UTILIZATION OF MAGNESIUM COMPOUNDS FOR WASTEWATER MANAGEMENT IN THE ELECTRONICS INDUSTRY

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Prepared for Presentation at 1995 AIChE Summer National Meeting
Boston, MA 30 July - 2 August 1995
Wastewater Management in the Electronics Industry -- Session #48

**Utilization of Magnesium Compounds for Wastewater Management
in the Electronics Industry**

by Aileen Reyes Gibson

As environmental regulations become more stringent on the quality of effluent discharged into natural waterways and municipal treatment facilities, electronic component manufacturers must employ effective treatment methods to meet these more strict discharge requirements. One treatment method which has proven itself as a viable technology for approaching zero discharge is the utilization of magnesium compounds for neutralizing acid waste streams and removing metals such as zinc, trivalent chromium, lead, nickel, iron, copper, and cadmium from wastewater via chemical precipitation and adsorption.   Magnesium compounds, such as magnesium hydroxide and magnesium oxide, have been used in the treatment of acid rinse water from drag-out stations, process solutions from etching baths, floor spills, spent plating baths, and other wastewater streams generated by printed circuit board manufacturers, semiconductor manufacturers, electroplaters, and metal platers.   The benefits of magnesium compounds over the other commonly used alkalis such as caustic soda, lime, and soda ash make it a cost-effective alternative for acid neutralization and metal precipitation.

CONVENTIONAL ALKALIS

Acid neutralization of wastewater is generally accomplished by adding a conventional alkali such as caustic, lime, soda ash, or one form of the magnesium compounds to raise the pH of the waste stream. Caustic soda, or sodium hydroxide (NaOH), is the most commonly used chemical for acid neutralization due to its ease of addition by relatively straightforward and inexpensive feed systems. However, caustic is a toxic and corrosive chemical that must be handled cautiously. Workers that use caustic must strictly adhere to safety procedures and wear appropriate protective clothing and goggles. One inadvertent splash of caustic in the eye can cause permanent loss of vision, while contact with the skin can cause severe burns. In addition, caustic spills must be cleaned up immediately by a hazardous clean-up crew to prevent environmental damage since sodium salts entering the environment can cause adverse effects in animals and vegetation. With a relatively high freezing point of 13.9°C (57^0F), 50% caustic requires indoor storage or heat-tracing equipment (Teringo, 1990).

Lime, the least costly source of hydroxide ion available, is slaked to calcium hydroxide (Ca(OH)$_2$) prior to acid neutralization, therefore requiring the additional cost associated with the installation and maintenance of feed and slaking equipment. If quicklime (CaO) is used, it must be stored in air-tight bins to prevent air-slaking since it is hygroscopic. Moisture in the air produces a destabilizing effect by air slaking quicklime into agglomerated particles, which may eventually coat and plug up pipes. Maintenance problems also arise when lime is used for acid neutralization due to an insoluble calcium sulfate (gypsum) scale formation on equipment, excessive wear on valves and pumps due to undissolved lime grit, and increased suspended solids in the treated water. Hydrated lime slurry tends to bulk and bridge in storage tanks, and therefore requires special agitation systems on cone bottom tanks. Like caustic, lime can cause permanent eye damage and severe irritation or systemic injury to the skin due to absorption. Also, lime dust can cause intolerable irritation to the nose and throat thus necessitating special dust collection systems and protective clothing.

Soda ash, or sodium carbonate (Na$_2$CO$_3$), is not particularly corrosive by itself, but like caustic,

can impact the environment by contributing sodium salts which are harmful to animals and vegetation. It is not a difficult alkali to dissolve, however, it requires heat-traced or insulated storage tanks since its freezing point, once dissolved in water, is at 26.7°C (80°F) (Louchart and Papamarcos, 1988). When neutralizing acidic wastewater, soda ash causes foaming which can be difficult to handle.

As opposed to the aforementioned alkalis, magnesium hydroxide (Mg(OH)$_2$) and magnesium oxide (MgO) pose little danger to the environment and human health. Magnesium hydroxide, an aqueous white slurry containing 55% to 60% solids, is essentially the same ingredient as "Milk of Magnesia" which is used for medicinal purposes to neutralize stomach acids. This magnesium hydroxide slurry, however, is a non-pharmaceutical grade alkali utilized for neutralization of acidic wastewater. Although relatively low in toxicity, magnesium hydroxide slurry can cause abdominal cramps or diarrhea if ingested in large quantities.

Because they are classified as low-degree health hazards and non-corrosive materials, these magnesium compounds are safe to handle and require no special safety procedures. Unlike lime and caustic which liberate heat with the addition of water, magnesium hydroxide is not exothermic, and is classified as a weak base, making it much safer to handle (Teringo, 1987). Magnesium oxide, on the other hand, will liberate heat when hydrated to magnesium hydroxide, but this conversion is not needed to neutralize acids as the unhydrated form is just as effective in most cases. Provisions for dust control, however, may be necessary as magnesium hydroxide and magnesium oxide powders may be dust nuisances. In the event of a spill, minimal environmental impact would result since magnesium hydroxide has low solubility, and magnesium is considered an essential nutrient to normal plant, animal, and human growth.

Freezing of magnesium hydroxide slurry is not a common occurrence as with caustic or soda ash since its freezing point is the same as water (i.e. 0°C (32°F)). In cold climates, precautions should be taken to heat-trace or insulate the storage tanks. Mild, intermittent agitation is required to keep the solids from settling over a prolonged storage; however, some magnesium hydroxide manufacturers can supply stabilized slurry that needs only infrequent agitation. Since the quality of magnesium hydroxide varies depending upon the manufacturer, the slurry can be highly viscous (i.e. >0.4 Pas (>400 cps)), thus requiring careful selection of agitators, pipes, valves, and pumps.

