Chemical Facts Pertaining to Environmental Uses for Lime

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FOREWORD

The purpose of this booklet is not to make a chemist out of anyone. Rather, we are attempting to present and explain a few chemical considerations which should help the lime salesman to become more knowledgeable in and more conversant with the chemistry of lime in the environmental protection program (EPA). Lime is a major chemical reagent in this program. However, there is developing competition from other chemical reagents. In order that the market for lime in the environmental field can be maintained and promoted, it is necessary that some basic lime chemistry be understood by those interested in this versatile chemical. Some chemical accuracy has been sacrificed in the interest of simplicity.

Section 1 · NOMENCLATURE

The chemical terms most often encountered in the field are:

- limestone, calcium carbonate ($CaCO_3$)

- quicklime, calcium oxide (CaO)

- hydrated lime, calcium hydroxide ($Ca(OH)_2$)

- phosphate, a chemical union of phosphorus and oxygen (PO_4)

- nitrate, a chemical union of nitrogen and oxygen (NO_3)

- sulfur (S)

- sulfur dioxide, a chemical union of sulfur and oxygen (SO_2)

- sulfur trioxide, another chemical union of sulfur and oxygen (SO_3)

- stack gas scrubber sludge, calcium sulfite ($CaSO_3$)

- gypsum, calcium sulfate ($CaSO_4$)

- sulfuric acid, hydrogen sulfate (H_2SO_4)

- ferric chloride, a compound of iron and chlorine ($FeCl_3$)

- alum, a compound of aluminum, sulfur and oxygen ($Al_2(SO_4)_3$); also may contain chemically combined water (H_2O)

- soda ash, sodium carbonate (Na_2CO_3)

- caustic soda, sodium hydroxide ($NaOH$)

- hydrofluoric acid, a compound of hydrogen and fluorine (HF)

- municipal waste sludge, mostly organic solids from sewage treatment

- precipitation, causing a dissolved material to come out of solution as a solid

AUTHOR'S NOTES

Lime is the most versatile chemical in the world. However, because of its different geographical and geological origins and the varying circumstances surrounding its production, there are differences in the physical and chemical properties. These must be taken into account by design engineers, lime salesmen and purchasing agents. Lime, as a chemical, has, and will continue to have, competition from other chemicals which may substitute for lime.

Because lime has its origin in antiquity, and for hundreds of years was looked upon as a menial product of interest mainly for soil sweetening and mortar preparation, lime has not yet received its due recognition as a chemical. This chemical is often handled without due regard for its perishable nature and the equipment necessary for its efficient performance is improperly engineered or inadequately maintained. Many lime handling installations which might be quite neat are monuments to indifference and lack of knowledge. These situations give rise to frustrations and concessions which have nothing to do with the lime, but rather the attitude of those using it. It is hoped that those involved with lime will not only find something useful in the preceeding pages, but will also attempt to educate all involved with the importance of recognizing lime as a chemical.

Advantage: Highly effective as a final clean-up reagent for removing small amounts of undesirable substances which have not been removed by previous processing steps. Can be regenerated.

Disadvantage: Relative initial high cost and rapid saturation and inactivation if being used to remove more than small amounts of undesirable substances.

· precipitant, the reagent which reacts with the dissolved substance to cause precipitation

· precipitate, the material which comes out of solution

- coagulation, used interchangeably with precipitation

· coagulant, used interchangeably with precipitant

· flocculant, a material which causes a light, fluffy snowflake-like precipitate

· flocculating reagent, the material which causes floc-

- floc, the light, fluffy, snowflake-like precipitate

The foregoing names and formulae pretty-well cover the chemical materials about which the lime salesman should have some understanding, as far as the use of lime in the environmental clean-up program is concerned.

Section 2 - SOME "BITS" OF LIME CHEMISTRY

The chemical terminology a lime salesman is most likely to encounter in the field includes the following:

Elements

Name	Symbol
Calcium	Ca
Magnesium	Mg
Oxygen	O
Sulfur	S
Carbon	C
Hydrogen	H
Heavy metals (iron, aluminum, etc.)	R_2O_3
Phosphorus	P
Silicon	Si
Sodium	Na

Compounds

Name	Formula
High calcium limestone	$CaCO_3$
High calcium quicklime	CaO
High calcium hydrate	$Ca(OH)_2$
Dolomitic limestone	$CaCO_3 \cdot MgCO_3$
Dolomitic quicklime	$CaO \cdot MgO$
Normal dolomitic hydrate	$Ca(OH)_2 \cdot MgO$
Dolomitic pressure hydrate	$Ca(OH)_2 \cdot Mg(OH)_2$
Soda ash	Na_2CO_3
Caustic soda	$NaOH$
Sulfur dioxide	SO_2
Sulfuric acid	H_2SO_4
Carbon dioxide	CO_2
Phosphate	PO_4
Silica	SiO_2

do the work of one ton of high calcium lime. Limestone cannot develop a pH sufficiently high to precipitate all heavy metals and sometimes not sufficiently high to meet EPA requirements on pH of discharge waters.

7. Polymers-complex organic compounds

    Use: Sludge conditioning ahead of dewatering and flocculation. Can be purchased as a water solution or as dry solids, which can then be dissolved in water.

    Advantage. Ease of handling and application.

    Disadvantage: Fragile nature of the dewatered sludges produced and the fact that polymers are inert as pH control reagents, and likewise generally inert as far as reacting with metals, phosphate, nitrates or odor-producers.

8. Waste carbide sludge - from acetylene production

    Use: Can be, and is substituted for slaked lime slurry in many applications.

    Advantage: Relatively low delivered cost per ton of available calcium oxide if source is near point of application. Usually delivered as a 40-45% calcium hydroxide slurry, thus eliminating quicklime storage and a lime-slaking operation.

    Disadvantage: May contain impurities, such as cadmium, zinc and chromium in amounts far exceeding the content of these and other impurities in commercial quicklime. Such impurities may report in the sludges or effluent from the operation, exceeding EPA limitations. Relatively coarse particle size, minimizing surface area.

9. Activated carbon - a material not unlike an ion-exchanging resin and capable of absorbing metals and other impurities from water

    Use. As an absorbant for removing relatively small quantities of metals and gases, usually from water. Popular in tertiary municipal waste treatment plants as a final clean-up reagent.

