MAGNESIUM HYDROXIDE AS A TREATMENT FOR ACID MINE DRAINAGE IN NORTHERN MINNESOTA[1]

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Abstract. Three alkaline materials were investigated for their suitability to treat acid mine drainage generated by a research facility located at a remote site in northern Minnesota. The materials investigated were hydrated lime, sodium hydroxide, and magnesium hydroxide. All three reagents were successful at raising pH and removing trace metals from the drainage, but the magnesium hydroxide had the added benefit of producing a maximum pH of approximately 9.5, while the other two reagents resulted in pH values of 12 and greater. In addition, the magnesium hydroxide was available as a high solid content slurry (58%) which simplified application and handling, and which produced the lowest volume of sludge of the materials tested.

Additional Key Words: copper, nickel, cobalt, zinc

Introduction

Acid mine drainage is a serious environmental problem. Thousands of miles of streams have been affected by acid drainage from both coal and metal mines (U.S. Bureau of Mines 1985). The common approach used to control this problem is to increase pH and precipitate metals by the addition of an alkaline material. Lime is the chemical usually used in this treatment process. Lime, although generally available and inexpensive, has several problems associated with its use. It is available only as a dry product which requires care in handling, produces a large mass of low-density sludge, and, if dosage is not carefully controlled, will raise pH to around 12.5. While these concerns can be handled relatively easily in a fully staffed treatment plant, they can cause serious problems at remote locations without full time on-site personnel.

The Minnesota Department of Natural Resources (MnDNR) has conducted field research on the prediction and mitigation of mine drainage problems since 1977 at a remote site in northeastern Minnesota. This site was operated by a mining company in conjunction with their evaluation of a sulfide base metal prospect until 1989. Six test stockpiles of Duluth Complex material, which contain subeconomic amounts of copper and nickel sulfides, are located at the site (Eger et al. 1981). Each pile is underlain with an impermeable 36 mil hypalon liner, and all drainage from the piles is collected in a central sump and pumped to a settling basin.

Drainage from the test piles varies with precipitation and approaches zero during extended dry periods. Peak daily flows ranging from approximately 23-27 liters per minute (l/min) have been observed during summer rainstorms. About 25% of the total annual flow occurs when daily flow exceeds 7.5 l/min, but

90% of the time the flow is less than 3.8 l/min. The annual average volume draining from the six test piles is about 580,000 liters. The composite drainage from all the piles has a pH of around 4.0 and an acidity of 700-800 milligrams per liter (mg/l) as $CaCO_3$. Concentrations over 100 mg/l of both copper and nickel and 10 mg/l of both cobalt and zinc are typical for the site. The drainage from the test pile that produces the most acidic water has a pH of around 3.5 with an acidity over 2000 mg/l (Table 1).

In 1989, the mining company chose to abandon the prospect and reclaim the site. The MnDNR wanted to preserve the research portion of the facility so existing projects could continue and new projects could be initiated. In order to take over operations at the site, it was necessary to develop an acceptable treatment system design before necessary environmental permits would be issued.

MnDNR's long-term goal is to develop and research wetland treatment technologies for treatment of this drainage. However, due to funding limitations, it was decided to actively

treat the drainage with an alkaline material for the short term.

The treatment goal is to reduce all metals in the drainage to less than 1 mg/l. Then the drainage can be further treated by wetland treatment or hauled to the nearest municipal wastewater treatment plant. Power is available at the site but personnel visit the site only once per day during the work week. Any treatment system must require very little maintenance to be successful. It is also important to utilize as much of the existing collection system as possible to minimize costs. A program was initiated to investigate the use of different alkaline materials and develop a treatment system appropriate for this site.

Methods

Laboratory tests were conducted to compare the effectiveness of lime $(Ca(OH)_2)$, magnesium hydroxide $(Mg(OH)_2)$ and sodium hydroxide (NaOH) at neutralizing acid mine drainage and removing trace metals from solution. The tests were designed to determine the contact time, sludge production, and required dosage for each neutralizing agent.

