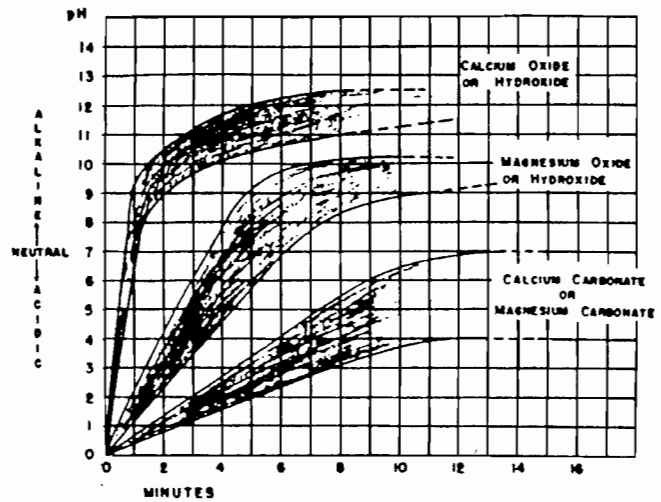


Figure 3 — Reaction Rate Ranges for Liming Material Constituents (4)

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

Agent	Room temperature	60°C
NaOH	a	a
Na ₂ CO ₃	0.75	0.75
MgO (reactive)	3 hr.	0.72
CaO	0.25	0.25
CaO·MgO	1.88	3.14
Ca(OH) ₂	0.5	0.5
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.

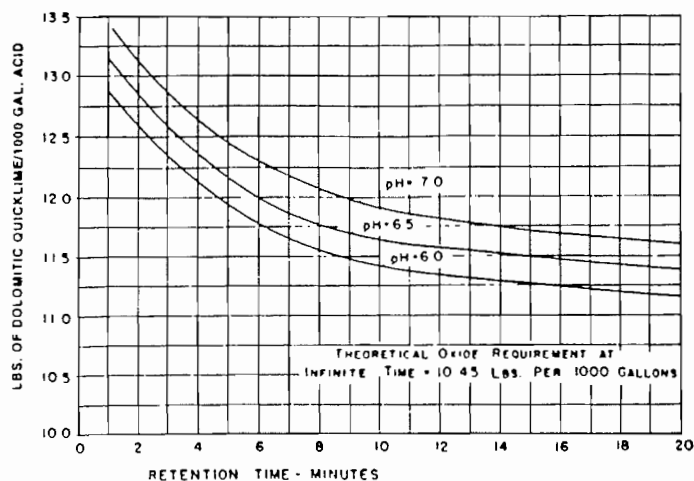


Figure 4 — Lime Requirement for Neutralizing 1/4 Percent Sulfuric Acid Using a Dolomitic Pebble Quicklime Slaked and Slurried (4)

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

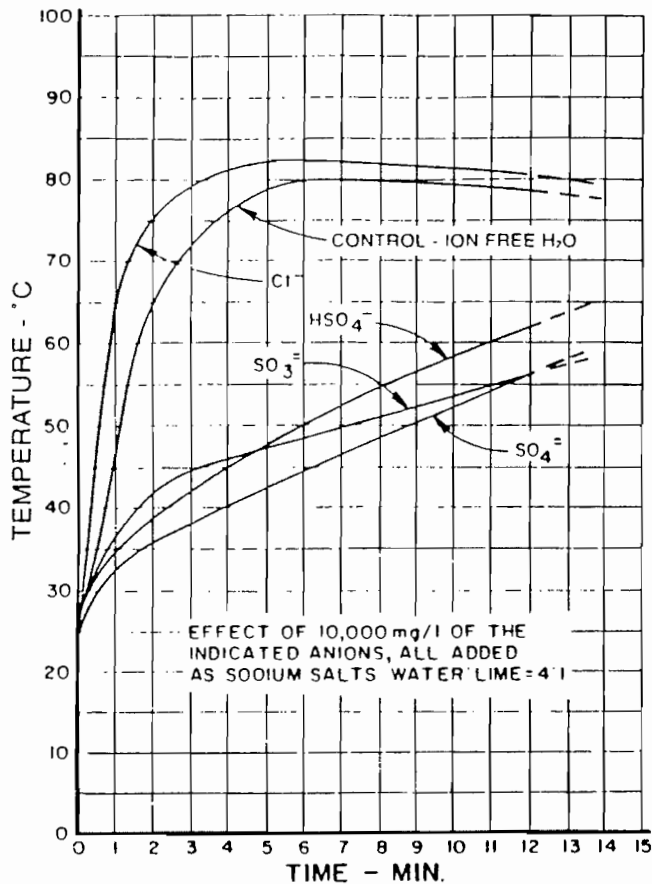


Figure 5 — Slaking Rate Test (10)

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.

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 of Lime Slurry 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. 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 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, 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. Sids. 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**

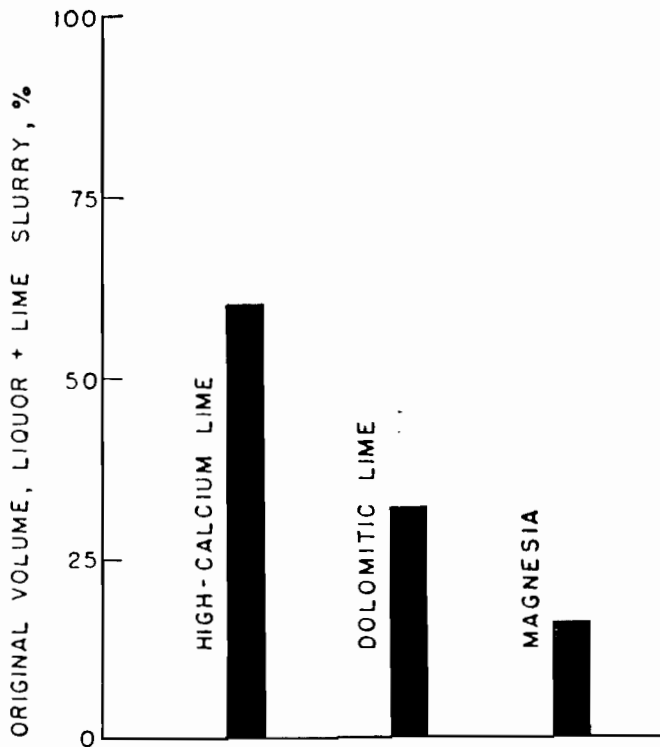


Figure 6 — Sludge from Neutralized Pickle Liquor (1)

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 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 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-

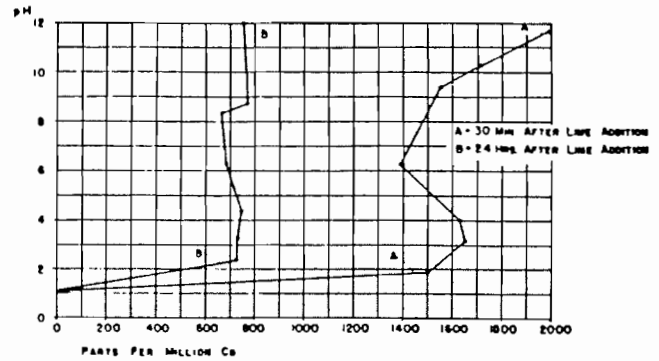


Figure 7 — Calcium in Effluent from Approx. 1/4 Percent H₂SO₄-Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