Disadvantage: Same as alum. Seldom used unless local-
ly available as a waste product from a local indus-
try, particularly an industry cleaning steel with
sulfuric acid.

4.   Soda ash (sodium carbonate) (Na_2CO_3)

Use: Acid neutralization, heavy metals precipitation and
as a stack gas-scrubbing reagent for sulfur ox-
ides removal.

Advantage: None in particular unless locally available at
an attractive price. In stack gas scrubbing, has
the advantage of all sodium compounds being
soluable to thus eliminate scaling in a scrubber.

Disadvantage: The scrubber effluent is usually regener-
ated with lime to recycle caustic soda and the
soda ash thus becomes a makeup reagent. Other-
wise, the scrubber effluent must be impounded.
If used in a dry scrubbing process, the sodium
salts, mixed with fly ash, are leachable. This may
also render the fly ash unsuitable for use in con-
crete.

5.   Caustic soda (sodium hydroxide) (NaOH)

Use: Acid neutralization and to precipitate heavy metals.

Advantage: A minimum of sludge is produced because
all sodium salts are water-soluble. Can be pur-
chased as a liquid or as a solid, which is easily
dissolved in water — hence ease of handling and
application.

Disadvantage: High cost. Environmental protection
authorities frown on soluable sodium salts in
discharges entering public domain.

6.   High calcium limestone (calcium carbonate) ($CaCO_3$)

Use: Acid neutralization, precipitation of some heavy
metals and as a reagent for sulfur oxides control
by scrubbing or dry injection.

Advantage: Local abundancy, relatively low cost and
relative ease of handling and application.

Disadvantage: About 2 tons of limestone are required to

An element is a chemical building block, the smallest
particle of which still retains all of the chemical and physical
properties of any amount of the element. For example, the
smallest conceivable particle of the element calcium has the
same chemical and physical properties of a pound, a ton or a
thousand tons of calcium.

A compound is a combination of two or more elements
in a definite, fixed and unchanging ratio of the elements by
weight. For example, water (H_2O) is a compound of hydrogen
and oxygen, which can be broken down into the elements
hydrogen and oxygen. As in the case of the elements, the
smallest conceivable particle of a compound has all the
chemical and physical properties of any amount of the com-
pound.

Science has been able to determine the relative
weights of the approximately 100 chemical elements now
known. It is very important to understand the use of the term
"relative" because it is doubtful if the actual weight of the
smallest particle of any element is known. However, by
simply assigning an arbitrary weight of 16 to the element ox-
ygen (O), the relative weights of the known elements have
been established and, for those already mentioned, these,
rounded off to the nearest decimal point, are:

Element	Relative Weight
Calcium	40
Magnesium	24
Oxygen	16
Sulfur	32
Carbon	12
Hydrogen	1
Heavy metals	Not applicable
Phosphorus	31
Silicon	28
Sodium	23

If the list of chemical compounds of principal interest to the
lime salesman is examined, it can be seen that these are
essentially combinations of the foregoing elements and that
the number of elements and compounds involved in the
chemistry of lime is relatively small.

When the formula of a compound involving lime in a chemical reaction is known, the amount of lime or limestone involved can be calculated by simple arithmetic by using the atomic weights as indicated. It should be borne in mind that the following examples are based on theoretical chemistry and pure compounds. This would not hold true in all applications since lime and limestone always contain some impurities. This means that the amount of lime or limestone calculated from rounded-off atomic weights and formulae will usually be from 5 to 10% by weight less than that realized in field practice. So, after the theoretical quantity of lime required has been calculated, it is a rule-of-thumb to add at least another 5% of this weight as a contingency.

Example 1

Let us consider the formula for high calcium limestone — this is $CaCO_3$. The formula weight is

$$Ca (40) + C (12) + 3 \text{ times } O (16) \text{ for a total of } 100$$

Of this total, the quicklime (CaO) portion is

$$Ca (40) + O (16) \text{ equal to } 56$$

So, the potential quicklime in high calcium limestone is

$$\frac{56}{100} = 56\%$$

Obviously, the carbon dioxide (CO_2) content is

$$\frac{44}{100} = 44\%$$

So, if 1000 tons of chemically pure high calcium limestone were completely calcined to high calcium quicklime, 560 tons of quicklime product would be produced.

Example 2.

Let us consider high calcium hydrated lime — $Ca(OH)_2$. Its formula weight is

$$Ca (40) + 2 \text{ times } O (16) + 2 \text{ times } H (1)$$
$$\text{for a total of } 74.$$

Section 11 - COMPETITIVE MATERIALS

In the environmental clean-up program, the lime salesman will encounter reagents which can be used in place of lime. In the fields of sewage treatment, and acids neutralization, as well as heavy metals precipitation and fixation, major competitive reagents are:

1. Alum (aluminum sulfate) [$Al_2(SO_4)_3$]

   Use: Phosphate precipitation and flocculation. Can be purchased as a solution or as a solid, which can be dissolved in water.

   Advantage: Ease of handling and application.

   Disadvantage: The sulfate part of this reagent remains dissolved in the water. Also lowers pH and sometimes requires subsequent lime addition for sulfate removal and pH control.

2. Ferric chloride ($FeCl_3$)

   Use. Municipal waste sludge conditioning, phosphate precipitation and sometimes for flocculation. Can be purchased either as a solution or as a solid, which can be dissolved in water.

   Advantage. Ease of handling and application.

   Disadvantage: The chloride portion remains dissolved in the water and lime cannot remove this because calcium chloride ($CaCl_2$) is water-soluable. However, ferric chloride lowers pH and lime may be subsequently needed for pH control. Also, ferric chloride has the disadvantage of being a very corrosive material. When $FeCl_3$ is used for sludge conditioning, lime is almost always required as an additive.

3. Copperas (ferrous sulfate) [$Fe_2(SO_4)_3$]

   Use. Flocculation and phosphate precipitation but rarely for municipal sludge conditioning.

   Advantage. Ease of handling and application.

When using pulverized limestone as a reagent for neutralizing sulfur oxide gases in scrubbers, the effect of carbon dioxide evolution is negligible.