Drainages from two different stockpiles were selected for bench tests. One represents the most acidic case (minimum pH, maximum metal concentrations; test pile 5) and one represents the average concentrations in the combined drainage from all the test piles (test pile 6; Table 1). Lime dosages were determined from a previous study (Lapakko et al. 1986), while a titration was conducted to determine the appropriate amount of sodium hydroxide to add to the stockpile drainage. Lime and magnesium hydroxide were added to 150 ml of drainage at doses of 1.0, 2.0, 5.0, and 10.0 grams per liter (g/l). A 15% sodium hydroxide solution was added to 150 ml of drainage at doses of 0.23, 1.53, 1.76, and 2.35 g/l. All solutions were agitated continuously, and samples were collected at 1, 2, 4, 7.5, 24, and 96 or 120 hours.

Table 1. Typical test pile drainage quality.

	Composite Drainage; Average Conditions (test pile 6)	Most Acidic Drainage (test pile 5)
pH	4.09	3.52
Acidity	756	2340
Copper	119	128
Nickel	133	180
Cobalt	9.3	18
Zinc	9.2	12
Iron	0.5	2.2
Manganese	13.2	20.5
Aluminum	23.6	101

Note: Acidity values are expressed as mg/l as $CaCO_3$, pH values are in standard units, and metals values are all mg/l.

The pH of each solution was measured after the sample was allowed to settle for several minutes. Aliquots of the samples were then taken for analyses of metals and suspended solids. Samples analyzed for metals were filtered through a 0.45 micron Millipore filter, and samples used for suspended solids determinations were passed through a Gelman type A/E glass fiber filter. Solution pH was determined with an Orion Model 720 pH meter. Metals were analyzed using flame atomic absorption with a Perkin Elmer 303 Atomic Absorption Spectrophotometer. Suspended solid samples were dried at 105°C and weighed on a Sartorius analytical balance (Model 2848).

Laboratory Results

Since all reagents were successful in elevating pH and removing trace metals from both test pile drainages, only the results for the most acidic drainage, Test Pile 5, are presented. Treatment behavior for the average drainage was similar to the most acidic drainage, except that lower doses of neutralizing agents were required.

Solution pH increased with time and dosage, but at different rates (Figure 1). For lime, pH increased to within 10% of the equilibrium value within 1 hour for all doses. Solution pH ranged from 4.5 to 5.0 for a dose of 1.0 g/l, and increased to between 12.0 to 12.5 for the highest dose of 10.0 g/l. For magnesium hydroxide, pH increased more slowly at the lower doses of 1.0 and 2.0 g/l, and did not reach the equilibrium value until about 24 hours. For the higher doses of 5.0 and 10.0 g/l, final pH was approached after 4 hours. The maximum pH obtained with this reagent was 9.5. Equilibrium was approached more quickly with Test Pile 6 drainage.

Sodium hydroxide was added as a 15% solution (by weight). As a result, the neutralizing capacity was more readily available than with the solid sources of alkalinity. Lower dosage rates were used, and, in general, pH was

within 1% of equilibrium value within 1-2 hours.

Since metal solubility is a function of pH, all treatment chemicals were successful in removing over 99% of the metals from solution. The pH required to achieve the goal of reducing metals to less than 1 mg/l decreased as contact time increased. For contact times of 2-4 hours, pH had to be in the range of 8.0-8.5. However, when equilibrium was approached (after 24 hours) the pH range decreased to 7.5-8.0 (Figure 2). The pH required to remove each metal from solution increased in the order: copper < zinc < cobalt < nickel. Copper was the easiest metal to remove, and concentrations decreased to less than 1 mg/l when pH was between 6.0-6.5. Zinc, cobalt and nickel concentrations were reduced to less than 1 mg/l when pH ranged from 6.5-7.0, 7-7.5 and 7.5-8.0, respectively. This removal pattern is consistent with the solubility products for each metal hydroxide (Smith and Martell 1976). However, concentrations in solution were as much as several orders of magnitude less than predicted by hydroxide solubility alone, suggesting that some of the metals were removed by other mechanisms, such as co-precipitation with other metal hydroxides (Table 2).

Table 2. Comparison of measured metal concentrations with solubility of metal hydroxide.

Metal	pH	Measured[1] Concentration	Predicted from[2] Hydroxide Solubility
Copper	7	0.1	0.32
Nickel	8	0.2	37
Cobalt	8	0.1	74
Zinc	8	0.02	1.4

[1] Estimated from least squares smoothing curves depicted in Figure 2.