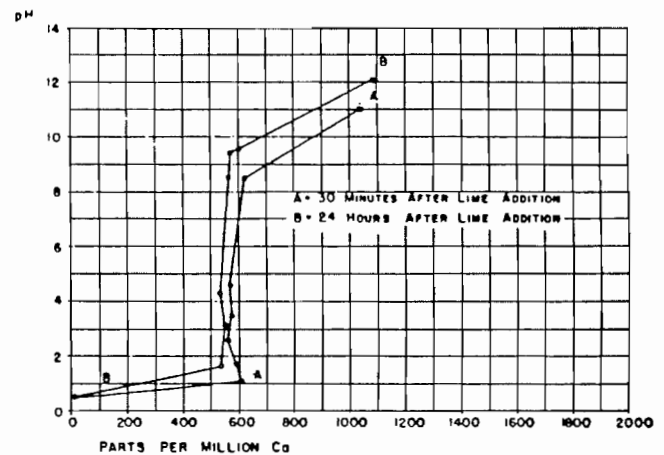


Figure 8 — Calcium in Effluent from Approx. 3 Percent H₂SO₄-Water System Treated With Slaked and Slurried High-Calcium Quicklime (4)

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-

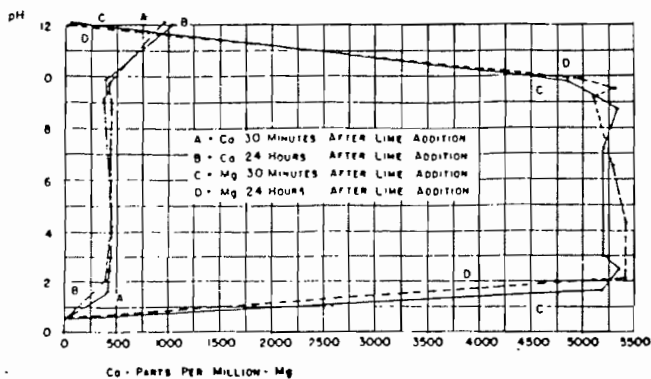


Figure 9 — Calcium and Magnesium in Effluent from Approx. 3 Percent H_2SO_4 -Water System Treated With Slaked and Slurried Dolomitic Quicklime (4)

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.

References

1. How to Buy and Use Lime As a Neutralizing Agent, Richard D. Hoak, *Water and Sewage Works*, December, 1953.
2. Chemical Lime Facts, Bull. 214. National Lime Association. Arlington, VA 22203.

3. Chemistry and Technology of Lime and Limestone, Robert S. Boynton, Chemical Publishing Co., New York, NY.
4. Lime in Waste Acid Treatment, C. J. Lewis and L. J. Yost, *Sewage and Industrial Wastes*, v. 22, p. 893, July, 1950.
5. The Role of Limestone in The Environmental Field, Clifford J. Lewis, 1974 *Mining Yearbook*, Colorado Mining Association.
6. Removing Heavy Metals from Wastewater, John G. Dean et al, *Environmental Science and Technology*, v. 6, N. 6, June, 1972.
7. Basicity Factors of Limestone and Lime Evaluation as Neutralizing Agents, Richard D. Hoak et al, *Industrial and Engineering Chemistry*, v. 36, p. 274, March, 1944.
8. Preparation and Handling of Lime Slurries, TP-80-M, Pennwalt, Wallace & Tiernan Division, Belleville, N.J. 07109.
9. Lime Handling. Application and Storage. Bull. 213, 7th Ed., 1995. National Lime Association. Arlington, VA 22203.
10. Effect of Dissolved Solids in SO_2 Scrubber Water Used for Lime Slaking, Robert J. Baker et al, Bull. TA-1050-C, Pennwalt, Wallace & Tiernan Division, Belleville, N.J. 07109.
11. Progress in Scrubber Sludge Disposal, J. L. Jordan, Dravo Corp., Denver, Colorado.

Other References

12. Chemical Treatment of Sewage and Industrial Wastes. William A. Parsons. National Lime Association. Arlington, VA 22203.
13. An Evaluation of Acid Waste Treatment, Pennwalt, Wallace & Tiernan Division, Belleville, N.J. 07109.
14. Neutralization of Acid Wastes, H. L. Jacobs, *Sewage and Industrial Wastes*, 23.100, July, 1951.
15. Treatment of Spent Pickling Liquors with Limestone and Lime, Richard D. Hoak et al, *Industrial and Engineering Chemistry*, v. 37, p. 553, June, 1945.
16. Wet Slaking Speeds Lime Reactivity, Ralph L. Carr, *Water & Sewage Works*, August, September, 1976.

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. "Water Supply & Treatment" (12th edition), 1995, by Nicholas Pizzi.
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, (7th edition), 1995.
5. "Lime in Municipal Sludge Processing," Bull. 217, 1980.
6. "Lime—The Versatile Chemical" Brochure.

In addition, NLA has available three VHS videos related to the treatment field:

1. "Lime—The Versatile Chemical." 30 min.
2. "Taming A Hazardous Waste with Lime." 15 min.
3. "Lime and the Earth — A Natural Balance." 26 min.

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CHAPTER III

COAGULATION AND SEDIMENTATION

Coagulation

Almost all surface water supplies are turbid, colored, and contain bacteria. The turbidity is due to finely divided matter held in suspension. It usually is too light to settle unless allowed long periods of time. Color is caused by dissolved organic material resulting from algae, decayed vegetation and bacteria. Ordinarily these impurities may be removed readily by the use of coagulants. However, surface supplies which receive sewage and/or industrial wastes may require specialized treatment; first, because of the presence of detergents, which retard the coagulation process, and, secondly, because of color-bearing substances which may not be affected by coagulation.

The reactions involved in coagulation have been the subject of much research. Studies in recent years have broadened the original concepts to cover the principles of neutralization of the electrostatic charges on the suspended colloidal particles that are to be removed by the process. The dissociating coagulating chemicals, when added to alkaline water, produce a gelatinous, sticky precipitate. However, for the suspended colloidal particles to be effectively entangled or absorbed in the "floc" that the coagulant forms, it is necessary that their mutually repellent "like" charges be neutralized either by the action of the coagulant or coagulant aid.

The nature and extent of the electrostatic charges on the colloidal suspended particles in the water are determined by the measurement of their mobility or "zeta potential". This measurement is beyond the scope of many laboratories, but if it can be determined, it will assist in the selection of the types of coagulant and/or coagulant aid.

In introducing the coagulant to the water, a rapid mixing action of five to ten minutes is needed to distribute the chemicals properly; then, a moderately slow agitation (15-60 minutes) may be used to allow the gelatinous mass to form the floc or clumps which will settle easily. Some coagulant aids are most effective when added with or prior to the coagulant; others are best added a few minutes after the original dosage.

The coagulants generally used are aluminum sulfate, ferrous sulfate and lime, ferric chloride, ferric sulfate, and sodium aluminate and lime. Others have been used but not to any great extent. Coagulant "aids" are varied in nature, and include the following: magnesium

low in cost. They may be used in various ratios. Ferrous sulfate may be used alone for secondary coagulation if there is sufficient oxygen in the water to insure complete oxidation. Where prechlorination is practiced, chlorine may be used with ferrous sulfate instead of lime.