ACID NEUTRALIZATION

In the manufacturing of electronic components such as semiconductors, capacitors, transformers, and printed circuit boards, vats of sulfuric, hydrochloric, and nitric acid are used to clean and polish metal chips and boards. As a result, the acidic rinse water that is generated must be neutralized with an alkali prior to being discharged. When comparing the "neutralization value" of the neutralizing agents, magnesium compounds have an advantage over the other alkalis. Less magnesium hydroxide or magnesium oxide by weight is required to neutralize the same amount of acid as caustic, hydrated lime, and soda ash.   The reason for this is that the percent hydroxide, or that portion of the chemical which actually neutralizes the acid, is 27% greater for magnesium compounds as compared to hydrated lime, 37% greater than caustic, and 82% greater than the hydroxide equivalent of soda ash.   Figure 1 shows that less magnesium hydroxide and magnesium oxide are required to neutralize one ton of sulfuric or hydrochloric acid than other conventional neutralizing agents. Table 1 compares the properties of each alkali.

Kilograms of Neutralization Agent
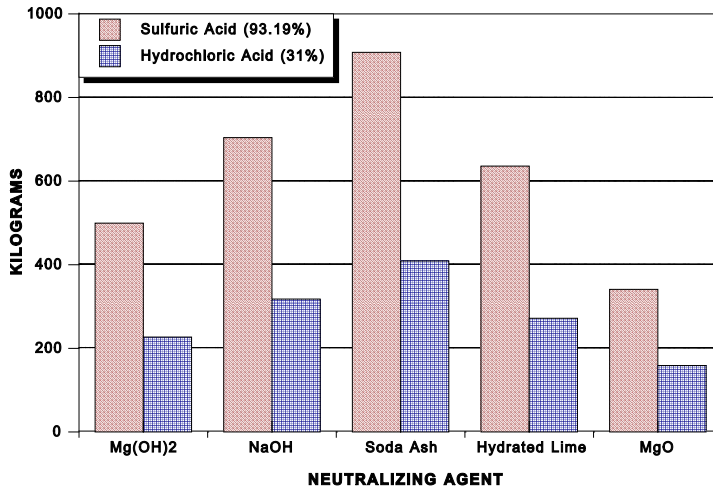
Required to Neutralize One Ton of Acid

Figure 1

Table 1
Physical and Chemical Properties
of Different Alkalis

Property	NaOH	Ca(OH)$_2$	Na$_2$CO$_3$	Mg(OH)$_2$	MgO
Molecular weight	40.01	74.09	105.99	58.32	40.30
Ratio to Mg(OH)$_2$	1.37	1.27	1.82	1.00	0.69
Percent hydroxide	42.51	45.91	*	58.32	------
Solubility in water[1], g/L H$_2$O	1030[2]	1.70[3]	294.00[3]	0.0117[3]	0.0062[4]
Freeze point[9], °C	13.9[5]	0[6]	26.7[7]	0[8]	------
Reactive pH maximum	14	12.5	11.6	9.0	9.5

[1] Linke, 1965.	[5] 50% solution	[9] Louchart and Papamarcos, 1988.	
[2] 12°C	[6] 30% solids slurry	* Na$_2$CO$_3$ indirectly provides hydroxyl ions	
[3] 25°C	[7] 15% solution	by providing carbonate ions that combine	
[4] 20°C	[8] 58% solids slurry	with hydrogen ions, thus deionizing water.	

Since less magnesium compound is required in the neutralization of hydrochloric acid, the total dissolved salt in the effluent stream is reduced. However, in the neutralization of sulfuric acid, there is less magnesium sulfate dissolved in the effluent than there is sodium sulfate. When lime is used to neutralize sulfuric acid, calcium sulfate (gypsum) precipitates from solution leaving less total dissolved salt than magnesium compounds and caustic, but significantly increases the amount of sludge produced. Gypsum can produce supersaturated solutions resulting in further precipitation downstream of the neutralization (Foreman, 1993). From Table 2, comparison of sulfuric acid treatment with different alkalis shows the amount of insoluble substances (i.e. sludge) produced versus the total dissolved substances left in solution.

Table 2
Comparison of Sulfuric Acid Treatment
With Different Alkalis
(1 Ton of 100% H_2SO_4)

Alkali	Insoluble Substances, kg	Total Dissolved Substances, kg
$Mg(OH)_2$, MgO	< 9	1108
Caustic Soda	< 9	1308
Lime[*]	1594	< 22.7

* Forms Insoluble $CaSO_4 . 2H_2O$ (Gypsum)

In many localities, the maximum pH limit for wastewater discharge is 9.0 to 10.0. Compared to other common acid neutralizers, magnesium compounds are less likely to exceed this limit in the event of over-addition. Magnesium compounds have a unique, built-in pH buffering capability known as the common ion effect, which prevents the pH from exceeding 9.0 for magnesium hydroxide and 9.5 for magnesium oxide. A saturated solution of magnesium hydroxide or magnesium oxide has a pH of 10.5, whereas a 1N solution of caustic has a pH of 14, a 0.1N solution of soda ash has a pH of 11.6, and a saturated solution of hydrated lime has a pH of 12.4.

Due to their buffering ability, magnesium compounds, even in large excesses, will not cause the pH to rise much above 9.0 - 9.5 when neutralizing sulfuric acid. The excess solid does not dissolve until more acid is added due to the low solubility of magnesium hydroxide. Hydrated lime and caustic, on the other hand, can exceed pH 12 and 13, respectively, even with small excesses when neutralizing the same acid.   As a result, many facilities must use acid to readjust the pH in cases of over-addition to bring the pH within the discharge limit.   Magnesium compounds are therefore much more forgiving in terms of over-addition, and less likely to cause the pH to be out of compliance.

