Competitive Reagent Primer:

Use of Lime Products in Water Treatment

Lime products are an ideal choice for adjusting pH, adding alkalinity and precipitating metals and in almost all drinking water or waste water treatment applications. Carmeuse’s products are certified NSF 60 Drinking Water Treatment Chemicals and all of our high calcium products exceed AWWA B202-07 Standards for Drinking Water.

For the vast majority of water treatment applications, the end user needs a high quality and low cost source of hydroxide anions, which is exactly what Carmeuse’s Quicklime and Hydrated Lime offer. Both Quicklime and Hydrated Lime offer pH-adjusting hydroxide anions for much less cost than sodium hydroxide, sodium carbonate, magnesium hydroxide and magnesium oxide.

Lime products have many properties in water that make them superior to sodium or magnesium based reagents.

- Lime product pricing has been stable throughout the years and is not subject to large swings in variation due to byproduct demand.

- Quicklime and hydrated lime reagents are delivered dry with no water. This means the end user is not paying for 42% water (in the case of magnesium hydroxide) or 50% water (in the case of the most concentrated sodium hydroxide solution available) to be delivered to their plant. Lime products generally have shorter, greener lead times and delivery distances since magnesium hydroxide and sodium hydroxide are often shipped across the US to the user. There are many more lime plants in the US compared to sodium and magnesium reagent manufacturing plants which ensures cost-competitive pricing and less transportation cost for the end user. It also ensures a shorter delivery time.

- Long transportation distances adds cost by making the user pay to ship water a great distance to their facility. These practices are not sustainable and should be considered in the selection of reagents. The end user should also investigate where the sodium or magnesium reagent originates from, not just the terminal location to evaluate real transportation distances. Further, the energy used in the manufacturing process of pH adjusting reagents should be considered when choosing the best reagent. Both sodium and magnesium reagents’ energy requirements in the manufacturing process are inherently higher than lime products which adds additional cost for the end user.

- Quicklime has the highest neutralizing capacity per pound of dry solids compared to any other alkaline reagent. See the table at the end of this report for data on neutralizing capacity per pound of dry solids. Since lime products are much less expensive they are the overwhelming reagent of choice for neutralizing acids.

- Stoichiometry dictates that approximately 20% less magnesium needs to be dosed in alkaline conditions to provide alkalinity in biological treatment when compared to lime products. However, the much lower cost of lime products outweighs any benefit of marginally lower dose rates.
• Lime products produce fewer total dissolved solids (TDS) when neutralizing sulfuric acids compared to sodium or magnesium reagents since these reagents create soluble reaction byproducts. With some states restricting TDS in waste water discharges, this could be an important factor to avoid more expensive forms of TDS removal.

• Carmeuse performed acid neutralization tests to quantify the benefits of fewer dissolved solids when using lime products to neutralize sulfuric acid. We used two different commercial grade hydrated lime products and reagent grade sodium carbonate, sodium hydroxide and magnesium hydroxide to neutralize 1.5 weight percent sulfuric acid. The dissolved species in mg/L left in the neutralized liquor can be seen in the table below. Note the initial pH was 0.7 and final pH was 9.3 for all reagents except magnesium hydroxide; where the end pH was 8.8 (since pH would not rise higher). This table shows the much lower dissolved solids numbers lime creates when neutralizing sulfuric acid.

<table>
<thead>
<tr>
<th>Dissolved species in finished effluent in mg/L</th>
<th>Hydrated Lime 1</th>
<th>Hydrated Lime 2</th>
<th>Sodium Carbonate</th>
<th>Sodium Hydroxide</th>
<th>Magnesium Hydroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>641</td>
<td>603</td>
<td>2</td>
<td>2</td>
<td>37</td>
</tr>
<tr>
<td>Mg</td>
<td>85</td>
<td>150</td>
<td>1</td>
<td>0</td>
<td>3,795</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>1,843</td>
<td>1,900</td>
<td>15,304</td>
<td>15,680</td>
<td>15,504</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>2</td>
<td>8,091</td>
<td>7,763</td>
<td>7</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>2,570</td>
<td>2,655</td>
<td>23,398</td>
<td>23,445</td>
<td>19,343</td>
</tr>
</tbody>
</table>

• Precipitation applications are best suited for lime products because of the physical properties of lime sludges. Lime products precipitate heavy metal contaminants readily and form a Blanket Floc sludge mechanism. Blanket Floc mechanism occurs when lime precipitates adhere to other lime precipitates while settling to the bottom of a tank or clarifier. As lime precipitates settle, they contact other suspended solids (ie metals, non-metals and nutrients) which pulls suspended solids into the floc; decreasing turbidity, suspended solids and effectively filtering the effluent. The particles become physically entrapped within the settling floc and are subject to adsorption to ensure particles stay in the sludge. Once lime precipitates reach the bottom of the tank or clarifier, they compact in volume due to the weight of the sludge, forcing moisture out of the sludge and thus dewatering readily. Sodium and magnesium precipitates are very small, require long times to settle, larger reactor residence times and are extremely sensitive to any mixing during the settling process. Sodium and magnesium precipitates do not compact and often require expensive coagulants and flocculants to aid settling. As a result, these sludges are difficult to dewater due to high moisture content.

• In precipitation applications, lime products are the least expensive source of alkali to precipitate equivalent amounts of metals. This means from a treatment and cost standpoint, lime products are the best solution to optimize treatment for less.