[2] Calculated from solubility products reported by Smith and Martell (1976).
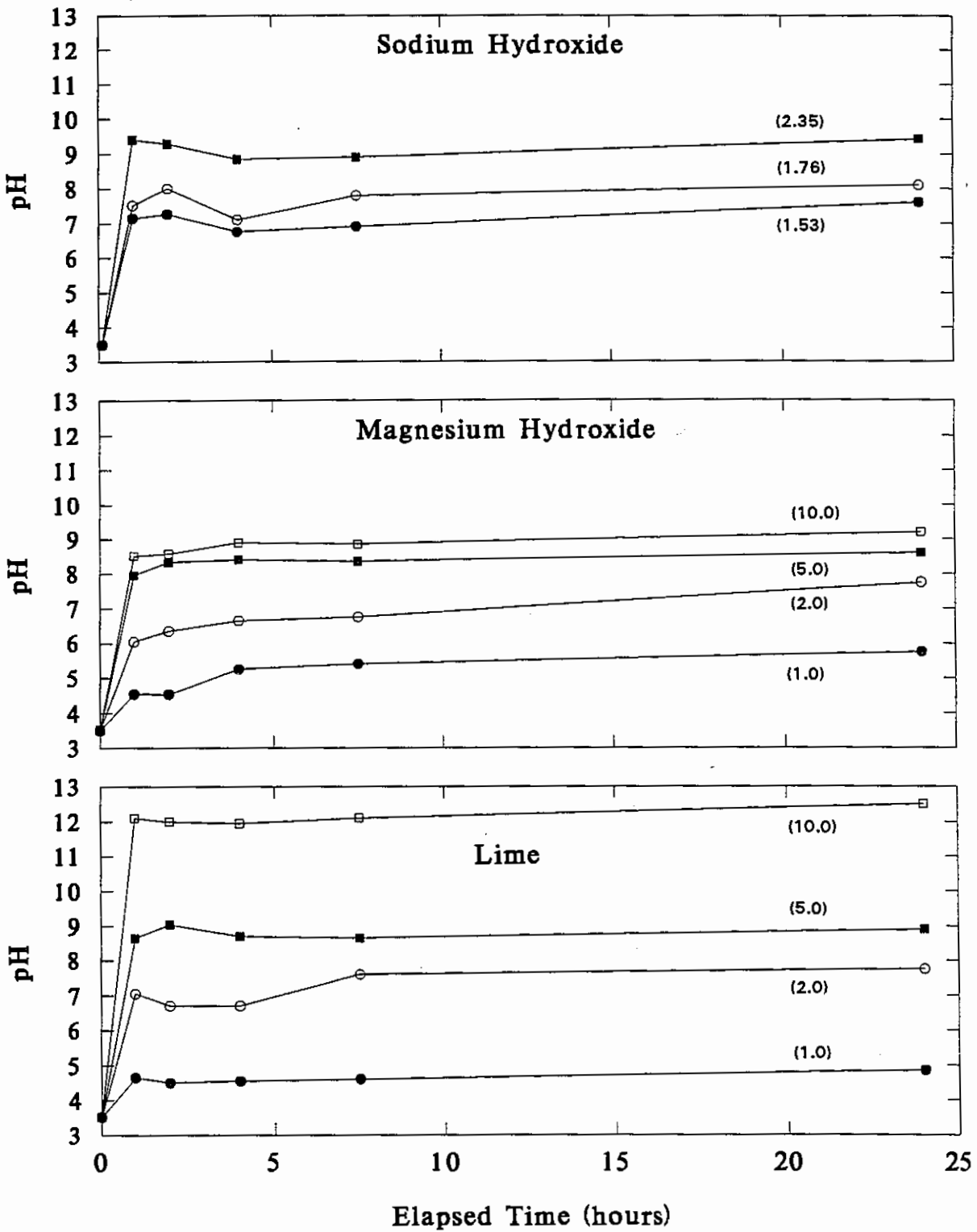
Figure 1.   Solution pH as a function of time and dosage for Test Pile 5 drainage. The numbers in parentheses indicate the dosages of the alkaline reagents (in grams/liter).
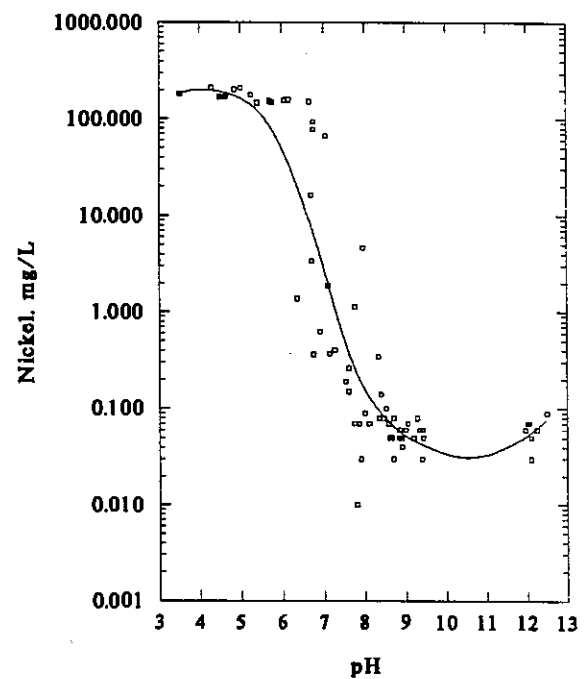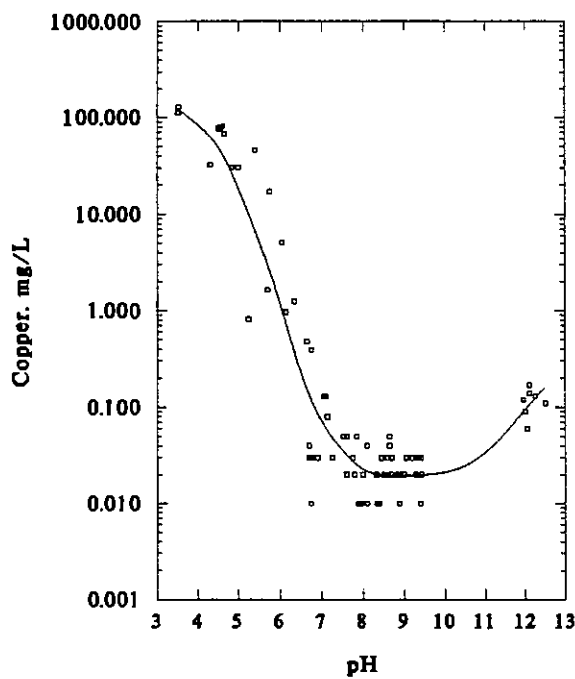