Magnesium Hydroxide Conversion Project

From Quicklime Alone to "Mixed Mode Treatment" with FloMag® H Magnesium Hydroxide Slurry and Quicklime

EXECUTIVE SUMMARY

A major United States metal processing company [hereafter to be known as "MPC"] has implemented a mixed-mode treatment strategy at its dedicated industrial wastewater treatment plant. The project has demonstrated several beneficial effects including:

- Environmental Discharge Permit compliance improved. Magnesium hydroxide and lime together can be more efficient than using lime alone;
- Greater alkali efficiency. One ton of magnesium hydroxide has the same treatment potential as 1.27 ton of hydrated lime. Reduced quicklime purchase and slaking requirements by 66%;
- Eliminated the vast majority of scaling and fouling due to insoluble calcium salts. The pre-existing hard gypsum scale slowly dissolved and did not return;
- Reduced hazardous waste haul-away by 50%. Annual treatment capacity increased by 1MM lbs of waste sulfuric acid (H_2SO_4);
- Clarifier capacity doubled. Operations are based on a SINGLE Claricone for the first time since 1989;
- Filter press capacity improved. Reduced sludge haul away by at least 50%;
- Magnesium hydroxide has a demonstrated buffering effect, resisting sudden pH changes and upsets. Acid requirements for pH control-back are reduced;
- Coagulant polymers are more efficient and effective;
- FloMag® H slurry is non-hazardous compared to lime and much safer for operators to handle.

In summary, for a $48,000 capital investment for a new magnesium hydroxide slurry storage tank with mild mixing, MPC switched to a combination of Magnesium Hydroxide (FloMag® H) and lime in fall 2012. MPC's own analysis saw approximately $136,000 of annual cost savings plus averted over $5MM in capital costs by replacing 66% of the quicklime with magnesium hydroxide slurry. Plant Operations see benefits including better effluent permit compliance. MPC remains a satisfied customer of Martin Marietta Magnesia Specialties LLC.

Case Study

Supplementing Lime with Magnesium Hydroxide Slurry In Acidic Metal-Laden Wastewater Treatment

A global leader in production of high-quality steel processing continues its 85-year tradition of providing customers with unparalleled value by investing in new technologies that enhance the quality of its products, shortens lead times and save customers money over the long term. This is a case study of how the MPC discovered a strategic technology that saved over $136,000 in operating costs annually, avoided a minimum of $5,000,000 in capital spending, improved uptime, improved safety, significantly reduced environmental liability due to reduced hazardous waste trucking and saved uncounted man-hours of labor.

Figure 1: Gypsum sludge fouled the process when using lime alone to treat sulfuric acid wastewater. This problem has been eliminated with a combination of magnesium hydroxide slurry and lime.

Martin Marietta Magnesia Specialties, LLC ("Martin Marietta") supplies MPC with FloMag® H. FloMag® H is a concentrated, stabilized, highly reactive magnesium hydroxide aqueous suspension with excellent flow and storage properties. FloMag® H has been manufactured for industrial wastewater treatment for over 20 years in Manistee, Michigan by Martin Marietta Magnesia Specialties, LLC, a division of Martin Marietta Materials, Inc. Magnesium hydroxide slurry is delivered as a non-hazardous liquid (by D.O.T. standards) which provides buffered acid and metals neutralization, and generates significantly less sludge compared to lime slurry.

Figure 2: Martin Marietta Magnesia Specialties FloMag® H stabilized magnesium hydroxide slurry.

The MPC wastewater treatment plant was constructed in two phases, in 1969 and 1989. With the exception of the recently installed equipment, the majority of the treatment plant equipment is over 25 years old. The treatment plant currently processes waste pickle liquor, cleaner solution, rinse water, boiler water, and cooling water containing numerous heavy metals, phosphorus, oil and grease and suspended solids. While running the lime-only treatment scheme, the treatment plant experienced numerous problems including: regular upsets, imposing limitations on pickling, extreme scaling and fouling of plant fixtures, and a general overloading of the sludge handling capacity.