Since magnesium compounds are sparingly soluble in water, they produce a limited amount of hydroxyl ions, which must be consumed by the acid before more magnesium hydroxide particles dissolve to provide additional hydroxyl ions.   As a result, the rate at which neutralization occurs is slower than

that of the other alkalis. Below a pH of 5, the reaction is rapid; above a pH of 5, the rate of neutralization is slower as the rate controlling mechanism changes from being a surface reaction with protons to being a diffusion of magnesium hydroxide from the surface into the solution (Foreman, 1993). Therefore, as neutrality is approached, the rise in pH becomes slower. Since hydrated lime and caustic are more soluble than magnesium compounds, they dissociate rapidly in water to provide hydroxyl ions for neutralization, and once either of these alkalis are added to wastewater, the pH rises almost immediately to the final pH. With magnesium compounds, the pH rise is more gradual as seen in Figure 2.   For magnesium oxide powders that are added directly into the wastewater, the rate of neutralization is faster than that for magnesium hydroxide slurry due to the exothermic reaction taking place as magnesium oxide hydrates. Based upon the surface area of the magnesium oxide particle, the rate of neutralization is faster for high surface area MgO than for low surface area MgO (see Figure 2).

Figure 2
Comparative Neutralization Rates For
1N Sulfuric Acid Solution
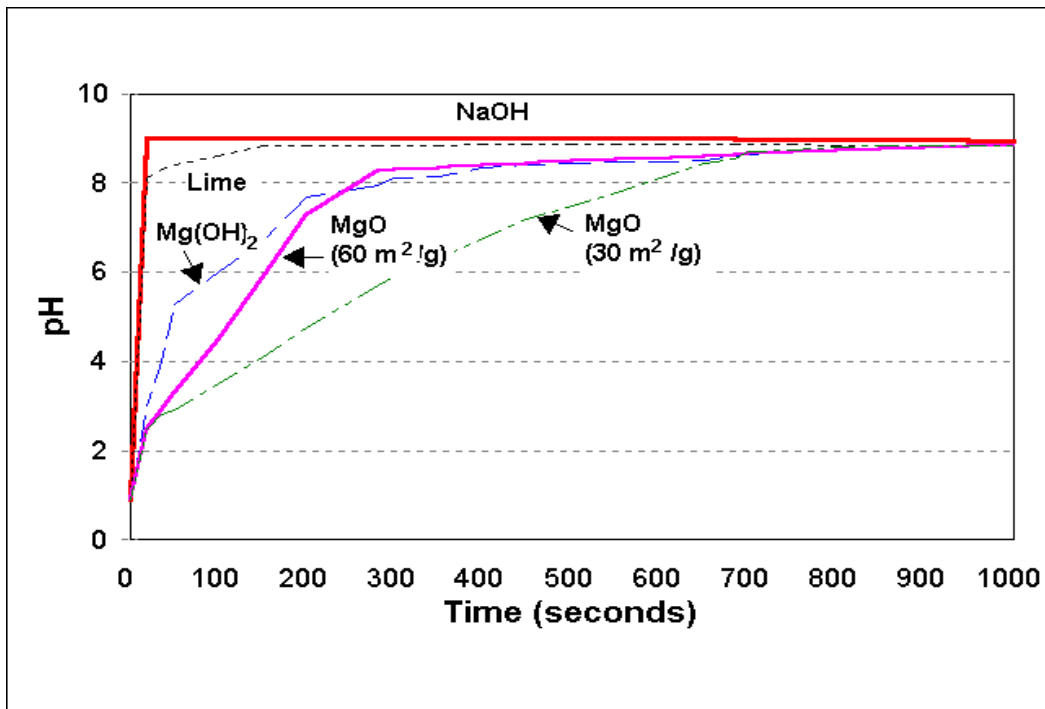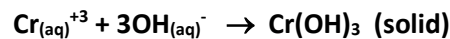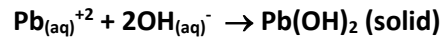

METAL PRECIPITATION

Metals are essential to all electronic components due to their conductive and resistive properties. The most common forms of application are electroless and electrolytic plating in which an adherent metallic coating is deposited on an electrode to produce a surface with properties or dimensions different from those of the basic metal. Chemical etching, which is used in the electroplating preclean operations

or in the removal of excess surface metal, is also a major source of metallic contaminants (Nunno et al., 1988).

In the printed circuit board and electroplating industry, process wastes and rinse water, which are generated from the etching and metal plating baths, typically contain metal concentrations in the final effluent that exceed pretreatment standards for discharge. Conventional treatment methods such as chemical precipitation have been used to reduce the metal concentrations in these effluents to meet specific discharge limits.

Chemical precipitation of metals such as copper, lead, zinc, chromium, nickel, and cadmium can be achieved by addition of an alkali such as caustic, hydrated lime, or one of the magnesium compounds to acidic wastewater. Precipitation occurs as the pH of the wastewater is raised to a point where the metal (cation) reacts with the hydroxyl ions to form an insoluble metal hydroxide.

Examples: $Pb_{(aq)}^{+2} + 2OH_{(aq)}^{-} \rightarrow Pb(OH)_2 \text{ (solid)}$

$Cr_{(aq)}^{+3} + 3OH_{(aq)}^{-} \rightarrow Cr(OH)_3 \text{ (solid)}$

Metal hydroxides precipitate at various pH levels depending upon the type of metal. Metals such as chromium become more insoluble as the pH is increased to its minimum solubility point, which is in the pH range of 8.0 - 9.0. Figure 3 shows the solubility curve of trivalent chromium as a function of pH. As the pH is increased beyond this optimum pH, the insoluble metal hydroxide starts to go back into solution. However, because the maximum pH that can be achieved by magnesium hydroxide is 9.0, resolubilization of the precipitated metal is less likely to occur than if caustic or hydrated lime were employed.

