

TYPES OF CALCIUM REAGENTS AND THEIR APPLICATION IN ACID MINE DRAINAGE AND ABANDONED MINE LAND RECLAMATION¹

M.C. Schrock² and J.K. Mercer³

Abstract: Lime is a generic term applied to a variety of calcium based reagents. This paper will discuss the different types of calcium reagents available, their origin and their physical characteristics. The paper also discusses application methods for calcium reagents and the effect preparation has on the utilization efficiency of the reagent, as well as the reagent's suitability for use in acid mine drainage treatment and abandoned mine land reclamation.

A research project undertaken by Carmeuse Lime & Stone (CLS) examined the effects of water temperature on the reaction between quicklime and water. While mine drainage water was not specifically used for the experiments, certain extrapolations can be made based on the results. Suggestions will be given to maximize utilization efficiency for quicklime products.

Cool slaking water temperature retards reaction rate, lowers final slaking temperature, and decreases the utilization efficiency of reagent. Testing showed an increase in particle size as slaking water temperature was decreased. Low utilization efficiency and larger particle size increases the amount of residue left at the end of slaking.

Water chemistry can have a large impact on slaking and should be of interest when using lime for the treatment of mine drainage. Waters containing more than 500 mg/l of sulfates, sulfites, or bisulfites are considered unsuitable for slaking.

Calcium reagent costs can differ greatly, as can their relative utilization efficiency in a given process. Low reagent cost does not always equate to lowest operating cost if utilization efficiency is low. A simple comparison tool is presented to illustrate the relative costs of a variety of calcium reagent materials and forms.

Additional Key Words: lime, limestone, quicklime, hydrated lime, lime kiln dust, waste lime, slaker, slaking.

¹ Paper was presented at the 2010 National Meeting of the American Society of Mining and Reclamation, Pittsburgh, PA *Bridging Reclamation, Science and the Community* June 5 - 11, 2010. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

² Michael Schrock, Technical Marketing Manager-Environmental Industries, Carmeuse Lime & Stone Co., 3600 Neville Rd., Pittsburgh, PA, 15225, ³Julia Mercer, Engineering Specialist, Carmeuse Lime & Stone Co., 3600 Neville Rd, Pittsburgh, PA, 15225, Proceedings America Society of Mining and Reclamation, 2010 pp 1018-1039
DOI: 10.21000/JASMR10011018

<http://dx.doi.org/10.21000JASMR10011018>

What is Lime?

Lime is a generic term that may be applied to several different materials. It is important to understand the different forms of lime that are available when selecting one for a specific process or application. By strict definition, the term lime may refer to quicklime (CaO) or hydrated lime (Ca(OH)₂). It is very different from limestone (CaCO₃) which is often confused with lime because pulverized or granulated limestone is frequently marketed as agricultural lime (ag-lime). Limestone is the raw material from which quicklime is made. Hydrated lime is produced by combining quicklime and water at the appropriate ratio using specialized equipment.

Types of Quicklime

High calcium limestone is comprised mainly of CaCO₃, while dolomitic and magnesian limestones are comprised of both MgCO₃. Limestone is heated in a kiln at high temperature using a process called calcination. When limestone is heated, CO₂ is released from the stone. Quicklime is the product of calcination. Quicklime is comprised of the oxides of calcium and magnesium (CaO and MgO, respectively).

High calcium quicklime is produced from high calcium limestone via the following reaction:



Dolomitic or magnesian quicklime is produced from dolomitic or magnesian limestone via the following reaction:



High calcium, magnesian, and dolomitic quicklimes may be classified by the fraction of magnesium oxide they contain.

Table 1. Classification of Quicklime Based on Magnesium Oxide Content (Oates, 1998)

Type of Quicklime	Amount of MgO Wt-%
High Calcium	0 - 5
Magnesian	5 - 35
Dolomitic	35 - 50

A Note on Quality

While quicklime product quality can vary depending on what type of kiln is used for calcining, it is important to understand that the calcination process can affect only some of the quality characteristics of the final product like residual CO₂ and reactivity. Other characteristics like chemical impurities are a “heritage” of the stone chemical quality and the calcination process will only amplify their concentration, as carbon dioxide leaves the stone. As a rule of thumb, we can consider that the weight percentage of impurities in the stone will double with calcination.

Some typical quality parameters for quicklime, hydrated lime, and co-products of lime such as lime kiln dust and waste lime include:

- Available lime (AvCaO)
- Magnesium oxide content (MgO)
- Calcium carbonate equivalence (CCE)
- Reactivity
- Size and/or particle size distribution
- Moisture (hydrate and co-products)
- Viscosity (slurry)
- Sedimentation rate (slurry)
- Other quality parameters may be specified depending on the application.

Foundation of Hydration / Slaking – the Conversion of Quicklime to Hydrated Lime

Quicklime is sometimes called hot lime because of the amount of heat released when it is mixed with water. Hydration is the reversible exothermic chemical reaction between quicklime and water. During slaking, water also serves as a dilution agent.

It is not the purpose of this paper to discuss hydration and/or slaking in detail, though certain aspects of these processes are pertinent to a discussion on reagent utilization in acid mine drainage treatment. Relevant synergies are presented and discussed in the appropriate sections that follow. For more detailed discussion of slaking or hydration and the equipment used to accomplish both, readers may choose to review the resources listed in the Reference list that accompanies this paper.

By convention, the two processes (hydration and slaking) can be distinguished by the physical differences between the finished products:

Hydration → water addition is minimized and the product is a dry powder

Slaking → water addition is controlled, though in excess of that required for hydration; the product is a slurry or suspension of hydroxide particles in water

Hydration

By mixing quicklime with water in the correct proportion, hydrated lime is created and heat is released. Hydrated lime is a dry, fine, white powder – as such, its production process is sometimes referred to as “dry slaking.”

Theoretically to produce high calcium hydrated lime, 24.3% of water (by weight) is needed to accomplish a complete hydration of 100% pure quicklime. In real life, around 50% of water is required to achieve full hydration due to the water losses in steam, un-combined water, etc. Quicklime adsorbs water into its pores readily. As water penetrates the lime, heat is produced and this exerts pressure on the lime physical structure. The lime fractures into multiple pieces in a chain reaction.

High calcium quicklime hydrates / dehydrates via the following general reaction:

High Calcium Quicklime + Water ⇌ Hydrated Lime + Heat



Dolomitic lime may also be hydrated, though the process is somewhat different than the hydration of high calcium lime. When dolomitic quicklime is hydrated at atmospheric pressure, Type N dolomitic hydrated lime is produced. In Type N dolomitic hydrated lime, only the calcium oxide fraction of the quicklime hydrates. Only a small portion of the magnesium oxide hydrates at atmospheric conditions.

