Magnesium Hydroxide for Neutralizing Acid Waste Containing Metals

By John Teringo III

Magnesium hydroxide has several advantages for neutralizing metal-containing acid wastes. Because it generates a low volume of sludge that is easily dewatered, it is more cost effective than other alkalis when solids separation and disposal are taken into consideration.

Magnesium hydroxide is an alkali that has been used for many years to neutralize acids. It is the major ingredient in milk of magnesia, a familiar remedy for neutralizing stomach acids.

In wastewater management, a common and cost-effective way to treat acid streams containing dissolved metals is chemical precipitation of the metal hydroxides with alkalis such as caustic (NaOH), lime (CaO), and soda ash (Na₂CO₃). Magnesium hydroxide, Mg(OH)₂, is also effective for neutralizing acids and removing unwanted metal contaminants in wastewaters from plating and other finishing operations.

The unique characteristics of magnesium hydroxide and its capability to produce a low-volume, easily dewatered metal hydroxide sludge are addressed here.

Property Information
Magnesium hydroxide is available as an aqueous white slurry of agglomerated particles (0.6 to 1.0 μm) composed of 55 to 60 percent Mg(OH)₂, with a bulk density of 1.5 kg/L (12.5 lb/gal). This thixotropic slurry has a high viscosity of 4 to 40 poise, resembles latex paint upon movement, freezes at 32° F, and must be agitated mildly during storage. The solubility is very low at both ambient (0.0009 g/100 mL of H₂O at 18° C) and elevated temperatures (e.g., 0.0004 g/100 mL of H₂O at 100° C). Magnesium hydroxide is similar to concentrated milk of magnesia and is therefore safe to handle.

Table 1
Comparison of Physical and Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>NaOH</th>
<th>Ca(OH)₂</th>
<th>Mg(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular wt</td>
<td>40.0</td>
<td>74.1</td>
<td>56.3</td>
</tr>
<tr>
<td>Hydrate content, percent</td>
<td>42.3</td>
<td>45.9</td>
<td>57.7</td>
</tr>
<tr>
<td>Heat of solution, kg-cal/mol</td>
<td>9.9</td>
<td>2.78</td>
<td>6.0</td>
</tr>
<tr>
<td>Solubility in water, g/100 mL H₂O</td>
<td>42°</td>
<td>0.185</td>
<td>0.0009</td>
</tr>
<tr>
<td>Reactive pH maximum</td>
<td>14</td>
<td>12.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Wt. equivalence</td>
<td>1.37</td>
<td>1.27</td>
<td>1.0</td>
</tr>
<tr>
<td>Freezing point, °C</td>
<td>16</td>
<td>0°</td>
<td>0°</td>
</tr>
</tbody>
</table>

*Measured with a Brookfield viscometer (No. 4 spindle, 20 rpm), Brookfield Engineering Laboratories, Inc., Stoughton, MA.
Magnetism is one of the most common elements on earth and is an essential nutrient for normal plant, animal and human growth. These characteristics, in conjunction with the low solubility of magnesium hydroxide, result in minimal environmental impact in the event of a spill.

Table 1 compares the physical and chemical properties of common alkalis, showing several advantages of magnesium hydroxide. For example, there is 27 percent more hydroxide, which neutralizes acids and precipitates metals, in magnesium hydroxide than in hydrated lime and 37 percent more than in caustic. Thus, fewer pounds of magnesium hydroxide are required to neutralize the same amount of acid.

Because less magnesium hydroxide is required in the neutralization of hydrochloric acid (Table 2), a reduction of total dissolved solids (TDS) in the effluent stream is realized. Likewise, for neutralization of sulfuric acid waste, less magnesium hydroxide is required. A reduction in TDS will occur compared with caustic; however, hydrated lime will form gypsum (CaSO₄·2H₂O), which will minimize TDS in the effluent but create a large volume of sludge.