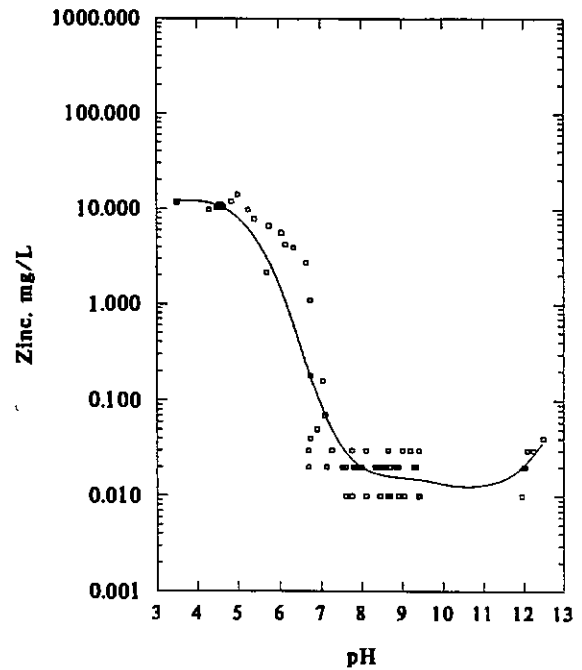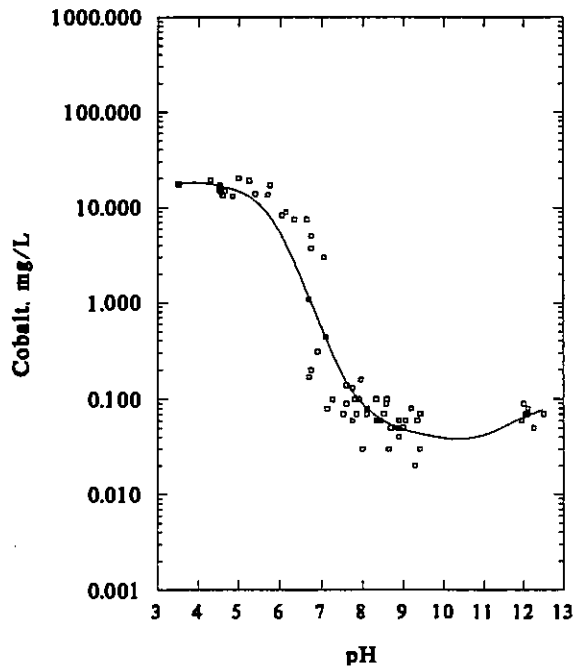
Figure 2.   Metals concentrations as a function of pH in treated Test Pile 5 drainage.   The data presented is from the laboratory experiments (with data from all reagents and doses), and is intended to depict how metals concentrations in solution are a function of the pH of the solution.