Dolomitic Quicklime + Water @ atm pressure ⇌ Type N Dolomitic Hydrated Lime + Heat



When dolomitic quicklime is hydrated under pressure, Type S dolomitic hydrated lime is produced. In Type S dolomitic hydrated lime, both the calcium oxide and the magnesium oxide fractions of the quicklime are hydrated.

Dolomitic Quicklime + Water + pressure \Leftrightarrow Type S Dolomitic Hydrated Lime + Heat



By the nature of its production process, hydrated lime is comprised of very fine particles. The chemical composition of hydrated lime reflects the composition of the quicklime from which it was produced, as well as the method of hydration and the physical classification (air classification, milling, or screening) steps after hydration. When hydrated lime is mixed with water, no heat is released.

Slaking

The term slaking is generally understood to refer to “wet slaking” or the hydration of quicklime in the presence of an excess of water. In terms of the reactions occurring, the chemistry of quicklime hydration in a slaker is identical to that taking place in a hydrator. There is a wide variety of slaking equipment manufacturers and slaker designs available in the marketplace to manufacture lime slurry. Ultimately, the goal of lime slaking is to produce lime slurry with a high quality that can be used in an efficient manner. Preferred quality attributes include:

- Small calcium hydroxide particle size
- finely divided calcium hydroxide particles
- minimal unreacted quicklime
- minimal contaminant material
- appropriate density
- acceptable viscosity

It is very difficult to completely slake dolomitic quicklime and magnesian quicklimes with high magnesium oxide (MgO) levels using conventional slaking equipment. Practice has shown that once MgO level in quicklime rises above about 10 wt-%, the hydration efficiency of the MgO declines rapidly. This is due not only to the chemical equilibrium constraints imposed by trying to hydrate MgO at or near atmospheric pressure, but also due to the fact that increased levels of MgO impede reaching an adequate temperature for efficient hydration of calcium oxide, let alone MgO. Magnesian quicklimes with less than 8% MgO are slaked efficiently in conventional slaking equipment and several million tons are used annually in flue gas desulfurization systems in the Ohio Valley.

Factors that affect slaking/hydration:

- Purity of quicklime
- MgO content of quicklime – too high of a MgO level can affect efficiency
- Size and form of quicklime – quicklime is available in a variety of size ranges
- Temperature of hydration/slaking water – warmer water increases efficiency
- Operating temperature of the hydrator/slaker –temperature has a direct correlation on efficiency and final product quality
- Amount of water (Water to Lime or W:L ratio, by weight) – dependent on the type of equipment used and in the case of slakers, the density of the slurry produced
- Quality of water (specifically total dissolved solids or TDS content) – waters with high concentrations of dissolved solids decrease efficiency
- Agitation/mixing in the hydrator/slaker – good agitation helps increase efficiency
- Residence time in the hydrator/slaker – adequate residence time coupled with a reactive quicklime ensures complete hydration of the quicklime

A Note on Delivered Lime Slurry (Milk-Of-Lime or MOL)

Some suppliers sell pre-made hydrated lime slurries that can be easier to use, though more expensive on a CaO equivalent basis. These slurries may be manufactured using the cold route – mixing hydrated lime and water to produce a slurry of desired physical properties, or the hot route – slaking quicklime under exact conditions to yield a slurry with desired physical properties. Care should be exercised when choosing a slurried product, as some manufacturers add other materials to stabilize the slurry. These additives may result in exceeding a pH of 12.5 or add additional compounds that may not be desirable in the receiving stream.

Lime Kiln Dust

Lime Kiln Dust (LKD) is a co-product from the manufacture of quicklime and is sometimes referred to as baghouse lime. Lime kiln dust contains un-reacted limestone (calcium/magnesium carbonates), quicklime (calcium/magnesium oxides), fly ash when the kiln is coal fired (the ash component of the combusted coal), and some minor levels of gypsum (calcium sulfate produced from the reaction in the kiln of residual sulfur with quicklime). These components are products of commerce and lime kiln dust is currently sold into market applications that use limestone, quicklime, or fly ash products.

Physically, lime kiln dust is a dry, finely divided powder that will vary in color depending on the limestone fired, the type of kiln used, and the kiln fuel used during its production. The quicklime fraction in the LKD will react with water to produce heat. Sometimes lime kiln dust is available as a mulled, or wetted product that more closely resembles a crumbled filter cake or wetted soil.

Lime kiln dust has been used in product applications including soil stabilization for sub-bases prior to highway and other pavement construction (as a substitute for quicklime and/or fly ash), land remediation projects, i.e. abandoned mine land reclamation or acidic overburden neutralization (as a substitute for quicklime or limestone), solid waste treatment (as a substitute for quicklime), and as a cement additive (as a substitute for limestone).

Waste Lime

Waste lime or yard waste is a co-product from the manufacture of quicklime. Its production rate varies, depending on kiln operation, housekeeping and other operational factors at the lime plant. Waste lime typically contains un-reacted limestone (calcium/magnesium carbonates), quicklime (calcium/magnesium oxides), hydrated lime (calcium/magnesium hydroxides), and lime kiln dust. The material collected as waste lime is usually collected separately or segregated from typical product streams as it typically originates from spills, or is comprised of off-spec material produced during start up or shut down of kilns and hydrators, that cannot otherwise be sold and is thus excluded from product silos or bins.

Physically, waste lime may contain finely divided powder reminiscent of lime kiln dust or hydrated lime, pebble or lump quicklime, and unfired raw stone that may be 1 ½ to 2 inches in size. The quicklime fraction in waste lime will react with water to produce heat. Sometimes waste lime is available as a mulled, or wetted product that more closely resembles a crumbled filter cake or wetted soil.

Waste lime has been used in product applications that include ag-liming (with size reduction and/or screening), land remediation projects, i.e. abandoned mine land reclamation or acidic overburden neutralization (as a substitute for quicklime or limestone), and in solid waste treatment (as a substitute for quicklime or limestone).

Storage of Lime Products

The shelf life of lime products is dependent on the packaging and storage methods used. Bags are typically multi-walled in construction and may have an added ply that is moisture proof. Although these bags are designed to be effective against humid air, they are not designed to be effective against liquid water. If exposed to water, the heat generated from slaking and the resulting swelling may cause bags of quicklime to burst. Bulk silos must be weather-tight and handling equipment such as screws or feeders should be emptied after use to prevent plugging.