Another unique characteristic of magnesium hydroxide is the maximum pH that can be obtained in neutralization. Excess additions of lime or caustic can cause the pH of waste streams to go to 12.5 and 14, respectively. The pH of a magnesium hydroxide slurry is 10.5, but when used to neutralize acidic streams containing diverse ions, it can only reach a maximum of 9. This buffering effect at pH 9 is beneficial in the event too much alkali is added and fortuitously coincides with the upper pH limit under the Clean Water Act of 1977. It also prevents resolubilization of some heavy metals. Metal hydroxides precipitate at various pH levels depending on the type of metal. Graphic representations of equilibrium data for hydroxides of metals such as chromium, copper, zinc and lead show a decrease in solubility as the pH is increased to about 9 and an increase in solubility because of complex ion formation as the pH is further increased.

The safety aspect of magnesium hydroxide is another advantage. Lime and caustic liberate heat during reactions with water and are strong alkalis that cause severe irritation or burns on contact with skin. Magnesium hydroxide is a weak base and is not exothermic; therefore, it is a safe product to handle.

**Reaction Rates**

Acid neutralization with hydrated lime or caustic (Fig. 1) is a single-step reaction and is faster than with magnesium hydroxide, considered a two-step reaction. Magnesium hydroxide, being sparingly soluble, is in equilibrium with the water to produce a limited amount of magnesium and hydroxyl ions. These hydroxyl ions must be consumed by the acid before more magnesium hydroxide particles dissolve to provide additional hydroxyl ion. As more acid is neutralized, fewer hydroxyl ions are consumed and the reaction rate slows.

The neutralization rate with magnesium hydroxide is dependent upon various factors in addition to the usual kinetic effects of increased temperature and agitation. The quality of alkali added affects the rate of neutralization. Increasing the amount of magnesium hydroxide beyond that necessary for 100 percent neutralization will increase the rate. The concentration of acid also affects the rate. As shown in Fig. 2, a pH of 7 is reached with a 5 percent sulfuric acid solution in about 1 min. By contrast, it takes 10 min to obtain the same pH when treating 0.25 percent sulfuric acid.

Other factors that affect the reaction rate of magnesium hydroxide are the type and concentration of metal to be removed. As shown in Fig. 3, 100 mg/L of ferric iron is removed faster than 200 mg/L of ferric iron or 100 mg/L of copper.

Often a waste stream will contain several metals that need to be removed. Using magnesium hydroxide, the pH will increase until the level at which the first metal to be precipitated is reached, remain constant until the metal is removed, and then proceed upward. For example, with a system containing both ferric iron and copper, the pH will rise to 4.5 and remain there until all the ferric iron has been removed and then rise to 7 when copper hydroxide precipitation begins.

Not only does magnesium hydroxide provide hydroxyl ion for metal removal as metal hydroxide, it can remove metals through surface adsorption. It has been observed that metals can even be removed from waste streams with unacceptable pH levels. For example, adding magnesium hydroxide to a solution containing 500 mg/L of copper to raise the pH to 5.6 reduced the copper concentration to 37 mg/L. At this pH, it should be greater than 100 mg/L according to established profiles of concentration vs. pH. The magnesium hydroxide was just as effective in lowering the copper to an equivalent level at approximately 1 pH unit less than the caustic. At pH 8.4 the Mg(OH)₂ reduced the copper concentration to 0.2 mg/L. By comparison, adding
sodium hydroxide to raise the pH to 9.3 reduced the concentration of copper to 0.4 mg/L.

Early additions of flocculant will cause the unreacted Mg(OH)$_2$ particles to coagulate with the sludge and the reaction of Mg(OH)$_2$ is terminated.

There are several factors that can affect the reaction rate of magnesium hydroxide with acidic metal waste streams. Due to a culmination of these effects, longer residence times are required with magnesium hydroxide than with hydrated lime or caustic for acid neutralization and metal removal. This additional residence time may appear to be a negative feature, but is the basis for the process attractive from a sludge-production and handling-point-of-view.

**Sludge Characteristics**

The type of metal hydroxide precipitate that forms when using hydrated lime and caustic tends to be extremely light and friable. The instantaneous formation/precipitation results in numerous small particles that are interdispersed with water to form a gelatinous sludge. The type of sludge formed with magnesium hydroxide is more particulate in nature and can be attributed to the longer reaction time, which is conducive to crystal growth. The difference between a particulate and gelatinous sludge can be seen in Fig. 4, which shows the result of treating a sulfuric acid waste stream containing 1000 mg/L of chromium. On a dry-weight basis, the amount of sludge precipitated in the three tubes is approximately the same with the exception of the CaSO$_4$·2H$_2$O portion of the sludge formed with hydrated lime.