In the so-called "dry" stack gas scrubbing operations even very finely pulverized limestone is not practical because of the relatively slow reaction rate of the limestone as compared with a slurry of high calcium lime. The EPA has conducted much research in an effort to increase the reaction rate of limestone neutralizations, particularly in wet scrubbers for sulfur oxides control. It has been established that a group of organic acids do increase the reaction efficiency sometimes sufficiently to obtain almost theoretical (stoichiometric) use of the limestone. Of these acids, adipic acid is currently being used in wet scrubbers operating on pulverized limestone. However, the savings resulting from better limestone usage may be offset by the cost of the organic acid.

As before stated, limestone at the source may be relatively inexpensive and even though its other cost factors may result in its final cost approaching, or even exceeding that of lime, it must be borne in mind that many producers of lime also market limestone. The foregoing comments have been presented to indicate the parameters between limestone and lime which should be taken into account when making an evaluation of the relative merits of these materials in acid neutralization operations.

Of this formula weight, the quicklime (CaO) is

$$\frac{56}{74} = 76\%$$

In other words, high calcium hydrated lime is theoretically 76% calcium oxide and 24% water.

Example 3.

Let us consider the use of atomic weight relationships for estimating the quantity of lime required when removing sulfur dioxide by scrubbing the stack gases from coal-burning operations. All coal contains some sulfur which during the combustion of the coal forms mostly sulfur dioxide (SO_2). This sulfur dioxide in either wet type or "dry" type stack gas scrubbers forms a chemical compound known as calcium sulfite containing some chemically-bound water. Its formula is $CaSO_3 \cdot \frac{1}{2}H_2O$. Whether this waste material from the scrubber is in the form of a wet sludge or a dry baghouse product, its formula is the same. The various impurities accompanying this material, such as fly ash, unreacted lime, etc., do not affect the calculations for estimating the amount of limestone or lime needed to theoretically react with the sulfur dioxide from coal-burning.

It is first necessary to obtain information on the amount of coal to be burned per hour or per day, the sulfur content of the coal or the weight of sulfur dioxide gas which will go up the stack. In the case of utilities, a rule-of-thumb is that it requires about one-half ton of coal to generate one megawatt of power. So, if the megawatt capacity of the generating station is known, the amount of coal to be used per hour can be estimated. The next step would be to ascertain the sulfur content of the coal. Usually this figure can be obtained from the user.

Let us assume the quantity of coal per hour and its sulfur content is known. We may then use the formula of the end product scrubber sludge [$CaSO_3 \cdot \frac{1}{2}H_2O$] and visualize this compound as $CaO \cdot SO_2 \cdot \frac{1}{2}H_2O$. Based on atomic weights, it is obvious that 56 units of CaO involve 32 units of sulfur (atomic weight of S is 32). This gives a lime to sulfur conversion factor of 56/32 or 1.75. In other words, if the weight of sulfur scrubbed per hour is multiplied by 1.75, this gives the theoretical quantity of

high calcium lime required per hour. Of course, the actual quantity in practice will depend upon the efficiency of the system and actual amount of lime used will be more than theoretical. However, this example affords a starting point in assessing the lime requirement for any particular amount of sulfur.

Section 10 - LIMESTONE VERSUS LIME FOR NEUTRALIZATION

High calcium limestone ($CaCO_3$) may be used in place of lime in acid neutralization. Limestone will react with acids and is used where a pH on the alkaline side of the scale is not required. Limestone can develop a pH somewhere between pH 5.5, and pH 6.0, as contrasted with lime which can develop a pH in excess of 12.0. This is not true for dolomitic limestone which reacts with acids at an impractical rate.

Usually the selection of limestone, rather than lime, is based on an abundance of high calcium limestone near its point of use. Its relatively low price FOB the mine or quarry may afford it an economic advantage. However, there are a number of factors other than origin and price which affect the economics of limestone use. Transportation cost is important because, theoretically, it requires about 100 pounds of high calcium limestone to produce the neutralizing effect of 54 pounds of calcium oxide. The limestone should be pulverized to about 200 mesh to obtain any kind of reaction efficiency. Various experiences in the field indicate that about 1.5 times the theoretical quantity of limestone is required; thus further adding to its relative cost. In addition, more than twice the weight of limestone must be handled as compared with lime. Finally, if hardening of limestone-produced sludge is desired, it is more difficult to harden as compared with a lime sludge. Other cost factors may affect the bottom line for limestone versus lime, but the foregoing are the major ones which should be taken into account.

It has been well-established that the presence of magnesium carbonate in the crystal structure of a high calcium limestone retards the rate of acid neutralization to a point where the limestone cannot be used. An unacceptable amount of magnesium carbonate is considered to be any amount in excess of 5% of the limestone. It is for this reason that dolomitic limestone is not used for acid neutralization. (However, this is not true for dolomitic lime, which is not similarly affected by the presence of magnesium).

In the neutralization of waste acids with limestone, copious amounts of carbon dioxide gas are liberated. This can become a hazard if the neutralization is carried out in a closed area.

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In recent years, it has been ascertained that sulfur oxide emissions from industrial operations in central Europe have destroyed fresh water lakes in Scandinavian countries. Still more recently, it has been ascertained that sulfur oxide emissions from the greater sulfur dioxide-producing areas in the United States have destroyed lakes in the northeast and in Canada. Indeed, there have been reports of acid rain injuring the health of forest lands in the Rocky Mountain west.

In the Scandinavian countries, the addition of limestone to the lakes to neutralize acidity is being practiced. At present, there is considerable interest in the continental United States and Canada to apply lime or limestone to lakes in order to combat the effects of acid rain. This situation is becoming increasingly serious because some lakes in the northeast and Canada have been completely destroyed for recreational purposes. In terms of sulfuric acid and acid rain and the need for control and neutralization, and the potential market for lime to control SO_2 emissions or neutralize acidity in this area staggers the imagination.

Section 3 - CONVERSION FACTORS

Other factors for converting weight of a material to the equivalent weight of high calcium quicklime are as follows:

| Weight Pounds, Tons, etc.	Conversion Factor
Sulfur (S)	1.75
Sulfur dioxide (SO_2)	0.88
Sulfur trioxide (SO_3)	0.70
Sulfuric acid (H_2SO_4)	0.57
Hydrochloric acid (HCl)	0.77
Phosphate (PO_4)	0.87
Ferric chloride ($FeCl_3$)	0.52
Ferrous sulfate [$Fe(SO_4)$]	0.37
Hydrogen fluoride (HF)	1.40
Bicarbonate (HCO_3)	0.46
Alum [$Al_2(SO_4)_3$]	0.49
High calcium hydrated lime	0.76
High calcium limestone	0.56

Weight of material multiplied by conversion factor gives weight of calcium oxide (theoretical).

