

Magnesium hydroxide reduces sludge/improves filtering

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In treating acid waste streams containing metals, the cost of neutralization chemicals is generally the deciding factor in determining which treatment method to use. Closer scrutiny shows that, in many instances, sludge disposal costs should also be considered and may even overshadow treatment chemical costs. In many applications, the advantages of magnesium hydroxide in reducing sludge disposal costs can significantly outweigh the higher chemical cost.

Magnesium hydroxide is an alkali that has been used for many years to neutralize acid. The medicinal neutralization people are familiar with is neutralization of stomach acids using "Milk of Magnesia" in which the major ingredient is magnesium hydroxide.

In wastewater management, one common and cost effective way to treat acid waste streams containing dissolved metals is through chemical precipitation of the

metal hydroxide. Precipitation is usually accomplished with such alkalies as caustic (NaOH), lime (CaO) and soda ash (Na_2CO_3). Magnesium hydroxide [$\text{Mg}(\text{OH})_2$] has also been found to be effective in neutralizing acids, as well as in removing unwanted metal contaminants in electroplating and metal finishing wastewaters.

Magnesium hydroxide does not act nor react like conventional alkalies. Yet the unique characteristics of this alkali, when properly applied in a treatment system, can result in a lower volume and more dense metal hydroxide sludge that is easier to dewater.

Properties

Magnesium hydroxide is available as an aqueous white slurry [55-60 percent $\text{Mg}(\text{OH})_2$] of agglomerated particles (particle size distribution 0.6 to 10.0 microns) with a bulk density of 12.5 lb/gal. This highly viscous (4-40 poise, Brookfield Viscometer #4 Spindle at 20 rpm) thixotropic slurry resembles latex paint, see Figure 1. It freezes at 32 F and must be kept in mildly agitated storage. At ambient temperatures, the solubility of magnesium hydroxide is very low (0.0009 g/100 ml H_2O at 18 C) and decreases as the temperature is increased (0.0004 g/100 ml H_2O at 100 C).

As mentioned earlier, magnesium hydroxide is comparable to a concentrated milk of magnesia product and, therefore, can be classified as a low-degree health hazard from a handling point of view. Magnesium, as one of the most common elements on earth, is an essential nutrient to normal plant, animal and human growth. This, in conjunction with magnesium hydroxide's low solubility, would cause a minimal environmental impact in the event of an accidental spill.

When comparing physical and chemical properties of magnesium hydroxide with conventional alkalies such as hydrated lime or caustic, several distinct advantages can be noted as shown in Table 1. The first is percent hydroxide (that portion of the chemical which actually neutralizes the acid and precipitates the metals). Magnesium hydroxide has 27 percent more hydroxide than hydrated lime and 37 percent more than the caustic. This means that fewer pounds of magnesium hydroxide (and less storage volume) are required to neutralize a given volume of acid and remove metal(s).

In the neutralization of hydrochloric acid, Table 2, less magnesium hydroxide is required than either lime or caustic. With magnesium hydroxide neutralization, there is also a reduction in the total dissolved salt in the effluent stream than there would be if caustic or lime is the neutralizing agent.

Less magnesium hydroxide is also required in the neutralization of sulfuric acid than would be required for lime or caustic. As for total dissolved salt, less magnesium sulfate is generated when magnesium hydroxide is the alkali source than the amount of sodium sulfate