Properly packaged and stored lime products can last for months. Packaging & storage container design play a large role in carbonation. The National Lime Association (NLA) provides minimal comment on carbonation of bagged hydrated lime. They indicate that “carbonation during storage is usually evident only after storage for at least 6 months and then does not penetrate more than about one-half inch into the bag near the valve.” (NLA, 1995) Quicklime can deteriorate at a faster rate than hydrated lime when stored improperly. In either case, it is good practice to use material in the order it is received rather than maintain a large inactive reserve. Lime that has been stored for extended periods may not need to be discarded. However, it may be necessary to use more reagent than usual when using material that has been stored for an extended period.

Some lime products can be a challenge to store and use in water-powered dosing equipment. Quicklime fines, hydrated lime, and lime kiln dust may all experience bridging problems in silos that do not have mechanical vibrators or air pulse or sweep systems. These concerns certainly play a role in designing a water-powered dosing system that will have limited human attendance. Moisture intrusion from the receiving stream or hydraulic drive equipment can compound these problems, so care must be taken to ensure that no water from the receiving or carrier stream contacts dry lime products in the handling equipment.

Waste lime is typically stored outdoors, however it is good practice to store it under cover of some sort to prevent pile erosion and washing. Mulled lime kiln dust can also be stored outdoors and under cover. One must realize that motorized handling equipment is required to move materials that are wet/damp and at least partially exposed to the weather. Storage in a silo, like those used for quicklime or hydrated lime, is not recommended – though some open top hopper configurations might be feasible when designed specifically for these products. Additionally,

size reduction or screening equipment should be used to help increase utilization efficiency and prevent plugging or dam formation in the receiving or carrier stream.

The Quicklime – Water Reaction and its Correlation to Acid Mine Drainage

A great deal of qualitative comparison indicates that slaking water temperature has a direct effect on slaking time and lime utilization. However, it is often difficult to locate quantitative data to support this statement. A research project undertaken by Carmeuse Lime & Stone (CLS) examined the effects of water temperature on the reaction between quicklime and water. One of the goals of the project was to develop a dataset that could be used to illustrate the types of trends that can be expected when modifications are made to enhance slaker operation. While mine drainage water was not specifically used for the experiments, certain extrapolations can be made based on the results.

The water to lime ratio also affects slaking time by affecting the slaking temperature. Variations in this ratio were examined as part of the CLS project. Higher temperatures generally equate to shorter slaking times. Controlling a constant water to lime ratio in a slaker does not guarantee a constant operating temperature. Operating temperature will vary due to variations in water temperature, lime reactivity, and quality of water. It is preferable to adjust the water to lime ratio to control the slaking temperature.

A wide variety of quicklimes were tested as part of this program - originating from different limestone sources, having been fired in different kiln types at different operating conditions, and of several different size gradations. To present all of the data collected would be beyond the scope of this paper. Data from individual samples that illustrate trends exhibited by virtually all of the quicklimes tested are shown in this paper. Figures 1 and 2 illustrate the effect of slaking water temperature on both the reaction rate and final slaking temperature for one quicklime sample at a variety of water to lime ratios. Figure 1 shows a raw data set that illustrates the effects of both water to lime ratio and slaking water temperature on slaking rate and total temperature rise.

Figure 2 “smooths” the data set from Figure 1 to illustrate the greater impact that slaking water temperature has on slaking rate and total temperature rise. Figure 2 also illustrates that the ASTM method for measuring slaking rate and temperature rise is not always consistent with what is observed when slaking “as received” quicklime at 25°C, even though the ASTM method

uses 25°C slaking water. In the case of the sample shown in Figure 2, both the slaking rate and total temperature rise were apparently affected by the particle size reduction that the ASTM standard specifies (6 mesh particle size). As a trend across all of the quicklimes examined during the test program, initial slaking rate tended to be lower during the ASTM tests as compared to the “as received” tests at 25°C, while the final slaking temperatures were equal to or higher using the ASTM test method. The sample shown in Figure 2 is the exception to that trend.

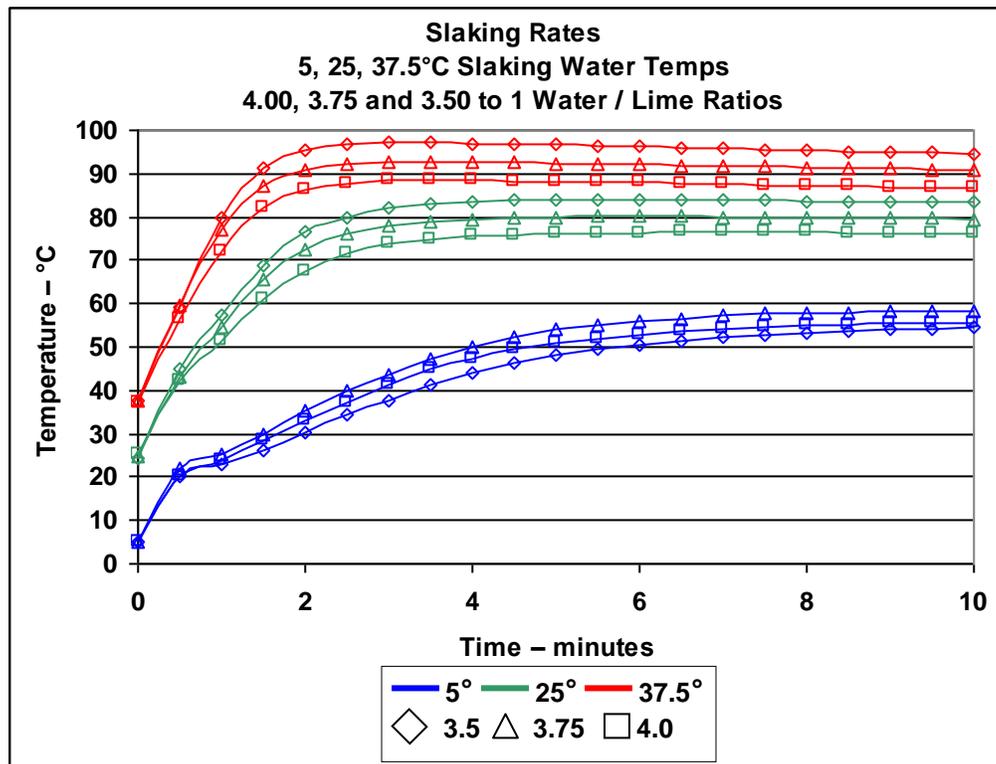


Figure 1. Slaking Rate vs. Slaking Water Temperature, CLS Test Data

As further proof of the negative effect of using cool water for slaking, it is interesting to note that most slaker manufacturers have implemented water jacket designs into their slakers to pre-heat cool slaking water before introducing it into the slaking chamber. If cool water is used for slaking without pre-heating, a condition called “drowning” can occur. Particles of hydrate formed under “drowning” conditions can be coarse and not very reactive.