The reaction of chlorine with water furnishes the oxygen necessary to oxidize the iron. The reactions for this coagulant take place best at high pH values.

Ferric Sulfate

Ferric sulfate as a commercial product for coagulation is comparatively new. Its wide pH zone of coagulation makes it applicable to various conditions. Iron salts do not form soluble compounds in the alkaline range, and for that reason very low residual metal is found at the high pH values. Except in special cases of color removal, coagulation with iron salts is best at a pH of 9.0 or above.

Chlorinated Copperas

Ferrous sulfate is used as a base material for the preparation of chlorinated copperas. The ratio is one part of chlorine to eight parts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. In practice, usually about 10 per cent excess chlorine is used to insure complete oxidation. This material has proved effective for removing certain types of color in soft waters. Results are best accomplished at pH below 7, due perhaps to complex ferric organic precipitates that are formed. Lime is used to raise the pH to prevent corrosion, just before or after filtration. In the alkaline pH ranges, certain colors may be accentuated by the use of iron salts. Here also, complex ions, or colloids, of the iron and coloring matter are formed but are not precipitated.

Ferric Chloride

Ferric chloride has a high optimum pH zone of coagulation but can be used in low pH ranges for color removal. Its greatest use has been as a precipitant and sludge conditioner in sewage treatment. Here a saving in ferric chloride on digested sludge is obtained by the use of lime in amounts sufficient to raise the pH to 9.0 or more.

Sodium Aluminate

Sodium aluminate is more expensive than other coagulants. Its application for municipal plants has been limited. It is especially effective when used with lime and soda ash in the treatment of boiler feed waters. It forms a floc rapidly. The free alkali present gives it some softening properties. Unlike aluminum sulfate it will not convert

available from an increasing number of suppliers: they may be purchased in solution or dry form and may be cationic, anionic, or non-ionic in nature. The dry material often requires special precautions in wetting down and putting into soluble or slurry form.

Some suppliers claim that their products can replace all metallic salt coagulants, but for the most part it has been found that a small amount of the aluminum or iron salt is necessary for satisfactory and economical clarification. Using the polymer to replace all the alum or iron salts usually requires so much polymer that the cost is greater than the cost of metal salts originally used.

Personal experience indicates that the metallic salt dosages can be *markedly reduced* by the use of small amounts of some polymers, effecting an overall reduction in chemical costs. A reduction of lime and/or soda ash dosage also may be accomplished with some polymers. The polymers are quite expensive in cost per pound; but since the dosages are, as a rule, very low, the increase in costs for the polymer dosage may be more than offset by the decreased dosage costs for alum (or iron) salts as well as lime and/or soda ash.

It is strongly recommended that an evaluation of the various types and brands of polymers first be made in the laboratory using jar tests; then the most promising type or types be evaluated for both cost savings and effect on water quality on a plant scale. However, before using any polymers on a plant scale, the operator is warned that written evidence of approval by State and Federal regulatory agencies must be obtained, covering (a) the manufacturer, (b) the *specific* product used, and (c) the maximum quantities or dosages of that specific polymer that can be applied without involving any hazard to the water quality.

See page 126 for a description of lime's function in precipitating trace amounts of heavy metals, some of which are toxic, along with radioactivity that are at unsafe levels in some surface waters.

Laboratory Jar Tests

There is no rule or set of rules for determining the quantity of coagulant required, or which one, or combination of them, is best suited to obtain maximum benefits. A very muddy water in which the turbidity is due to coarse particles will require less coagulant than a less muddy one in which the turbidity is due to fine particles. The presence of organic compounds, or too much or too little acidity or alkalinity (pH value), sometimes prevents coagulation reactions, or causes them to proceed to completion very slowly. Color may prove troublesome by combining with the coagulant to form soluble com-

paper filter. The minimum dose that produces a bright, sparkling effluent from the paper filter is the quantity needed.

In making comparative tests of different coagulants a very large number usually must be made. Tests should be made not only on each sample, as is, but also on the samples with acidity or alkalinity (pH value) adjusted to various ranges.

Laboratory results may be made to more accurately predict the plant requirements if the jar tests are run on samples maintained at nearly the same temperature as the raw water. A convenient way to do this is to procure a metal tank or "water bath", approximately the same height as the jars; short enough to fit under the stirring device and wide enough to permit easy handling of the jars. Tap water is introduced through a small jet set at the bottom in a horizontal position to cause agitation, and an adjustable over-flow provides a means to maintain the desired water level.

Mixing, Agitation, or Flocculation

After the chemical has been added to the water the two should be quickly and thoroughly mixed. Prolonged agitation is also desirable and often necessary. In the treatment of turbid water the precipitate of the coagulating compound should be kept in suspension until it has had sufficient time to collect into clusters a maximum number of the fine particles, which give the water its turbidity. Gentle velocities of from 0.6 to 1.5 feet per second are adequate. If the water and chemicals are given a quick mix ahead of prolonged gentle agitation, the

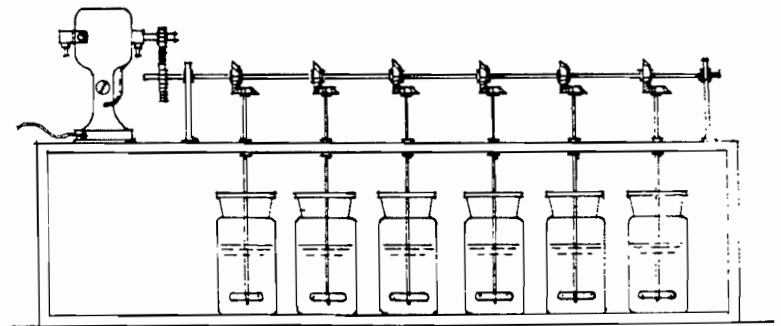


FIG. 3-1. LABORATORY STIRRING DEVICE

A laboratory stirring device is one of the most needed pieces of equipment in a water works laboratory. It is of especial use in coagulation, color removal, water softening reactions, and taste elimination studies, and for determining minimum quantities of coagulants required for treatment. The paddles usually rotate so as to produce a velocity of 1.5 feet per second.

at right angles to the flow of water. Paddles attached to this shaft rotate so that an outward travel is given to the upper stratum of water being mixed, and an inward motion to the lower stratum. This inward motion causes the settled floc to be gently swept back along the bottom of the basin, lifted by the upward motion of the paddles, and mixed with the incoming treated water. The introduction of already precipitated floc is believed to facilitate coagulation.

Views of four types of agitating devices are shown in Figs. 3-2 and 3-3. Properly designed baffled tanks are satisfactory, but mechanical tanks are less expensive to build. They remove the necessity of lifting the water the extra two or three feet necessary to pass it through baffled mixing tanks. Although agitators require power to keep them running, the cost of operation, if proper drive is provided, should be less than the cost of the additional lift of the water. They also provide greater accessibility and flexibility.