Section 4 - CHEMICAL EQUATIONS

Having considered atomic weights of the elements and how a formula can be used for calculating percentage composition and weight relationships, we will next take an elementary look at chemical equations.

The word "equation" is derived from the word "equal". In short, an equation states that one relationship is equal to another. For example, $2 + 2 = 4$ is an equation; also $2 + 7 + 12 = 9 + 8 + 4$ is an equation. In algebra, $(x + y)$ times $(x - y) = x^2 - y^2$ is an equation. For practical purposes, the units in equations can be weight units, volume units, time or distance units, etc., so long as the total units are the same on each side of the equation.

From a chemical point of view, however, a chemical equation is more than just a relationship between an equal number of units. A chemical equation also describes the chemical reaction which takes place. The chemical equation must not only relate equal units on each side of the equation but it must also be a true statement of what happen chemically. For example,

$$Ca(CO_3) + heat = CaO + CO_2$$

$$\begin{matrix} 40 \; 12 \; 48 & & 40 \; 16 & 12 \; 32 \\ 100 & & & 100 \end{matrix}$$
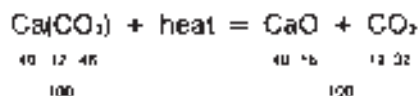
is a true chemical equation because the total weight of the elements on each side is the same and likewise, this reaction actually takes place when limestone is heated to produce calcium oxide and carbon dioxide.

Now, if we consider an equation in which high calcium limestone is reacted with sulfur dioxide in a stack gas scrubber, we could write:

$$Ca(CO_3) + SO_2 = Ca(SO_3) + C + O_2$$

$$\begin{matrix} 40 \; 12 \; 48 & 32 \; 64 & 40 \; 32 \; 48 & 12 & 32 \end{matrix}$$
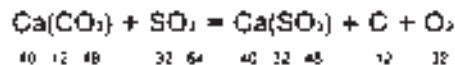
It can be seen that this equation satisfies the requirement that the total weight of all the elements is the same on each side of the equation. However, this is not a chemical equation because it does not state what actually takes place. Carbon and oxygen are not produced on the right-hand side. Instead, carbon dioxide is produced. Therefore,

consumption, can be assessed. Based on past experience and emerging data from the research underway, dry injection has little opportunity of success unless the present requirement for the removal of sulfur in the 90% range is reduced to around the 60% requirement, as indicated.

7. Sludge Hardening. This is a relatively new application for lime and the chemistry of the reactions involved is not yet well-understood. In some respects, sludge hardening may be visualized as "soil stabilization". It may be considered that the lime reacts with siliceous material and aluminum compounds added, or present, to form a crude cement. It has been established that fly ash from coal-burning reacts with excess lime in a wet scrubber sludge to bring about this hardening reaction. It has also been established that pulverized blast furnace slag will react with excess lime in a wet scrubber sludge to form a more or less hardened mass.

It is important, when considering lime for any sludge hardening process, that the precipitation and fixation of any heavy metals present be taken into account in terms of pH which must be developed. If hardened sludges are used for landfill, the EPA requires that the heavy metals present be "fixed" in such a manner that they cannot leach into surface waters or the underground water table.

8. Acid Rain. This section would not be complete without a brief reference to acid rain. Over many years of industrial growth, worldwide, vast quantities of sulfur dioxide have been released into the atmosphere. Likewise, over a long time period, this has moved in atmospheric patterns over great distances to finally be borne to earth by rain and snow in the form of acid rain:

$$SO_2 + H_2O = H_2SO_3 \text{ (sulfurous acid)}$$

$$SO_3 + H_2O = H_2SO_4 \text{ (sulfuric acid)}$$

Due to the reaction between sulfur dioxide and oxygen in the air, most of this rain has no doubt come down as sulfuric acid.

$$Ca(OH)_2 + H_2SO_3 \rightarrow CaSO_3 + 2H_2O$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$
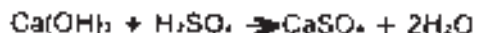
Both the calcium sulfite ($CaSO_3$) and the calcium sulfate ($CaSO_4$) are insoluable precipitates. It is the calcium sulfate (gypsum) which tends to stick to the internals of the scrubber and cause plugging. Both of these precipitates form an admixture of sludge which must be impounded or otherwise dewatered and used as land fill. As will be discussed later, these sludges can be hardened for possible other uses.

In the case of dry lime scrubbing, the chemical reactions are the same as in the case of wet scrubbing except these end products report as a dry sludge well-mixed with fly ash — all being collected in a baghouse. As far as lime is concerned, it is the weight relationship between the sulfur in the fuel and the calcium oxide required in the foregoing reactions that is important. While this can be calculated, more than the theoretical amount of lime is necessary, depending on the efficiency of the scrubbing system.

6. Dry Injection. Currently, there is renewed interest in the dry injection of alkaline material into coal-fired boilers for sulfur dioxides control. These materials; such as pulverized limestone, high calcium hydrated-lime, dolomitic pressure-hydrated lime and various sodium alkalis, may be dry-injected, mixed with the coal or as a separate stream.

It is known that these systems can react with around 60% of the sulfur in the coal with the resulting reaction products and fly ash being collected in electrostatic precipitators or baghouses. Revival of interest in these' systems largely resulted in increasing public concern over acid rain and the belief that Congress will enact legislation reducing requirements to all coal-burning operations. On this basis, the dry injection process appears promising as far as sulfur oxides control is concerned.

However, much research and pilot-plant testing will be required before the effect of the procedure on boiler operations; such as scaling, fuel efficiency and reagent

to satisfy the requirements of a chemical equation, this should be written

$$CaCO_3 + SO_2 = CaSO_3 + CO_2$$

This equation now satisfies both requirements. (For simplification, the fact that water is present has been ignored.)