Figure 3
Solubility of Chromium (III) Hydroxide as a Function of pH
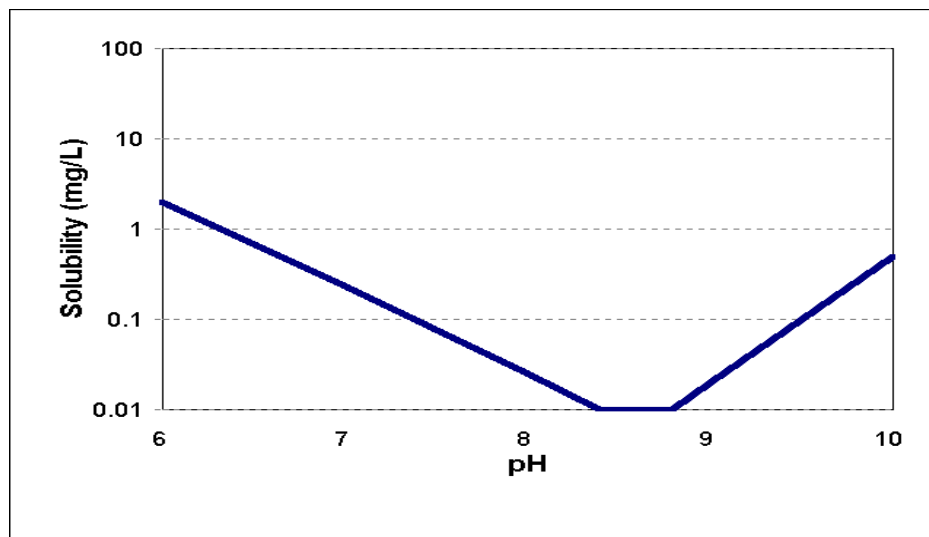
As mentioned previously, acid neutralization using hydrated lime and caustic occurs rapidly as compared to using magnesium compounds. This is also true for precipitating metals from acid waste streams as seen in Figure 4 which shows neutralization of a 290 mg/L trivalent chromium solution. During the dissociation of hydrated lime or caustic in the presence of metals, the hydroxyl ions combine with the metal ions so quickly that there is little time for crystal growth of the metal hydroxides.   Instead, small friable particles result that entrain large amounts of water thus contributing to the overall sludge volume produced. The sludge formed is gelatinous making filtration difficult and time consuming.

Figure 4
Comparative Neutralization Rates for
290 mg/L Cr (III) Solution
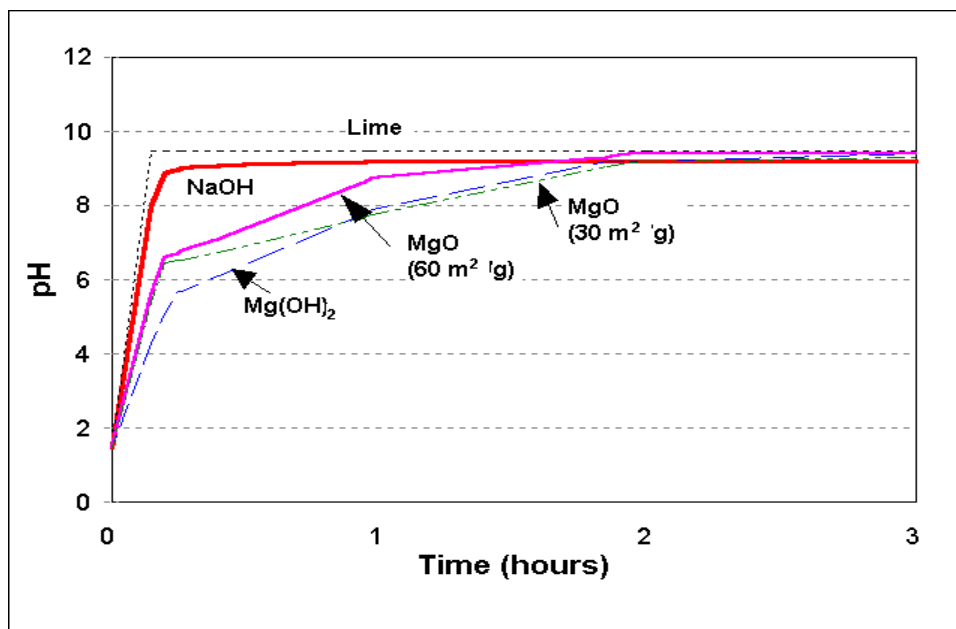
Due to the low solubility and slow dissociation of magnesium compounds, the pH of the wastewater increases until it reaches the point where the metal begins to precipitate out of solution. At this pH level, the magnesium compound dissolves at the same rate at which the released hydroxyl ions are reacting with the metal (Teringo, 1990). The pH remains stable through this quasi-equilibrium until all the metal hydroxide is precipitated and a buildup of hydroxyl ions causes the pH to increase again. In a multi-metal contaminated waste stream, the pH will proceed upward to the next metal's minimum solubility pH. In cases where high metal concentrations are present (i.e. > 100 mg/L total metal), the reaction time is slower than if low concentrations were present. This longer reaction time, however, allows for crystal growth development which results in larger particles. The sludge produced is a dense, compact sludge which is much easier to dewater.

As magnesium compounds require this extra reaction time, sufficient retention time for neutralization must be provided. To increase the rate of reaction, however, an excess of magnesium

hydroxide needed for 100% neutralization (typically 1% to 20% excess) may be added without exceeding the buffer pH of 9.0. (Excesses beyond 15% - 20% of the stoichiometric dosage may not be economical. The excess must be limited to prevent driving up the cost of solids disposal.)

Depending upon the composition of the waste stream, magnesium compounds can reduce sludge volume by as much as 60%. This benefit, along with a higher percent solids sludge, decreases the amount of filter press time needed and reduces sludge disposal costs. Figure 5 and Figure 6 depict the typical sludge characteristics produced by magnesium compounds after neutralizing lab prepared chrome and copper solutions of the same concentration. After a 30 minute settling time, the volume of particulate sludge produced is less for magnesium hydroxide slurry than for the other alkalis. In addition, this sludge is of a higher percent solids with increased porosity and permeability thus making dewatering an easier process. Since the sludge produced by magnesium compounds is dense and not gelatinous, the sludge settles faster and may not require as much flocculent usage as when caustic and hydrated lime are used as the neutralizing agents.

