THE USE OF MAGNESIUM HYDROXIDE SLURRY FOR BIOLOGICAL TREATMENT OF MUNICIPAL AND INDUSTRIAL WASTEWATER

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ABSTRACT

In wastewater treatment, microorganisms transform the wastes into cell tissue and gaseous, liquid, or solid conversion products. Optimum growth conditions, such as pH, nutrient availability, and alkalinity, must exist in order for the microorganisms to continue to reproduce and function properly. Municipal wastewater typically contains adequate amounts of alkalinity to support the biological conversion of organic waste; however, in some cases, there is insufficient alkalinity to maintain optimum bacterial growth conditions. Typically, an alkali such as caustic soda or lime must be added to the wastewater stream in order to provide the alkalinity and maintain the pH within the optimum range. Currently, caustic soda and lime users are switching to magnesium hydroxide slurry because of the advantages it offers for biological treatment. Magnesium hydroxide slurry, which is recognized as "the milk of magnesia" for wastewater treatment, has been widely utilized for heavy metal precipitation and acid neutralization of industrial wastewater. Many industrial and municipal wastewater facilities are now converting over to magnesium hydroxide for utilization in aerobic and anaerobic biological treatment systems.

With magnesium hydroxide slurry, a nutrient in the form of magnesium is readily available to the microorganisms. Magnesium hydroxide provides more $CaCO_3$ equivalent alkalinity on an equal weight basis when compared to hydrated lime and caustic soda which lowers chemical consumption. Additional benefits which make magnesium hydroxide slurry more attractive to end users are its buffering ability which provides the added benefit of excellent pH control, and its handling properties. Unlike caustic soda, magnesium hydroxide is non-hazardous and non-corrosive when used properly which makes handling safer and easier.

Magnesium hydroxide slurry, such as FloMag®H, has been used effectively in aerobic and anaerobic biological treatment systems at meat processing facilities, bakeries, chemical processing facilities, and municipalities, just to name a few. This paper will discuss the advantages of magnesium hydroxide over hydrated lime and caustic, and present case studies on the successful utilization of FloMag®H Magnesium Hydroxide slurries for both aerobic and anaerobic treatment of municipal and industrial wastewater.

INTRODUCTION

Physical, chemical, and biological treatment processes are used both in municipal and industrial wastewater treatment systems. For municipal wastewater, these processes are employed to coagulate and remove nonsettleable colloidal solids, reduce the organic fraction of wastewater (usually measured as BOD (biochemical oxygen demand), total organic carbon (TOC), COD (chemical oxygen demand)), remove phosphorus, and nitrify ammonia. For organic waste-based industrial wastewater, biological treatment is used primarily to reduce the concentration of organics which are amenable to biodegradation and to remove inorganic compounds such as heavy metals.

The biological processes are carried out by a variety of microorganisms, principally bacteria, which transform the organic matter in waste into cell tissue and gaseous, liquid, or solid conversion products. Since environmental conditions such as pH and alkalinity have a significant effect on the survival and growth of microorganisms, it is important that optimum conditions are maintained throughout the biological process. Some municipal wastewaters typically contain adequate amounts of alkalinity to support the biological conversion of organic waste. Industrial wastewaters, on the other hand, may not have sufficient alkalinity to sustain optimum bacterial growth. In these cases, alkalinity addition may be necessary in order for the bacteria to function properly. By utilizing magnesium hydroxide slurry for biological treatment, alkalinity and a nutrient supply in the form of magnesium is readily available to bacteria while magnesium hydroxide's buffering ability can provide the added benefit of optimum pH control.

DISCUSSION

The organic matter present in wastewater can be biologically degraded in the presence or absence of oxygen. In aerobic biological treatment, simple and complex organics are eventually decomposed to water and carbon dioxide in the presence of oxygen. In anaerobic biological treatment, simple organics such as carbohydrates, proteins, alcohols, and acids are decomposed to methane and carbon dioxide in the absence of oxygen.