Selection of Treatment Chemical

Each chemical was evaluated based on the following criteria:

1.   sludge mass and volume
2.   reaction time
3.   maximum pH
4.   ease of handling and application
5.   residual neutralizing capacity
6.   cost
7.   sludge classification
       (hazardous or non hazardous)

Although each of these factors are important, the most important in this application are ease of handling and application, residual neutralizing capacity, and maximum pH. Since the site is only inspected periodically, the control of these factors seemed most likely to provide protection against unanticipated problems.

Sludge Mass and Volume

Lime treatment produced the largest mass of sludge, due primarily to the precipitation of $CaSO_4$, and to the presence of unreacted lime. At comparable levels of treatment, lime produced about 50% more sludge than magnesium hydroxide and almost three times as much sludge as sodium hydroxide (Figure 3, Table 4). The limited solubility of magnesium hydroxide contributed to the additional sludge with magnesium hydroxide while the sludge produced with sodium hydroxide was due primarily to the formation of metal hydroxides.

Although sodium hydroxide treatment produced the lowest mass of sludge, the density of sludge was also the lowest. The magnesium hydroxide formed the densest sludge. The volume of sludge produced decreased in the order of sodium hydroxide > lime > magnesium hydroxide. Sodium hydroxide produced about an order of magnitude more sludge volume than magnesium hydroxide while lime produced about 6 times more sludge volume than magnesium hydroxide.

Reaction Time

Sodium hydroxide, due to its high solubility, increased pH the quickest, reaching 99% of equilibrium pH within 2 hours for all doses (Figure 1). Lime increased pH quickly at doses of 5.0 and 10.0 g/l, but at doses of 1.0 and 2.0 g/l was somewhat slower acting, reaching a value equal to 95% of the equilibrium value after 2 hours. Magnesium hydroxide was the slowest acting of the reagents. At a dose of 2.0 g/l, the pH after 2 hours was only 78% of the equilibrium value. This percentage increased to 92% for the higher doses of 5.0 and 10.0 g/l.

Maximum pH

Since the site is remote and only inspected periodically, over-treatment of the drainage could produce an unacceptably high pH water in the settling basin. The magnesium hydroxide, as a result of its limited solubility, maintains pH below 9.5, while lime does not buffer until 12.5, and sodium hydroxide can increase pH to around 14.0.

Ease of Handling and Application

Lime is available as a dry product which can be added to the drainage or prepared into a slurry on site. Lime is fairly corrosive and represents a moderate risk to the employees handling the product.

Sodium hydroxide is generally available either as a solid or as a liquid containing about 50% NaOH. Although this solution is easy to apply, it will freeze at temperatures below 14° C (58° F). If the solution is diluted to 15% NaOH by weight, the freezing point drops to around -18°C (0° F). Solutions of sodium hydroxide are very caustic and must be handled carefully to avoid injury.

