Removal of Metals from Metal Finishing Waste Water Using a Granular, Magnesium-based Adsorbent*

by Matthew D. Walter, Joseph T. Witkowski, and Aileen Reyes

This paper details a granular, Magnesium-based Adsorbent which has been used to remove various metals from surface finishing waste water streams. The metals treated in this study include copper, nickel, and zinc. Effluent concentrations of the treated metals are typically less than 0.5 mg/L.

Environmental regulations have become increasingly severe regarding the types and amounts of pollutants that may be released into the environment. In particular, metal finishers are commonly restricted to the metal concentrations and pH of waste water that may be discharged into natural waterways, municipal sewers, etc. Various treatments have been utilized to remove metal ions from water while rendering the pH suitable for discharge. The most widely used method for treating waste water streams is chemical precipitation. Using this method, the pH of the stream is raised with an alkali (e. g. $Mg(OH)_2$, NaOH, Lime, etc.) until the metals precipitate as the insoluble hydroxides. Often, chemical precipitation is not completely successful in reducing metal concentrations in the waste water stream to comply with discharge regulations. Additional treatment techniques such as reverse osmosis, ion exchange, and activated carbon are often necessary to reduce the metal concentration sufficiently for discharge. The adsorbent described herein is a novel Magnesium-based adsorbent from Martin Marietta Magnesia Specialties, LLC that has been shown to remove heavy metal ions from mildly acidic to mildly alkaline surface finishing waste water while simultaneously neutralizing the acidic components of the waste. Three case studies are presented detailing the performance of this granular medium as well as information about how this granular, Magnesium-based product removes metals from solution.

Mechanism

The medium operates by the principal of ion exchange, where an Mg^{++} ion exchanges with a metal ion (M^{+x}) as shown in the following equation:

$$Mg(OH)_{2\,(adsorbent)} + M_{eq}^{+2} \ ? \ M(OH)_{2\,(adsorbent)} + Mg^{+2}$$

Equation (1)

Though the metal is shown to be divalent in this equation for simplicity, it may be of any valence provided the ion exists as a cation in solution. Anionic species (e. g. $Cr_2O_7^{-2}$, Cu-EDTA, etc.) cannot exchange for the magnesium in the medium, and are, therefore, not adsorbable by this material.

A general tendency exists for the solubility of the hydroxides of successfully treated metals to be lower than that of $Mg(OH)_2$ as shown in Table 1.

* ***FloMag® G is a product of Martin Marietta Magnesia Specialties LLC, 195 Chesapeake Park Plaza, Suite 200, Baltimore, MD 21220, (800) 648-7400.***

In order for the medium to effectively remove target metals from solution a minimum empty bed contact time of eight minutes is recommended. Laboratory tests have shown that effluent metal concentrations can be lowered to 0.010 mg/L or less with sufficient contact time. Shorter contact times may result in insufficient removal of the target metal. The medium is regenerable with a dilute acid backwash. In addition, periodic backwashing with air and water is recommended.

Table 1: Solubility Data for Target Treatment Metals

Metal Hydroxide	KsP	Solubility, mole/L	Temperature	Ref.
$Cu(OH)_2$	2.2×10^{-20}	2.8×10^{-7}	Room Temp.	1
$Cd(OH)_2$	1.7×10^{-15}	1.2×10^{-5}	25ºC	2
$Cr(OH)_3$	1.7×10^{-24}	1.2×10^{-8}	Room Temp.	3
$Ni(OH)_2$	6.5×10^{-18}	1.9×10^{-6}	Room Temp.	4
$Zn(OH)_2$	1.66×10^{-16}	5.5×10^{-6}	25ºC	5
$Pb(OH)_2$	1.1×10^{-20}	2.2×10^{-7}	22ºC	6
$Mg(OH)_2$	1.1×10^{-11}	2.2×10^{-4}	18ºC	7

Case Studies

Case Study #1

The first case study involves an electronics component manufacturer with copper in the waste water stream. Chemical precipitation with both $Mg(OH)_2$ and NaOH was first used to both adjust pH and precipitate copper as $Cu(OH)_2$. An inclined plate clarifier removed most of the sludge, while a paper filter further clarified the waste stream. A schematic of the treatment system is shown in Figure 1. The Magnesium-based granular adsorbent was added to the system (as shown in Figure 1) to reduce soluble copper levels from ~1.5 mg/L after the primary treatment to below 1 mg/L for discharge. Figure 2 shows the performance of the granular adsorbent in removing copper from this waste water stream. The stream, at a flow rate of approximately 5 Gallons per Minute (~18.9 Liters/Min), entered the column containing 300 pounds (~136 kg) of the granular,

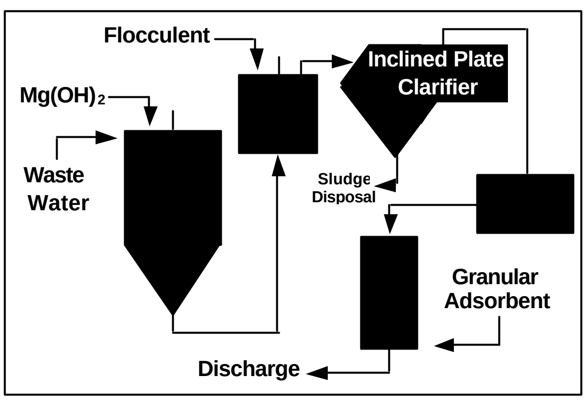


Figure 1: Schematic of Treatment System for Case Study #1

Magnesium-Based Adsorbent. This provided an empty bed contact time of approximately six minutes (as opposed to the recommended eight to ten minutes). All of the measurements showed the medium to substantially reduce the copper concentration in the effluent. For the most part, the effluent copper concentrations were 0.5 mg/L or less. One reading had a concentration of 1.36 thought to be the result of channeling in the bed.