Aside from chemical precipitation, magnesium compounds have another added benefit of being able to remove metals through surface adsorption. If a certain pH level cannot be achieved within a specified retention time by magnesium compounds, the metals may be adsorbed onto the surface of the magnesium hydroxide or magnesium oxide particles despite the lack of an acceptable pH level (Teringo, 1987). A patented granular, magnesium-based adsorbent utilizes this mechanism to remove metals from mildly acidic waste streams prior to discharge.
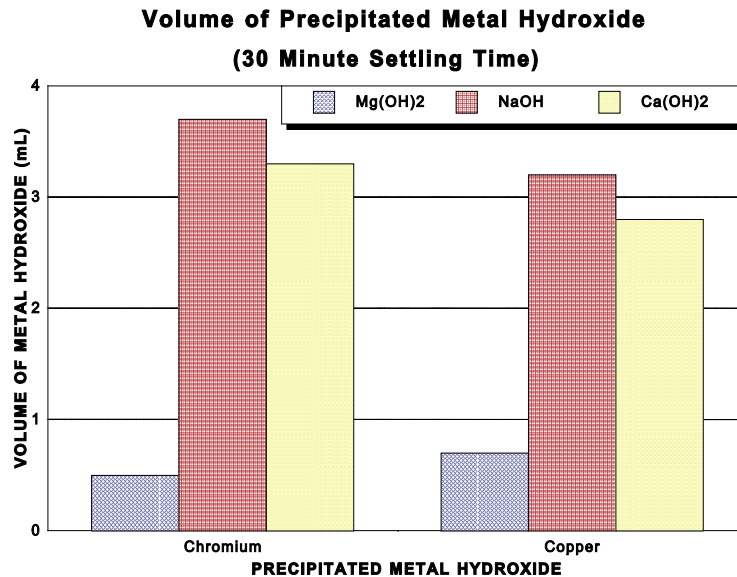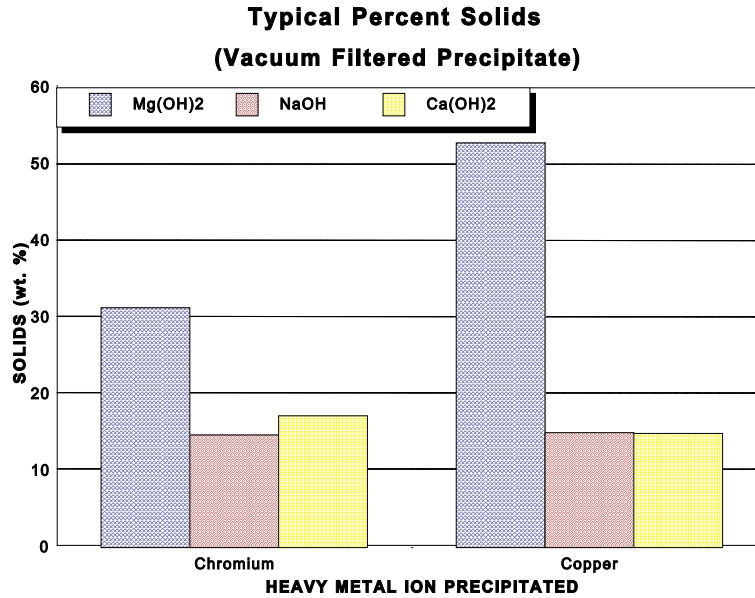

Figure 5

Typical Percent Solids

(Vacuum Filtered Precipitate)

Figure 6

GRANULAR, MAGNESIUM-BASED ADSORBENT

In cases where chemical precipitation is not completely successful in reducing metal concentrations in the wastewater to comply with discharge regulations, additional treatment techniques such as reverse osmosis, ion exchange, and activated carbon are often employed to reduce the metal concentrations sufficiently for discharge. One new approach to tertiary treatment is a patented granular, magnesium-based adsorbent that uses surface adsorption via ion exchange to remove metal ions from mildly acidic (pH 4.0) to mildly alkaline (pH 8.5) rinse water and plating baths, while simultaneously neutralizing the acidic components of the waste stream. The medium is often used as a polishing filter downstream of primary and secondary treatment to remove trace soluble metals (< 20 mg/L) and filter out the insoluble metals. Typical applications, however, have included wastewater with metal concentrations up to 220 mg/L.

The granular adsorbent functions as an inorganic ion exchange medium where a Mg^{++} ion exchanges with a metal ion (M^{+x}) as shown in the following equation:

$$Mg(OH)_{2\ (adsorbent)} + M_{(aq)}^{+2} \rightarrow M(OH)_{2\ (adsorbent)} + Mg_{(aq)}^{+2}$$
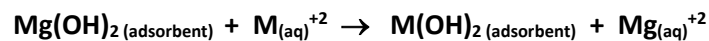
In this equation, the metal ion is shown as divalent, but any multivalent metal ion may be adsorbed provided the ion exists as a free cation in solution. Anionic species, such as complexed or chelated metals

(e.g. $Cr_2O_7^{-2}$, Cu-EDTA, etc.), cannot exchange for the magnesium, and are therefore not adsorbable by this medium.

Metal hydroxides that are less soluble than magnesium hydroxide can be successfully treated and are shown in Table 3. Metal hydroxides such as copper and lead hydroxides both have solubilities (2.8 x 10^{-7} and 2.2 x 10^{-7} respectively) much lower than magnesium hydroxide (2.2 x 10^{-4}) and are readily adsorbed by the granular, magnesium-based adsorbent. Calcium hydroxide, however, is much more soluble (2.5 x 10^{-2}) than magnesium hydroxide, and is therefore not adsorbed by the medium.

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 0.01 mg/L or less with sufficient contact time. Shorter contact times may result in less efficient removal of the target metal.