Magnesium hydroxide is available either as a solid or as a high solid content slurry (58% by weight). Since the pH is controlled by the limited solubility of the product, this slurry is both easy to apply and safe to handle.
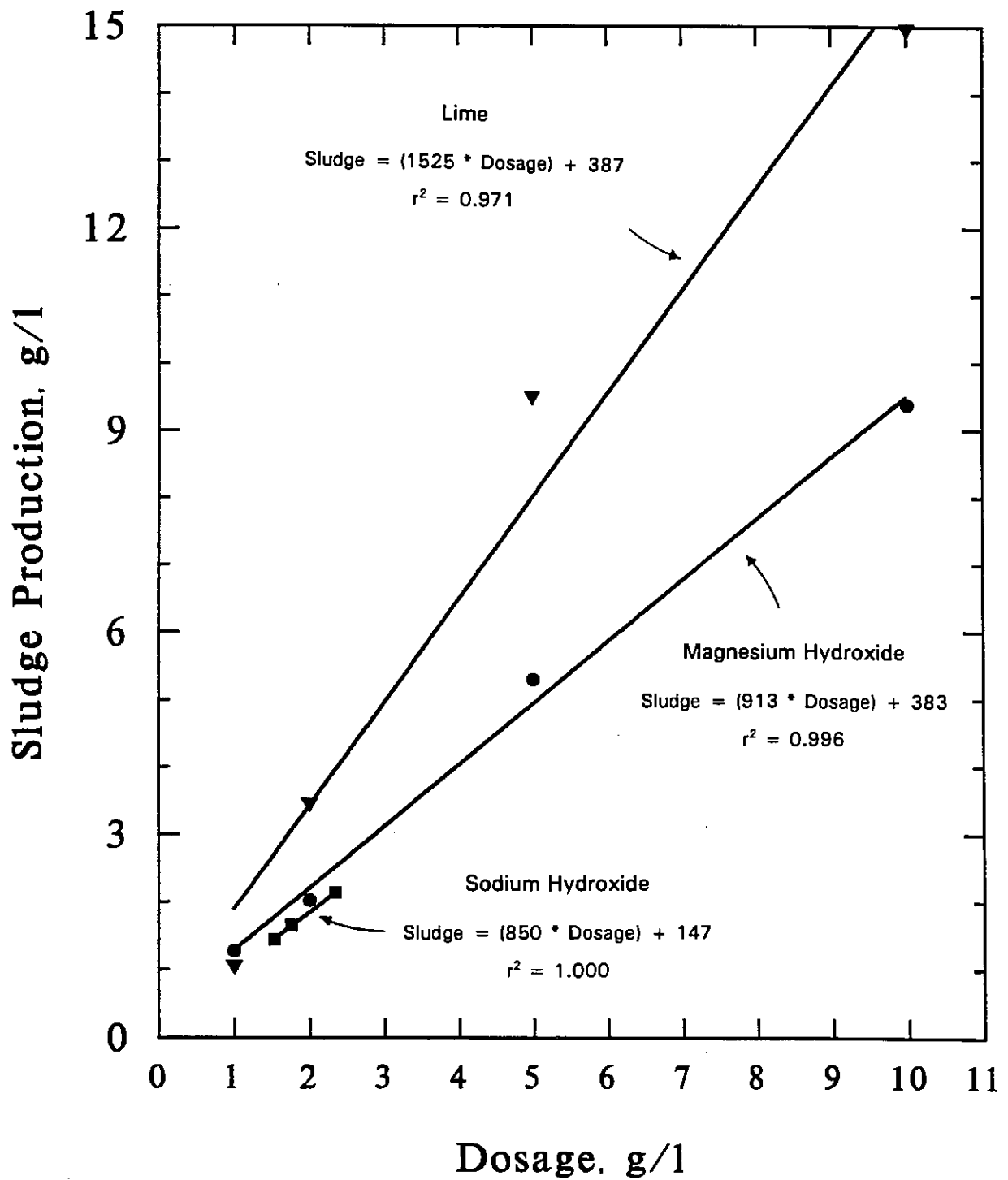
Figure 3. Sludge production measured after 24 hours for test pile 5 drainage as a function of dosage for lime, magnesium hydroxide, and sodium hydroxide.

Residual Neutralizing Capacity

Due to the limited solubility of lime and magnesium hydroxide, these materials are generally applied in excess of the theoretical requirements of neutralization. As a result, unreacted neutralizing capacity remains in the sludge, which can be used to neutralize additional acid input. This provides some level of protection in the settling basin in case of any problem with the dose of alkaline material. Since the sodium hydroxide completely dissolves, no residual neutralizing capacity is available.

Cost

Table 4 compares the cost per kg of chemical, the cost per kg of base, and cost estimates for the treatment of 1000 liters of average concentration drainage to a pH of 8 in 2 hours. Lime is substantially cheaper than the other chemicals.