Care should be exercised to insure uniform velocities throughout the tank. The paddle area should be at least 25 per cent of the area of the central vertical section of the tank, or 25 per cent of the area of diameter of tank times its height. In the case of large tanks, when water is admitted through an inlet at the side or bottom of the tank and discharged at an outlet at the side and top, as is usually done,

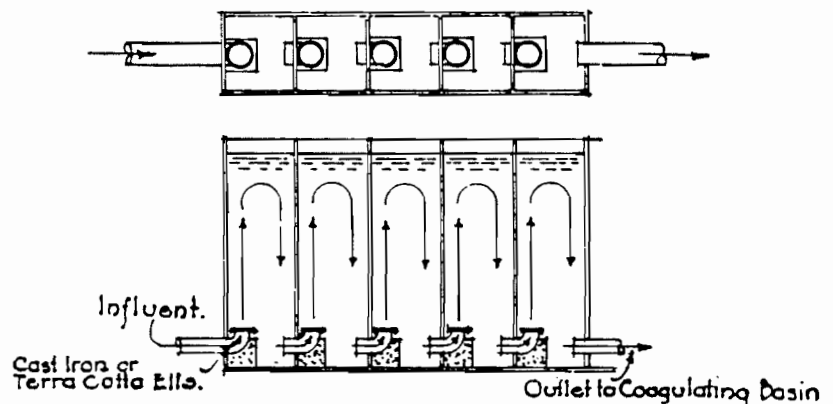


FIG. 3-3. MIXING TANKS DUAL FLOW COMPARTMENT TYPE

Arrows show path of water through mixer. The upflow is induced by the jet action of orifices in the ells, and the downward flow by gravitation. The general dimensions used are: chamber area in proportions of 18 sq. ft. per million gallons per day, depth equal to coagulating basin, preferably between 9 and 15 feet. Connecting ells in proportions of one sq. ft. per million gallons per day. Ell discharge ends should not be in excess of 8 ft. below water level. Nipples may be added to bring about these conditions. This scheme is adaptable to square, rectangular, or circular basins.

older plants provided with inadequate mixing tanks, but deep coagulating basins (20 to 25 feet), produce satisfactorily settled water no doubt because of the depth of the basins. In other words, if water is not thoroughly coagulated before it reaches the basin, the depth is then a distinct advantage.

The design of sedimentation units has been the subject of much research, especially in regard to improving the quality of the effluent with reduced detention times. The conventional 10 to 12 feet of depth has been found to be unnecessary—much shallower basins can be effective if the sludge can be removed satisfactorily. One company (Micro-Floc) has patented a unique "tube settler" device which can be installed in old or new clarifiers of any shape. These units are a radical change from the conventional design but are said to be very efficient. (See Figs. 3-4 and 3-5.)

Two basins usually are provided for small plants; three or more for larger ones. It is advisable to make provisions so that one can be out of service for cleaning or repairs, while the remainder can be operated. The velocity of flow through a basin usually does not exceed one foot per minute. It should be as uniform as possible.

Water may enter the sedimentation basin through pipes or channels traveling at a much greater velocity than it will or should have going through the basin. This velocity must be reduced at the inlet of the basin and the water started through the basin at a slow uniform velocity over the entire path of its flow. In circular tanks this is accomplished by admitting the water into a circular central well extending from slightly above the surface of the water to within a few feet of the bottom. The water discharges from the bottom and is collected over a weir extending around the entire circumference of the tank. In rectangular and square tanks, perforated or slatted baffles may be built across the inlet and outlet ends of the tank. These baffles generally are located about three feet out from the basin walls.

Combined coagulation and settling should produce a water with a turbidity of around 10 mg/l; in some plants turbidities as low as 0.5 mg/l are achieved in the settled water. In the treatment of flood water this often means a reduction in turbidity of over 99 per cent. The sludge produced by coagulation or softening may be allowed to accumulate in the basin. It can be discharged intermittently or removed continuously by special equipment which has been developed for that purpose. Almost all softening plants are equipped with continuous sludge-removing devices because the quantity of sludge produced by softening is often twenty times as much as that produced by coagulation.

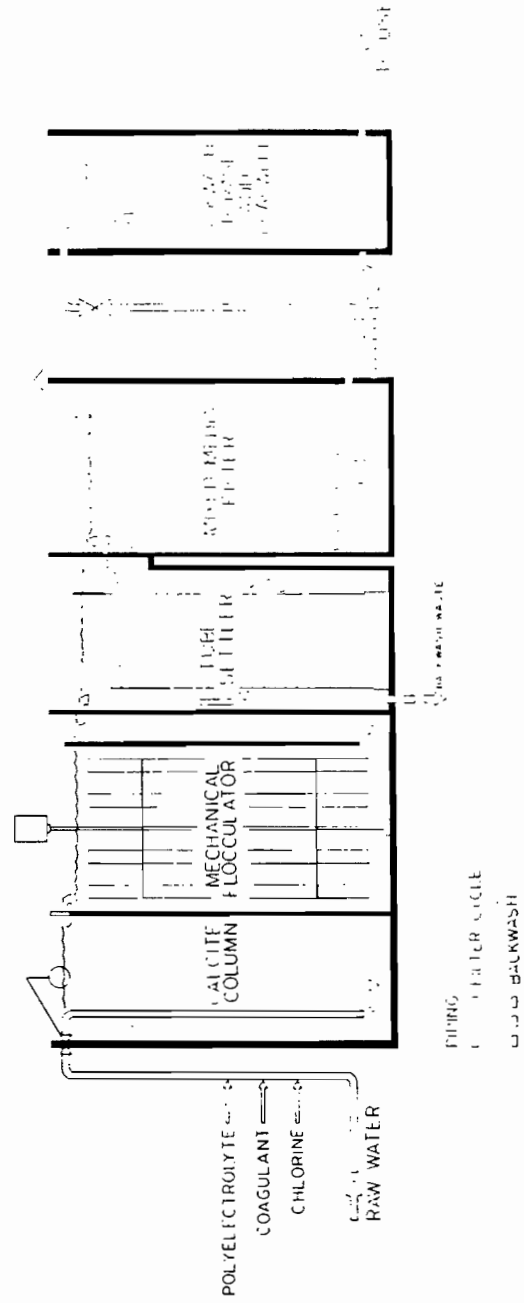


FIG 3.5. FLOWSHEET INCORPORATING NEPTUNE TUBE SETTLER

Control of the sludge blanket level may be difficult, particularly where fluctuations in raw water quality require frequent changes in chemical dosages. Also, best performance is obtained when these units are operated at a uniform rate. After the operator learns by actual experience just what he can do with a unit of this type, excellent results are to be expected.

The marketed devices are shown in the accompanying sketches in Figs. 3-7 to 3-9.

The Spiractor

The Spiractor is a recent development in lime-soda ash water softening equipment. It consists of an inverted conical tank in which the softening reactions take place in the presence of a suspended bed of granular calcium carbonate.

The advantages claimed for this type of softener are:

1. Equipment is small, 5 to 10 minutes detention period only is required.
2. The precipitant and removed hardness are discharged in a granular form instead of the usual wet, pasty sludge. The granular material is easy to handle as it drains to less than 5 per cent moisture in a relatively short time.

The process involves the principle of catalytic precipitation, the granules serving as nuclei around which the precipitated compounds of calcium and magnesium build up.

