

The Application of Lime Sorbents in Municipal Waste Combustors

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ABSTRACT

Lime is the sorbent most utilized to control acid gas emissions from Municipal Waste Combustors (MWCs) throughout the world. Lime is safe, economical, and easy to handle. In addition to acid gas controls, lime has been demonstrated to reduce mercury and dioxin emissions when used in spray dryers. Lime also has applications in controlling the leachability of heavy metals from MWC ash.

Although lime is used throughout our industry, we see many misapplications and misunderstandings of this technology. We have seen the wrong type of silos used as well as the wrong size silos. Slaking is a major problem for some plants because they use the wrong water and lime products. This paper will discuss the selection criteria and economics for lime handling and feeding systems with design data. Definitions and the chemistry of lime will be presented to enable design engineers to better prepare systems specifications. This paper will be beneficial to plants planning to upgrade for the MACT standards.

INTRODUCTION

Chemical and Physical Properties of Lime

Chemical lime is a term designating a type of quick or hydrated lime low in impurities and possessing a high degree of reactivity making it suitable for use in chemical processes. Commercially, chemical lime is obtained through the controlled calcination of high quality limestone. Quicklime, the product of calcination, consists of the oxides of calcium and magnesium, and in this country it is available in three forms:

- *High calcium quicklime* (CaO): containing 0.5 to 2.5% magnesium oxide.
- *Dolomitic quicklime* (CaO • MgO): containing 35 to 40% magnesium oxide.
- *Magnesian quicklime*: containing 5 to 10% magnesium oxide.

Hydrated lime is a dry powder obtained by treating quicklime with sufficient water to satisfy its chemical affinity for water, thereby converting the oxides to hydroxides. Depending upon the type of

quicklime used and the hydrating conditions employed, the amount of water in chemical combination varies, as follows:

- *High calcium hydrated lime*: High calcium quicklime produces a hydrated lime containing 72 to 74% calcium oxide and 23 to 24% water.
- *Dolomitic hydrated lime (normal)*: Under atmospheric hydrating conditions only the calcium oxide fraction of dolomitic quicklime hydrates, producing a hydrated lime of the following chemical composition: 46 to 48% calcium oxide, 33 to 34% magnesium oxide, and 15 to 17% water.
- *Dolomitic hydrated lime (pressure)*: This lime is produced from dolomitic quicklime under pressure, which results in hydrating almost all of the magnesium oxide as well as all of the calcium oxide, producing the following chemical composition: 40 to 42% calcium oxide, 29 to 30% magnesium oxide, and 25 to 27% water.

Chemical lime is a white solid having a crystalline structure. Table 1 contains physical and chemical data for lime products. Quicklime is highly reactive with water, generating considerable heat in the hydration process. This material will react with the moisture in the air, and as such, it has found application as a desiccant. In the presence of moisture, the lime reacts slowly with the carbon dioxide of the air, forming water insoluble carbonates. As a chemically active material, it is desirable to reduce atmospheric exposure during handling and storage to a minimum. Hydrated lime, though only slightly soluble in water, forms suspensions easily; the resulting solution and suspension is strongly alkaline, possessing a pH of 12.4 at 25°C.

Quicklime is commercially available by the carload, in bulk or in paper bags, in a number of more or less standard sizes as follows:

- *Lump lime*: the product with a maximum size of eight inches in diameter.
- *Crushed or pebble lime*: the product ranging in size from about 2 ½ to ¼ inches.
- *Ground lime*: the product resulting from grinding the larger sized material. A typical size is substantially all passing a No. 8 sieve and 40 to 60% passing a No. 100 sieve.
- *Pulverized lime*: the product resulting from a more intense grinding than is used to produce ground lime. A typical size is substantially all passing a No. 20 sieve and 85 to 95% passing a No. 100 sieve.
- *Pelletized lime*: one inch sized pellets or briquettes, molded from quicklime fines.

Hydrated lime is generally shipped in 50-pound paper bags, 1,000 lb. “super sacks” and in bulk tank trucks. It is difficult to unload rail cars with hydrated lime without special equipment. Due to the hydration process, hydrated lime is by necessity of fine particle size. Normal grades of hydrate suitable for most chemical purposes will have 85% or more passing a 200-mesh sieve, while for special applications air classified hydrated lime may be obtained as fine as 99.5% passing a 325-mesh sieve.

LIME STORAGE SYSTEMS

Two problems that we have noticed in designing lime storage silos are related to the sizing of lime silos and the cone angle. Lime silos need steep angles at the bottom of silos in order to insure proper

material handling and feeding. The need for such steep slope angle is based on the relatively high angle of repose for quicklime of 50 - 55° and hydrated lime 70°. Therefore, for quicklime the silo should have a 60° cone in the silo while hydrated lime needs a 72° cone. Silos need to be equipped with air pads and vibrators to assist in lime feeding. Dry air should be used for air pads to prevent the lime from reacting with the moisture in the air.

We have seen several projects where the silos have been undersized which increases the cost of lime being delivered to the project. Bulk trucks can carry 23 tons of quicklime and 20 tons of hydrated lime. Silos must be sized so that the project can accept at least a full truck and have no less than 50% reserve in the silo when the truck arrives. If the silos are sized any smaller, the plant may not be able to accept full truck loads and the plant must pay the same transport cost whether it buys 15 tons or 23 tons, or the plant may run out of lime. For sizing silos, we recommend a bulk density of 23 lbs./cu. ft. for hydrate and 55 lb./cu. ft. for quicklime. For structural designs bulk densities of 35 and 60 lbs./cu. ft. should be used for hydrate and quicklime respectively.

For detailed information on the handling and storage of lime, equipment for application of lime, and the factors affecting the selection of lime, please refer to Bulletin 213, "Lime Handling, Application and Storage in Treatment Processes," published by the National Lime Association.

LIME SLAKING AND SLURRY HANDLING

The term "slaking" applies to the combining of varying proportions of excess water and quicklime which can yield a milk-of-lime, a lime slurry, or a viscous lime paste (or putty) of widely varying degrees of consistency. In contrast, the term "hydration" by popular usage in the lime industry connotes the process utilized by the commercial lime industry to produce dry, finely powdered hydrated lime. Less water is used in such commercial hydration than in slaking where invariably the reaction hydrate product contains considerable excess water. With the dry hydrates, other than a trace up to 1%, all of the water is chemically combined as a hydroxide. From a chemical standpoint, however, both "slaking" and "hydration" are really synonymous in that both act exothermically by emitting appreciable heat of hydration and form hydroxides.

It is beyond the scope of this paper to discuss the production of dry commercial hydrates. Therefore, the following will be confined to slaking of quicklime by the consumer. Of course, where hydrated lime is being used, the slaking process or step has already been performed by the lime manufacturer.