Aerobic Biological Treatment: Nitrification

One of the primary pollutants in municipal and food processing wastewasters is ammonia. The *nitrification* process is used to convert the ammonia in the wastewater to nitrate. Nitrification is a two step aerobic biological process utilizing two species of nitrogen converting bacteria. These species of bacteria are most active in the pH range of 7 to 8. At pH 6.1 to 6.2, the microorganisms are seriously inhibited (Martin, Davis, and Chewning, 1991). During the nitrification process hydrogen ions are released and alkalinity is consumed as the acid is neutralized. For oxidation of ammonia, the expression for growth is (Henze, Harremoës, Jansen, and Arvin, 1995):

$$15\ CO_2 + 13\ NH_4^+ \rightarrow 10\ NO_2^- + 3\ C_5H_7NO_2 + 23\ H^+ + 4\ H_2O \qquad (1)$$

For every 1.0 mg of ammonia converted to nitrate, 7.14 milligrams (mg) $CaCO_3$ equivalent are consumed. The generation of acid during ammonia conversion, and the need to maintain the proper pH necessitates alkali addition to the system.

Nitrification of the wastewater is the single largest factor which leads to the consumption of alkalinity. *Alkalinity* can be defined as the ability of a water to neutralize acid or to absorb hydrogen ions. It is the sum of all acid neutralizing bases in the water. In municipal wastewater, there are many factors which contribute to alkalinity. Such factors include the type of dissolved inorganic and organic compounds present in the water, the amount of suspended organic matter in the water, whether the water is strongly or weakly buffered, the presence or absence of free hydroxyl alkalinity, the amount of bicarbonate in the water, the bicarbonate to dissolved CO_2 ratio, and indirectly, the amount of dissolved solids in the water.

The bacteria and other biological entities which play an active role in wastewater treatment are most effective at a neutral to slightly alkaline pH of 7 to 8. In order to maintain these optimum pH conditions for biological activity there must be sufficient alkalinity present in the wastewater to neutralize acids generated by the active biomass during the ammonia conversion process. This ability to maintain the proper pH in the wastewater as it undergoes treatment is the reason why alkalinity is so important to the wastewater industry.

How much alkali is added to the system is dependent on a number of interrelated factors. The amount of alkali added is determined by the amount of pollutants in the incoming waste, the type of treatment that is used in the plant, the amount of natural alkalinity in the influent water, the pH of the influent waste stream, the permitted pH of the effluent discharged from the plant, the number of gallons of waste processed by the plant, and whether the plant denitrifies the effluent prior to final treatment and discharge.

One of the most common alkalis used to provide alkalinity in wastewater treatment is caustic soda. However, magnesium hydroxide has properties which make it a clearly superior product in providing alkalinity and pH control to wastewater treatment systems. Unlike caustic soda and hydrated lime, magnesium hydroxide slurry has extremely low solubility in water which results in the limited production of hydroxyl ions for neutralization. Neutralization takes place as the soluble hydroxyl ions from magnesium hydroxide are consumed by the acid (Martin, Davis, and Chewning, 1991). Additional hydroxyl ions are released as the magnesium hydroxide particle dissolves when more acidity is generated. As a result, magnesium hydroxide provides long lasting alkalinity and better pH control. The chemical properties comparing magnesium hydroxide and other alkalis are summarized in Table 1.