One advantage of a particulate sludge is its increased porosity and permeability; this is dramatically seen in its handling and dewatering characteristics. The data in Table 3 are based on experiences with several chromium plating operations. They show that sludge volume is much greater when caustic or lime rather than magnesium hydroxide is used for neutralization. With lime, it is not uncommon to see a volume nearly two times greater.

Dewatering is enhanced in the case of magnesium hydroxide. Also, filtration time for separating solids is much faster due to the particulate nature of the sludge.

As a result of these advantages, the costs of acid neutralization, solids separation and disposal are much lower with magnesium hydroxide than with calcium hydroxide (Table 4). The data show that magnesium hydroxide is a cost-effective neutralization agent, chiefly because it reduces the volume of and generates an easier-to-dewater sludge.

The estimates in Table 4 do not include maintenance expenses associated with the scaling effects of lime or the incremental cost of operating equipment for extended periods. A further saving is possible with magnesium hydroxide by reducing the amount of polymer used for flocculation. Due to the higher density of the sludge and a faster settling rate, polymer usage has been cut in half in several cases.

**Operating Techniques**

As indicated earlier, certain minimum reaction times are necessary for the magnesium hydroxide to produce a particulate sludge. Consequently, it is necessary to address this time requirement and determine how it can be incorporated in a waste-treatment system.

Hydrated lime and caustic are generally added to the waste until a desired pH is reached. This procedure cannot be followed with magnesium hydroxide if it is going to be used efficiently. Instead of adding magnesium hydroxide
until a desired pH is reached, a simple calculation should be made beforehand. With a batch neutralization system, 100 mL of sample is taken from the batch and titrated with 1N sodium hydroxide to the desired pH. The volume of sodium hydroxide (caustic) in the titration is then used to determine the amount of caustic required to neutralize that batch by the following calculation:

\[
gal of 50\% NaOH = \text{gal waste} \times mL of 1N NaOH \times 0.000523
\]

After determining the amount of caustic required to neutralize the batch, multiplication of that amount by 0.65 will provide an equivalent volume of 57.5 percent magnesium hydroxide. That quantity is then added all at once, and time is allowed for the pH to reach the desired level. Experience has shown that most of the sludge is formed in the first 20 min. If time is not available for the full reaction, the batch can be "topped off" with lime or caustic (typically less than 10 percent of the total alkali) to remove the remaining metals immediately. Although this procedure will yield a slightly greater volume of sludge than that produced using only magnesium hydroxide, it is still of better quality than the sludge generated with conventional alkalis alone.

When using magnesium hydroxide in a continuous neutralization system, a 100-mL sample of waste is titrated with 1N NaOH to ascertain the amount of alkali needed to achieve the desired pH. Then an equivalent amount of magnesium hydroxide is added, using the following calculation:

\[
\text{grams Mg(OH)}_2 = \frac{\text{mL of 1N NaOH} \times 0.03061}{\% \text{ Mg(OH)}_2}
\]

An equivalent amount of magnesium hydroxide should be added to another 100-mL sample of waste while pH is determined as a function of time. Figure 2 can be used as a guide to show the initial required pH for ultimately reaching the final desired value. After the system is in operation, it is often necessary to fine tune by adjusting the initial targeted pH up or down.

If sufficient time is not available, several courses of action can be taken:
1. Alkali can be added in upstream sumps or collection lines.
2. Neutralization tanks and basins can be partitioned to prevent short circuiting.
3. Agitation can be increased.
4. Additional tankage can be incorporated.
5. The stream can be topped off with caustic soda or lime.

To use magnesium hydroxide as an alkali for neutralization, it is necessary to make modifications in waste-treatment operating procedures and/or equipment. Based on extensive experience, these changes should be easy to make.

**Summary**
Magnesium hydroxide has some unusual characteristics that make it cost-effective for neutralizing acid waste containing metals. Because it generates a low volume of sludge that can be dewatered easily, magnesium hydroxide is becoming more attractive as disposal costs continue to escalate. It does not behave like conventional alkalis; therefore, modest modifications in waste-treatment operations and/or equipment are required. Reduced maintenance requirements, safety in handling, and minimal environmental impact are additional benefits.

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