• Fluoride, Sulfate and Phosphate are precipitated with lime products but not with sodium or magnesium reagents.
• Lime products are able to raise pH adequately to precipitate heavy metals. Since magnesium reagents’ maximum pH is 9.0, it is not able reach high pH to precipitate the majority of metal hydroxides, which generally precipitate from pH 9.0-11.0. For example, magnesium hydroxide cannot precipitate Lead (pH 9.3), Silver (12.0), Zinc (9.1), Nickel (10.1) and Cadmium (pH 10.8) to their least soluble points. Lime products are able to reach pH 12.45 and precipitate metal hydroxides readily, but do not reach a hazardous pH while doing so.

• Magnesium reagent solubility is ten times less than calcium reagent solubility. This means in a water application lime products will react with the water faster and will deliver pH correction easily in an upset situation. This also means when using lime products reactors don’t have to be sized larger to allow for the slow equilibrium time of magnesium reagents to react with water or to allow more residence time for sludge to completely settle. When building a new plant, less residence time equates to less capital expense.

• Further, because magnesium products take substantially more time to react with water and because the sludge is amorphous, it is very easily overdosed into processes. This practice is not sustainable and can become very expensive with the cost of magnesium reagents. Since lime products react quickly with water, the user can ensure pH is correct without fear of overdosing and wasting reagent.

• Lime products provide calcium micronutrients to biological treatment systems and provide alkalinity and pH adjustment, not only pH adjustment as occurs when using sodium hydroxide. Lime products will not form drastic pH hot spots of pH 14 that can kill microbes.

• When treating biosolids, lime products’ pH of 12.45 will aid in BOD reduction, pathogen removal, virus destruction and reducing vector attraction. Quicklime can be used to add heat to stabilize biosolids per EPA’s 503 B regulations, which cannot be done with sodium or magnesium reagents. Lime treatment allows biosolids to be beneficially reused which reduces or eliminates landfill costs and space in landfills. Magnesium hydroxide’s pH of 9.0 is not high enough to disinfect biosolids, reduce pathogens, viruses or discourage vector attraction. Sodium hydroxide’s hazardous pH of 14 cannot be used safely for land application.

• Lime products precipitate phosphorous to very low levels without the need for biological treatment systems. Waste water plants use lime products to ensure that when phosphorous levels fluctuate, the discharge levels are still in compliance. Sodium and magnesium reagents alone cannot precipitate phosphorous in a simple 1-step precipitation process like lime products can.

• Finally, Lime products are not hazardous and don’t require heating. According to Dow, the freezing point of 50% sodium hydroxide solutions is 58°F and viscosity increases rapidly below 65°F (http://www.dow.com/causticsoda/offer/physical.htm).

Unless specific sodium or magnesium precipitation chemistry is warranted in the drinking water or waste water application, lime products can be used to provide a high quality, cost effective solution for your water treatment application. Many applications simply require a reagent which is affordable and quickly reacting with good settling properties. When coupled with the better availability of lime
products to the market, lime products make a better reagent of choice for almost all water treatment applications.

<table>
<thead>
<tr>
<th>Product</th>
<th>Lime (Calcium Oxide or Hydroxide)</th>
<th>Soda Ash (Sodium Carbonate)</th>
<th>Caustic Soda (Sodium Hydroxide)</th>
<th>Magnesium Hydroxide</th>
</tr>
</thead>
</table>
| Form of Material | Solid - CaO  
Powder-Ca(OH)₂  
Shurry 55%-Ca(OH)₂ | Powder - Na₂CO₃  
Solution 15%-Na₂CO₃ | Solution 50%-NaOH  
Shurry 58%-Mg(OH)₂ |
| Alkali Requirement Per Ton H₂SO₄ Per Ton HCl | As CaO:  
1,240 lbs.  
1,670 lbs. | 2,160 lbs.  
2,900 lbs. | 1,630 lbs.  
1,690 lbs. | 1,190 lbs.  
1,600 lbs. |
| Cost Per Ton of Neutralizing Agent (on a dry basis) | CaO - $60  
Ca(OH)₂ - $80  
Shurry Ca(OH)₂ - $100  
Cost Stable | Na₂CO₃ - $80  
Cost Variable | NaOH - $280  
Cost Highly Variable | Mg(OH)₂ - $300  
Cost Increasing |
| Cost to Neutralize 1 Ton of H₂SO₄ | CaO - $37  
Ca(OH)₂ - $66  
Shurry Ca(OH)₂ - $82 | Na₂CO₃ - $86  
Cost Variable | NaOH - $228  
Cost Highly Variable | Mg(OH)₂ - $179  
Cost Increasing |
| Maximum pH @ 25° C | 12.45  
>11 | 14  
10.6 |
| Sludge Profile | Heavy, Low Volume, but easy handling, even if heavy metals present | High Volume, gel-like when heavy metals present | High Volume, gel-like when heavy metals present | Heavy, Low Volume |
| Salts | Insoluble calcium metal hydroxyl salts | Soluble sodium salts | Soluble sodium salts | Soluble magnesium metal hydroxyl salts |
| TDS (total dissolved solids) | Low  
High | High | High | |
| Reaction Time | Moderately fast-acting to complete neutralization | Moderately fast-acting to complete neutralization | Extremely fast-acting to complete neutralization | Fairly slow-acting to 95% complete neutralization |

Source: National Lime Association (NLA) Publication entitled “Using Lime for Acid Neutralization”

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