Given these facts, it is not surprising that dry-dosing quicklime in mine drainage treatment results in less than optimal quicklime utilization. Surface waters can approach freezing during

the winter months in the north, and underground discharges, while of constant temperature, generally aren't much above about 15°C, which presents much less than an optimal temperature for slaking water. Slaking water should be at least 65°C (150°F) by the time it is mixed (contacted) with the quicklime. (Hassibi, 1999)

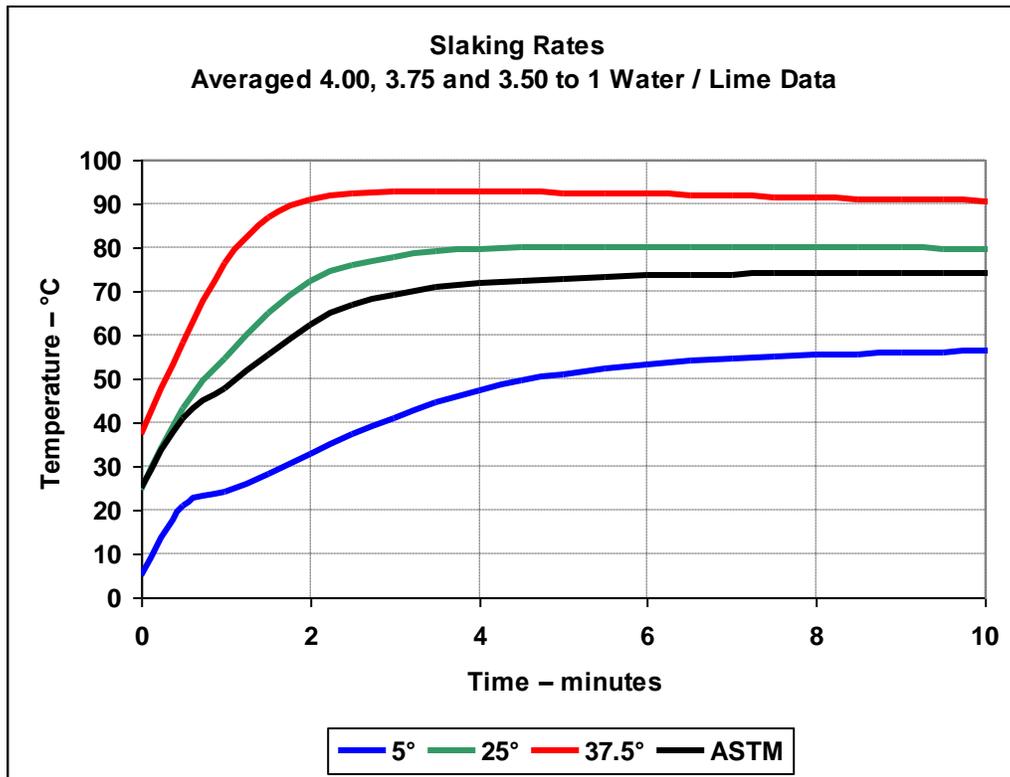


Figure 2. Smoothed Data - Slaking Rate vs. Slaking Water Temperature, CLS Test Data

After slaking tests were run, the final slurry was screened to gauge the impacts of water temperature and water to lime ratio on the amount of residue left at the end of slaking. The amount of residue larger than 60 mesh (250 um) should be removed rather easily by screening or settling equipment after slaking. Samples were also screened at 200 mesh (75 um) because experience has shown that the fraction retained at 200 mesh is a good (and quickly measured) indication of slaking efficiency. Figures 3 and 4 demonstrate the effect of decreasing slaking water temperature on the quantity of residue gathered during the reactivity tests illustrated in Fig. 1 and 2.

The data shown represents the weight percent retained on the screen size shown, therefore the fraction retained on a 200 mesh screen includes all of the material retained on the 60 mesh

screen, i.e. the >200 mesh number is the cumulative percent retained on both the 60 and 200 mesh screens.