Figure 3: MPC Wastewater Treatment Plant prior to starting the trial. Note the control cells to the left, the overloaded Claricone at bottom right, trial tanks and control shelter supplied by Martin Marietta for receiving trailers, storage and pH-controlled metering of FloMag® H magnesium hydroxide slurry during the trial – located at top right.

While several paid consultants recommended treatment plant expansion (projected cost of $5 million), MPC engineers researched other innovative solutions to these issues. MPC engineers contacted Martin Marietta Magnesia Specialties based on a search for a new technology that could reduce sludge generation while increasing wastewater treatment capacity and improving the permit compliance, with the overriding goal of saving money.

BEFORE MAGNESIUM HYDROXIDE CONVERSION

Before the magnesium hydroxide conversion, the clarifiers and sludge presses were a significant production bottleneck in the plant. Several consulting engineers provided estimates that it would require millions to bring sludge processing up to capacity to meet even present production requirements. Due to capacity limitations, pickling waste needed to be shipped off-site for paid disposal approximately three times per week.

Sludge disposal and its associated handling costs are significant. In addition, scheduling and managing sludge disposal and hauling requires significant planning and scheduling to execute without causing delays. Often minor issues including weather conditions, equipment breakdowns, and hauler and driver availability contributed to sludge back-ups and production slow-downs.

Figures 4 & 5:

Typical red gypsum scale on the treatment cell walls, and typical pipe fouling prior to the magnesium hydroxide trial.

Calcium sulfate created a thick scale deposit on all tank and clarifier interiors, pipe walls and sensor surfaces. Scale-encrusted sensors required constant cleaning and were often damaged during cleaning. MPC took several approaches to control scale but these methods had not been successful.

Figure 6: Two Claricones in parallel. Both clarifier cones were overloaded when using lime alone, but only one was needed with mixed treatment (FloMag® H and lime).

MAGNESIUM HYDROXIDE CONVERSION

Magnesium hydroxide slurry ($Mg(OH)_2$) provides similar chemistry to lime due to its divalent cation and two hydroxide anions, but $Mg(OH)_2$ does not create gypsum sludge as shown in the following equations.

(Sulfuric acid) H_2SO_4 + (Lime) $Ca(OH)_2$ ⇨ Insoluble $CaSO_4 \bullet 2H_2O$ precipitate or scale

(Sulfuric acid) H_2SO_4 + (FloMag® H) $Mg(OH)_2$ ⇨ Soluble $MgSO_4$ forms no scale + (Water) $2H_2O$

MPC's engineers determined that the benefits of reduced sludge handling and disposal yielded benefits over quicklime treatment particularly when total capacity and capital cost savings were compared.

"We have always strived to go beyond the status quo and investing in new technology that allows us to better serve our customers has been an integral part of our continued success over the years."