There is one more consideration involving elementary chemical equations. This is known as "balancing" the equation. For example, if we consider the reaction between caustic soda and sulfurous acid, this may be written

$$Na(OH) + H_2SO_3 = Na_2(SO_3) + HOH \text{ (water)}$$

This equation is chemically true for the first two materials do react to form the second two materials. However, if the weights are added on each side of this equation, these will not be equal. To balance this equation, one must use two weight parts of caustic soda in order to have the two sodium atoms which are necessary to complete the formula on the right-hand side of the equation. The balanced equation then appears as follows

$$2Na(OH) + H_2SO_3 = Na_2(SO_3) + 2HOH \text{ (water)}$$

Of course, by using the weight relationships on each side of a balanced and true chemical equation, it can be calculated how much lime, limestone, caustic or other chemical is needed to react with some other chemical to produce still other chemicals, etc. This is very similar to calculating the same practical weight relationships using atomic weights and formulae as previously discussed. Chemical equations can become complicated and it really requires some background in chemistry to wrtie chemical equations correctly. However, it is hoped, that from the foregoing brief discussion, the significance of a chemical equation can be better understood when an equation is encountered in the course of lime applications.

Section 5 - A LAYMAN'S LOOK AT pH

When promoting the use of lime in the environmental clean-up program, the lime sales engineer often hears the term "pH". pH is a measure of acidity or alkalinity, pH is a measure of neutralization (NLA Bulletin No. 216), a guide for the precipitation of many metals, and it is one of the most frequent terms encountered in EPA specifications for liquid waste discharge.

To better understand the meaning of pH, we must first recall some arithmetic. Consider the following table:

$$10 \times 1 = 10$$
$$10 \times 10 = 100 = 10^2$$
$$10 \times 10 \times 10 = 1000 = 10^3$$
$$10 \times 10 \times 10 \times 10 = 10,000 = 10^4$$

Note that the exponent of 10 indicates the number of zeros following the numberal "1". Also note that in multiplying 10 x 10, these exponents are <u>added</u> — the exponents are <u>not</u> multiplied. For example, consider the following:

$$10^2(100) \times 10^2(100) = 10^4 = 10,000$$
$$10^2(100) \times 10^3(1,000) = 10^5 = 100,000$$

Now, the pH scale makes use of these exponents of 10, as will be explained. pH, in simple terms, means the concentration of hydrogen ion* in a water solution. Science has determined that water is neutral. The chemical formula for water is H_2O. However, this may be written as $H(OH)$. The important point here is that all acids in water solution cause a preponderance of hydrogen ion, whereas all alkalis in water solution cause a preponderance of (OH) ion, commonly referred to a hydroxyl.

Science has further established that in a neutral water solution, the concentration of hydrogen ion is $1/10^7$. A neutral solution is therefore considered to be a solution which has a pH of 7 and the acid-forming hydrogen ion and the alkaline-forming hydroxyl ion are of equal concentration.

* In water solution, some molecules break apart to form atoms having an electrical charge. These atoms are called ions. The hydrogen ion has a plus charge of one (+) and the hydroxyl ion has a negative charge of one (-)

metals. Lime is an excellent reagent for precipitating and "fixing" heavy metals. For example, the reaction between lime and ferric sulfate is

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Fe(OH)_3$$

Some of the heavy metals and the pH values at which they begin to precipitate are as follows:

| Metal	pH	Metal	pH	Metal	pH
Ferric		Ferrous		Zinc	7.0
iron	2.0	iron	5.5	Mercury	7.3
Aluminum	4.1	Lead	6.0	Manganese	8.5
Chromium*	5.3	Nickel	6.7	Cobalt	6.9
Copper	5.3	Cadmium	6.7		

Not every metal is completely precipitated from solution at the pH indicated. Ferrous iron begins to precipitate at a pH of about 5.5., but its precipitation is not completed until a pH of about 10.5 is achieved. Some heavy metals which are completely precipitated by lime at the start of precipitation form compounds which redissolve if the pH is too high. Examples of such metals are aluminum and zinc. Magnesium in solution is precipitated by calcium hydroxide at a pH of about 9.0. However, for practical purposes it may be assumed that almost all heavy metals can be precipitated by a lime slurry. Most of these precipitates are quite insoluable and, in terms of sludge behavior particularly for land disposal, may be considered as "fixed". Over a period of time, these precipitates tend to react with chemicals in the soil, air or water to revert toward their natural state as earthy minerals.

5. Stack Gas Scrubbing for Sulfur Oxides Control. In stack gas scrubbing, the principal chemical reaction in the scrubber is between the lime slurry and sulfur dioxide (SO_2). When fuel is burned, particularly coal, the sulfur is converted to sulfur dioxide by reacting with the oxygen in the combustion air. Since there is always some excess combustion air, some of the sulfur dioxide then goes on to react with the remaining oxygen to form sulfur trioxide (SO_3). The simplified equations for the reaction of these gases with lime are:

* Lime does not precipitate chromate chromium (CrO_4). The chromate must first be reduced to a lower valence state.

procedures but, rather, its use is minimized depending upon whether heavy metal fixation in the compost is necessary or whether incomplete incineration yields an odorous ash which is then treated with lime to destroy the odor. When trenching is used, either raw or treated sludge is simply buried in a trench and covered with earth. In this changing technology, there is yet a growing market for lime in the direct addition of high calcium quicklime to dewatered sludge cake from belt filter presses or centrifuges. Current technology is to add quicklime on the sludge conveyor belt which then discharges into a pug mill or other mixing device. This incorporates the quicklime into the sludge, consuming sludge water as the lime slakes. The end product is a friable odor-free material in which the heavy metals have been fixed and the pathogens destroyed.

3. Industrial Waste Acid Neutraliztion. The only acid of real interest to the lime salesman is waste sulfuric acid (H_2SO_4). Where nonrecoverable fluorides (F) are involved, lime can be used to treat these by precipitation of insoluble calcium fluoride (CaF_2). Phosphoric acid (H_3PO_4) is usually too valuable to be considered as a waste and is recovered. Hydrochloric acid (HCl) and nitric acid (HNO_3) are not only worth recovering but even in cases where recovery is not feasible, lime is not generally used for neutralization because the end products, calcium chloride ($CaCl_2$) and calcium nitrate [$Ca(NO_3)_2$], are completely water-soluble. The reaction between lime slurry and sulfuric acid is

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 \text{ (gypsum)} + 2H_2O$$
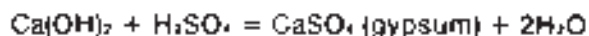
The gypsum (calcium sulfate) is the insoluble precipitated end product and is usually settled out as a sludge or it may be further dewatered on filters. This gypsum has little or no market potential because it is usually contaminated with heavy metals which are in the waste sulfuric acid.