In operation, the conical-shaped tank (see Fig. 3-10) is slightly more

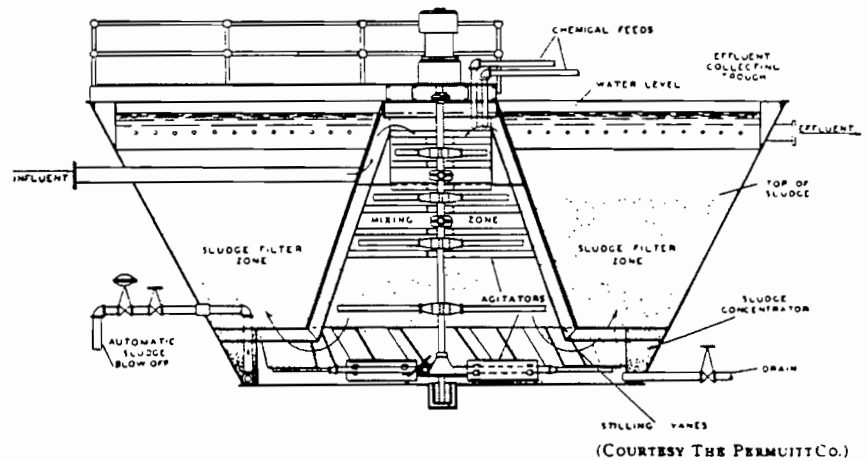


FIG. 3-7. COLD LIME-SODA ASH PRECIPITATOR WATER SOFTENER

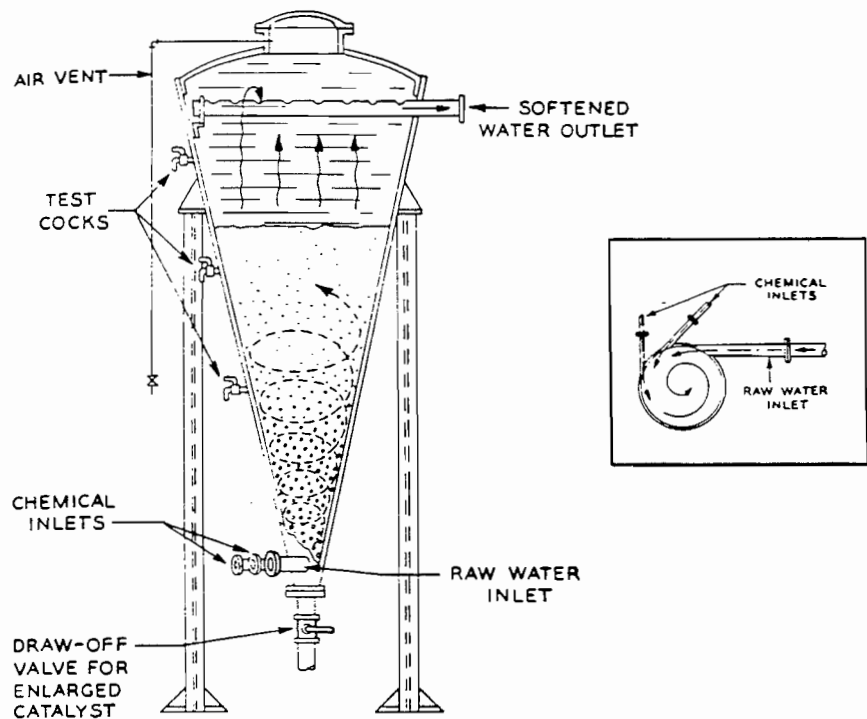


FIG. 3-10. CROSS-SECTIONAL VIEW OF PERMUTIT SPIRACTOR SHOWING FLOW. INSET GIVES DETAIL OF ARRANGEMENT OF RAW WATER AND CHEMICAL INLETS

than half filled with fine granules of calcium carbonate (0.1 to 0.2 mm. in size). Raw water enters the bottom through a special fitting containing a tangentially disposed nozzle. Through another opening in this fitting the dosage of lime or lime-soda ash suspension is introduced. The chemicals mix with the upward swirling water and in the presence of the calcium carbonate granules the softening reactions take place—a contact reaction similar to that which occurs in sand filters softening unstabilized lime-soda softened water. The calcium carbonate granules grow in size just as filter sand does. As the granules grow in size and the bulk of material increases, its level is kept down to that desired by withdrawals of the largest particles from the bottom. Periodic additions of new material are required, and this new material may be produced by regrinding and screening a portion of the discharged material.

The water discharged from the Spiractor usually is stabilized and filtered through a sand filter.

erence to ClO₂. For laboratory procedures to determine break-point chlorination or chlorine dioxide dosages, see Chapter XVIII, pages 203 and 204.

Sterilization with Lime

The late Dr. A. C. Houston, chemist of the Metropolitan Water Board, London, England, first proposed the excess lime method of sterilizing water*. His results were first confirmed by Hoover and Scott at Columbus, Ohio**, and have since been confirmed at a number of water softening plants. The following table shows the average *B. coli* indices on raw surface and lime-softened, filtered, but unchlorinated water in six Ohio municipalities:

	B. coli per 100 ml.		Hours Detention Period			
	Raw Water	Lime Softened Filtered Water	Mixing	Clarifier	Sedimentation	Total
Columbus	402	0.40	1.0	..	10.0	11.0
Fremont	3274	1.00	1.5	3.0	6.0	10.5
Greenville	1537	1.40	1.6	0.8	6.7	9.1
Newark	1376	0.40	2.5	0.75	20.0	23.2
Piqua	1004	0.30	1.5	4.0	6.0	11.5
Youngstown ..	6052	0.05	15.0	15.0

The results show that all of these plants produced water that met the U.S. Treasury Department standards without the use of chlorine. The average load of all the plants is 2274 *B. coli* per 100 milliliters, whereas the treated water averages only 0.6 *B. coli* per 100 milliliters. Some of the plants named in the table do not use chlorine at all. Some use it all the time, and others only occasionally. Where it is used as an additional factor of safety it is applied after filtration. The plants studied have detention periods, on design bases, varying from 3.5 to 9.1 hours. However, they are not operated at full capacity, therefore the detention periods shown in the table are based on 1929 average consumption records, and vary from 9.1 to 23.2 hours. On the other hand, some of the plants operate at full capacity during a portion of the day, and then shut down, so that the period of contact may be said to range from 3.5 to 23.2 hours.

The important factors in lime sterilization are:

1. Quantity of excess lime used.
2. Time or reaction.
3. Quantity of mud, organic matter, and bacteria present in raw water.

* Eighth Research Report of the Metropolitan Water Board, London, England.
 ** Engineering Record, September 6, 1913, page 257.

durations of 60 to 120 min. But with three strains of bacteria at 120 min. exposure only about 70 to 95% of the bacteria was killed.

While it has been found that some types of bacteria can be removed at a pH as low as 9.5, other strains may require a pH of over 11.0, such as 11.5 or even 12.0. Generally the higher the pH the less contact time is needed, or longer contact times can produce comparable bacterial reduction at slightly lower pH levels. Bacteria is more resistive at low temperatures, i.e., 1 to 15° C, but Morrison and Martin found that rapid destruction of coliform bacteria occurred at pH levels of 11.5 to 12.0 even at 1° C temperature, whereas pH levels just below 11.0 were ineffective. Doyle found that salmonella typhosa bacteria that causes typhoid fever, is destroyed at pH 11 after 2 hr.