For maximum efficiency in using quicklime in chemical processes involving aqueous solutions, it is desirable to slake lime at or near optimum conditions. Since many limes have different slaking characteristics, owing to different chemical analyses (purity), methods of calcining the lime, size and gradation of the quicklime particles, etc., these optimum conditions are usually determined empirically with some "trial and error" tests necessary. Usually, the lime manufacturer can simplify this determination by providing data or recommendations on the slaking behavior of its quicklime. However, the way the lime is slaked can mean the difference between a slaked lime of very minute particle size, high surface area, and porosity that is slow settling and chemically very reactive and another hydrate that is much coarser, possibly incompletely hydrated, that settles rapidly and has slow reactivity. In either case, however, the particle sizes of slaked lime particles are minuscule, 95 to 100% sub-sieve sizes of substantially 1 to 5 microns for soft burned limes and 3 to 25 microns for limes of lower reactivity with submicron particles also present.

THEORY OF SLAKING

Briefly, the variables exerting a profound effect on slaked hydrate quality are:

- 1) *Reactivity of the quicklime*: Whether the quicklime is hard, soft, or medium burned, influences speed of slaking and temperature attainment. An operator needs to ask each supplier which type of lime they supply i.e. hard burned or soft burned since a typical chemical analysis will not provide this information. Slakers used in MWCs function better with a soft burned lime and therefore, when purchase orders or contracts are written, soft burned lime must be specified.
- 2) *Particle size and gradation of quicklime*: Whether the quicklime is lump, pebble, ground, pulverized, or run of-the-mill gradation. The finer sizes of the same quality slake most rapidly. Paste slakers work better with “fine” lime while detention slakers can use both fine and pebble lime.
- 3) *Optimum amount of water*: Whether too much or too little water is used. Limes vary in their optimum water: lime ratios.
- 4) *Temperature of water*: Whether slaking water is too cold or possibly too hot (steam) for the particular slaking conditions. Slow reacting limes need heated water; reactive limes do not. However, if the water temperature falls below 70°F, the operator can have trouble with unreactive lime in the system. For optimum slaking, it is best to maintain the water temperature around 100 °F.
- 5) *Distribution of water*: Whether water is introduced into the slaking chamber unevenly as surges. An even flow is desired.
- 6) *Agitation*: Whether too vigorous or insufficient agitation or quicklime and water is employed. Some agitation is necessary.
- 7) *Water quality*: Wallace and Tiernan conducted research to show the importance of water quality in efficient lime slaking. They concluded it is desirable to use water of (or near) potable quality. In particular, they observed that waste or recycle process waters containing sulfites and sulfates acted as a retarder to the slaking process. Not only was more time needed to complete the slaking step, but the quality of the resulting lime slurry was impaired. The lime hydrate particles became much larger and the surface area smaller, which in turn, retarded its neutralization reaction with acids. In fact, some of the lime did not hydrate and was wasted. The only explanation is that the lime precipitates the SO₃ and SO₄ ions on the quality of the diluted lime slurry ranged between nil and negligible. The chloride ion in reasonable amounts does not appear to exert any deleterious effect on slaking or in the dilution water.

Rate of Slaking

The most important test in determining optimum slaking conditions for a given quicklime is to measure its reactivity in water, specifically how much temperature rise occurs and in what length of time. This test comprises adding a specific weight of quicklime of a prescribed degree of fineness to a specified volume of water at 77 °F (25 °C) temperature, and then with a calorimeter and stop watch measure the temperature at intermediate points and at completion of hydration. This test is standardized by the American Water Works Association (AWWA B202) and the ASTM in specification C 110 on Physical Tests of lime.

The results, based on the AWWA test and covering the number of minutes to achieve a temperature rise of 40°C, will reveal if the quicklime has:

	<u>No. Of Minutes</u>	<u>Time for Completion</u>
high reactivity	3 or less	10 minutes or less
intermediate reactivity	3-6	10-20 minutes
low reactivity	more than 6	20 minutes or more

Generally, limes of high reactivity are soft-burned, i.e. calcined at lower temperatures, or at high temperatures (but under closely-controlled temperature conditions) for a short duration. The result is a reactive, porous quicklime of lower density that slakes rapidly with a high temperature rise. Limes of low reactivity are the converse, i.e., hard-burned, denser and heavier that slake much more slowly and evolve heat much more gradually so that the temperature rise is appreciably less. Dolomitic limes are inherently slowly reactive in varying degrees, regardless of how they are calcined. Slakers used in MWCs do not perform at their optimum level with dolomitic lime.

However, this heat of reaction can be artificially accelerated by using hot water for slaking quicklime of finer size, such as pulverized, and using more vigorous agitation. By such measures, it may be possible to so increase the slaking rate that a medium reactive time may approximate the behavior of a high reactive time. By applying these methods to a reactive time, it is possible to obtain extremely rapid, almost instantaneous slaking so that the lime and water literally explode on contact. Striving for such explosive slaking as this, however, is inadvisable; complete slaking time of 5 to 10 minutes is considerably more desirable. Conversely, a high quality, reactive lime's efficiency can be seriously impaired by using too much water at cold temperature, especially with lump or large pebble quicklime that is inadequately mixed or agitated. A coarse particle, fast settling, often incompletely slaked hydrate can result. Consequently, it is possible to enhance the efficiency of a lime of mediocre (possible poor) quality and impair the efficiency of a high quality lime by altering the slaking conditions.

Two extreme conditions should be avoided. If too great an excess of slaking water is used, particularly if the water is cold, an adverse reaction called "drowning" occurs. The surface of the quicklime particle hydrates quickly, but the mass of hydrate formed impedes the penetration of the water into the center of the particle delaying rupture of the particle into micro particles. The rise in temperature is stifled and slaking is delayed, resulting in coarser hydrate particles and badly delayed or incomplete hydration. The other extreme is adding insufficient water to the lime, causing the hydrate to be "burned," due to generation of excessive temperatures (250°-500°F) instead of the desired temperatures of just below boiling. Too much of the hydration water is lost as steam, and there may remain considerable unhydrated particles. The heat can be so intense that paint on the equipment can blister or ignite and lime particles that initially hydrated can be dehydrated. There is also a danger to operating personnel under these conditions.

Water to Quicklime Ratio

The two methods of slaking, batch versus continuous, require an understanding of the implication of percent solids in the final slaked lime product. For example, 2000 lb. of CaO when slaked will yield about 2,640 lb. of Ca(OH)₂ solids. This means that if 6,000 lb. of water are used to slake 2,000 lb. of high calcium quicklime with a final total weight of 8,000 lb., the concentration of solids in the final slaked lime product is 2,640/ 8,000, or about 33%. To obtain a 26% final lime slurry product, 8,000 lb. of water per 2,000 lb. of lime would be required (i.e., 2,640/10,000). In other words, water to lime ratios, to result in the best slaking temperature, must also be viewed in terms of the desired concentration of the final slaked lime product. This same approach applies to the slaking of dolomitic quicklime to yield a slurry of partly hydrated dolomitic lime (Ca(OH)₂ • MgO) or completely hydrated dolomitic lime (Ca(OH)₂-Mg(OH)₂).

Generally, with high calcium quicklime, about 3 lb. of water to 1 lb. of lime are used; with slower reacting limes, such as dolomitic quicklime, the ratio of water may be reduced to perhaps 2.5 to 1. As indicated in the previous paragraph, such proportions should result in a rather heavy paste, possibly too stiff to pump when cool. The resulting slaked lime should not be used until 30 minutes after mixing to allow ample time for complete hydration. Additional aging, up to several days, in which the paste is covered from the air to prevent carbonation, improves the product.