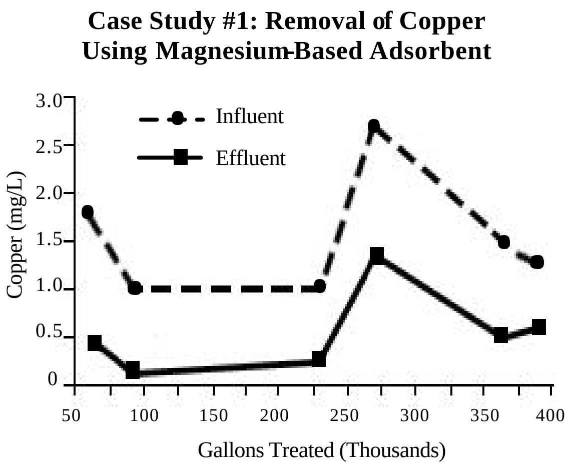
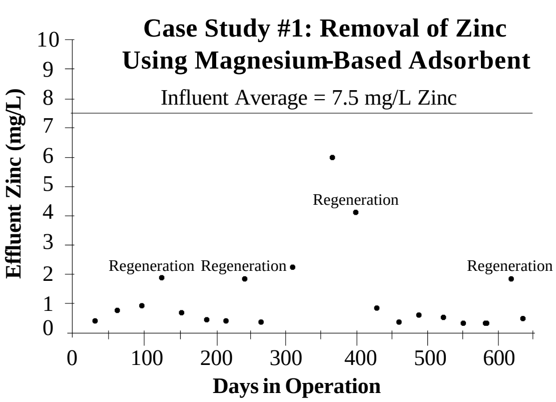


Figure 2: Performance of Granular, Magnesium-Based Adsorbent in Case Study #1

Backwashing restored good copper adsorption in the subsequent measurements.

Case Study #2

The second case study involved a hardware plating shop treating a zinc-containing stream.



In this application, primary treatments with NaOH to pH 10-11 had been unable to reduce the zinc concentration of the effluent to less than 5.75 mg/L, on average, while the discharge limit was 2 mg/L. By incorporating the Granular, Magnesium-Based Adsorbent as a polishing filter, this company was able to reduce the target pH of the primary treatment to pH 8 while removing the residual zinc with the adsorbent. Specific influent data is not available but the monthly averages for the effluent are plotted in Figure 3. Even though the flow rate of 25 Gallons per Minute (94.6 Liters/Min) allowed only about three minutes empty bed contact time, the medium consistently reduced the zinc levels to well below the 2 mg/L discharge limit. The user regenerated the adsorbent approximately every one hundred days of operation, as shown in Figure 3, to restore the adsorption capacity of the medium.

Case Study #3

The third case study involved a metal finisher with zinc, copper, and nickel in the waste water stream. Conventional chemical precipitation techniques using NaOH had been unable to consistently reduce the concentrations of the three target metals to below 1 mg/L. To reduce the metals in this 6 Gallons per Minute (22.7 Liters/Min) waste water stream, this plater added a column containing 300 pounds (136 kg) of the Granular, Magnesium-Based Adsorbent as a polishing filter. Even though the unit only has a 5.2 minute empty bed contact time, the company has not experienced a surge in any of the metal concentrations exceeding 0.98 mg/L. Figure 4 shows the metals content of the waste water stream before the addition of the Granular, Magnesium-Based Adsorbent in March

1993, as well as the metals content of the unit.

Multi-Metal Removal
Using Magnesium-Based Adsorbent

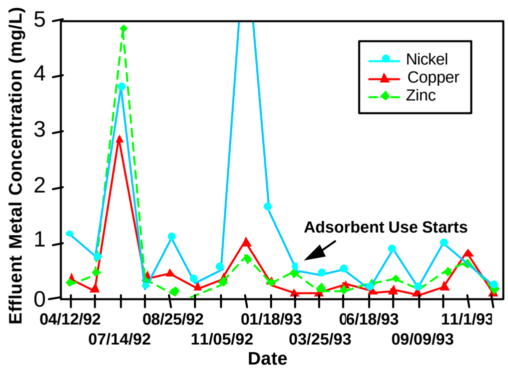


Figure 4: Multi-Metal Removal in Case Study #4

Conclusions

The Granular, Magnesium-Based Adsorbent is effective in removing many cationic metals from waste water streams. Laboratory testing, and small scale industrial trials have shown that metal concentrations of 0.01 mg/L or less may be achieved with this product when used properly. Though none of the case studies cited in this paper consistently achieved these levels, all consistently reduced the metal concentrations in the effluent to well below stream after the addition of the polishing discharge limits. It is presumed that more appropriately sized units, providing the recommended eight to ten minute empty bed contact times, would result in even better performance.

References

1. R. Nasanen and V. Tamminen, J. Am. Chem. Sec., 21, 1994-1998 (1949)

2. W. Feitknecht and R. Reinmann, Helv. Chim. Ada, 34, 2255-2266 (1951)

3. Y. Oka, J. Chem. Sec. Japan, 41, 311-320, (1940)

4. K. H. Gayer and A. B. Garrett, J. Am. Chem. Sec., 2L 2973-2975, (1949)

5. W. Feitknecht, Metaux et Corrosion, 23, 192-203m, (1947)

6. I. M. Korenman, F. S. Frun, and V. G. Chebakova, Zh. Obshch. Khim., 22, 1731-1734, (1952)

7. J. K. Gjalbelt, Z. Anorg. Allgem. Chem., 144, 145, 269, (1925)