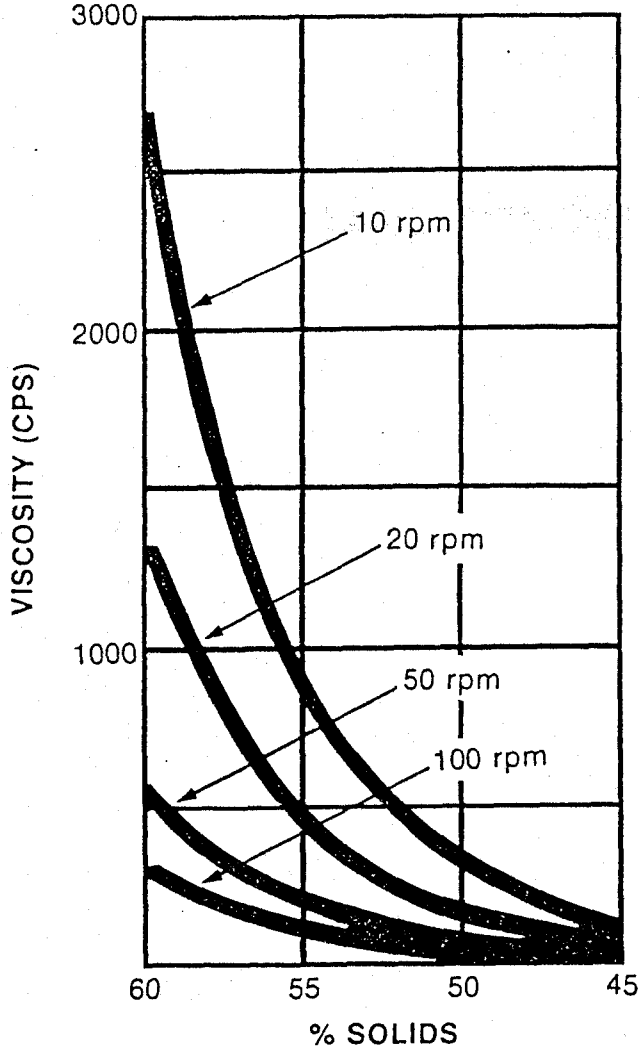


Figure 1. Brookfield viscosity vs percent solids of magnesium hydroxide in water.

generated by caustic. Calcium sulfate, generated when lime is the alkali source, is virtually insoluble so total dissolved salt in this case will be extremely low.

Another characteristic unique to magnesium hydroxide is its reactive pH maximum. Excess addition of lime or caustic causes the pH of waste streams to rise to 12.5 and 14.0, respectively. The pH of a magnesium hydroxide slurry is 10.5, but when it is used to neutralize acidic streams containing diverse ions, magnesium hydroxide can only obtain a maximum pH of 9.0. This phenomenon is known as a common ion effect (buffering) and is of special benefit when more alkali is accidentally added to the effluent than is needed for neutralization.

The maximum magnesium hydroxide pH of 9.0 happens to coincide with the upper pH limit cited in the Clean Water Act of 1976. This pH also prevents resolubilization of some of the heavy metals (precipitate) that are being removed.

Metal hydroxides precipitate at various pH levels, depending upon the type of metal. Observing various concentrations of metal hydroxides versus pH, it can be noted that several metals such as chrome, copper, zinc and lead, to name a few, will become more insoluble as the pH is increased. Then a minimum solubility point is reached after which, upon the further addition of hydroxide ion to the media, the insoluble metal hydroxide becomes more soluble via complex formation.

The buffering effect of the pH at 9.0 can also be beneficial for disposing of alkaline wastes downstream of the neutralization without concern for exceeding maximum effluent pH limits. Although magnesium hydroxide will begin to precipitate out beyond a pH of 9.0, a considerable amount of alkalinity is required to do this.

A final advantage of magnesium hydroxide over hydrated lime or caustic is its safety. With hydrated lime or caustic, heat is liberated in the presence of additional water. These strong alkalies (bases) can cause severe irritation or burns with skin or eye contact. Magnesium hydroxide is not exothermic and is classified as a weak base, making it much safer to handle.

Reactivity

Acid neutralization reactions with hydrated lime or caustic may be considered one-step reactions in which the alkali dissociates immediately to provide an abundance of hydroxyl ions that neutralize the acid and cause a rapid increase in pH. Magnesium hydroxide does not react like conventional alkalies, as shown in Figure 2. Using magnesium hydroxide for neutralization involves a two-step reaction.