With rapid-slaking limes, it is preferable to add the lime into the requisite amount of water. With slow-slaking limes, it is preferable to add the water to the lime so that sufficient heat can be developed initially to prevent the water dosage from "drowning" the lime. In either case, the objective is to bring the lime and water together in such a way that the temperature of the slaking mass approaches that of boiling. In all cases, proper precautions should be taken to avoid the hot slaking lime contacting the body.

Methods of Slaking

There are two basic types of continuous lime slakers: 1) *the paste slaker* which operates at a minimum practical water-to-lime ratio, thus discharging a paste or even a "near" putty, and 2) the *detention slaker* which uses a somewhat greater water-to-lime ratio and can discharge a hydrated lime slurry ranging from a creamy suspension in the range of 30% solids, to a thin slurry in the range of 10% solids. In both types of continuous slakers, a minimum slaking temperature should be maintained in order to achieve good slaking as may be measured by the particle size of the resulting hydrated lime product. This temperature may range from 170°F in ball mill slakers to near boiling in paste slakers.

Obviously, the variance in the proportions of water and lime used will depend on the characteristics of the lime and the type of continuous slaker. For detention slakers, this averages about 3.5 to 4 lb. of water to 1 lb. of high calcium quicklime and 3-3.5:1 for dolomitic quicklime. With paste slakers, the average proportions are near two parts water to one part high calcium lime and less water for dolomitic lime. On the other hand, if the detention slaker is equipped to provide auxiliary heat and is mechanically designed to handle a slaked product approaching the consistency of paste, the water to lime ratios in a detention slaker can then approach those of a paste slaker.

The paste slaker uses a pug mill type of equipment to agitate the lime and water, i.e., two sets of paddles on counter-rotating shafts, with water being automatically added if the paste becomes too stiff. The detention type uses an impeller-type mixer, which agitates the slurry to prevent local overheating and "hot spots" in the slaking chamber. Provision is made in both types for classification of the slaked lime by continuous removal of grit and core (impurities) from the slurry or paste and for a dilution tank to reduce the concentration of the slaked lime for feeding into the reaction chamber. Other auxiliary equipment common to all modern slakers are automatic temperature recording devices in order to control quality of the slaked lime; thermostatic control to prevent accidents; a vapor remover which prevents the moisture of evaporation, laden with lime dust, from rising into the feeder or slaking room and corroding equipment or prematurely slaking the lime at the mouth of the feeder or in storage above the feeder. This latter device is operated by water jets, which condense the vapor and wash dust from the air, permitting clear air discharge into the room.

Chemically, from the standpoint of reacting quicklime with water, all properly designed slakers, whether batch or continuous detention or paste type, will handle any kind or quality of commercial quicklime. This statement assumes that provision for temperature control of the slaking operation is adequate. To this end, slakers generally contain temperature sensing instruments and automated devices in which both quicklime feed and water feed are temperature controlled.

The principal problems encountered during mechanical lime slaking are:

- 1) The breakage of moving parts due to oversized lime or non-lime impurities (grit),
- 2) The removal of non-lime impurities, and
- 3) The control of water vapor and dust originating in the slaker.

Most machines will handle quicklime from 2 inches top size down to pulverized forms although 3/4 to 1 inch top size is generally preferred. Since there may be an occasional piece of unburned limestone, kiln refractory or even a piece of tramp iron of 2 inch size or more, the slaker parts should be designed to accommodate such occasional hard objects without jamming the paddles or agitator or other conveying mechanisms.

As for impurities in the lime, these are considered to be any material which will not stake or at least crumble to a small size. All lime contains some unburned material in the form of the parent limestone (core) as well as other non-lime materials (silica, silicates, aluminates, ferrites, etc.), which are called grit. With the exception of ball mill slakers, which grind up the impurities, all mechanical slakers must be provided with a core and grit removal system. Such systems are discussed in a subsequent section. When these systems fail to operate properly, an unacceptable amount of core and grit report in the lime slurry holding tank and generate problems downstream from the slaker.

As for water vapor and dust, continuous lime slakers should be designed to operate under negative pressure. This is because of almost unavoidable dusting as the quicklime enters the slaker and the presence of steam or highly saturated water vapor due to the operating temperature of the slaker. When dust escapes, it is obviously a nuisance in the area around the slaker and lime handling system. Escaping steam and water vapor are likewise nuisances in the area. However, from an operating point of view, the important objective of negative pressure within the slaker is to prevent the moisture from working backwards into the quicklime feeding system. When this occurs, the lime feeder will cake and jam and must be shut down for clean out. In most continuous lime slakers, negative pressure is maintained by an aspirating system which is an integral part of the slaker design.

Degritting Lime Slurries

With high quality chemical quicklimes that have been thoroughly calcined and have a loss-on-ignition of 1 to 1½% or less as CO₂, the total grit content that must be wasted will be only 1 to 2% of the weight of the quicklime. However, grit losses may range on up to 5% or more with decreasing lime qualities. When the grit is ejected from the slaker, it resembles a mass of wet sand-like particles ranging from ¼ inch to # 100 mesh in size.

- Degritting is performed to improve lime quality and to reduce abrasion and wear on equipment. Cast iron centrifugal pumps have been worn out within a month in extreme cases when pumping a slurry that had not been degrittied. By degritting, the same equipment can operate for two years or more without maintenance.
- Degritting is performed in the dilution tank adjacent to the slaking chamber. The slurry or paste as it passes over a weir into the dilution chamber is dispersed and diluted by water sprays. The much heavier grit particles settle rapidly on the bottom and are removed automatically by rakes or screws which drag the grit up an incline and out of the chamber or to a classifier in the bottom of the dilution chamber. Here, the grit is washed, recovering in the waste water a small amount of slaked lime particles that can be reintroduced again as

slaking or dilution water in the system. A vibrating screen is used for grit removal in one slaker model.

- The washed grit is disposed of manually or automatically. Slakers with a capacity of 500 lb./hr. or more usually employ automatic removal by ejection with water-jet eductors, similar to sand washing eductors. Meanwhile, enough turbulence is maintained so that nearly all of the slaked lime in the diluted slurry remains in suspension for introduction through pipes or directly into reaction chambers or storage for later use or for further adjustment in concentration.

Dilution of Slurry Concentration

Consumer preference as to the concentration of CaO or lime solids in the milk-of-lime used in their processes naturally varies-generally from about 5 to 15% CaO or about 6.25 to 18.75% lime solids as a hydroxide.

One manufacturer advocates diluting the slurry to at least a 10% lime solids concentration before it leaves the slaker. However, there is no set rule; certain processes seem to operate more smoothly with stronger or weaker concentrations than this. Where the lime dosage is minute, a few mg/l, the more dilute suspensions are believed by some to provide better dispersion in the reaction chamber.