Like ion exchange mediums, this adsorbent is regenerable with dilute acid backwash. The spent acid regenerant is returned to the primary precipitation step for treatment or to metal recovery. If regeneration is not preferred, proper disposal of the saturated medium in accordance with local, state, and federal regulations is employed. Periodic backwashing with air and water is highly recommended to keep the bed friable and free of particulates.

Table 3
Solubility Data for Target Treatment Metals

Metal Hydroxide	K_{sp}	Solubility, mole/L	Temperature
[1]$Cu(OH)_2$	2.2 x 10^{-20}	2.8 x 10^{-7}	Room temp.
[2]$Cd(OH)_2$	1.7 x 10^{-15}	1.2 x 10^{-5}	25°C
[3]$Cr(OH)_3$	1.7 x 10^{-24}	1.2 x 10^{-8}	Room temp.
[4]$Ni(OH)_2$	6.5 x 10^{-18}	1.9 x 10^{-6}	Room temp.
[5]$Zn(OH)_2$	1.7 x 10^{-16}	5.5 x 10^{-6}	25°C
[6]$Pb(OH)_2$	1.1 x 10^{-20}	2.2 x 10^{-7}	22°C
[7]$Mg(OH)_2$	1.1 x 10^{-11}	2.2 x 10^{-4}	18°C
[8]$Ca(OH)_2$	5.5 x 10^{-6}	2.5 x 10^{-2}	25°C

[1] Nasanen et al., 1949.
[2] Feitknecht et al., 1951.
[3] Oka, 1940.
[4] Gayer et al., 1949.
[5] Feitknecht, 1947.
[6] Korenman et al., 1952.
[7] Gjalbek, 1925.
[8] Dean, 1992.

The advantages of this magnesium-based adsorbent over conventional ion exchange resins are low sensitivity to Total Dissolved Substances (TDS) and can withstand high metal concentrations in the influent. If there is an abundance of TDS such as calcium and sodium, conventional ion exchange resins may stop functioning. The magnesium-based adsorbent can tolerate these substances without loss of its adsorption capacity. If the metal concentration is too high when entering the ion exchange bed, very little metal removal will occur. The magnesium-based adsorbent, on the other hand, will saturate faster with high metal loadings, but still reduce the metal concentration.

CASE STUDIES

Case Study #1: Electronic Component Manufacturer

This plant manufactures components for printed circuit boards which introduces copper into their wastewater stream. Chemical precipitation with $Mg(OH)_2$ topped off with NaOH to increase the rate of neutralization is used to adjust pH and precipitate copper as $Cu(OH)_2$ at a pH of 8.0. The stream and precipitated metals are dosed with flocculent and fed to a large inclined plate clarifier which removes the bulk of the solids. The copper containing sludge is dried and sold to copper reclaimers while the supernatant is filtered through gravity paper to remove flocculated precipitate prior to discharge to the river. Soluble copper in the discharge water often reached 1.5 mg/L which exceeded their 1.0 mg/L copper discharge limit. As a result, the granular, magnesium-based adsorbent was added as a polishing filter after the gravity paper filter. A schematic of the treatment system is shown in Figure 7.

FIGURE 7
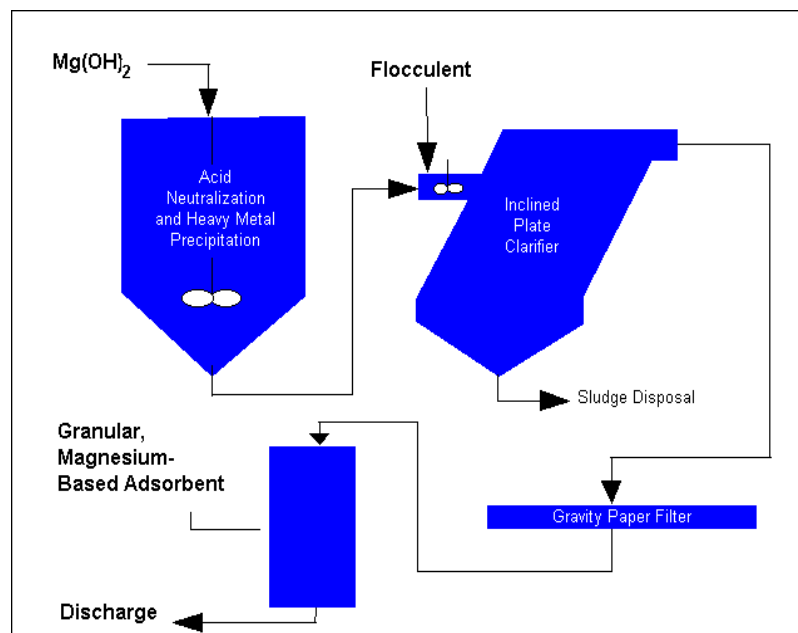
Approximately 113.5 kg (250 lbs) of the granular, magnesium-based adsorbent were charged in the filter vessel. The flow rate, which was regulated after installation to provide an eight minute contact time within the bed, was later increased for a six minute contact time in order to treat more wastewater. After one month of testing the magnesium-based adsorbent, 286,525 L (75,700 gal) of wastewater were treated and approximately 0.74 kg (1.64 lbs) of copper was removed. Based on the 113.5 kg of adsorbent in the filter vessel, the theoretical amount of copper that could be adsorbed until saturation was 2.27 kg (5 lbs). The average copper concentration in the effluent was < 0.5 mg/L when using the adsorbent. One reading, however, showed the copper concentration to be 1.36 mg/L which was due to channeling in the

bed.

Daily backwashing with fresh water and air was employed which restored good copper adsorption in the subsequent measurements. Figure 8 shows the performance of the granular, magnesium-based adsorbent in the removal of copper from this wastewater stream.