Magnesium hydroxide, being sparingly soluble, is in equilibrium with the water and produces a limited amount of magnesium and hydroxyl ions. These hydroxyl ions must be consumed by the acid before more magnesium hydroxide is solubilized.

The rate of neutralization for magnesium hydroxide is dependent upon several conditions beyond the usual kinetic effects of increased temperature and agitation. One factor that influences the rate of neutralization is the amount of alkali used. By adding more alkali than necessary for 100 percent neutralization, the reaction rate will increase. However, the buffering capability of magnesium hydroxide will prevent the pH from exceeding 9.0.

The rate of neutralization is also affected by the con-

Table 1. Comparison of Physical and Chemical Properties

Property	NaOH	Ca(OH) ₂	Mg(OH) ₂
Molecular weight	40.0	74.1	58.3
Percent hydroxide	42.5	45.9	58.3
Heat of solution, Kg-Cal/mol	9.94	2.79	0.0
Solubility in water, g/100 ml H ₂ O	42 ¹	0.185 ¹	0.0009 ²
Reactive pH maximum	14	12.5	9.0
Weight equivalency	1.37	1.27	1
Freeze point, F	61 ³	32 ⁴	32 ⁵

¹ - 0 C

² - 18 C

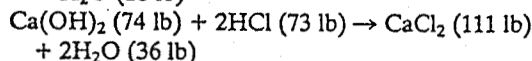
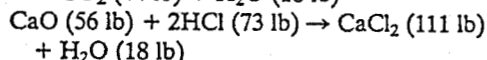
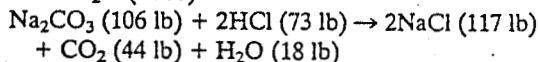
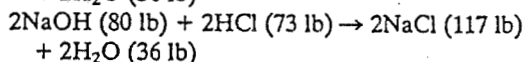
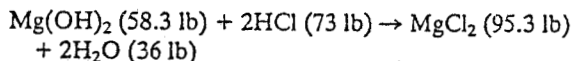
³ - 50% solution

⁴ - 30% slurry

⁵ - 58% slurry

Table 2. Neutralization of Hydrochloric Acid (HCl)

For two moles (73 lb) of HCl (hydrochloric acid) to be neutralized, the following chemical reactions would occur:



Using the above equations, we can arrive at the following significant conclusions:

Neutralizing Agent	Lb Required to Neutralize 1 Ton HCl	Ratio to: Mg(OH) ₂	Total Dissolved Solids in Effluent: (100% Basis) Acid Per Ton
Mg(OH) ₂	1600	1.0	2610
NaOH	2190	1.37	3210
Na ₂ CO ₃	2900	1.82	3210
CaO	1530	0.96	3040
Ca(OH) ₂	2027	1.27	3040

centration of acid being neutralized. As shown in Figure 3, a 5 percent sulfuric acid solution reaches a pH of 7 in approximately one minute. It takes ten minutes to obtain the same pH when treating 0.25 percent acid.

Waste streams usually contain a multitude of metals that need to be removed. Other factors that affect the reaction rate of magnesium hydroxide are the concentration and type of metal to be removed. As can be seen in Figure 4, the residence time required to remove 100 ppm ferric-iron is much less than for removal of 200 ppm of ferric iron. The removal of 100 ppm copper takes longer than 100 ppm ferric iron.

With the addition of magnesium hydroxide, the pH will increase to the level at which a particular metal precipitates. It will remain at that pH until the metal is removed and then will proceed upward to the next metal's precipitation pH. For example, if a system contained both ferric iron and copper, the pH would rise to 4.5 where ferric hydroxide precipitates and remain there until all of the ferric iron has been removed. The pH would then rise up to 7.0 where the onset of copper hydroxide precipitation begins.

There are two other reactive characteristics that need to be mentioned. Magnesium hydroxide not only provides hydroxyl ions for metal removal, but can remove metals through surface adsorption. It has been observed that metals can be removed from waste streams despite the lack of an acceptable pH level. Table 3 illustrates such a phenomena.