Vice President of Sales and Marketing for MPC

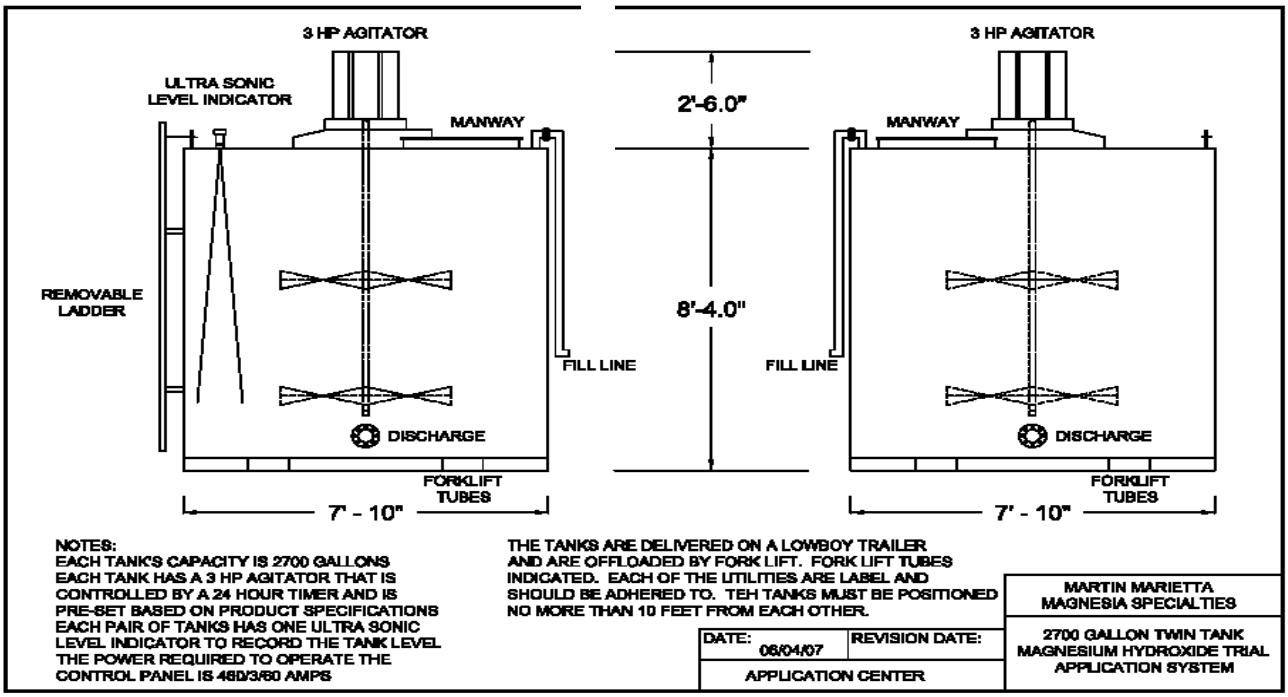


Figure 8: Martin Marietta Magnesia Specialties "Twin Tanks" with 5,000-Gallons combined working volume.

MPC's engineers contacted Martin Marietta Magnesia Specialties, LLC to investigate FloMag® H, a high-solids, stabilized magnesium hydroxide slurry, as a partial replacement for quicklime. Martin Marietta's laboratory evaluations of a wastewater sample from MPC projected that the chemistry and economy of replacing 75%-80% of the quicklime would be viable. Using trial equipment and engineering assistance from Martin Marietta's Application Center, MPC and Martin Marietta ran a three-month long trial at the

MPC location to verify the feasibility of magnesium hydroxide conversion. Although the chemical cost of $Mg(OH)_2$ slurry is higher per dry ton than CaO, the results of the three-month trial were very positive. The plant converted to a mixture of FloMag®H and lime during the fall of 2012. A long time treatment plant union employee noted:

"We haven't seen the bricks in the walls of the cells in years, due to the thick scale. Since the Mag project, now we can."

AFTER MAGNESIUM HYDROXIDE CONVERSION

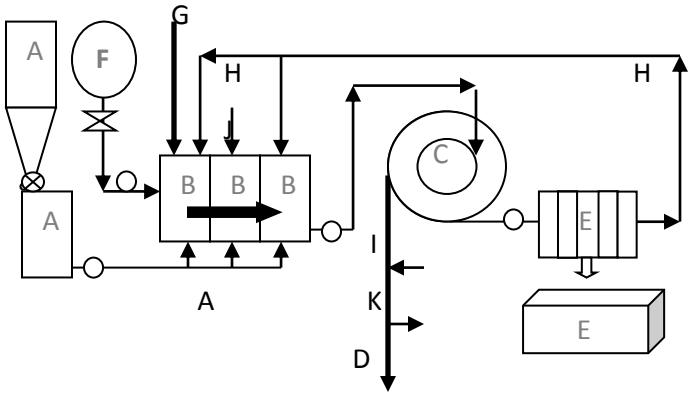
The magnesium hydroxide conversion took place in 2012, and MPC remains a satisfied customer. Since that time, a number of benefits, both financial and operational have been identified and quantified including:

- Greater alkali efficiency: Plant experience shows that one ton of magnesium hydroxide has the same treatment potential as 1.27 tons of hydrated lime in the MPC process;
- Magnesium hydroxide has a demonstrated buffering effect, resisting sudden pH changes and upsets;
- Discharge Permit compliance has improved;
- Eliminated the vast majority of scaling and fouling of instruments and valves due to insoluble calcium salts;
- Reduced hazardous waste haul away by 50%;
- Reduced sludge haul away by at least 50%;
- Reduced lime purchase by 66%;
- Operations are based on a SINGLE Claricone for the first time since 1989;
- More efficient and effective use of coagulant polymer.