4. Precipitation and Fixation of Heavy Metals. A chemical element is either a metal or a non-metal; although there are a few elements which are either, depending upon the chemistry involved. For example, sodium, potassium and lithium are classified as light metals. Iron, zinc, copper and nickel are examples of heavy

Finally, as far as this brief explanation of pH is concerned, science has also established that the concentration of hydrogen multiplied by the concentration of hydroxyl always equal $1/10^{14}$. This is the key point to understanding the pH scale.

The pH instrument is actually measuring an electrical impulse caused by the concentration of hydrogen in a water solution. Therefore, if the hydrogen concentration is $1/10^3$, the concentration of hydroxyl must be $1/10^{11}$, because (adding) 3 + 11 equals 14. On the other hand, if the concentration of hydrogen is $1/10^9$, the concentration of hydroxyl must be $1/10^5$ since (again adding) 9 + 5 equals 14.

Finally, let us consider what these concentrations of hydrogen mean. If the pH is 2, the concentration of hydrogen is $1/10^2$, which is 1/100. And this means that the concentration of hydroxyl must be $1/10^{12}$, which is 1/1,000,000,000,000. Obviously, a concentration of 1/100 is a lot stronger that 1/10,000,000,000,000. So, hydrogen predominates and at a pH of 2, this system is very acidic. Now let us consider a pH of 10. This means that the hydrogen concentration is 1/10,000,000,000 ($1/10^{10}$), while the hydroxyl concentration is 1/10,000 ($1/10^4$). In this case, the hydroxyl concentration is obviously greater than the hydrogen concentration, which means that hydroxyl (alkalinity) predominates, rather than hydrogen (acidity). So, a pH of 10 means the system is very alkaline.

As can be noted from the foregoing, only the exponents of 10 are used when referring to the pH scale. The arithmetic, as explained, is inferred. Neutrality is represented by a pH of 7, acidity is represented by those values below 7 and alkalinity is represented by those pH values above 7. The pH scale, simplified, is therefore the concentration of hydrogen using the exponents of 10 between 0 and 14.

Since slaked high calcium lime, $Ca(OH)_2$ and dolomitic lime [$Ca(OH)_2 \cdot MgO$] or [$Ca(OH)_2 \cdot Mg(OH)_2$] contain OH, they are hydroxyl donors, and hence are ideal materials for neutralizing the hydrogen concentration of acids. This is because hydrogen (H) + hydroxyl (OH) unite to form water (H_2O), which is neutral. In other words, the addition of slaked lime to an acid system with a low pH can increase the pH of this system to around pH 12.5, which is about the maximum pH that lime can develop.

This change in pH, using lime, causes most metals in solution to precipitate out as solid compounds as the pH is increased. The EPA prefers liquid waste discharge in the range of pH 6.5 to pH 8.5. However, in some cases, when certain metals are present, it is necessary to increase the pH beyond 8 in order to "fix" the metal and remove it from solution. This is probably how the term "fixing" heavy metals by pH control of municipal waste sludge originated.

a. incineration
b. landfill
c. trenching
d. fertilizer production

Since this sludge originates as a water slurry containing between 3 and 5 percent solids by weight, it usually must be dewatered before it can be further processed. Lime destroys sludge odors, kills sludge pathogens and fixes the heavy metals in sludge. In addition, lime imparts a residual alkalinity to neutralize the acids formed when sludge decays on the land.

Traditionally, sludge dewatering has been accomplished by adding a mixture of ferric chloride and high calcium lime slurry (as filter aides) to the sludge and then dewatering the mass on conventionl rotary vacuum filters. The resulting semisolid filter cake, practically odor-free, is then ready for some form of land disposal. This lime usage continues to represent a substantial market.

The availability of land for sludge disposal is diminishing and newer techniques for sludge dewatering and disposal are gaining ground. Organic reagents known as polymers are replacing the lime-ferric chloride systems and the belt filter and centrifuge are gaining in popularity over the rotary vacuum filter. One reason for this is to avoid the increase in weight of total solids in the dewatered sludge resulting from the addition of lime and ferric chloride. The amount of polyelectrolyte for sludge dewatering may be as little as 5 to 10 pounds per weight of dry solids. However, an even more important reason favoring polyelectrolytes is the growing popularity of composting the dewatered sludge cake or incinerating it. In the composting process with polyelectrolytes, dewatered sludge is mixed with wood chips and allowed to decay under controlled conditions of temperature and aeration to yield a material which can be used on forest lands and certain crop lands as a fertilizer. Likewise, the dewatered sludge, without the added burden of the inert lime and ferric chloride solids, is amenable to incineration to an ash which requires a minimum of disposal area. Lime is not necessarily eliminated by composting or incineration

timum flocculating and sludge settling conditions. Because some public waters cannot tolerate even the overflow from the secondary treatment basin, and because the reuse of sewage effluent may be desirable, some municipal waste treatment plants have, or are moving to tertiary treatment.

Tertiary treatment involves both the primary step and the secondary step and, in addition, a third step which removes heavy metals, phosphates and nitrates. Many of the heavy metals are toxic to aquatic life, and phosphates and nitrates are well-known fertilizers which cause excessive plant growth in rivers and lakes. Also, the heavy metals and phosphates are objectionable in water which is to be recycled for industrial purposes. Some tertiary treatment plants contain steps which finally yield an almost potable water.

Some, or all of the tertiary treatment steps may be juggled with reference to their position in the flowsheet of the tertiary process. The chemistry, as far as lime is concerned, is that lime precipitates phosphates and heavy metals. Also, pH adjustment with lime sets the stage for nitrate removal. This can be accomplished in the overflow from the secondary treatment by elevating the pH to some desired level. One procedure is to increase the pH to around pH 11, settle out the precipitated materials, and then blow the relatively clear overflow with air in ammonia "springing" towers. At the elevated pH, the nitrates in the sewage effluent are converted to ammonia (NH_3) which is then released to the air as the effluent cascades downward through a tower and meets the upcoming stream of forced air. In another system, the secondary effluent, at a carefully adjusted pH on the alkaline side, is impregnated with a bacteria which converts the nitrate to nitrogen which is then released into the air. It is obvious that the role of lime in the tertiary sewage treatment is both that of a precipitant and a pH adjuster.