Increasing interest is evident in the effect of high pH on another pathogen—*virus*—since chlorine has many limitations in virus elimination. Thus, high alkalinity treatment with lime may prove to be a valuable complement to chlorine in effecting greater public protection from diseases. Lime is devastating to poliovirus I, an example of which is taken from research by Berg et al. using lime flocculation and sand filtration as follows:

LIME TREATMENT		
pH	Virus Remaining pfu/l (a)	% Virus Removed
9.27	336	99.0
10.13	685	98.7
10.88	1.7	99.995
11.10	5.1	99.998
11.20	<1.4	>99.997

(a) Concentration of virus expressed as plaque-forming units per volume or pfu/l. Initial virus concentration was 33,000 to 55,000 pfu/l.

Other researchers have indications that high pH may be nearly as effective as with polio in eradicating virus from water that causes hepatitis and other diseases, as well as some parasite eggs from worms in fecal matter. While the eggs flocculate readily with lime or other coagulants and settle with other sediment, the high pH destroys those parasite eggs with thin shells after a short duration. However, some eggs with thick shells will resist even the highest pH for up to several weeks.

In all of this bacteria, virus, parasite, and parasite egg removal with lime treatment, and unlike treatment with other coagulants and chlorine disinfection that functions in *one manner*, lime attacks these pathogens in *two ways*:

CHAPTER VII

TASTES AND ODORS

Tastes and odors in water may be caused by:

1. Dissolved organic matter.
2. Dissolved organic gases.
3. Hydrogen sulfide.
4. Mineral substances, such as sodium chloride, sodium sulfate, magnesium sulfate, and iron.
5. Earthy constituents.
6. Algae and microorganisms.
7. Phenols and other oily or tarry waste products.
8. Chlorine products, especially chlorinated hydrocarbons.

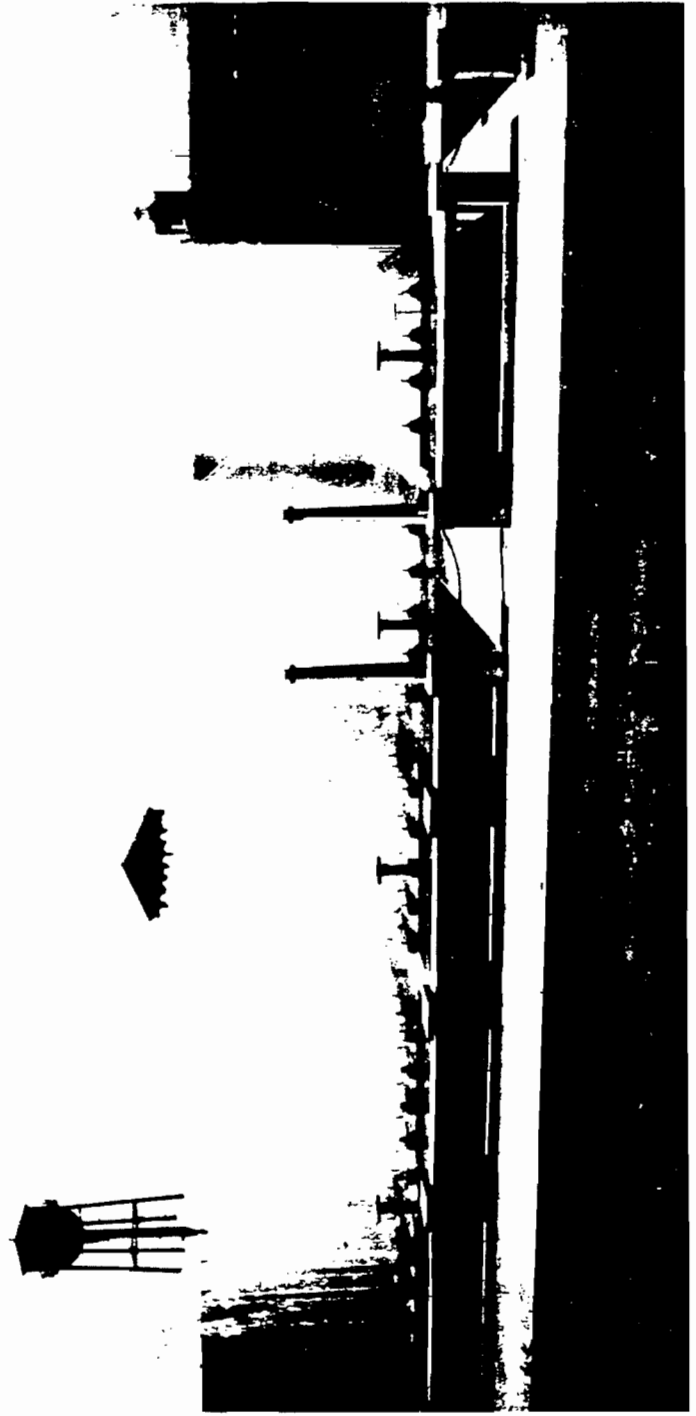
Methods used for reducing or removing tastes and odors are:

1. Aeration.
2. Coagulation (using excess coagulants and/or coagulant aids).
3. Lime softening.
4. Break-point chlorination.
5. Chlorine dioxide.
6. Ammonia.
7. Permanganate.
8. Activated carbon.
9. Ozone.
10. Various combinations of the above.

Water containing mineral matter in sufficient quantity to produce an unpleasant taste seldom is fit for domestic use. Almost all other tastes and odors can be removed by careful use of the proper kind and amount of treatment.

Aeration is effective for removing tastes due to dissolved gases but helps little in oxidizing organic matter. However, iron is oxidized and made insoluble so that it can be removed. Coagulation, using larger quantities of coagulant than required for clarification only, sometimes is effective in removing or reducing tastes due to earthy constituents.

When sufficient lime is used to soften the water, organic matter is more effectively removed than under ordinary conditions of coagulation, thus assisting in the elimination of tastes and odors. Lime softening can produce a bacteriologically safe water without the use of chlorine. Lime softening also has been used to remove tastes and odors due to sulfides.



AERATORS AT MARSTON LAKE, NORTH SIDE FILTER PLANT, DENVER, COLO.

If it is possible to do so, application of the carbon prior to any other chemical feed may be the most efficient. One plant has had good results by application of carbon at a low service pumping station; thus allowing about three hours contact time before addition of coagulant and the lime and soda.

Another factor to consider is that carbon will adsorb chlorine, so if the two materials are added at or near the same point, the effectiveness of both are very greatly reduced.

Break-point chlorination may be used to decompose or break down some taste- and odor-forming compounds, and is generally effective for phenols, but not in all cases. It must be used properly so that the dosage does not fall below that required for break-point. Also if the dosage is too high, a dechlorinating agent may be required.

Chlorine dioxide has been even more effective in some cases, due to its higher oxidizing power. It has been shown to be effective in removing phenolic tastes, especially where these tastes have been "set" by lime softening. The disadvantage lies in the costs of sodium chlorite and in the hazards involved.

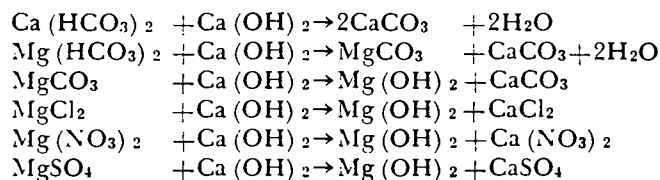
Ammonia is used to combine with chlorine to reduce chlorinous tastes. This also has been found effective in treating well supplies, particularly where the distribution system becomes fouled with odors created by sulfur-reducing bacteria. Break-point chlorination can cause an excessive oxidation potential, thus intensifying the red-water troubles by loosening old scale and tubercles. Chloramines can effectively hold the bacterial growth in check without intensifying the iron difficulties.