Figure 9:

Clarified operates "clear and efficient" with combined magnesium hydroxide and lime.

Figure 10. Simplified Continuous Process Schematic of MPC's Wastewater Treatment Plant



Schematic Key:
A - Lime Silo, Slaker, Storage, and Feed
B – pH Treatment Cells
C – Clarifier Cones (2 in Parallel)
D – Treated Discharge
E – Filter Press & Sludge Roll-Off
F – FloMag® H Agitated Storage & Feed
G – Influent from Plant, pH <1
H – Filtrate Recirculation
I – Acid Overshoot Control
J – Flocculant Addition
K – Automated Monitoring & Sampling

CHEMISTRY:

Magnesium hydroxide ($Mg(OH)_2$) is purchased as a high solids (60%) stabilized slurry composed of fine (median diameter of 3 microns) particles suspended in water. The product does not require slaking. Like lime, magnesium hydroxide may be metered into the process as slurry and requires gentle mixing in storage. Because the magnesium hydroxide slurry trialed at MPC is a synthetic product, it has far less grit and far less settling tendency than lime slurry or other naturally-mined products. Like lime, magnesium hydroxide dissolves in acid to release hydroxide ions capable of neutralizing acids and creating metal hydroxides. "Mag" slurry provides more alkalinity per gallon than lime slurry.

Unlike lime, magnesium hydroxide does not combine with sulfate ions to create insoluble gypsum (Calcium Sulfate) or any other solid precipitate or scale. Instead, magnesium ions remain in solution as Magnesium Sulfate. Metals, on the other hand, precipitate as desired without excess sludge.

For best process efficiency, metal hydroxide precipitation should ideally be continuously controlled within the target range of pH values needed for the neutralization reactions of the contaminants to be removed, and these reactions must continue for a period of time until the required amount of each contaminant is removed as hydroxide precipitant or flocculated solids. Through simple process adjustments, MCP avoided or compensated for conditions that impeded or reversed the desired reactions.

A major difference between lime and magnesium hydroxide is the difference in solubility. This means "Mag" is less soluble than lime, and less soluble the higher the pH; *"Mag hydroxide has a demonstrated buffering effect, resisting sudden pH changes and upsets"* as stated in the executive summary.

The pH of lime (dry or slurry) can exceed 12. Lime is corrosive, can cause severe skin burns and must be transported, stored, and handled as a corrosive material. Simple calculations will show that the pH of magnesium hydroxide slurry will not exceed a pH much above 10. This explains why magnesium hydroxide slurry is non-hazardous and not D.O.T.

regulated. Both personal safety & process safety can be improved by using Mg(OH)2.

In metal-hydroxide precipitation, using magnesium hydroxide alone often does not exceed 8.5 pH. In some cases, dual alkali treatment with magnesium hydroxide and lime might be required to precipitate metals that require a higher pH level. In the experience of MCP, the majority of neutralization can be accomplished with magnesium hydroxide, and the remainder of the precipitation can be accomplished by "topping off" with lime slurry.

Since magnesium hydroxide is more soluble at low pH values than at high values, as pH is raised to between 10 and 11 for nickel precipitation, a small amount of magnesium hydroxide that had dissolved at more acidic conditions reforms into microscopic particles of magnesium hydroxide. It does not form scale. If the new particles form, additional dissolved metals may be removed from solution through surface adsorption onto the particle and also into the interior of the particle as it gets bigger and engulfs any materials adsorbed onto the surface. Particles with adsorbed metals on the surface get denser, and settle along with the metal hydroxides particles created under traditional means. Because the particles settle, this phenomenon contributes to even higher efficiency in total dissolved solids (TDS) removal than would be expected.