TABLE 1
PROPERTIES OF MAGNESIUM HYDROXIDE vs OTHER ALKALIS

	MAGNESIUM HYDROXIDE	**CALCIUM HYDROXIDE**	**SODIUM HYDROXIDE**
TRADE NAME	FloMag®H	Hydrate Lime	Caustic Soda
CHEMICAL FORMULA	$Mg(OH)_2$	$Ca(OH)_2$	NaOH
% SOLIDS	62	34	50
LBS DRY SOLID PER GALLON	7.965	3.54	6.043
ALKALINITY, LBS $CaCO_3$ EQUIVALENT PER DRY LB	1.68	1.32	1.23
ALKALINITY, LBS $CaCO_3$ EQUIVALENT PER DRY TON	3360	2640	2460
ALKALINITY, LBS $CaCO_3$ EQUIVALENT PER GALLON	13.38	4.68	7.43

As can be seen from Table 1, magnesium hydroxide provides 1.68 lbs of $CaCO_3$ equivalent alkalinity per dry pound as opposed to 1.23 lbs of $CaCO_3$ equivalent alkalinity per dry pound of caustic soda and 1.32 lbs of $CaCO_3$ equivalent alkalinity per dry pound of hydrated lime. Magnesium hydroxide provides 37% more alkalinity than caustic soda and 27% more alkalinity than hydrated lime on a per dry pound basis. However, it is on a delivered product basis that magnesium hydroxide demonstrates its superiority to the other alkalis. The data in Table 1 shows the advantages of either FloMag®H over 50% caustic soda and 34% hydrated lime slurry. FloMag®H provides 13.38 lbs of $CaCO_3$ equivalent alkalinity per gallon. Caustic soda delivers only 7.43 lbs of $CaCO_3$ equivalent per gallon while hydrated lime provides 4.68 lbs of $CaCO_3$ equivalent per gallon. FloMag®H provides 80% more alkalinity per gallon when compared to caustic soda and 2.9 times more than hydrated lime.

Other benefits of magnesium hydroxide slurry are that it buffers to a pH of about 9.0, is much safer to handle than caustic soda, and does not scale equipment like hydrated lime. These benefits combined make magnesium hydroxide slurry superior to caustic soda and hydrated lime when selling into the wastewater treatment industry. Municipal wastewater treatment plants that are currently using caustic soda and hydrated lime to provide alkalinity during nitrification would be good candidates for conversion to magnesium hydroxide.

Anaerobic Biological Treatment

Biological degradation of organic matter can also be achieved anaerobically (in the absence of oxygen). The most common anaerobic process utilized for the treatment of wastewater is the *anaerobic digestion* process.

In anaerobic digestion, bacteria are used to convert colloidal and dissolved carbonaceous organic matter into methane, carbon dioxide, hydrogen sulfide, ammonia, and cellular materials. Anaerobic digestion is a two-stage process in which complex organic substances are first converted into simple organic acids or volatile acids (*acetogenesis)* and then converted to methane and carbon dioxide (*methanogenesis)* (Osborn, 1992):

Stage 1: ***Acetogenesis***

Complex organics + Acid forming bacteria → Simple organic acids + More acid forming bacteria

Stage 2: ***Methanogenesis***

Simple organic acids + Methane forming bacteria → Methane gas (CH_4) + More methane forming bacteria + Other end products

The general anaerobic transformation of organic matter into stable end products can also be described as follows:

$$\text{Organic matter} + H_2O + \text{nutrients} \xrightarrow{\text{bacteria}} \text{new cells} + \text{resistant organic matter} + CO_2 + CH_4 + NH_3 + H_2S + \text{heat}$$

The acetogenesis steps can proceed over a broad range of environmental conditions such as pH and temperature. However, the methane-forming bacteria in the methanogenesis stage are more sensitive to environmental conditions such as pH, temperature, and inhibitory compounds than are the acid-forming bacteria. Since the growth rate of methanogenic bacteria is lower than the acid-forming bacteria, it would take more time for the methanogenic bacteria to recover from inhibition or shock conditions than it would for the acid-forming bacteria. For these reasons, the methane-forming bacteria are the key bacteria in anaerobic digestion.