FIGURE 8

Case Study #1: Copper Removal Using Magnesium-Based Adsorbent
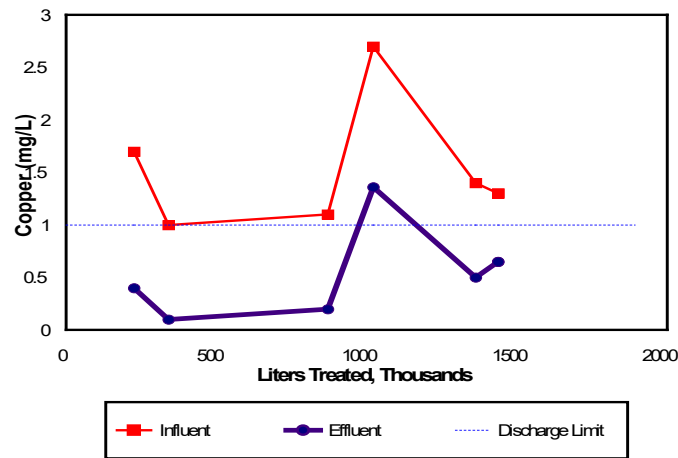
Case Study #3: Semiconductor Manufacturer

Case Study #2: Metal Plater for Printed Circuit Boards

In this second case study, a metal plater for printed circuit boards generates wastewater containing zinc, copper, and nickel from the process. Chemical precipitation using NaOH was not effective in reducing the three target metals to below this facility's discharge limit of 1.0 mg/L and effluent metal concentrations often exceeded 4.0 mg/L. As a result, a filter vessel containing 136 kg (300 lbs) of granular, magnesium-based adsorbent was installed as a polishing filter prior to discharge. Instead of the eight-minute contact time recommended, this facility maintained a 5.2 minute contact time within the adsorbent bed. Despite the short contact time, the metal plater did not experience a surge in any of the metal concentrations exceeding 0.98 mg/L. Figure 9 shows the metal concentrations before and after installing the magnesium-based adsorbent.

**Case Study #2: Multi-Metal Removal
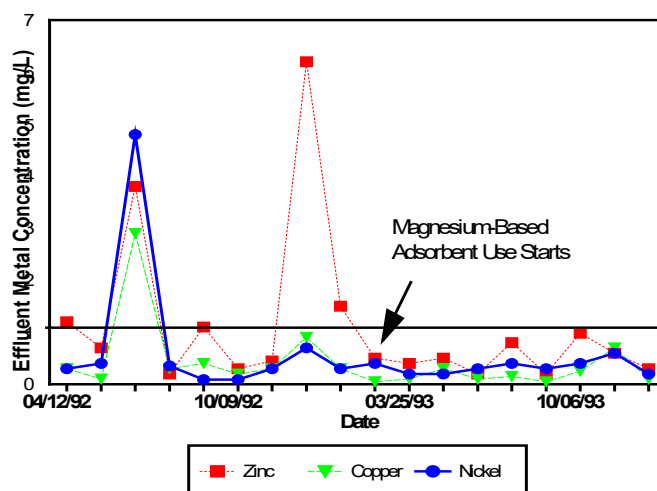Using Magnesium-Based Adsorbent**

Figure 9

Case Study #3: Semiconductor Manufacturer

This semiconductor manufacturer uses vats of acid to clean and polish metal between chips resulting in acidic rinse water that must be neutralized prior to discharge. The influent is a combination of acidic waste streams -- hydrochloric, nitric, and sulfuric acid -- with a composite pH of 4.0. In their continuous treatment process, a three mix-tank system is employed for acid neutralization with magnesium hydroxide slurry. Approximately 3785 L/min (1000 gal/min) are neutralized to a pH of 8.0 - 9.0 within their sixty minute retention time. Since their target pH is 8.0 - 9.0, the company chose magnesium hydroxide slurry for its buffering ability and safety. With caustic, the company did not want to deal with the safety issues when handling the corrosive material. They also found that a pH adjustment tank was needed after neutralization since caustic did not buffer to a controlled pH like magnesium hydroxide slurry, but often overshot their discharge limit of 6.0 - 11.0. This company currently consumes three truckloads of magnesium hydroxide slurry a month.

Case Study #4: Metal Fabricator for the Electronics Industry

At this facility, metal is fabricated for electronic components manufacturing. The wastewater generated from the process contains mainly trivalent chromium, which must be treated to meet discharge requirements. In the original treatment, approximately 1.31 kg per 1000 L (10.9 lbs per 1000 gallons) of caustic and 0.24 kg per 1000 L (2 lbs per 1000 gallons) of alum were used to precipitate the chromium. This treatment, however, was only effective in reducing the chromium level down to 1.8 mg/L. The

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amount of sludge generated was 13,620 - 18,160 kg (30,000 - 40,000 lbs) per year, which was subsequently disposed in a landfill.

The company switched to magnesium oxide for chemical precipitation of the chromium. Chemical consumption was reduced as they only used 0.74 kg of magnesium oxide per 1000 L(6.1 lbs per 1000 gallons), and eliminated the need for alum since a better settling precipitate was formed by magnesium oxide. The chromium concentrations in the effluent were <0.2 mg/L while sludge production was reduced to <9080 kg (<20,000 lbs) per year. Switching to a magnesium compound in their treatment system allowed this facility to use less neutralizing agent, eliminate alum, lower the chromium in their discharge, and reduce sludge disposal costs by reducing the amount of sludge generated by 50%.

Case Study #5: Electroplating Facility[1]

Wastewater from zinc electroplating, chrome dipping, and zinc phosphate baths are generated at this facility. Significant concentrations of dissolved zinc, iron, and chromium are present in the wastewater stream which is neutralized using conventional precipitation methods via caustic. Frequent effluent treatment and disposal problems prompted this facility to test magnesium hydroxide as their primary neutralizing agent.