At one time it was believed desirable to standardize on a fairly specific concentration of "milk" or thin slurry so that when gallons were metered into a process, it could be quickly calculated as to the total amount of lime as CaO or oxides being fed. From such a concentration, like one lb. CaO per gallon, it could be determined if the pre-calculated amount of time required for a given reaction was being added. It was felt that better control would be exercised over the process and less lime would be wasted. The concentration of lime was generally checked with a hydrometer; and from the specific gravity reading, it was possible to correlate the degrees Baumé, the lime concentration in g/l, lb./gal. as CaO or Ca(OH), by using a chart, such as shown in Table 8. If less or more lime was needed in the process, the flow of gallons was altered, not the lime concentration. In some processes this is still the preferred approach, but to do this precisely requires a separate solution tank in addition to the dilution tank.

However, increasingly in recent years, at least, for many chemical processes, this approach to feeding has been abandoned for reliance on the automatic recording pH meter and controller. By calculation the operator knows that if the reaction chamber records a pH within two tenths, plus or minus, of the required pH level of, say, 9 that enough time is being added. If the pH suddenly changes to 8.5 or 9.5, he increases or decreases the rate of flow. With this approach he has no interest whether the milk-of-lime contains one or two pounds of CaO per gallon. In continuous slaking and feeding processes, he can also double check the rate of feed from automatic recording of the weight of quicklime per minute or hour and the volume of water over the same period being introduced into the system. Regardless of what approach is used in controlling the lime feed, it is necessary to maintain the lime in suspension and prevent settling in order to maintain a uniform feed.

Some engineers have been imprecise in defining concentrations of slurry or milk-of-lime. For example, some feel that percent lime solids is synonymous with percent CaO (or oxides in case of dolomitic lime). It is not. Since quicklime can be slaked into a dry powder, like commercial hydrated lime, in this hydroxide form it is a *solid*, even though it contains about 25% chemically combined water. Therefore, percent lime solids, at least for high calcium lime, means strictly a hydroxide (Ca(OH)₂), and not the oxide (CaO). Table 2 shows the equivalencies of Ca(OH)₂, as CaO. Also, when percent lime solids or CaO is used, sometimes engineers fail to include the weight of water. To determine what concentration of lime solids is present, the following simple equation is suggested:

$$\% \text{ Solution} = \frac{\text{lb. of Ca(OH)}_2}{\text{lb. of Ca(OH)}_2 + 8.345 \times \text{No. of gal. water}} \times 100$$

USE OF LIME FOR AIR POLLUTION CONTROL

Two sorbents that have been used to control acid gas emissions are lime in two forms as quick lime (CaO) and hydrated lime (Ca(OH)₂) and sodium bicarbonate (NaHCO₃). Most utility and MWCs air pollution control systems have selected lime-based products since lime is generally more cost effective and the solubility of sodium based products can lead to leaching of metal. NaHCO₃ has a lower stoichiometric ratio than lime for acid gas absorption. However, the net cost per ton of acid gas removed is significantly higher. Quicklime at most MWCs costs between \$70 and \$90/ton while NaHCO₃ sells for more than \$400/ton.

The following table summarizes the calculated theoretical reagent requirements per tonne of gaseous pollutants.

Pollutant	Gas Temperature °C	Stoichiometric ratio		Ca(OH) ₂ consumption in tonnes (94%)	NaHCO ₃ consumption in tonnes (100%)
		Ca(OH) ₂	NaHCO ₃		
SO ₂	120-160	3.0	1.2	3.7	3.2
	160-220	3.5	1.5	4.3	3.9
	220-280	5.0	1.8	6.2	4.7
HCl	120-160	1.5	1.2	1.6	2.8
	160-220	1.8	1.5	2.0	3.5
	220-280	2.0	1.8	2.2	4.2
HF	120-280	1.0	1.0	2.1	4.2

A typical MWC emits approximately 5 lbs. of SO₂ and 7 lbs. of HCl per ton of MSW burned. Using the information in the above table means that you would need approximately 25.5 lbs. of Ca(OH)₂ or 14.4 lbs. of NaHCO₃ to control the acid gas emissions from a ton of waste. Since lime costs approximately \$0.04 per lb. and NaHCO₃ costs \$0.20 per lbs. it is easy to see that lime is the most economical choice as a sorbent. It costs \$1.02 for lime and \$2.88 for NaHCO₃ per ton of MSW to control the acid gas emissions. However, beyond the higher cost associated with sodium based reagents, their solubility (leachability) and the inability to control the alkalinity of the resulting MWC ash are more troubling problems.

Theory of Lime

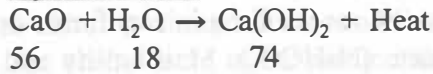
This Section discusses the various lime products involved in the process. Ca(OH)₂ is made from CaO by adding 32% by weight of water in a hydrator. Ca(OH)₂ is a powder with a mean particle size of 5 microns and is highly reactive.

CaO is not very reactive with acid gases for scrubbing at the temperatures and conditions that exist in MWC facilities and has to be converted into hydrate to be reactive in scrubbing systems. CaO converts to Ca(OH)₂ in the slaking process in which four parts of water are added to one part CaO to form Ca(OH)₂ in a slurry that has about 25% solids. This conversion requires two steps that take place in a slaker. The first step converts the CaO into Ca(OH)₂. The second step is to convert the hydrate

by mixing four parts of water (3.96 lbs. of free water) with one part hydrate (1.32 lbs.) that results in a 25% solids slurry (5.28 lbs.).²

The reactions of the chemical components (with their molecular weights) of Sorbalit are as follows:

A. Hydrated lime



1 lb. of CaO yields 1.32 lbs. of Ca(OH)₂

The stoichiometry of Ca(OH)₂ with acid gases is:

- It requires 1.156 lbs. of Ca(OH)₂ to capture 1.0 lbs. of SO₂
- It requires 1.014 lbs. of Ca(OH)₂ to capture 1.0 lbs. of HCl

The average MWC facility emits the following regulated acid gases: (lbs./ton of MSW burned)

SO₂ = 5.03 lbs./ton (212 ppmdv @ 7% O₂)
HCl = 7.03 lbs./ton (532 ppmdv @ 7% O₂)

The characteristic stoichiometric reaction of Ca(OH)₂ per ton of typical MSW is:

	<u>lb. Ca(OH)₂/ton MSW</u>
SO ₂ = 5.03 lbs. SO ₂ /ton MSW x 1.156 lbs. Ca(OH) ₂ /lb. SO ₂ =	5.815
HCl = 7.03 lbs. HCl/ton MSW x 1.014 lbs. Ca(OH) ₂ /lb. HCl =	<u>7.128</u>
TOTAL	12.943 (12.9)

B. Pebble Lime



The stoichiometry of CaO with acid gases is:

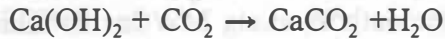
- It requires 0.875 lbs. of CaO to capture 1.0 lbs. of SO₂
- It requires 0.767 lbs. of CaO to capture 1.0 lbs. of HCl

The following is the stoichiometric reaction of CaO per ton of typical MSW:

	<u>lb. CaO/ton MSW</u>
SO ₂ = 5.03 lbs. SO ₂ /ton MSW x 0.875 lbs. CaO/lb. SO ₂ =	4.401
HCl = 7.03 lbs. HCl/ton MSW x 0.767 lbs. CaO/lb. HCl =	<u>5.392</u>
TOTAL	9.793 (9.8)

Since CaO contains about 7% unreactive material and inerts, the usage is adjusted to compensate for impurities. The adjustment is 1.07 x 9.8 = 10.5.