The first item to note is magnesium hydroxide at a pH of 5.6. At this pH the copper concentration should be above 100 ppm according to most concentration versus pH profiles. Next, note as the reaction neared completion the magnesium hydroxide was just as effective in lowering the copper to an equivalent level at approximately 1 pH unit less than the caustic; i.e., pH 8.4 for 0.2 ppm Cu; pH 9.3 for 0.4 ppm Cu. Finally, it can be seen that as the pH of the caustic increases from 10.3 to 10.9, the copper begins to resolubilize.

Another reactive characteristic of magnesium hydroxide pertains to flocculent (polymer) addition. Flocculent addition will cause the unreacted magnesium hydroxide particles to coagulate with the sludge and its reaction is terminated. While flocculent may be added in the early stages of neutralization when using caustic or lime, it is added in the final stage of neutralization when using magnesium hydroxide.

In summary, there are several factors that can affect the reaction rate of magnesium hydroxide with acidic metal waste streams. It is a culmination of these effects which requires longer residence times when using magnesium hydroxide in place of hydrated lime or caustic for acid neutralization and metal removal. This additional residence time may appear to be a deterrent for using magnesium hydroxide but slower reactivity is what makes magnesium hydroxide attractive from a sludge production and handling point of view.

Sludge Characteristics

The type of metal hydroxide precipitate that forms when using hydrated lime or caustic tends to be extremely light and friable. The strong bases cause nearly

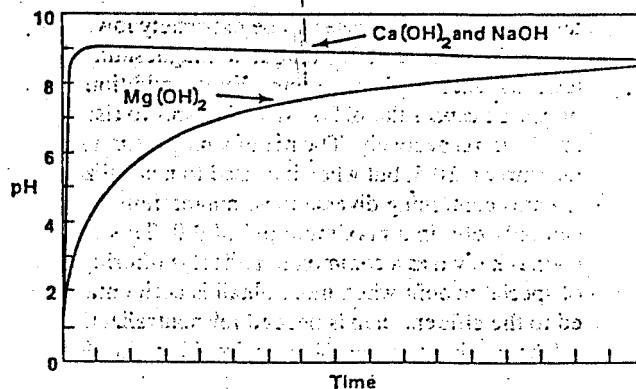


Figure 2. Rates of acid neutralization.