2. Municipal Sludge Disposal. All three of the foregoing treatment processes produce a municipal waste sludge. The disposal of this sludge may be a major problem. The developing options for sewage sludge disposal are:

Section 6 - MEASURING ACID RAIN*

The acidity of any solution, including rain or snow, is measured on a scale known as a pH scale. This scale is numbered from 0 to 14. A pH value of 7 is neutral, neither acidic nor alkaline. Values lower than 7 are more acidic — vinegar, for instance, with a pH of between 2.4 and 3.4. Values above 7, such as for ammonia or lye, represent alkalinity.
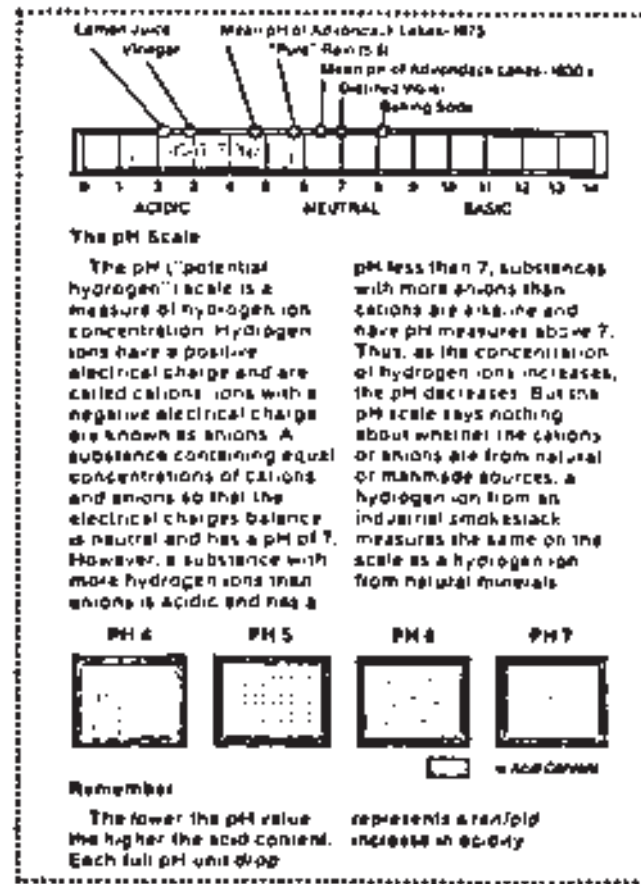
The pH scale is a logarithmic measure, that is, each change of one pH unit — say from 6 to 5 — represents a tenfold increase in acidity. Thus a drop from pH 6 to pH 4 represents a hundredfold increase and drop from pH 6 to pH 3 represents a thousandfold increase in acidity.

For rain or snow, acidity measurements reflect the balance of positive and negative ions in the precipitation (see box). The ions can come from a variety of compounds or elements (sulfur and nitrogen oxides, hydrogen, carbon oxides, chlorine, etc.) thus the total acidity of precipitation must take into account all of the sources of ions.

* EPA 600/9-79-036, Washington, D.C., July 1980

Section 7 · CHEMICAL CONSIDERATIONS INVOLVING LIME SLURRIES

Lime as a chemical reagent is usually applied in the form of a water slurry of suspended slaked lime particles. The objective of slaking is to obtain a high surface area of the hydrate in a water slurry which can be readily transported, metered, and mixed when applied. Depending upon the reactivity of the quicklime and the type of lime slaker used, slaking temperatures may range from as low as 160°F to near boiling. Higher slaking temperatures promote greater surface area. A well-slaked lime should result in hydrate particles of which about 95% will pass a 200-mesh standard sieve. Major considerations to keep in mind when producing and handling lime slurries are:

1. The chemical analysis of the water used for slaking is important. Sulfuric acid, heavy metal sulfates, phosphates, carbonates and other substances which form precipitates with lime are undesirable. The precipitates tend to coat the surface of the quicklime and prevent efficient contact with water. This retards the rate of slaking, the development of desired slaking temperature and causes an excess of gritty residue in the lime slaker. Such substances in the range of 10,000 ppm in the slaking water may be tolerated. When excessive, a ball mill slaker may be required since the grinding in the mill breaks up coating on the quicklime particles.

2. Precipitation in the lime slaker results in some loss of available lime. This is also true when water high in the referenced impurities is added to the lime slurry tank for dilution. However, using such water for dilution has no apparent adverse effect on the lime slurry since the precipitates adhere to the high surface area of the hydrate particles and scaling on the tank walls and agitation mechanism rarely occurs.

3   Scaling in lime slurry transport systems, including valves and pumps, can occur if dilution water containing the reference impurities is added down stream from the lime slurry holding tank. Such scaling occurs on the walls of the transport system (where velocity is theoretically zero) and can plug the system. Also, the inverse solubility of lime can cause serious scaling if the temperature of the transport system increases substan-

Section 9 · THE MAJOR USES FOR LIME IN THE ENVIRONMENTAL CLEAN-UP PROGRAM

These are presented with no particular order·

1. Municipal waste treatment (sewage).
2. Municipal waste sludge disposal.
3   Industrial waste acid neutralization
4. Precipitation and fixation of heavy metals.
5. Stack gas scrubbing for sulfur dioxides control.
6. Dry injection.
7. Sludge hardening.
8. Acid rain

1. Municipal Waste Treatment. This is divided into three categories; namely, primary, secondary and tertiary treatment. Primary treatment involves settling out such solid matter as will settle in a practicable time and the overflow from this settling operation goes directly into public waters or holding ponds. Usually no lime treatment is involved. Occasionally, a situation might exist in which the overflow water contains more heavy metals; such as iron, nickel, chromium, cadmium, zinc, etc., than can be tolerated. In this case, lime may be applied in the settling basin to precipitate heavy metals which then become a part of the sludge. The current goal of the EPA is to have all sewage treatment plants achieve at least a secondary treatment level.