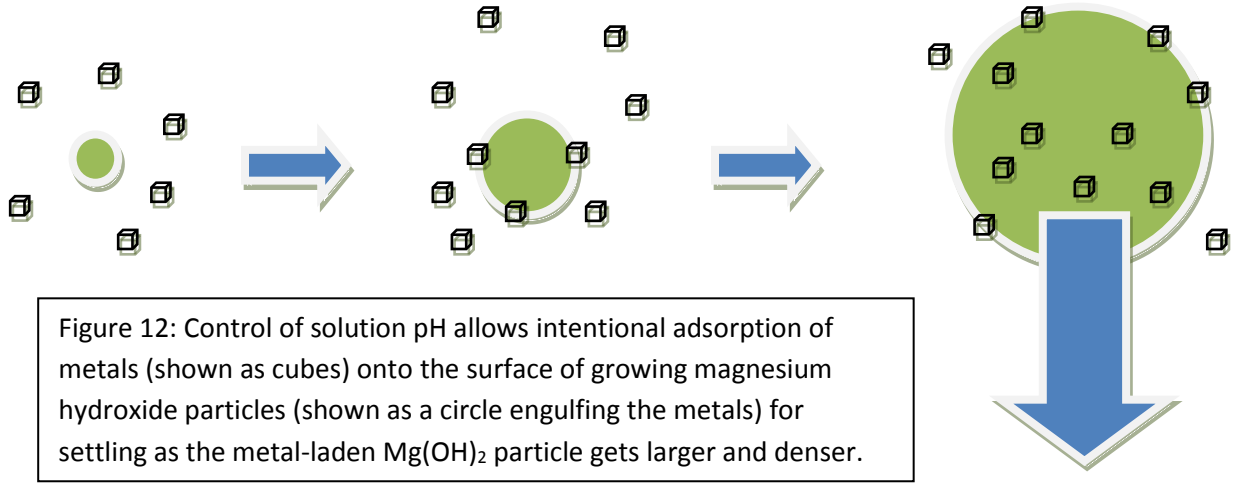


Figure 12: Control of solution pH allows intentional adsorption of metals (shown as cubes) onto the surface of growing magnesium hydroxide particles (shown as a circle engulfing the metals) for settling as the metal-laden $Mg(OH)_2$ particle gets larger and denser.

Gross over-addition of "mag" slurry does not cause a pH upset, but is indicated by turbidity in the clarifier. For this reason, the magnesium hydroxide pH set-point is chosen to balance process efficiency with clarifier clarity and TSS permit compliance. MPC has raised the first-stage (mag) pH set-point only to the level where clarifier turbidity is improved – in MPC's case, this is a pH of 6-7. The second-stage (lime) pH set-point is adjusted for metals precipitation; however, due to the surface adsorption effect, compliance may be achieved at pH values slightly lower than would be expected based on precipitation factors alone – in MPC's case this is about 10. The targets chosen are system-dependent.

Overall, MPC's clarifier now is twice as efficient as before, and provides a clear treated discharge. See Figure 3 versus Figure 9. The $5-million capital project to increase clarifier capacity – no longer needed – was cancelled.

Since the two-stage treatment continues to use lime, MPC's permit requirement to use lime for metals treatment is fulfilled.

Figure 13: Firm dewatered sludge formed with combined magnesium hydroxide and lime.

Magnesium hydroxide produces a faster-settling floc and higher sludge density compared to lime, as is well-documented in the literature. At MPC, this benefit is seen as increased clarifier efficiency, easier sludge dewatering, and denser sludge roll-offs. These improvements saved MPC money.

Finally, MPC's testing demonstrated that after a period of acclimitization, both plant and animal test species thrived in the treated discharge. All permit requirements have been met.

The MPC's own state Department of the Environment approved the process-change trial prior to installation of temporary equipment, supplied by Martin Marietta Magnesia Specialties, LLC (Figure 8). After a period of initial setup and training with Martin Marietta's Application Center engineers, MPC personnel systematically identified the limits of efficient operation and completed process optimization independently. The plant converted to a two-stage neutralization using both FloMag® H high solids stabilized magnesium hydroxide slurry in 2012, and has remained a satisfied Martin Marietta customer.

MPC generated real savings using FloMag®! A more detailed description of MPC's chemistry is available.

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