Theoretically, a typical MWC would require 12.9 lbs. of hydrated lime or 10.5 lbs. of pebble lime per ton of MSW burned to capture all of the SO₂ and HCl emitted. However, in actual applications this never occurs. Due to the inability to provide absolute contact between the lime and the acid gases, we need to put more lime into the process to achieve SO₂ and HCl emissions of less than 25 ppm. In addition, several unwanted chemical reactions take place that also use some undefined portion of the lime. For example, lime will react with carbon dioxide in the flue gas as follows:



The ratio of the actual amount of lime used to the theoretical amount required is called the stoichiometric ratio. A typical MWC equipped with a spray dryer and an ESP will require about 35 lbs. of pebble lime per ton of MSW while a MWC with a spray dryer baghouse will require about 20 lbs. per ton to meet the NSPS standards of 25 ppm of HCl (a 95.3% reduction) and 30 ppm of SO₂ (an 85.8% reduction). The stoichiometric ratio for a plant with an ESP would be:

$$35 \div 10.5 = 3.33$$

The Application of Lime Ash Stabilization

Many authors such as Chesner and Hasselriis have presented substantial data which demonstrates that if the pH of the TCLP extraction solution is in the range of 8 to 10, cadmium and lead are least soluble (see Figures 1 and 2). In this neutral-alkaline pH range, both the cadmium and lead are in the carbonate form and both lead and cadmium have a low solubility as carbonates. When the pH is greater than 10.5, the lead changes to a hydroxide which is more soluble than the carbonate. One of the major problems with the EPA TCLP test is that the extraction process takes 16 hours. Due to the extended duration associated with this process, facilities have no opportunity to adjust the lime feed system in order to attempt to control the pH of the ash. When a facility has to wait in excess of 16 hours for results, a substantial amount of ash can be generated before the facility can adjust the system thus reducing the ability of the facility personnel to meet the TCLP criteria. The following procedure was developed by Dravo Lime to facilitate and expedite ash TCLP analysis while providing a close approximation to the results of the EPA TCLP test by using a screening test procedure.

Controlling pH / Alkalinity in Ash

Figure 3 illustrates the change in pH with time and shows that most of the change in pH for the TCLP test occurs in the first 30 minutes. Beyond the first 30 minutes, pH changes about 0.5 pH units in total. Using this phenomenon, it is possible for plant personnel to adjust the alkalinity of the ash produced by using the results of an ash screening test presented in Figure 4. Based on the 30 minute extraction period used in the screening test, if the resulting pH value of the ash extraction solution is below 7, the graph in Figure 4 is used in calculating the additional alkalinity required to bring the ash extraction solution to pH 7. The ideal screening test result for the ash extraction solution is a pH value of 7. This is considered the optimum value for the screening test result since the pH value for the full scale EPA TCLP test result will typically increase by 0.5 pH units to a pH value of 7.5. This pH value of 7.5 is the point at which the solubility of cadmium and lead are lowest. Typically, however MWCs will try to operate at a pH level of 10.5 which represents a mid-range value for minimum solubility of cadmium and lead. Maintaining a pH of 10.5 reduces the chances of failing the TCLP test due to plant upsets / operational variations which can sufficiently move the ash pH either up or down enough to cause the lead and/or cadmium to leach.

Figure 4 indicates how much additional alkali is needed to raise the pH to 7 if the pH is below 7. The additional alkali could be supplied by increasing the lime feed rate to the spray dryer. For example, if the pH reading is 5.0, the Figure 4 shows that 70% of the acidity in the TCLP test is neutralized. Therefore, the alkali content of the ash must be increased by 30/70 or about 40% to result in a pH of 7 in the TCLP test. The plant personnel, by knowing the approximate ratio of ash to MSW and how

many pounds of lime the facility is using per ton of MSW burned, can calculate changes in the lime feed system.

Effects of Alkalis on pH

Most MWCs that use spray dryer / fabric filter technology, consume on average about 24 lbs. of lime (CaO) per ton of MSW burned to reduce the acid gas emissions to limits established by U.S. EPA. Based on the tests conducted by the authors at six MWCs, the amount of lime required to result in a TCLP final pH of 10.5 ranges from 25 to 35 lbs. of lime per ton of MSW. Some MWCs are limited in how much lime they can put into the spray dryer/air pollution control system due to design restrictions which are imposed to minimize build up of lime slag on the inside walls of the spray dryers caused by high lime slurry feeding rates.

Another problem associated with feeding too much lime into the system is the increase in unreacted lime added to the ash stream. Since the maximum pH of lime is 12.5 and lead is amphoteric, the lead will become soluble again above pH 10.5. Once you reach a pH of 7, the addition of lime at this point can quickly result in free alkalinity and a pH higher than 10.5. If there is too much lime, lead could leach from the ash; cadmium, however, does not exhibit this property.

One alternative to resolving the rapid variation in the ash pH is the addition of magnesium oxide or magnesium hydrate to the lime mixture. Magnesium is a natural buffer and has a pH end point of 9.5. The ideal formulation of lime and magnesium would be to use only as much lime as needed in the mixture to remove the acid gases and bring the TCLP extraction solution to a pH of 7. Any additional alkalinity should come from the magnesium component. In this ideal case, lead would not become soluble in the extraction solution. In the event that there is too much lime in the ash, the magnesium salts in the ash would tie-up the hydroxides when the pH becomes greater than 10. This prevents the lead from changing from the less soluble carbonate to the more soluble hydroxide form.

Given that the magnesium can effectively prevent lead from leaching from the ash at high pH values, why not use magnesium as the major alkali in the acid gas air pollution control system? The answer is that the use of magnesium as the major alkali in a dry scrubber acid gas removal system is not a good application because magnesium does not react as well with the acid gases as does lime at the temperatures at which MWC spray dryers operate. Therefore, more pounds of magnesium than lime are required per pound of acid gas removed. Since most facilities have to pay for ash disposal on a tonnage basis and the price of ash disposal is high, the goal of MWCs is to limit excess alkali leaving with the ash. Magnesium is, however, an excellent sorbent for acid gases in wet scrubbing systems.

Some facilities have tried to use a dolomitic quicklime at MWCs equipped with spray dryers to remove acid gases and modify the behavior of the pH in the combined ash stream. Dolomitic quicklime is approximately 40% MgO and 57% CaO while high calcium quicklime is 93 to 98% CaO. There are several problems associated with dolomitic quicklime for MWCs: 1) since dolomitic quicklime is 40% MgO, a facility would need 40% more quicklime to achieve the same acid gas removal and there would be additional ash for disposal; 2) the MgO component in dolomitic quicklime slakes very slowly (convert to a hydroxide) in the paste-type slaker used in most MWCs, and 3) MgO only partially converts from an oxide to a hydroxide.

The most practical solution for existing MWCs to minimize their capital and operating costs would be to use a quicklime that has a 5 - 10% MgO content. This amount of MgO should have little effect on the slaker and would minimize unreacted alkali from passing through the spray dryer. Sulfur helps to immobilize heavy metals in the ash in its sulfide form.