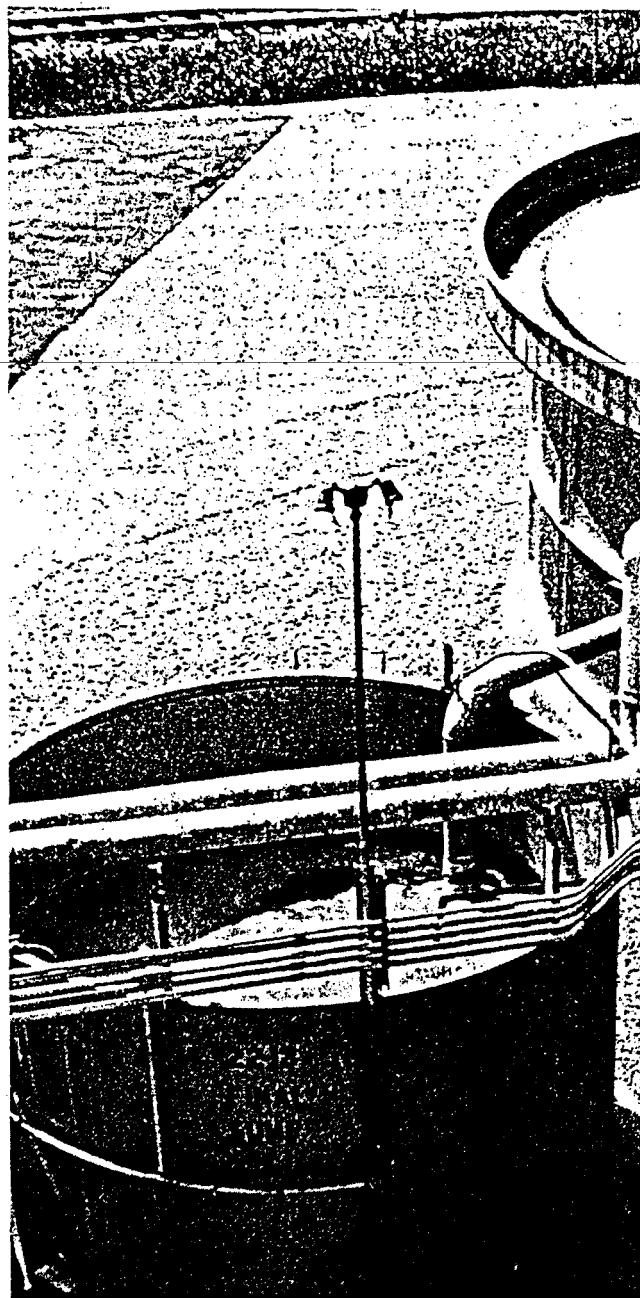
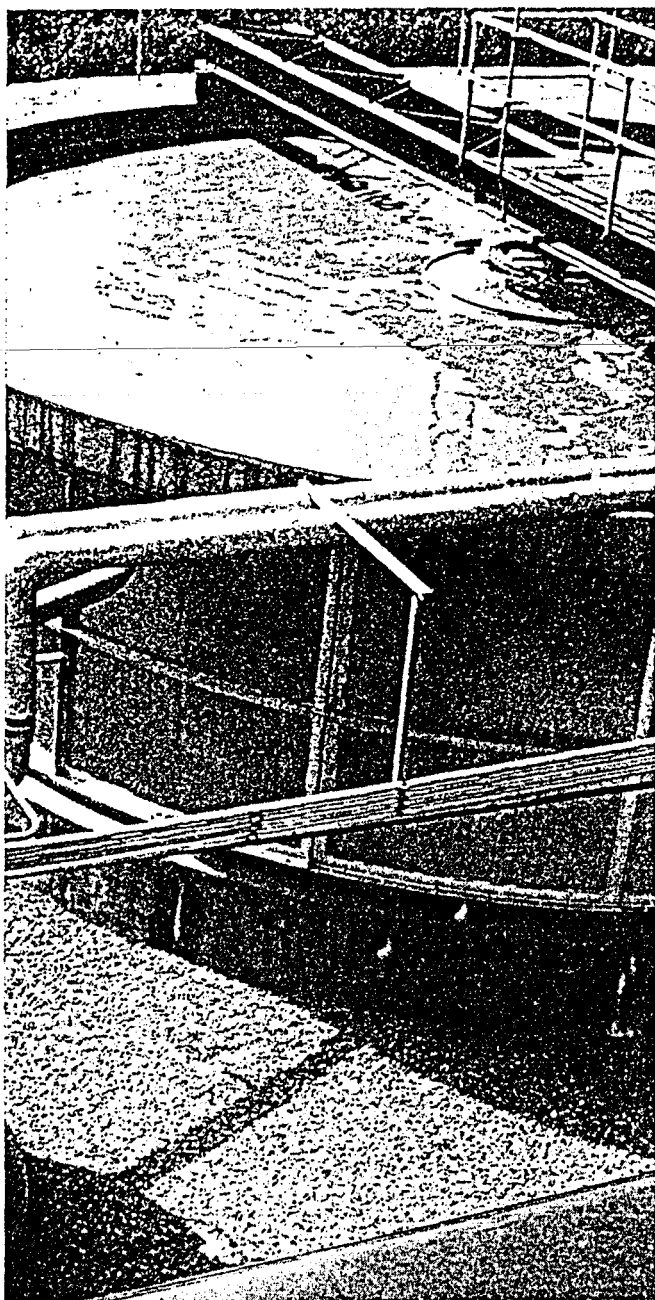


Table 3. Surface Adsorption

Alkali	pH	ppm Cu
None	1.5	500
NaOH	6.9	3.6
Mg(OH) ₂	5.6	37
Mg(OH) ₂	8.4	0.2
NaOH	9.3	0.4
NaOH	10.3	0.3
NaOH	10.9	0.5



instantaneous precipitation of metal hydroxides. This results in numerous small particles that are inter-dispersed with water to form a gelatinous type sludge.