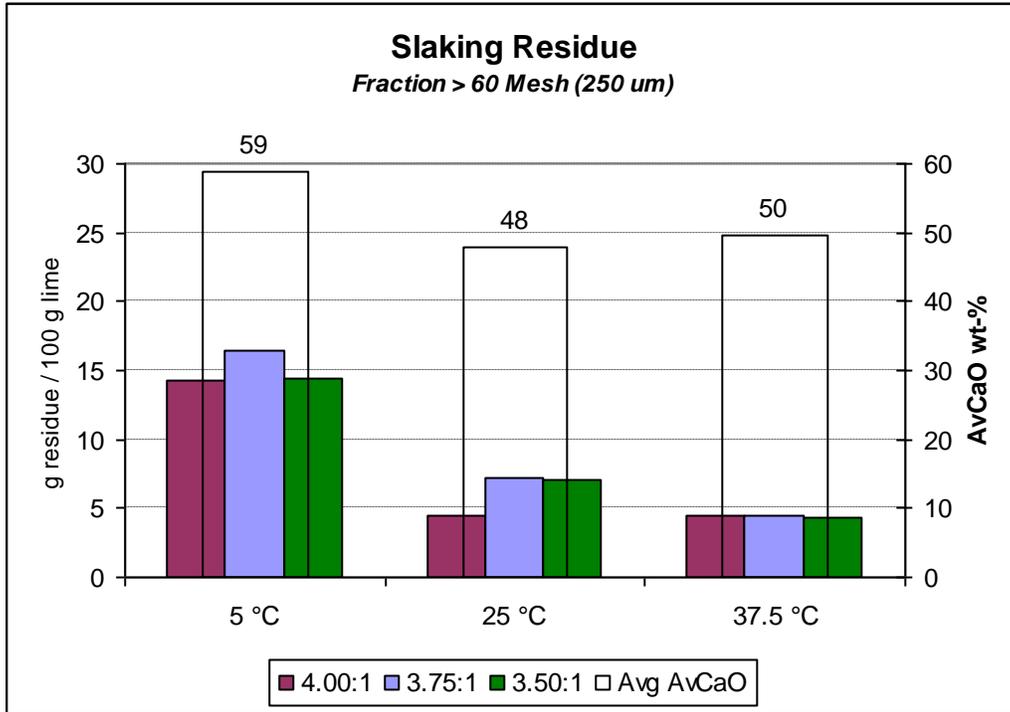


Figure 3. 60 mesh Slaking Residue vs. Slaking Water Temperature, CLS Test Data

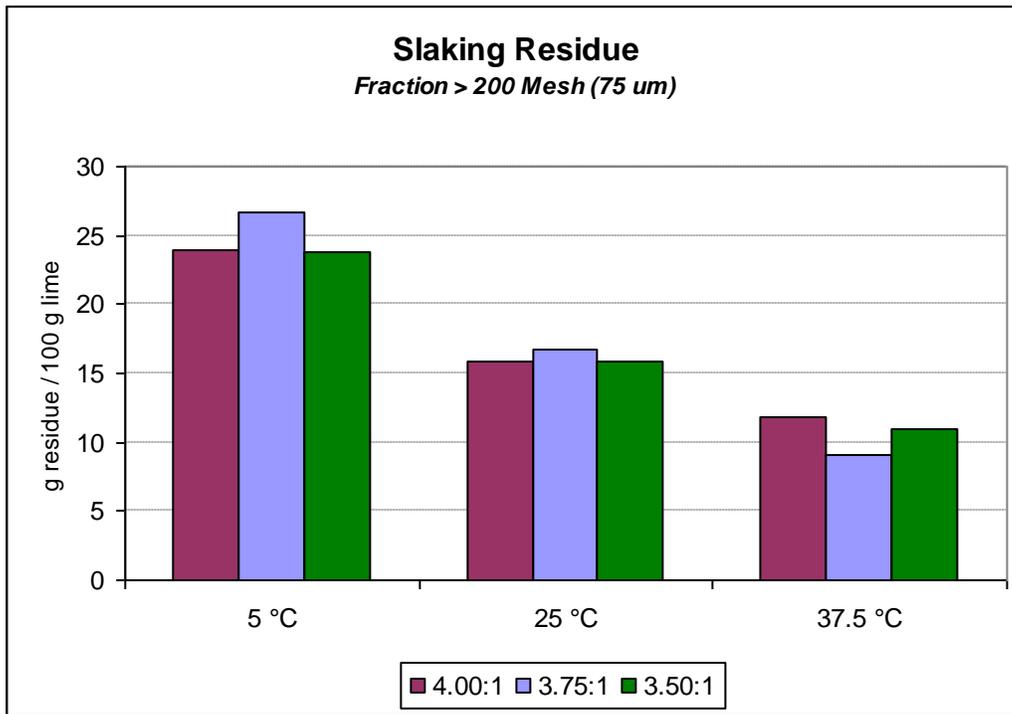


Figure 4. 200 mesh Slaking Residue vs. Slaking Water Temperature, CLS Test Data

Residue collected on the 60 mesh screens was tested to determine the amount of available lime (AvCaO) in the material. This material represents quicklime that did not slake and is thus waste from the system. One can see that increasing the starting water temperature had decreased both the quantity of residue collected and generally the amount of AvCaO in the residue. The AvCaO test was not conducted on the 200 mesh residues collected during the test program.

Figures 3 and 4 clearly show that poor slaking conditions can result in very large amounts of wasted quicklime exiting a slaking system. The values shown on these graphs are the weight of residue per 100 weight of quicklime slaked. Therefore, we can calculate that for every 100 grams of quicklime slaked using 5°C slaking water, we are wasting almost 9 g of available lime, assuming the 60 mesh material is removed from the prepared lime slurry.

Based on experience with similar residue samples gathered from a variety of sources, it is not unreasonable to assume that the available lime in the 200 mesh is similar (if not higher) than that seen in the 60 mesh samples. In a mine treatment application where 200 mesh material enters a quiescent or semi-quiescent zone, it is likely that these particles will settle from the receiving stream and few if any will react (slake) to completion. Carrying our calculations one step forward, if the available lime in the 200 mesh sample is similar to the 60 mesh sample, almost 15 g of available lime could be wasted per 100 g of quicklime fed to the system. These numbers are actually optimistic in a dry dosing situation, because as poor as the results are, they were run in a controlled atmosphere where slaking temperature was maximized – which is obviously not the case in a field deployed dry dosing system.

Table 2 shows summary particle size distribution data from several screened slurry samples made during testing. The numbers shown in the body of the Table represent the particle size that a specified fraction (volumetric percent) of the particles in suspension are smaller than. As an example, for the 5°C data in the Table, 10 vol-% of the particles in the sample analyzed were smaller than 1.52 micron (μm). It is interesting to note that for this sample, the particle size distribution of the slurry remained unchanged despite the dramatic changes in slaking water temperature. Other samples showed an increase in the amount of large particulate matter in the slurries being analyzed, as slaking water temperature was decreased – in some cases D90 values almost doubled with a decrease in slaking water temperature from 37.5°C to 5°C.

The values shown in Table 2 represent the averages of three samples made at different water to lime ratios, with the exception of the ASTM values which are from a single sample.

Table 2. Water Temperature Effect on Particle Size Distribution, CLS Test Data

Temperature	ASTM (25°C)	5°C	25°C	37.5°C
µm – 10%	1.54	1.52	1.50	1.67
µm – 50%	3.33	3.40	3.33	3.62
µm – 90%	6.03	6.56	6.28	6.54
µm – Mean	3.64	3.85	3.71	3.95

Figures 5 and 6 show particle size analysis results that compare the size distribution of a suspension of hydrated lime particles prepared by the “hot route” (Fig. 5) versus the size distribution of a suspension of hydrated lime particles prepared by the “cold route” (Fig. 6). The “hot route” implies production using wet slaking, while the “cold route” implies slurry manufacture using commercial hydrated lime. Both used the same quicklime feed. Note the similarities in the sizing of these two samples, despite being prepared using two different methods.