Alternate Approach

Dravo Lime has developed a formulation for both the Sorbalit (hydrated lime-based) and the Sorbalime (quicklime-based) products that contain magnesium to modify the pH properties of the ash as well as controlling the emissions of mercury, dioxins, and acid gases. One of the key features of this process is that Sorbalit is being applied for air pollution control purposes and not for "treating" the ash.

Sorbalit is a patented air pollution control system that reduces pollutants such as volatile heavy metals (mercury), organics (dioxin and PCBs), and acid gases (SO₂ and HCl). The Sorbalit process produces a special sorbent composed of lime, activated carbon, and other proprietary sulfur components. This unique lime-based product will reduce several pollutants in a single application and without replacing or adding significantly to a plant's existing air pollution control equipment.

Sorbalime, a quicklime-based product, can be applied at any facility that currently slakes lime for a spray dryer. For these facilities, a formulation with approximately 5% magnesium would be made and the application would be the same as the quicklime operation. For other facilities, Sorbalit can be injected before or after a dry scrubber, baghouse, or ESP. The lime in Sorbalit provides the alkalinity to raise the pH of the ash and reduces the acid gas emissions; the magnesium provides buffering at a pH of 9.5; and the carbon and sulfur in the Sorbalit formulation control the dioxins and mercury emissions. There are several advantages to dry injection although there may be some capital cost involved. These advantages are:

- By injecting the Sorbalit, extra "free" lime hydrate is being applied which is more reactive with the ash than the lime which has reacted with the acid gases; less product is produced and there is less alkaline material in the ash for disposal.
- The facility has independent control of both the acid gas removal process and the pH of the ash.
- The "free" sulfur from the Sorbalit reacts with the lead and cadmium in the ash and converts carbonates to sulfates which are less soluble.
- The sulfur in Sorbalit reduces the amount of carbon required to reduce mercury emissions and the amount of residue for disposal.

Summary

- 1) This section of the paper has described a screening procedure based on the full scale EPA TCLP test procedure that allows a facility to expeditiously and routinely test the ash, and make adjustments to reduce the solubility of cadmium and lead. This screening procedure reduces the risk that ash samples will not meet the TCLP criteria for disposal in non-hazardous waste landfills which can reduce the cost of plant operations.
- 2) By using lime and magnesium products, facilities can control and reduce the alkali content of the ash. If the final pH of the TCLP test is maintained, the facility is assured that the ash will have low lead and cadmium concentrations.
- 3) Magnesium is useful in helping to raise the pH to maintain the optimum level between 8 and 10.
- 4) Magnesium salts may be useful in reducing the pH of high lime ashes.

CONCLUSION

Lime is a very practical and economical sorbent for MWCs. There are certain material handling design criteria that engineers and operators need to utilize when lime products are used in a facility. With the proper design lime is a relatively easy and safe material to handle. In addition to controlling air emissions lime has a practical application in stabilizing MWC ash.

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Table 1: Lime physical and chemical data

Quicklimes

	High Calcium	Dolomitic
Primary Constituents	CaO	CaO & MgO
Specific Gravity	3.2-3.4	3.25-3.45
Bulk Density (Pebble Lime), lb./cu. ft.	55-60	55-60
Specific Heat at 100 °F. Btu/lb.	0.19	0.21
Angle of Repose (avg. for pebble)	50-55*	50-55*

Hydrates

	High Calcium	Normal Dolomitic	Pressure Dolomitic
Primary Constituents	Ca(OH) ₂	Ca(OH) ₂ + MgO	Ca(OH) ₂ + Mg(OH) ₂
Specific Gravity	2.3-2.4	2.7-2.9	2.4-2.6
Bulk Density (Pebble Lime), lb./cu. ft.	25-35**	30-40	30-40
Specific Heat at 100 °F. Btu/lb.	0.29	0.29	0.29
Angle of Repose (avg. for pebble)	70*	70*	70*

* Approximate average

** In some instances these values may be extended

Table 2: Strength of lime suspensions

Milk-of-Lime Suspensions				Lime Content		% Solids
Specific Gravity at 15 °C	Degrees Baumé (Bur. Stds. Scale)	Grams CaO per liter	Grams Ca(OH) ₂ per liter	lb. CaO per U. S. gal.	lb.. CaO per cu. ft.	Ca(OH) ₂ in Water
1.010	1.44	11.7	15.5	0.097	0.7	1.53
1.020	2.84	24.4	32.2	0.203	1.5	3.12
1.030	4.22	37.1	49.0	0.309	2.3	4.67
1.040	5.58	49.8	65.8	0.415	3.1	6.17
1.050	6.91	62.5	82.6	0.520	3.9	7.63
1.060	8.21	75.2	99.4	0.626	4.7	9.04
1.070	9.49	87.9	116	0.732	5.5	10.4
1.080	10.74	100	132	0.833	6.3	11.6
1.090	11.97	113	149	0.941	7.1	13.0
1.100	13.18	126	166	1.05	7.9	14.0
1.110	14.37	152	182	1.15	8.7	15.4
1.120	15.54	164	201	1.27	9.5	16.7
1.130	16.68	177	217	1.37	10.3	17.8
1.140	17.81	190	234	1.47	11.1	19.0
1.150	18.91	203	251	1.50	11.9	20.1
1.170	20.00	216	268	1.69	12.7	21.1
1.180	21.07	229	285	1.80	13.5	22.2
1.190	22.12	242	303	1.91	14.3	23.3
1.200	23.15	255	320	2.02	15.1	24.2
1.210	24.17	268	337	2.12	15.9	25.2
1.220	26.15	281	371	2.34	17.6	26.1
1.230	27.11	294	388	2.45	18.4	28.0
1.240	28.60	307	406	2.56	19.2	28.9
1.250	29.00	321	424	2.67	20.0	29.8