The type of sludge formed with magnesium hydroxide is more particulate in nature. Larger particles are formed because the longer reaction time is conducive to crystal growth. The difference between a particulate sludge and a gelatinous sludge can be seen in Figure 5. The sludge in the vials is the result of treating a sulfuric acid waste stream containing 1000 ppm chrome with caustic, hydrated lime and magnesium hydroxide.

Typically, magnesium hydroxide reduces sludge volume by 50 percent or more by producing a much denser sludge. This can be seen in the opacity differences at the tips of the volumetric centrifuge vials. On a dry weight basis, the amount of sludge in the three tubes is approximately the same with the exception of the CaSO₄ 2H₂O portion of the sludge formed with the hydrated lime. The magnesium hydroxide particulate sludge also has increased porosity and permeability, making it easier to dewater than gelatinous sludges.

Table 4 is data based on experience with several chrome plating operations. While there is an increase in the percent solids and sludge density using magnesium hydroxide, dewatering time (filter press time) is reduced. These results will vary from time to time, reflecting the change in wastewater due to changes in upstream production process.

How this reduction in sludge and ease of dewatering translates to actual savings is shown in the following example:

Basis:

1. 341 M lb/yr of lime at \$98/ton delivered
2. 267.5 M lb/yr of magnesium hydroxide at \$274/ton (includes freight to western Pennsylvania)
3. 1,238 yd³/yr of sludge produced by lime
4. 206 yd³/yr of sludge produced by magnesium hydroxide
5. \$40/yd³ sludge disposal cost
6. Labor: manpower cost only to operate solid/liquid separation equipment

	\$ Alkali Cost		\$ Sludge Disposal		Labor		Total
Ca(OH) ₂	16,709	+	49,520	+	15,000	=	\$81,229
Mg(OH) ₂	36,648	+	8,240	+	2,000	=	46,888

The estimated cost savings shown do not include maintenance costs associated with the scaling effect of lime nor the incremental maintenance costs for additional equipment operation.

Another economic benefit which has been observed in the use of magnesium hydroxide for neutralization is associated with the reduction in the amount of flocculent (polymer) used for flocculation. Several cases have been noted where flocculent usage has been cut in half and can be attributed to the increased density of the sludge. A sludge that settles faster will also provide an economic benefit with the downsizing of sludge holding tanks.

Operating Techniques

Hydrated lime and caustic are generally added to a waste until a desired pH is reached. This cannot be done with magnesium hydroxide because the reaction and pH changes are not instantaneous. One must first calculate the correct quantity of magnesium hydroxide to add. Determining this quantity is fairly simple in batch neutralization systems. Generally, a 100 ml sample of waste is taken and titrated with a one normal (1N) solution of sodium hydroxide to the desired pH. The volume of sodium hydroxide (caustic) consumed in the titration is then used to determine the amount of 50 percent caustic required to neutralize that batch by the following calculation:

$$\text{gal 50\% NaOH} = \text{gal of waste} \times \text{ml of 1N NaOH} \times 0.000523$$

After determining the amount of 50 percent 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 needs to be added.

That quantity of 57.5 percent magnesium hydroxide is added all at once; wait until the pH reaches the desired level. Do *NOT* add more magnesium hydroxide. Experience has shown that the bulk of sludge is formed in the first 20 minutes. Hence, if time is not available for the full reaction, the batch may be "topped off" with lime or caustic (typically less than 10 percent on an alkali basis) to remove the remaining metals immediately. This topping off will produce a sludge with characteristics not quite as good as magnesium hydroxide by itself, but one that will still be better than using conventional alkalies alone.