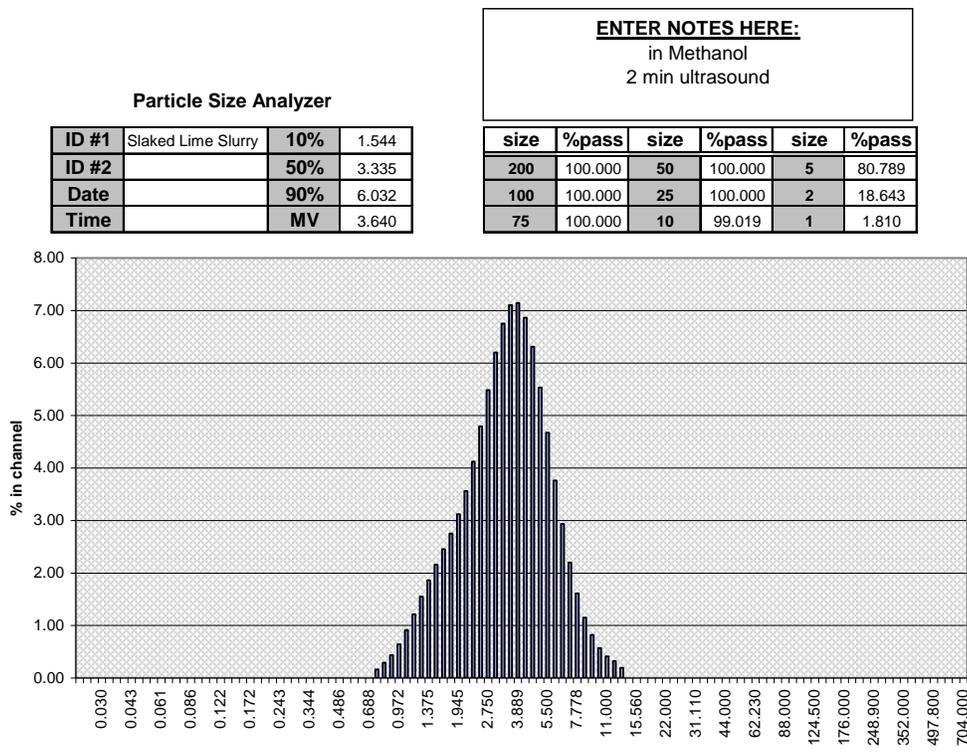


Figure 5. Slaked Lime Slurry Particle Size Distribution, CLS Test Data

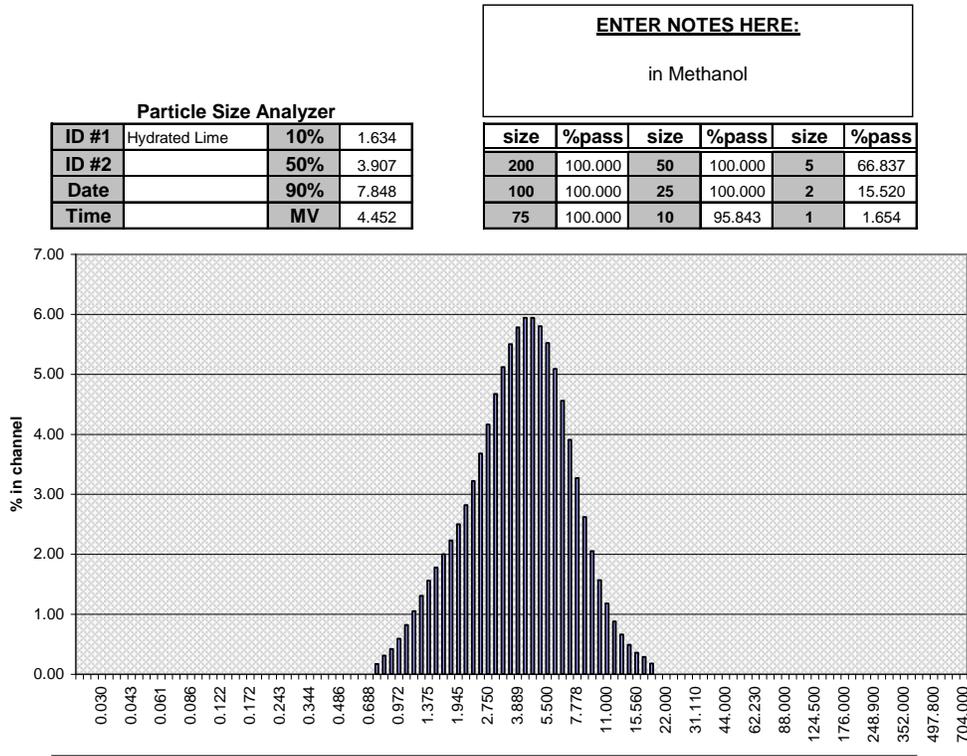


Figure 6. Hydrated Lime Slurry Particle Size Distribution, CLS Test Data

The Effect of Dissolved Salts on the Quicklime – Water Reaction

Water chemistry can have a large impact on slaking and should be of interest when using lime for the treatment of mine drainage. Some dissolved salts will accelerate the slaking process while others will retard it. Chlorides and sugars can have an accelerating effect on the slaking process. However, while brines have been used for slaking, corrosion becomes a driving factor when choosing the material of construction for the slaker. Figure 7 illustrates the effect of chlorides on the reaction of quicklime with water.

It should be noted that recent experiences trying to slake quicklime in a calcium chloride waste stream resulted in extremely poor quicklime utilization and the production of large amounts of coated quicklime particles that settled quickly and did not participate in the process. The results seen were in a system that had a very high calcium chloride concentration and based on the literature available; do not seem to be typical of what might be expected in dilute systems. It is thought that the majority of the coating material was comprised of a calcium hydroxichloride compound produced via the following reaction (Allal, et. al., 1997):

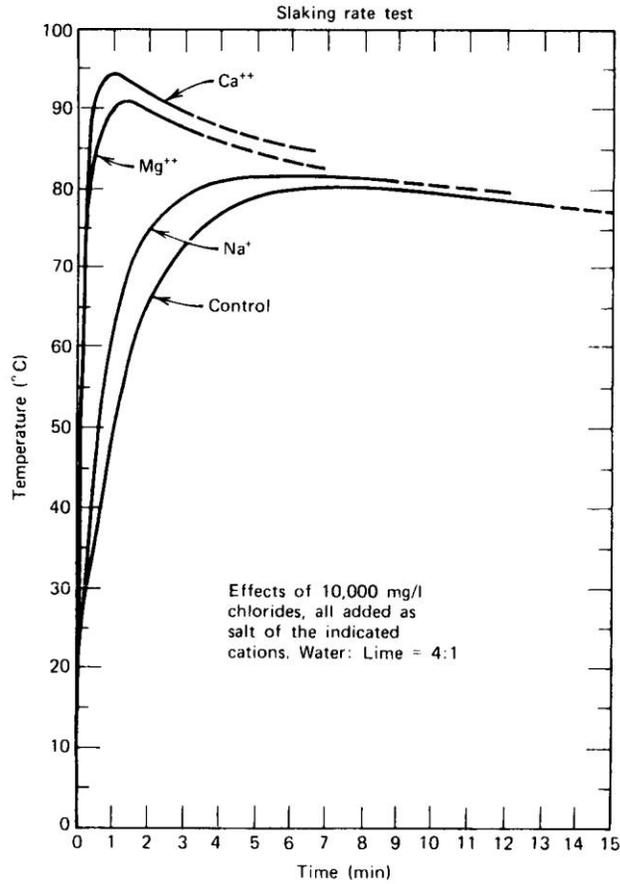
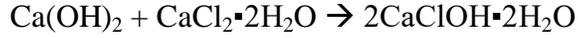


Figure 7. The Effect of Chlorides on the Quicklime – Water Reaction (Boynton, 1980)

Waters containing more than 500 mg/l of sulfates, sulfites, or bisulfites are considered unsuitable for slaking. Figure 8 illustrates the effects on temperature rise of sulfate containing slaking water. Calcium sulfate and sulfite salts of low solubility tend to precipitate on the surface of the quicklime pebbles and not allow water to penetrate the pores. The presence of sulfates, sulfites and bisulfites reduces hydrate yield, increases residue, and creates coarse particles that settle more rapidly than those produced from cleaner slaking water. Some of these issues can be overcome by in ball mill slaking systems that have the capability of exposing clean calcium oxide surface area to water through grinding, however as a rule, one would not recommend using these waters for slaking.