Potassium permanganate was employed as an oxidizing agent by a few plants for a number of years; but until the last few years its use was rather limited. However, it is being used increasingly, not only because it may be an effective treatment for certain tastes and odors, but also because it greatly improves sedimentation by adding weight to the floc particles. In order to assure that no pink color of unreacted permanganate carries through to the finished water, the dosage is controlled so the settled water has no pink color (not to be confused with the brown color imparted by the MnO_2 of the reacted material). A slight excess of permanganate can be expected to be absorbed by the filters and/or be reduced by the post-chlorination dosage.

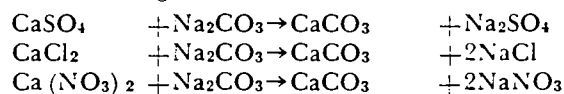
CHAPTER X

CHEMISTRY OF LIME-SODA ASH PROCESS OF WATER SOFTENING

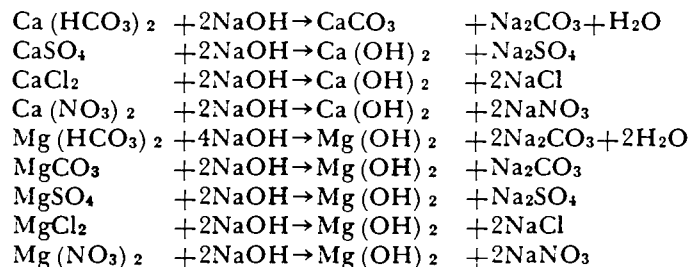
Reactions that take place when lime is added to a hard water containing both calcium and magnesium are:



Reactions involving the use of soda ash are:



Reactions involving the use of caustic soda are:



Note that in the second, third, and fourth reactions, hydrated lime $[\text{Ca (OH)}_2]$ is formed to further react with carbonate hardness or magnesium. In the first, fifth, and sixth reactions, soda ash (Na_2CO_3) is formed to further react with non-carbonate hardness.

The analytical data necessary to determine the approximate quantities of lime and soda ash required to soften a hard water containing calcium and magnesium salts are:

1. Free CO_2 .
2. Half-bound CO_2 (44 per cent of the alkalinity).
3. Non-carbonate hardness.
4. Total magnesium.

The methods for determining these constituents are given under Chapter XVIII.

material. Current market prices of caustic soda indicate that it cannot compete cost-wise with lime and soda ash.

During the fourteen years of operation of one municipal water softening plant, 10.7 pounds of lime per million gallons of water have been required to reduce the hardness 1 mg/l, and 11.5 pounds of soda ash per million gallons have been required for each mg/l of hardness reduced. Of this amount of soda ash, 2.3 pounds have been neutralized by alum added for coagulation purposes, leaving 9.2 pounds actually required as against a theoretical 9.1 pounds.

It is well to check the calculations for required lime and soda ash by actually adding the calculated quantities to small measured quantities of the water to be treated. The following procedure will be found convenient. Make up a standard lime solution using 17.1 grams of lime in one liter of boiled and cooled distilled water. If quicklime is used, slake it with a small quantity of water, just enough to make a boiling solution, then dilute to one liter. This solution is of such strength that 1 milliliter added to one liter of water is equivalent to 1 grain per gallon. Standard solutions of hydrated lime or soda ash may be made according to the same formula.

Place one liter of the water to be treated in a large beaker and add the calculated quantities of lime and soda ash necessary to soften it. Stir gently for 30 minutes, allow to settle until the liquid becomes fairly clear (usually requiring 10 or 15 minutes), siphon off about half of the clear solution, and warm to a temperature of about 120° F. or 49° C. Filter through filter paper and then analyze to determine whether or not proper amounts of chemicals have been added.

Methods for making these tests are given under Chapter XVIII.

Application of Analyses to Plant Operation

Determination of Proper Quantity of Lime

Determine the methyl orange (total) and phenolphthalein alkalinity of the treated water. If two times the phenolphthalein alkalinity is more than the methyl orange alkalinity (2P greater than M) the water contains caustic alkalinity or excess lime. If two times the phenolphthalein alkalinity is less than the methyl orange alkalinity the water is undertreated with lime. The following table shows the relation between alkalinity to phenolphthalein and methyl orange:

Determination of Proper Quantity of Caustic Soda

Caustic soda can be used in place of both lime and soda ash, but its reacting equivalent is in a fixed ratio (in approximate figures: 4 lbs. of caustic soda can replace about 3 lbs. of quicklime and 5 lbs. of soda ash). However, unless the water softening reactions require lime and soda ash in the ratio of about 3:5, then either lime or soda ash feed would be required in addition to the caustic soda.

If the computed lime to soda ash feed is less than 3 lbs. of lime to every 5 lbs. of soda ash, caustic soda for the lime equivalent, plus additional soda ash, will be needed. Usually the feed is more than 3 lbs. of lime for every 5 lbs. of soda ash; thus lime *plus* caustic soda feed would be indicated.

Expression of Water Softening Results

The chemistry involved in the determinations of alkalinity to methyl orange, alkalinity to phenolphthalein, and non-carbonate hardness, is extremely interesting because from these results the composition of water, expressed in the following terms, may be calculated:

Carbonate hardness.

Total hardness.

Bicarbonates of calcium and magnesium.

Normal carbonates of calcium and magnesium.

Caustic alkalinity as calcium hydroxide.

Caustic alkalinity as sodium hydroxide.

This calculation is of particular interest in water softening when excess lime and soda ash are used to produce water of low degree hardness.

Caustic alkalinity is present if two times the alkalinity to phenolphthalein exceeds the alkalinity to methyl orange. Examples 2, 3, 5, and 6. (See following tables.)

If the total hardness of an alkaline water is greater than the alkalinity, the difference between the two equals non-carbonated hardness. Examples 1, 2, 7, and 8.

In case of acid waters, all hardness is non-carbonate hardness.

If the total hardness is less than the alkalinity, the water contains negative non-carbonate hardness. In other words, the water contains free sodium carbonate or sodium hydroxide. The difference between the alkalinity and total hardness equals negative non-carbonate hardness. Examples 3, 4, 5, and 6.

From the results of analysis the following may be reported (all in terms of CaCO_3):

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Carbonate hardness	58	70	45	40	40	35	90	60
Non-carbonate hardness	30	35	0	0	0	0	30	20
Total hardness	88	105	45	40	40	35	120	80
Caustic alkalinity	0	10	30	0	20	20	0	0
Bicarbonates of Ca and Mg	18	0	0	0	0	0	90	0
Normal carbonates of Ca and Mg	40	60	40	40	40	35	0	60
Normal carbonate of sodium (Na_2CO_3)	0	0	0	20	0	5	0	0
Caustic alkalinity as $\text{Ca}(\text{OH})_2$..	0	10	5	0	0	0	0	0
Caustic alkalinity as NaOH	0	0	25	0	20	20	0	0

CHAPTER XII

REMOVAL OF IRON, HEAVY METALS AND OTHER UNDESIRABLE CONSTITUENTS

Iron is present in many ground water supplies whereas manganese is present only occasionally and then usually along with iron. In many states iron is present in ground waters rather generally. In Ohio, for example, dissolved iron (Fe) in well waters ranges from a few hundredths to 77 mg/l.