Figure 1. MSW ash TCLP results lead concentration vs pH

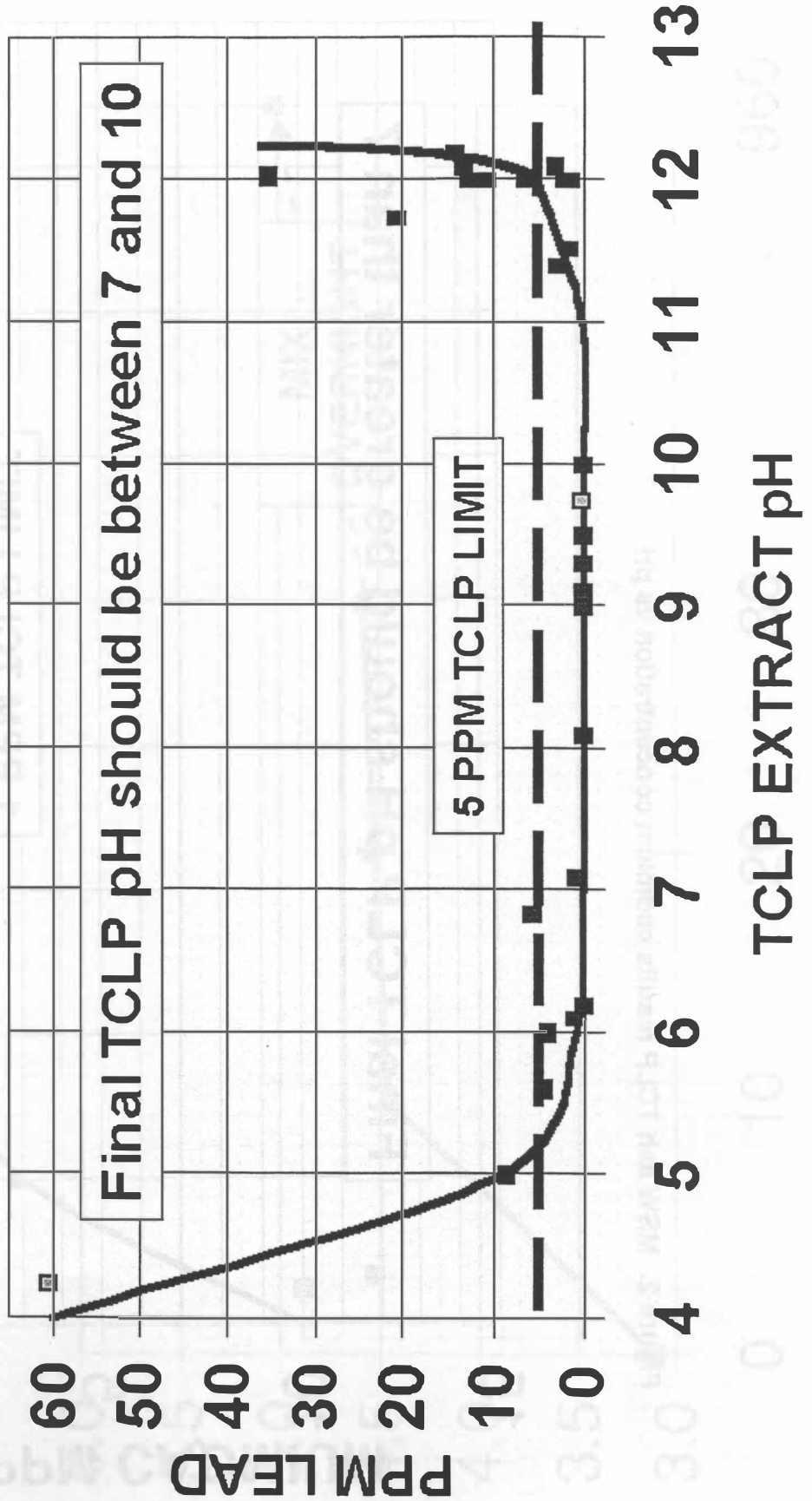


Figure 2. MSW ash TCLP results cadmium concentration vs pH

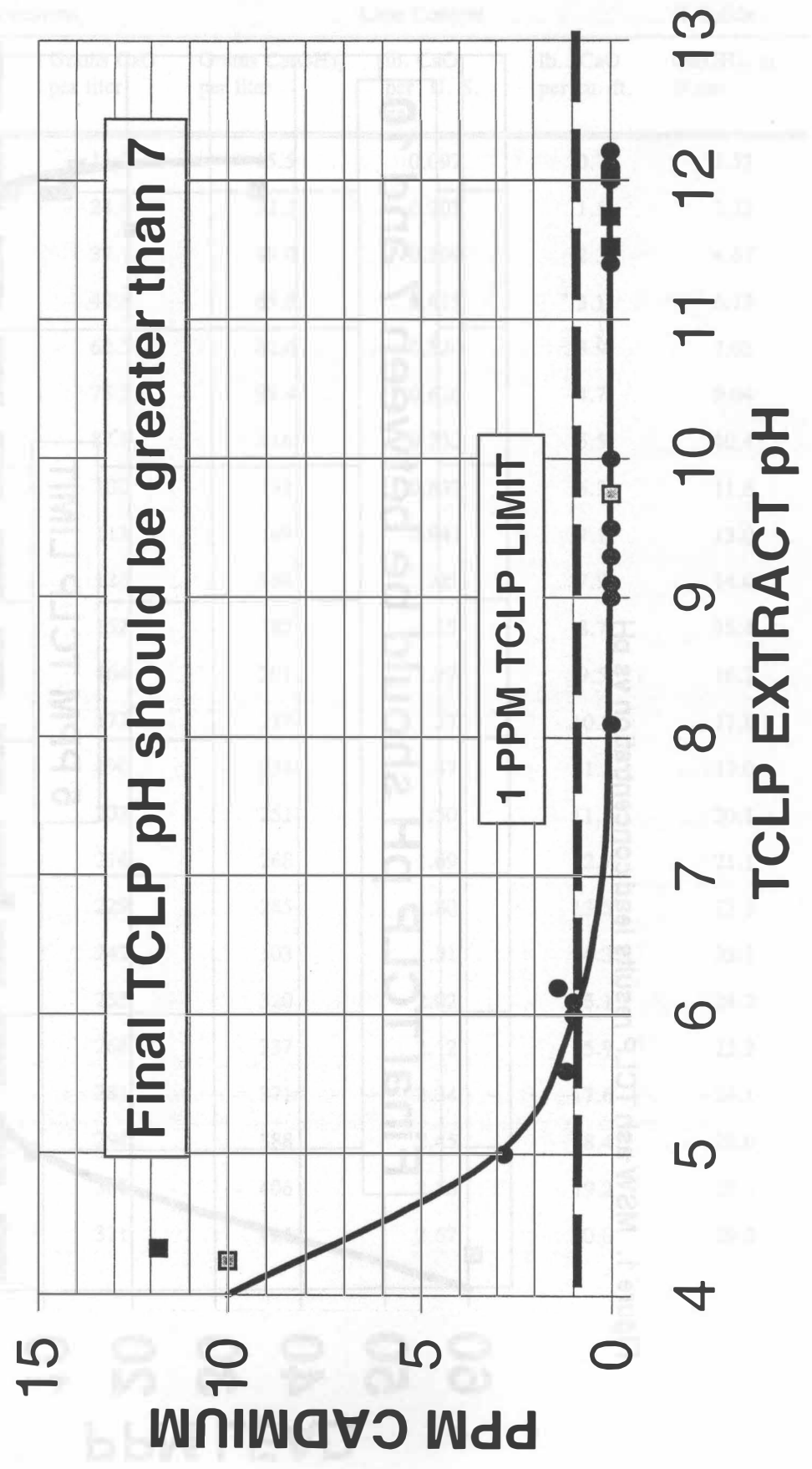
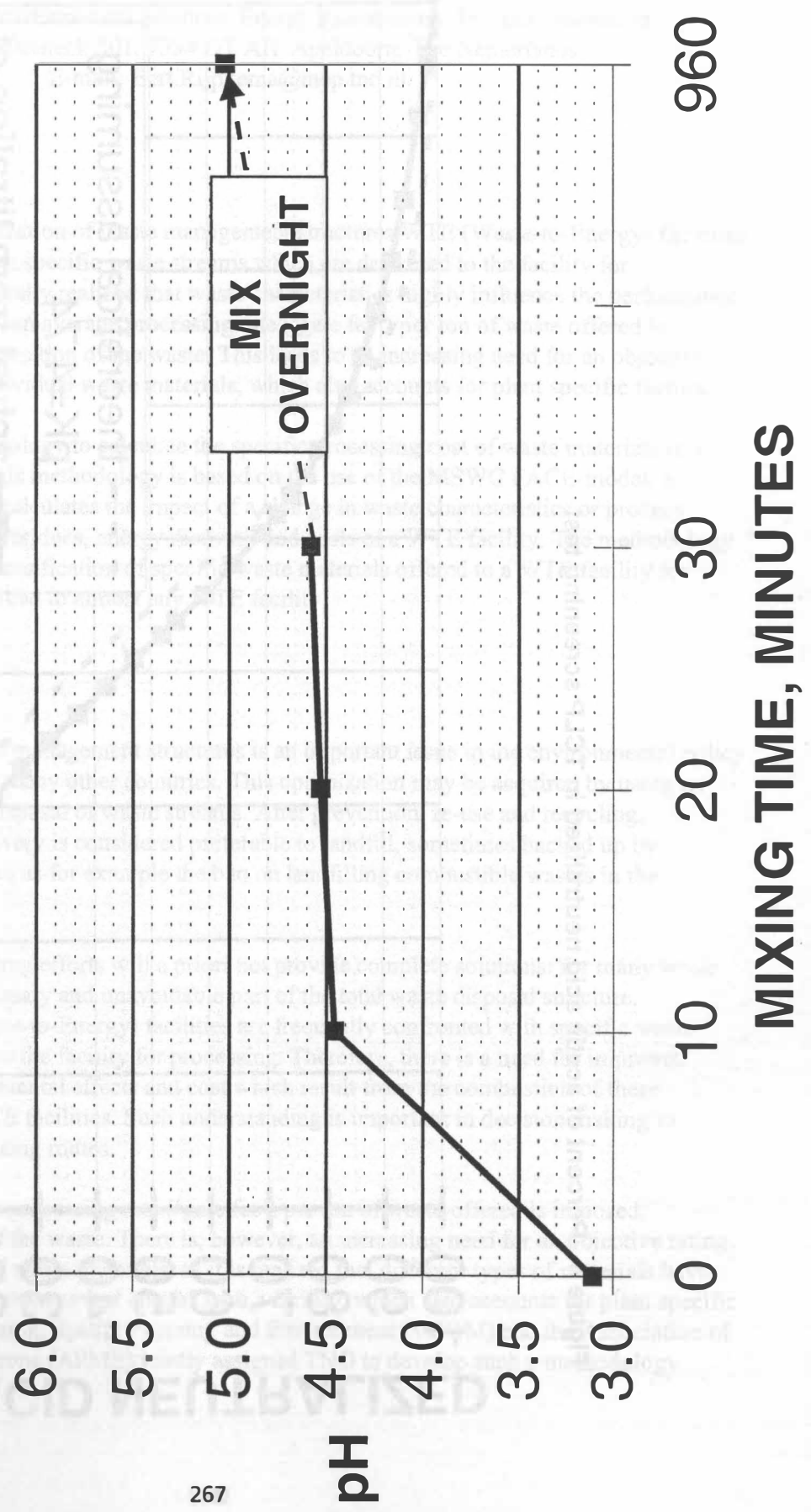