Secondary treatment starts the same as primary treatment but has the additional step of the overflow from the primary settling basin going to still another basin (or basins) wherein bacteria can digest the soluble organic matter in the primary basin overflow. Bacterial digestion produces a secondary sludge which is commonly referred to as activated sludge. The purpose of the digestion is to remove soluble organic matter so that this will not consume oxygen when it decays in the receiving waters. This is known as lowering biochemical oxygen demand (BOD). The sludge formed in the secondary digestion chambers may not settle-out too well. For this reason, a flocculating agent; such as alum or ferric chloride is sometimes added in the secondary basin and pH adjusted with lime to produce the op-

cidents involving lime are caused by the hot lime slurry, either in or coming from the lime slaker. If the slaking temperature is sufficiently hot, severe skin burns can occur from the temperature — not the lime, and adequate precautions in this area should always be taken.

tially downstream from the lime slurry holding tank. Another cause of scaling in systems where calcium sulfate ($CaSO_4$) is an end product of the reaction is the tendency of calcium sulfate to supersaturate its solution. As this supersaturation is relieved, severe scaling may result, particularly on the overflow of thickeners. One remedial procedure is to add magnesium to the system in the range of from 3 to 6% by weight of calcium oxide (CaO). Magnesium may be obtained in the form of dolomitic lime or magnesium sulfate.

4. The use of flexible lines to prevent scale in lime slurry transport systems merits special attention. Especially smooth surfaces, such as glass and plastic, have not been proved successful for preventing the adherence of scale. However, lines which can flex, such as thin-walled suspended plastic, rubber and flexible hose, in general, are very successful since if the transport line moves or is mechanically deformed, scale cannot adhere. Finally, in some situations where none of the foregoing procedures can be used for scale prevention, it is possible to keep the slurry transport lines open by "pigging" or by routine flushing of the lines with an inhibited acid.

5. Some quicklimes, when slaked with potable water or plant water, yield slurries having viscosities which are undesirable from a slurry handling point of view. This usually occurs when the hydrate solids are in excess of 15% by weight. Viscosity can be measured by the viscometer. However, a common practice to ascertain relative viscosities is to measure the rate of flow of the slurry from a pipette or through a laboratory filter funnel. Viscosity can be broken by the addition of chemicals to the quicklime before slaking or into the resulting lime slurry. There are organic chemicals which break viscosity. One of the more common materials is raw pulverized gypsum ($CaSO_4 \bullet 2H_2O$), which is usually added to the quicklime in the range of 0.5% to 1.0% by weight of calcium oxide. Also, the ash pond water of public utilities is an excellent viscosity breaker when used for slaking, whether or not the pond water is on the alkaline or acid side. This use of ash pond water has proved very successful when lime slurries in the range of 20 to 25% hydrate solids by weight are required for spray-dry scrubbers. It is prudent to undertake laboratory experiments when developing a procedure to "break" the viscosity of a slaked lime slurry.

Section 6 - LIME HANDLING

Pebble quicklime is usually shipped via rail in covered hopper cars, or in pneumatically-unloaded trucks. The hoppers may discharge into an air-conveying system or be unloaded by screw conveyor and elevator to the storage tank. Since so many deliveries of pebble quicklime are made by trucks, a well-designed system for handling truck deliveries can be described as follows:

1. The quicklime is in a size range of from about $1\frac{1}{2}$ inches to dust. The standard four-inch unloading line from the truck is connected to the lime receiving line with unloading pressure in the range of six to ten pounds.

2. The transport line is not horizontal. Rather, it is inclined to the maximum angle possible, with the line to the top of the receiving tank being near vertical. The line has no sharp bends but, rather, makes curving sweeps as necessary on about a four-foot radius. (This observation pertains to the relatively limited air volume and pressure of pneumatic truck unloading). When the lime is unloaded into a surge tank for transport to final storage some distance away, horizontal runs involving the necessary larger air volume and pressure are feasible.

3. The lime storage bin has a 60° sloping bottom including a "live bin" at the bottom of the cone to ensure that the lime does not hang up in the tank and is easily fed from the bottom. The storage tank also has a dust collector at the top and a heavy, loose-fitting manhole cover which can blow out if the dust collector should become plugged or the unloading system should otherwise undergo excessive pressure (this blow out port must be well anchored)

4. From this bin, the lime is discharged into a screw conveyor which transports the lime to a smaller "day tank" which discharges, again, through a live bin bottom to a belt conveyor which discharges the lime into the lime slaker.

5. The lime slaker is offset sufficiently from the day bin to prevent any steam or moisture from the slaking operation to work backward into the storage tank or conveying mechanisms. Also, the slaker is operated under negative pressure. The slaker, if not a ball mill, rejects the core into a mechanism which enables the core to be received in a suitable container for subsequent disposal.

6. The lime slurry is discharged from the slaker onto a screen which removes the remaining fine core to a size consistent with the end use of the lime slurry. The lime slurry is pumped to the lime slurry storage tank, which is maintained under mild agitation to prevent the slurry solids from settling and compacting. Dilution water is added in the slurry tank to produce a slurry of desired concentration.

7. From the slurry tank, the slurry is pumped by a positive displacement pump, which is well-sealed so that no inward air leakage can occur. At the end of the slurry line, the slurry is fed to point of application. At this point, there is sufficient agitation, or turbulence, to disperse the lime slurry quickly in the reaction system. The slurry feed is controlled by pH measurements sufficiently downstream from the slurry addition point to allow the reaction to be nearly completed at the point of pH measurement.

8. Finally, takeoff points along the lime slurry loop are vertical to prevent solids buildup behind the takeoff valve when it is closed. The valves are a flexible "squeeze-type" which aid in preventing lime solids from plugging the valve itself.

9. With reference to safety and health factors, lime is not a hazardous material per se. It is alkaline and can cause skin irritations on moist areas of the body. Indeed, some individuals may be allergic to lime, in which case, a physician should be consulted as to type of clothing, etc. for best protection. Lime has no record as a material which causes damage to the respiratory system. However, it can be dangerous to the eye and should always be washed therefrom promptly. Eye washes should be accessible within a few seconds. If lime, either dry or as a slurry, contacts the eye, the eye should not be rubbed because minor amounts of grit in the lime can scratch the eye. It is common practice to rub the eyeball with petroleum jelly or equivalent after the eye has first been thoroughly washed. Most ac-