Generally, the optimum pH for methane-forming bacterial growth lies between 6.5 and 7.5 (Metcalf and Eddy, 1991). The lower the pH and the longer the pH is maintained at that level, the more likely an upset can occur. It is very important that the pH be maintained above 6.5 and that sufficient alkalinity is present to ensure that the pH will not drop below this point. As a result, an alkali such as magnesium hydroxide slurry can be introduced into the digester to neutralize any excess acid that can not be consumed by the methane-forming bacteria.

Methane-forming bacteria are considered to be the most sensitive to toxicity of all the microorganisms involved in the anaerobic digestion process. However, like most microorganisms, they can still tolerate a wide variety of toxicants. Substances which stimulate and inhibit the growth of methane-forming bacteria are listed below in Table 2 (Cook and Boening, 1987):

TABLE 2

Species	**Stimulatory Concentration (ppm)**	**Moderately Inhibitory Concentration (ppm)**
Sodium	100-200	3500 - 5500
Potassium	200-400	2500 - 4500
Calcium	100-200	2500 - 4500
Magnesium	75-150	1000 - 1500

If the moderately inhibitory concentrations are present in the waste stream, the methane-forming bacteria will not be able to function resulting in septic conditions within the anaerobic digester. For example, if the magnesium level rises above 1000 ppm, bacterial growth will be inhibited; however, based on the stoichiometry for acid neutralization, the magnesium dosages should fall well below the moderately inhibitory concentration as seen in Table 2.

The following are case studies where magnesium hydroxide successfully replaced caustic soda or hydrated lime for biological treatment at industrial and municipal wastewater treatment facilities.

CASE STUDY 1: Activated Sludge and Nitrification Processes at a Meat Processing Plant

At this meat processing plant, approximately 1.3 million gallons per day of wastewater containing fatty tissue, oils, and animal scraps are treated aerobically in a complete-mix activated sludge (CMAS) tank. All the contents in the tank are mixed using diffused air for vigorous agitation. Single-stage nitrification is employed in this system to convert the ammonia to nitrates. Sufficient alkalinity must be provided and the pH must be maintained at 6.5 to 7.0 in order to support bacterial growth. After nitrification, the bacteria is clarified in a sedimentation tank and the supernatant is disinfected and subsequently discharged.

Previously, this facility consumed 200 gallons a day of 50% caustic soda in the CMAS system. After switching to Martin Marietta's Magnesium Hydroxide Slurry, their alkali consumption was reduced to approximately 100 gallons a day of magnesium hydroxide slurry giving the facility an economic advantage. Since there was a 1.3 day retention time in the CMAS and sufficient agitation was provided, magnesium hydroxide slurry was ideal. Magnesium hydroxide was able to maintain pH and satisfy the 90 ppm alkalinity needed for the nitrifying bacteria. This customer consumed one truckload of magnesium hydroxide slurry per month.

CASE STUDY 2: Anaerobic Digestion at a Bakery

This bakery processes 75,000 gallons per day of wastewater containing flour, yeast, and other organic ingredients at their wastewater treatment plant. In their treatment process, they used 75 gallons of 50% caustic soda to raise the pH of the waste stream to 7.0 prior to biological treatment in two anaerobic digesters in series. The pH within the digesters was maintained at pH 7.0 with caustic soda in order to nurture the growth of the methane-forming bacteria.