Figure 3. pH vs mixing time in TCLP screening test



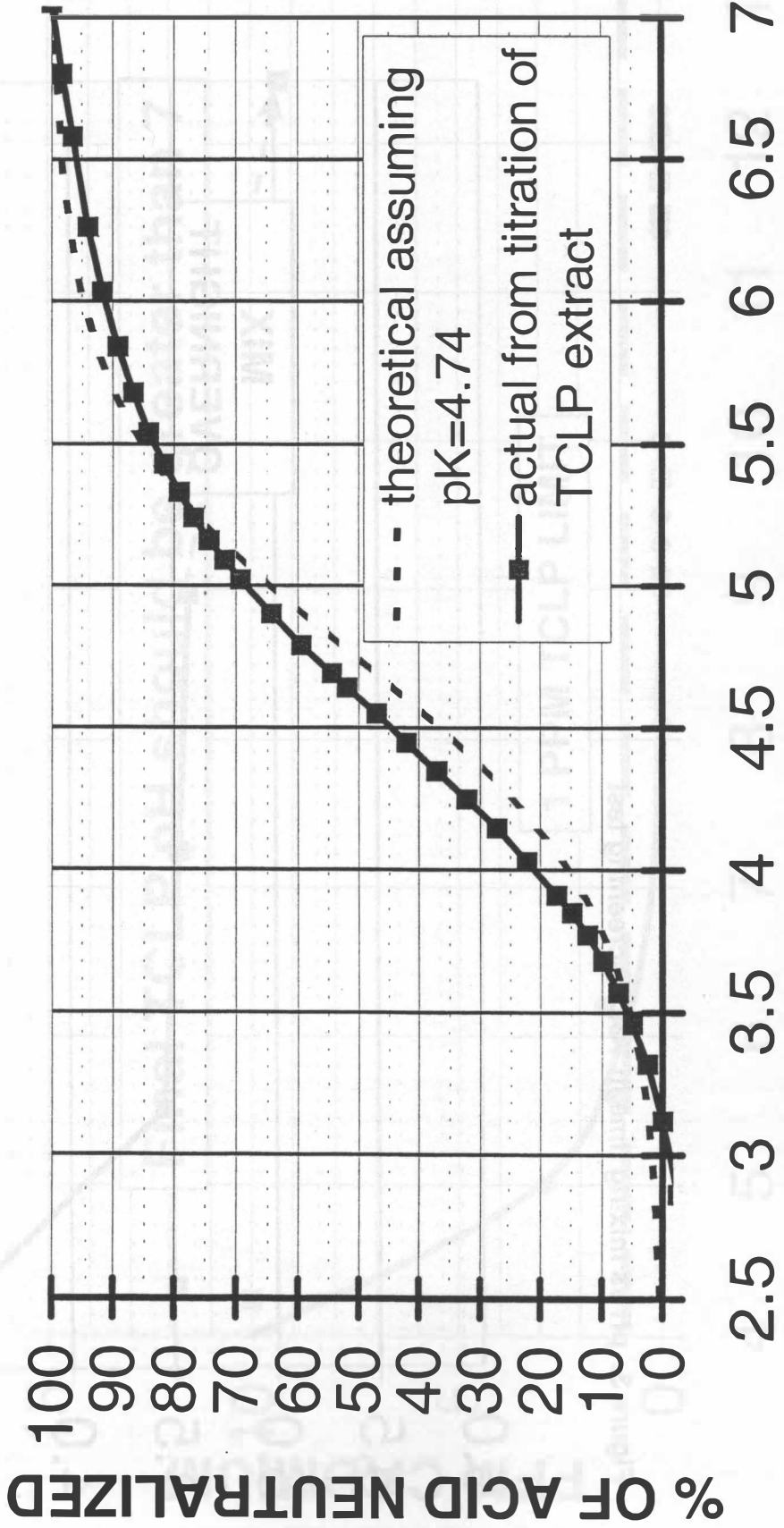


Figure 4. Percent of acetic acid neutralized in TCLP screening test

FINAL pH IN TCLP SCREENING TEST