With caustic, suspended solids were often found in the clarifier overflow and discharged with the effluent. Sludge filter cakes were soft and gelatinous, yielding a 15% to 30% solids cake. Due to the difficulty in dewatering the metal hydroxide sludge, there was increased demand on the filter press and increased maintenance times.   Although caustic quickly neutralized the wastewater stream, it produced a poor quality effluent, generated large sludge volumes, and made filtration a very time-consuming task.

As a result, the electroplating facility concluded that magnesium hydroxide slurry would be the best alternative to caustic by improving sludge properties and by providing a good quality effluent. Since the company did not want to greatly modify their current system to accommodate the longer retention time associated with magnesium hydroxide neutralization, caustic was utilized to "top off" the neutralization process. Preliminary testing showed that the magnesium hydroxide/sodium hydroxide combination would still reduce the sludge volume by 60% and settling time by 88%.   Figure 10 is a schematic of the treatment process utilizing both alkalis.

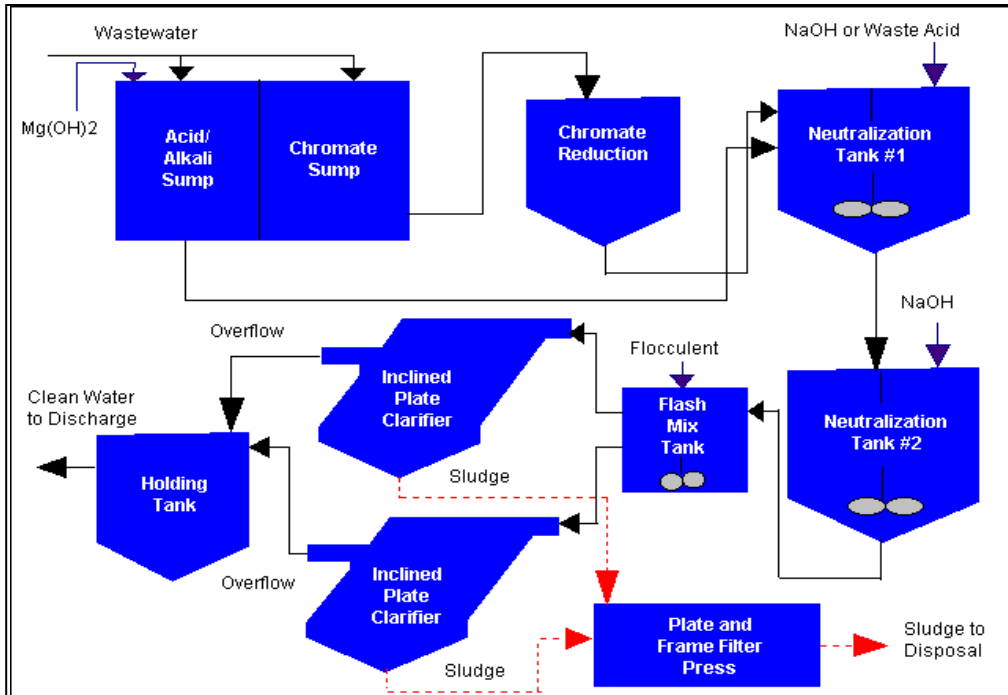[1]   Louchart and Papamarcos, 1988.

Figure 10

Magnesium hydroxide slurry is added to the acid/alkali sump in order to take advantage of the available mixing and retention time. Both acid/alkali and reduced chromate streams are pH adjusted in Tank #1 to a pH of 7.5 to 9.5 using sodium hydroxide or waste acid. Additional mixing and retention time in this tank accommodate the slow reaction of magnesium hydroxide. In Tank #2, the pH is raised to 8.5 to 9.5 with sodium hydroxide since the time for neutralization is only ten minutes.

The treated wastewater is then dosed with an anionic polymer in a flash mix tank prior to clarification in parallel inclined plate clarifiers. The overflow from the clarifiers are discharged to the municipal sewer while the sludge generated is thickened and dewatered using a 25-cubic-foot plate-and-frame filter press. The sludge produced by using a combination of magnesium hydroxide and sodium hydroxide yielded a solids content of 27% to 50% which increased with each trial run.

The electroplating facility found that the addition of magnesium hydroxide to their current system improved water quality, decreased sludge volumes, significantly increased sludge density and therefore, settling rates of the precipitate, and increased filterability of the sludge produced. These benefits led to a decrease in filter press cycle times and maintenance, reduced sludge disposal costs, and cutback on chemical costs. Average liquid sodium hydroxide consumption on a monthly basis prior to the addition of magnesium hydroxide was 30,882 L (8159 gallons). After adding magnesium hydroxide, the use of caustic was reduced to 15,727 L (4155 gallons) with the addition of 10,871 L (2872 gallons) of magnesium hydroxide slurry. This reduction in alkali consumption provided a 9% cost savings to the company.

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Sulfuric acid was eliminated with the addition of magnesium hydroxide since pH excursions were less likely due to buffering at a pH of 9.0. With caustic alone, the facility often overshot the target pH which required pH adjustment with approximately 3028 L per month (800 gallons per month) of raw sulfuric acid. After implementing magnesium hydroxide, the waste pickle liquor generated in the electroplating process satisfied their acid requirements. In addition, polymer costs were reduce by 36% because the incorporation of magnesium hydroxide in the treatment system allowed the company to use a less expensive polymer without compromising the quality of the effluent.

CONCLUSION

As these case studies show, the utilization of magnesium compounds for wastewater treatment in the electronics industry can provide significant economic and operational advantages by reducing chemical, maintenance, and sludge disposal costs. Electronic component manufacturers are looking towards magnesium compounds because of its safe and easy handling properties.   As compared to caustic, lime, and soda ash, magnesium compounds are environmentally friendly and pose little threat to human health. Although magnesium compounds are slower reacting than other conventional alkalis, the benefits associated with them, such as safety, providing more neutralization value per pound, removing heavy metals effectively, buffering to a controlled pH, and producing less sludge volume with improved sludge handling, make magnesium compounds attractive alternatives to caustic or lime for acid neutralization and chemical precipitation.

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