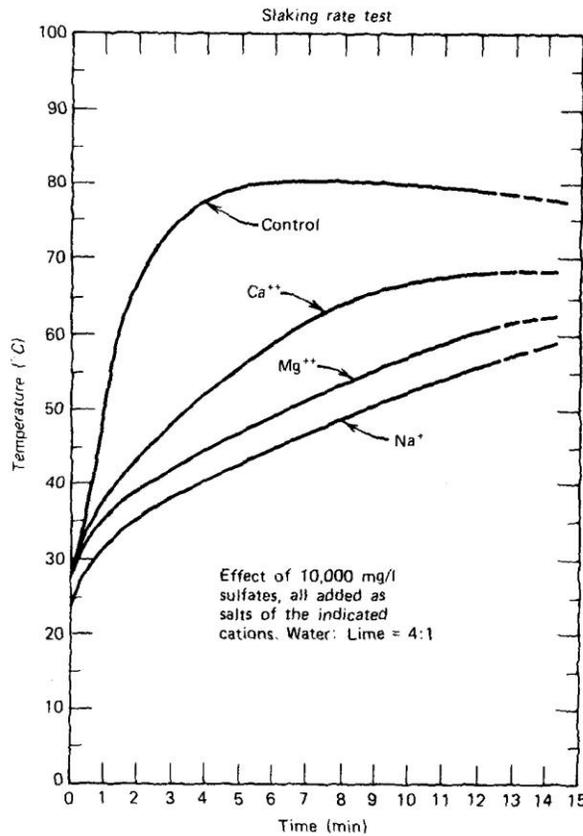


Figure 8. The Effect of Sulfates on the Quicklime – Water Reaction (Boynton, 1980)

Hydrated Lime and Purchased Hydrated Lime Slurry in Mine Drainage Treatment

Many of the problems associated with slaking quicklime can be overcome by purchasing hydrated lime directly from the manufacturer. As shown previously in Fig. 5 and 6, the particle size distributions of hydrated lime and hydrated lime in slurry produced via slaking can be very similar with the same quicklime source. The decision then becomes one of convenience. Table 3 lists some of the variety of reasons why one might choose one form of calcium reagent over another.

Table 3. Pros and Cons of Quicklime vs. Hydrated Lime

	Quicklime	Hydrated Lime
Cost per ton	cheaper	more expensive
Capital Cost (slurry production)	more expensive	cheaper
O&M (slurry production)	more expensive	cheaper
Material handling	easier	more difficult
Utilization efficiency	lower	higher

A note should be made about the purchase of pre-made lime slurry. Pre-manufactured lime slurry is available in various parts of the US and Canada for use in treating mine drainage. There are certainly advantages to purchasing a pre-made slurry, such as: no expensive silo, no slurring equipment (slaker or metering system), presumably less O&M due to less moving equipment, etc. However purchasing lime slurry can also have drawbacks, such as a need for agitation and freeze protection in northern climates. Ultimately, the choice of lime slurry vs. quicklime vs. hydrated lime becomes a combination of economics and site utilities availability.

Relative Cost of Lime Products

In terms of neutralizing capacity, or ability to raise pH, 1 ton of high calcium quicklime is theoretically equivalent to about 1.3 tons of high calcium hydrated lime. This is due to the water that was added to the material during the conversion of quicklime to hydrated lime, and to a lesser degree the difference in the amount of impurities in the two materials. Therefore, theoretically it will be necessary to add about 30% more hydrated lime on a weight basis to neutralize a given quantity of acid or to achieve the same pH rise.

The price of a lime product is made up of two costs, the actual reagent cost and the transportation cost to have the material delivered to the treatment site. The United States Geologic Survey (USGS) data indicates that the average cost of quicklime used for acid mine drainage treatment during 2008 was \$83.46 per short ton. The average cost of hydrated lime for acid mine drainage treatment during 2008 was \$96.63 per short ton.

Theoretically, 1.3 times as much hydrated lime is required to accomplish the same work (raising pH as well as precipitating metals & insoluble salts) as 1 ton of quicklime. Therefore, one must purchase \$125.62 worth of hydrated lime to do the equivalent work of \$83.46 worth of quicklime.

$$\$96.63 \times 1.3 = \$125.62 \quad \equiv \quad \$83.46$$

Now consider that transportation for the additional hydrated lime requirement must also be paid for. Assuming delivery costs \$20 per ton of material regardless of type, the delivered cost of quicklime rises to \$103.46 but the delivered cost of an equivalent amount of hydrated lime balloons to \$137.41

$$(\$96.63 \times 1.3) + (\$20 \times 1.3) = \$151.62 \quad \equiv \quad \$103.46$$

Theoretically, if 1 ton of quicklime is used for treatment, one would pay over 50% more on a delivered basis to utilize hydrated lime to treat the same waste.

However, one must try to take into account a variety of other factors when calculating the real economic advantage of one form of calcium versus another. Table 4 helps to illustrate the comparable costs of quicklime, hydrated lime, and hydrated lime slurry used to treat a hypothetical discharge where purities and utilization rates are less than theoretical. Quicklime and hydrated lime costs used are based on 2008 USGS data for lime products. Hydrated lime slurry cost is assumed and is given on a \$ / short ton of Ca(OH)_2 basis. Cost calculations are those associated with the reagents only – fob cost and transportation cost – and do not include any advantages associated with lower sludge production (pond dredging & disposal) realized by decreasing the quantity of un-utilized reagent being collected or differences in capital cost of equipment to store and dispense the materials.

The major assumption in Table 4 was the low utilization efficiency for quicklime (60%) - which may be relatively close to many actual results using dry pebble quicklime dosing. The hydrated lime utilization efficiency was then adjusted until the reagent cost on a dollar per day basis was identical to quicklime, which occurred at an 88% Ca(OH)_2 use efficiency. Lime slurry utilization was maximized at 100%, which minimized the slurry reagent cost (\$1,317/day). The authors acknowledges that this is a very crude calculator that does not account for many factors associated with reagent selection. However, it can be useful screening tool to determine relative reagent savings that might be spent on equipment and/or O&M with more complicated systems.