The presence in a water supply of over 0.3 mg/l of iron, or iron and manganese, is considered objectionable. The amount of manganese should be low, otherwise, troubles will result even with the combined amount being under the 0.3 mg/l level. Manganese of even 0.01 or 0.02 mg/l can be very objectionable. These compounds are objectionable because they stain everything with which they come in contact. This is especially true of plumbing fixtures and of clothes that are rinsed in the water. Iron-bearing water sometimes is so badly discolored that it is not pleasant to use. In extreme cases iron and manganese compounds in water interfere with culinary uses such as causing tea to turn black and darkening vegetables cooked by boiling. Iron-bearing waters do not always behave satisfactorily in the distribution system because they stimulate the growth of crenothrix and other bacteria which may impart disagreeable tastes and odors to the water. These crenothrix growths are stringy and gelatinous and may become so voluminous as to interfere with the flow of the water through the pipes. Chlorine treatment sometimes is used to prevent their growth.

One of the greatest annoyances of iron in water is that it precipitates out of solution and settles in the mains, especially in the outlying districts where the velocity of flow is low. Sudden demands for extra water, such as the opening of a fire hydrant, stir up this rust deposit to such an extent that the consumer has great difficulty in using the water from the mains. Manganese rust or stain, especially on clothes, is even more objectionable than iron rust or stain because it is darker. Deposits of manganese oxide are almost black.

Iron-bearing water when first pumped from the ground usually is clear because the iron is present as ferrous iron, and in that condition is soluble. Water may be perfectly clear, however, and still have several hundred mg/l of iron dissolved in it. As soon as it absorbs oxygen, the iron is changed from the ferrous to the ferric state and precipitates either completely or as a colloid. Iron in the colloidal

material available. The material soon becomes coated with iron or manganese hydroxide which promotes catalytic precipitation of iron and manganese from the incoming water.

Plain sedimentation is not very effective in removing iron. If the settling period is long (12 to 24 hours or more) and the iron is easily oxidized, then the following treatments for hastening sedimentation have been suggested:

1. Lime, plus aluminum sulfate, plus stirring (20 to 30 minutes), plus settling, plus recarbonation; i.e., if the lime treatment has increased the pH sufficiently to throw the water out of chemical balance.
2. Aluminum sulfate, plus stirring and settling.
3. Aluminum sulfate and bentonite plus stirring and settling.
4. Aluminum sulfate, along with specially treated silica, plus stirring and settling.

If sodium poly-phosphate is added to oxygen-free iron-bearing water, it tends to sequester or hold the iron in solution and prevents staining. However, it is important that the phosphate is applied to the water before there is any opportunity for oxygen to come in contact with the water. Even the air drawn in at the pump may reduce the effectiveness of the treatment.

Manganese removal is even more dependent upon contact reaction than iron. Pyrolusite (manganic oxide) is sometimes used as a contact medium in the aeration trays or filters when it is desired to remove manganese from water.

Special manganese ion exchanger also is used for removing manganese. These units when exhausted are regenerated with potassium permanganate.

Ordinary aeration and filtration are seldom adequate for manganese removal, and unless some special medium is used it is customary to aerate and then increase the pH of the water to about 9.4 before filtering. This procedure gives satisfactory results.

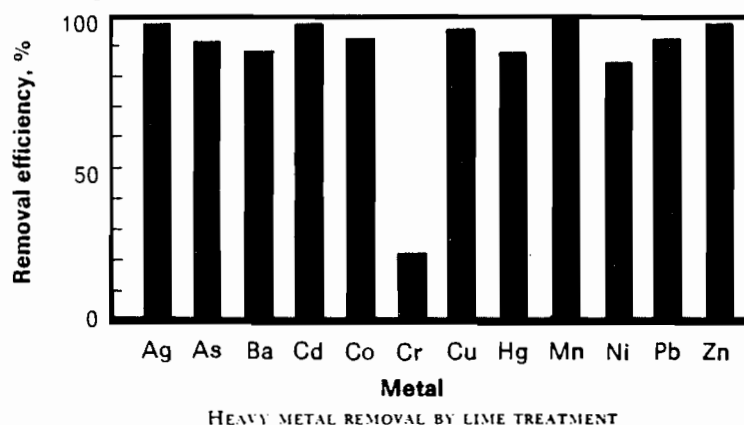
Conventional plants built to remove iron from a hard water supply should be designed so that they can be converted readily into softening plants. Sooner or later the public will insist on having soft as well as iron-free water.

Chlorine and chlorine dioxide have been used to oxidize manganese in filtration plants. Traces of copper, added as copper sulfate, speed up this oxidation. Potassium permanganate has been reported to be very effective in oxidizing the soluble manganese. The oxidized hydrated manganese dioxide may be difficult to filter out; coagulant aids have shown beneficial action in this regard.

Metal	Concentration (mg/l)	
	pH 6.7	pH 12.7
Cd	1.3	<0.02
Fe	6.0	<0.1
Ni	0.13	<0.05
Cu	5.3	0.05
Zn	31.25	0.11
Mn	26.5	0.04

Similarly, traces of radioactivity, such as radium 226, uranium and thorium 230, in excess of proposed 1975 Drinking Water Standards, can also be precipitated with lime, reducing the radioactivity to safe levels, according to EPA research. (From "Radioactivity Distribution in Phosphate Products, By Products, Effluents, and Wastes," by R. J. Guimond, S. T. Windham, ACS Meeting, Chicago, Ill., Aug. '75).

Actually water plants using lime for softening or purification with other coagulants generally have enough lime in their systems to automatically precipitate enough radioactivity and trace metals from a contaminated potable water source to meet the more stringent proposed 1975 EPA Drinking Water Standards. Thus, some of these seemingly very secondary, incidental attributes of lime, ignored or unknown by many before the environmental cleanup, are becoming increasingly important.



Silica

Silica may be present in water in colloidal form or in solution. Colloidal silica can be removed from water quite easily by coagulation and filtration. Silica in solution, however, is more difficult to remove and much study is being given to methods for its removal.

Ordinary ion exchange softening does not remove fluorides, but some types of exchange material have been found to absorb fluoride after the softening cycle is completed, then unload the fluoride after regeneration, during the start of the next softening cycle. This probably accounts for the fluctuations in the fluoride content of some water supplies.

At Bartlett, Texas* where the raw water supply contains 8 mg/l fluorides, a treatment plant was built using calcined (activated) alumina to absorb the fluoride. This alumina was placed in a contact tank through which the water was passed until the fluoride content of the effluent increased 1.0 mg/l. The unit was then regenerated with a strong caustic solution, followed by a water and dilute sulfuric acid rinse. Chemical cost was reported to be \$52.00 per million gallons for removal of 7 mg/l of fluoride.

Other materials that have been considered for fluoride removal are:—aluminum sulfate, tricalcium phosphate, calcium phosphate, and ground bone.

Household Fluoride Removal Units. Household fluoride removal units are available. They are similar in size to a household hot water tank and are filled with granular tricalcium phosphate. When they become exhausted they are regenerated with a 1 per cent caustic solution followed by 0.7 per cent hydrochloric acid, and a final rinse with clear water. The capacity of the regenerated phosphate is substantially less than the original capacity.

* Maier, F. J., Journal, A.W.W.A., Vol. 45, p. 879, Aug., 1953.