Application of magnesium hydroxide for a continuous neutralization system can be handled with ease once the correct information is obtained for the startup of the system. Like a batch treatment, a 100 ml sample of waste is first titrated with 1N NaOH to ascertain the amount of alkali that will achieve the desired pH. An equivalent amount of magnesium hydroxide is then added according to the following calculation:

$$\text{grams Mg(OH)}_2 = \frac{\text{ml of 1N NaOH} \times .03061}{\% \text{ Mg(H)}_2}$$

The equivalent amount of magnesium hydroxide is then added to another 100 ml sample of waste to determine a neutralization rate (pH versus time). This relationship will show an early targeted pH that must be obtained in order to reach the final desired pH.

Once the system is in operation, it is often necessary to fine tune the system by adjusting the initial targeted pH up or down to achieve the final desired pH. In the event that there is not a sufficient amount of residence time, several options can be used:

1. Alkali addition in upstream sumps or collection lines.
2. Partitioning of neutralization tanks or basins to prevent shortcutting.
3. Increase agitation.
4. Incorporate additional tankage.





5. Topping off as mentioned before.

In the use of magnesium hydroxide as an alkali for the neutralization of acid/metal waste streams, it will be necessary to make some modifications in waste treatment operating procedures and/or equipment. Based on extensive experience, this can easily be incorporated.

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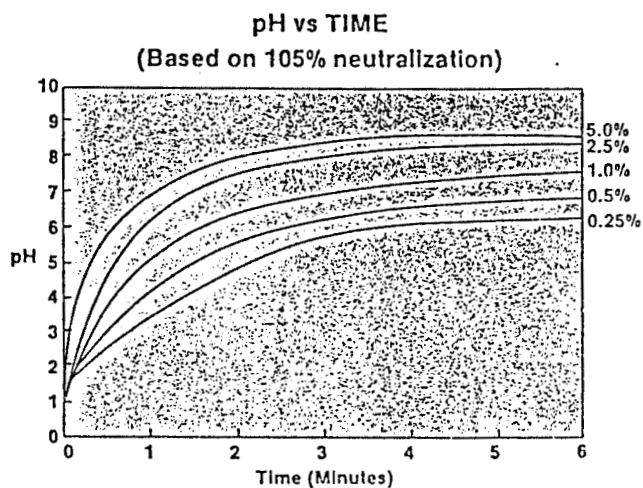


Figure 3. Neutralization of various concentrations of sulfuric acid.

Table 4. Typical Sludge Properties From a Plate and Frame Filter Press

Chemical	Percent Solids	Sludge Density (Lb/Ft ³)	Filter Press Cycle Times (Hr)	Yd ³ Sludge Per 10,000 Lb Solids Generated
NaOH	30	80	7-9	15
Ca(OH) ₂	35	85	7-9	12.5 ¹
Mg(OH) ₂	55	100-110	1.5-2	6.4

¹Consists of both metal hydroxide plus CaSO₄ 2H₂O from sulfuric acid in plating bath.

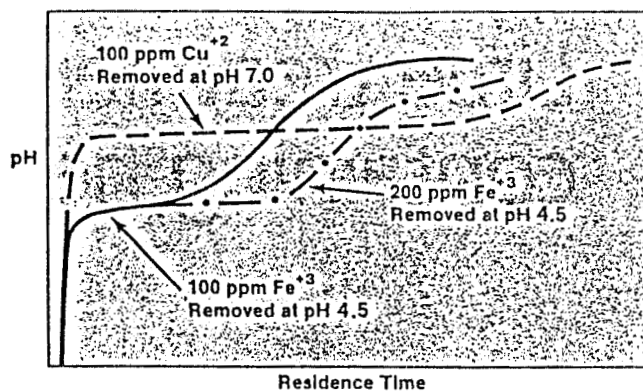


Figure 4. Profile chart showing pH vs time.

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