Conclusions

Lime is a generic term that is applied to several different materials. Not all materials called lime are suitable for all applications. Agricultural lime is actually limestone and may not provide the neutralization capacity as or may not have the same physical properties of quicklime or hydrated lime. Additionally, different types of quicklime (high calcium, dolomitic, magnesian) and different types of hydrated lime (high calcium, Type N dolomitic, Type S dolomitic) have different properties as well.

Table 4. Reagent Cost Contributions

SLURRY & SOLUTION CONCENTRATIONS AND CONVERSION FACTORS

SLURRY / SOL'N INFO	Quicklime CaO	Hydrated Lime Ca(OH)2	Hydrated Lime Slurry Ca(OH)2 slurry
Reagent slurry (by wt.) = reagent solids (dry lbs/gal)			35% 3.65

PRICING

TRUCK WEIGHT & VOLUME CALCULATIONS

Assume 25 ton max truck weight.
Assume 4,500 gal max truck volume.

	CaO	Ca(OH)2	Ca(OH)2 slurry
ton slurry or sol'n / truck			23
gal slurry or sol'n / truck			4,414
ton dry reagent / truck	25	24	8.1

REAGENT DELIVERED COST CALCULATION

FOB \$/ton dry solids	\$	83.46	\$	96.63	\$	200.00
Freight \$/ton dry mat'l on truck	\$	20.00	\$	20.00	\$	25.00
Freight \$/ton mat'l on truck	\$	20.00	\$	20.00	\$	8.75
ton dry solids / truck		25		24		8.1
ton water / truck						14.9

CHEMICAL PURITY & UTILIZATION EFFICIENCY ASSUMPTIONS

	CaO	Ca(OH)2	Ca(OH)2 slurry
Purity	93%	95%	95%
Utilization Efficiency	60%	88%	100%

ACIDITY LOADING AND REAGENT USE CALCULATIONS

Flow (gpm)	250
Acidity (mg/L as CaCO3)	5,000
Acid load (tpy as CaCO3)	2,629

	CaO	Ca(OH)2	Ca(OH)2 slurry
REAGENT NEEDED			
tons/year	1,473	1,946	1,946
REAGENT PURCHASED			
tons/year	2,640	2,341	2,048
SLURRY / SOLUTION			
ton/year			5,853
gal/year			1,123,189
WATER			
ton/year of H2O			3,804
gal/year of H2O			912,191
IMPURITIES			
tons/year	185	117	102
UNUSED REAGENT			
tons/year	982	278	-
COSTS			
\$/day	\$ 780	\$ 780	\$ 1,317
\$/year	\$ 273,095	\$ 273,047	\$ 460,915
\$/year reagent utilized	\$ 122,929	\$ 188,049	\$ 389,214
\$/year transportation	\$ 52,792	\$ 46,823	\$ 17,926
\$/year for impurity	\$ 15,421	\$ 11,311	\$ 20,485
\$/year for inefficiency	\$ 81,953	\$ 26,864	\$ -
\$/year free water			\$ 33,290

The shelf life of lime products is dependent on the packaging and storage methods used. Bags are designed to be effective against humid air, but not liquid water. Bulk silos should be weather-tight and handling equipment such as screws or feeders should be emptied after use to prevent plugging. Properly packaged and stored lime products can last for months. However, it may be necessary to use more reagent than usual when dosing with material that has been stored for an extended period.

A research project undertaken by Carmeuse Lime & Stone (CLS) examined the effects of water temperature on the reaction between quicklime and water, to develop a dataset that could be used to illustrate the types of trends that can be expected when modifications are made to enhance slaker operation. While mine drainage water was not specifically used for the experiments, certain extrapolations can be made based on the results. The water to lime ratio affects slaking time by influencing the slaking temperature and variations in this ratio were examined as part of the CLS project.

Higher temperatures generally equate to shorter slaking times. The effect of cooler slaking water temperature on both the reaction rate and final slaking temperature on quicklime at constant water to lime ratio is to reduce reactivity and reduce final slaking temperature. As further proof of the negative effect of using cool water for slaking, it is important to note that most slaker manufacturers have implemented water jacket designs into their slakers to pre-heat cool slaking water before introducing it into the slaking chamber.

Low water temperature not only retards slaking, but also increases the amount of residue left at the end of slaking. Typically the residue produced during inefficient slaking contains a large fraction of available lime. This material represents quicklime that did not slake and is thus waste from the system. Increasing water temperature generally decreases both the quantity of residue collected and the amount of available lime in the residue.

In general, testing showed an increase of the largest particle sizes in the slurries being analyzed, as slaking water temperature was decreased. Calcium hydroxide particle size distribution was very similar regardless of preparation method when using the same quicklime source.

Water chemistry can have a large impact on slaking and should be of interest when using lime for the treatment of mine drainage. Chlorides and sugars can have an accelerating effect on

the slaking process while waters containing more than 500 mg/l of sulfates, sulfites, or bisulfites are considered unsuitable for slaking. The presence of sulfates, sulfites and bisulfites reduces hydrate yield, increases residue, and creates coarse particles that settle more rapidly than those produced from cleaner slaking water.

Hydrated lime products can cost more on a weight basis than quicklime, but often times offer higher utilization efficiencies than quicklime. Sometimes the increases in efficiency are enough to overcome the difference in material price. However, one must try to take into account a variety of other factors when calculating the real economic advantage of one form of calcium versus another. There may be other advantages / disadvantages with some reagent forms such as: lower residue production (pond dredging & disposal), differences in capital cost of equipment, and differences in ease of storage and dispensing.

Literature Cited

- Allal, K.M. , Dolignier, Martin, 1997, Determination of Thermodynamical Data of Calcium Hydroxide, Institut Francais du Petrole, Vol. 52, No. 3, May-June 1997
- Boynton, Robert S., 1980, Chemistry and Technology of Lime and Limestone, John Wiley & Sons, Inc. Second Edition.
- Hassibi, M., 1999, An Overview of Lime Slaking and Factors that Affect the Process , 3RD International Sorbalit Symposium November 3-5, 1999, New Orleans, LA USA
- National Lime Association, 1995, Lime Handling Application and Storage Bulletin 213, 7th. Edition, Arlington, Va. 22203
- Oates, J.A.H., 1998. Lime and Limestone, Chemistry, Technology, Production and Uses, Wiley VCH. <http://dx.doi.org/10.1002/9783527612024>.