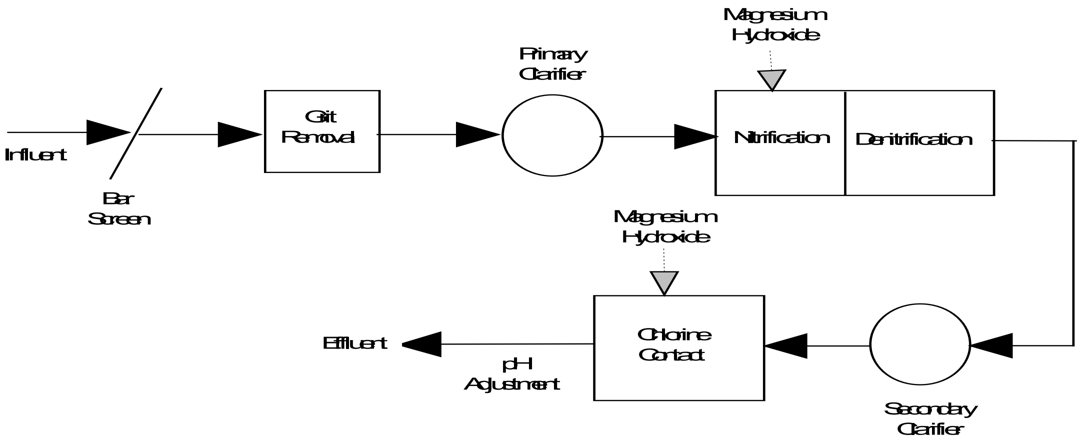
The facility often overshot the optimum pH of 7.0 when utilizing caustic soda in their system and as a result, caused adverse effects on the methane-forming bacteria which led to septic conditions. After switching to FloMag®H, the bakery found that FloMag®H was safer to handle and provided better pH control in their system with no cases of overshooting pH. In addition, less alkali was consumed since only 61 gallons of FloMag®H were required compared to 75 gallons of caustic soda. This magnesium hydroxide dosage imparted approximately 270 ppm of magnesium into the digestion process which was well below the range to cause bacterial growth inhibition. To date, the bakery is still using FloMag®H in their anaerobic digester.

CASE STUDY 3: Nitrification at a Municipal Wastewater Treatment Plant

Currently, this municipal wastewater treatment plant treats 13 - 14 million gallons a day of wastewater. Their wastewater treatment system as seen in Figure 1 consists of a nitrification/denitrification stage for ammonia removal.

Due to low influent alkalinity, alkali addition was necessary for the nitrification process and for pH adjustment. Before switching to Martin Marietta's Magnesium Hydroxide Slurry, the municipality utilized slaked lime and eventually caustic soda for supplemental alkalinity in the nitrification basin and pH control for the effluent. With lime, the municipality found its handling to be operator intensive due to cleaning of scaled equipment and caking in the feed bins. With caustic soda, handling of this corrosive chemical was always a safety issue. High pH excursions were frequent when using caustic soda which was detrimental to the bacteria in the nitrification basin and a violation of the municipality's discharge pH limit of 6.0 to 9.0. However, with magnesium hydroxide, the municipality achieved better pH control and was less likely to exceed their pH discharge limit. Since magnesium hydroxide is non-toxic and non-corrosive, handling was safer and easier which made magnesium hydroxide the more attractive alkali. This municipality uses one ton per year (dry solids basis) of magnesium hydroxide slurry in their biological treatment system for nitrification and pH adjustment.

FIGURE 1. MUNICIPAL WASTEWATER TREATMENT PROCESS



CONCLUSIONS

For biological wastewater treatment systems, particularly nitrification and anaerobic digestion, magnesium hydroxide slurry is the ideal replacement for caustic soda and hydrated lime. For both aerobic and anaerobic processes, magnesium hydroxide slurry provides the following advantages over the alkalis:

- Supplies more alkalinity per gallon than caustic soda and hydrated lime which means less magnesium hydroxide slurry is needed to treat the same wastewater as caustic soda and hydrated lime.

- Buffers to a moderately alkaline pH of 9.0, even with an over-addition. With this buffering ability, the pH can be better controlled making pH excursions less likely to occur.

- Safer to handle than caustic soda and hydrated lime since it is non-corrosive and non-toxic when used properly.

- Provides soluble Mg for cellular respiration.

- Does not cause scaling. Unlike hydrated lime, magnesium hydroxide slurry does not cause scaling in equipment which necessitates frequent cleaning and maintenance.

- Due to lower solubility than caustic soda and hydrated lime, magnesium hydroxide slurry provides long lasting alkalinity.

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