Sludge Classification

One of the primary tests to determine the hazardous nature of a sludge is to leach the material according to EPA's Toxicity Characteristic Leaching Procedure (TCLP) Test (U.S. EPA 1990). Before this test was adopted, sludge was leached with the Extraction Procedure Toxicity (EP Tox) test (U.S. EPA 1986). In this test acid is added until the pH stabilizes at 5. Although the new TCLP test prescribes a specific procedure for solids with pH > 5, it does not require that a specific pH be maintained during the leaching phase. Therefore the amount of metals removed from a sludge is a function of its residual neutralizing capacity. The other factor that will influence the classification of the sludge is the specific metals contained in the original drainage. Copper, nickel, cobalt and zinc are not listed metals and as a result neither of the extraction tests listed above were conducted.

Instead, the Minnesota Pollution Control Agency reviewed the data on the mine drainage and the proposed treatment system, and determined that the sludge would not be considered hazardous. In addition, the agency requested that a distilled water leach test (ASTM D 3987: Test for shake extraction (leaching) of solid waste with water) be conducted on the sludge. The sludge was extracted three times. Specific conductance decreased with each extraction. Trace metal concentrations in all extractions were low, ranging from <0.001 to 0.04 mg/l (Table 3).

Overall Comparison

Table 4 provides an overall comparison of the three neutralizing agents. Although magnesium hydroxide is the most expensive and has the slowest reaction time, it was selected primarily for its ease of handling and application

Table 3.   Release of trace metals from magnesium hydroxide sludge.

Parameter	Extraction		
	1	2	3
pH	7.62	7.56	7.14
S.C.	1850	800	590
Copper	0.04	0.03	0.02
Nickel	0.03	0.02	0.02
Cobalt	<0.01	<0.01	0.01
Zinc	0.05	0.04	0.03
Arsenic	0.008	<0.005	<0.005
Selenium	<0.005	<0.005	<0.005
Silver	<0.001	<0.001	<0.001
Chromium	<0.001	<0.001	<0.001
Cadmium	0.001	0.001	<0.001
Lead	0.005	0.008	0.009
Mercury	<0.001	<0.001	<0.001

Metals values are mg/l. Specific conductance (S.C.) values are in microsiemens. All values are averages of four samples. Procedure: 175 ml of distilled deionized water and 43.8 grams of dry sludge were agitated for 48 hours.

Table 4. Comparison of neutralizing agents.

Parameter	Hydrated Lime Ca(OH)$_2$	Magnesium Hydroxide Mg(OH)$_2$	Sodium Hydroxide NaOH
Cost [1] $/kg $/kg base $/1000 liters [2]	 0.33 0.72 0.35	 1.03 1.76 1.75	 0.88 2.07 0.60
Sludge Produced [3] (grams)	4.4	2.9	1.6
Maximum pH	12.5	9.5	13 - 14
Product Form	Solid	Solid or slurry	Solid or liquid
Risk associated with handling product [4]	Moderate	Low	Moderate to high
Ease of [5] application	Moderate	Easy	Easy
Reaction [6] time (hours)	1 - 2	2 - 4	~ 1
Residual [7] neutralizing capacity	Yes	Yes	No

1. Cost comparisons are approximate values for a small scale application. Costs are based on 50 lb bags and 55 gallon drums of product.
2. Estimated cost to raise pH of the average concentration drainage (test pile 6) to 8.0 within 2 hours.
3. Data from laboratory study. Based on the amount of reagent needed to raise the pH of test pile 5 drainage to 8.0 after 24 hours.
4. Based on risk to employee; data from material safety data sheets.
5. Subjective based on application at this site; liquid or slurry is much easier to dispense than solids.
6. Based on laboratory results.
7. Assumes that some undissolved lime and magnesium hydroxide exist in the sludge.

and for its ability to maintain pH below 9.5. Other positive factors are its residual neutralizing capacity, its low sludge volume, and its non-hazardous sludge classification.

Design of Field Treatment System

In order to effectively treat the drainage at the field site, a system had to be designed which would be compatible with the existing water collection system. This system consists of a central 3785-liter (1000 gallon) collecting sump with a float-activated pump (Figure 4).

As the sump fills, the float-activated pump discharges about 750 liters (200 gallons) of treated water to a settling basin. About 570
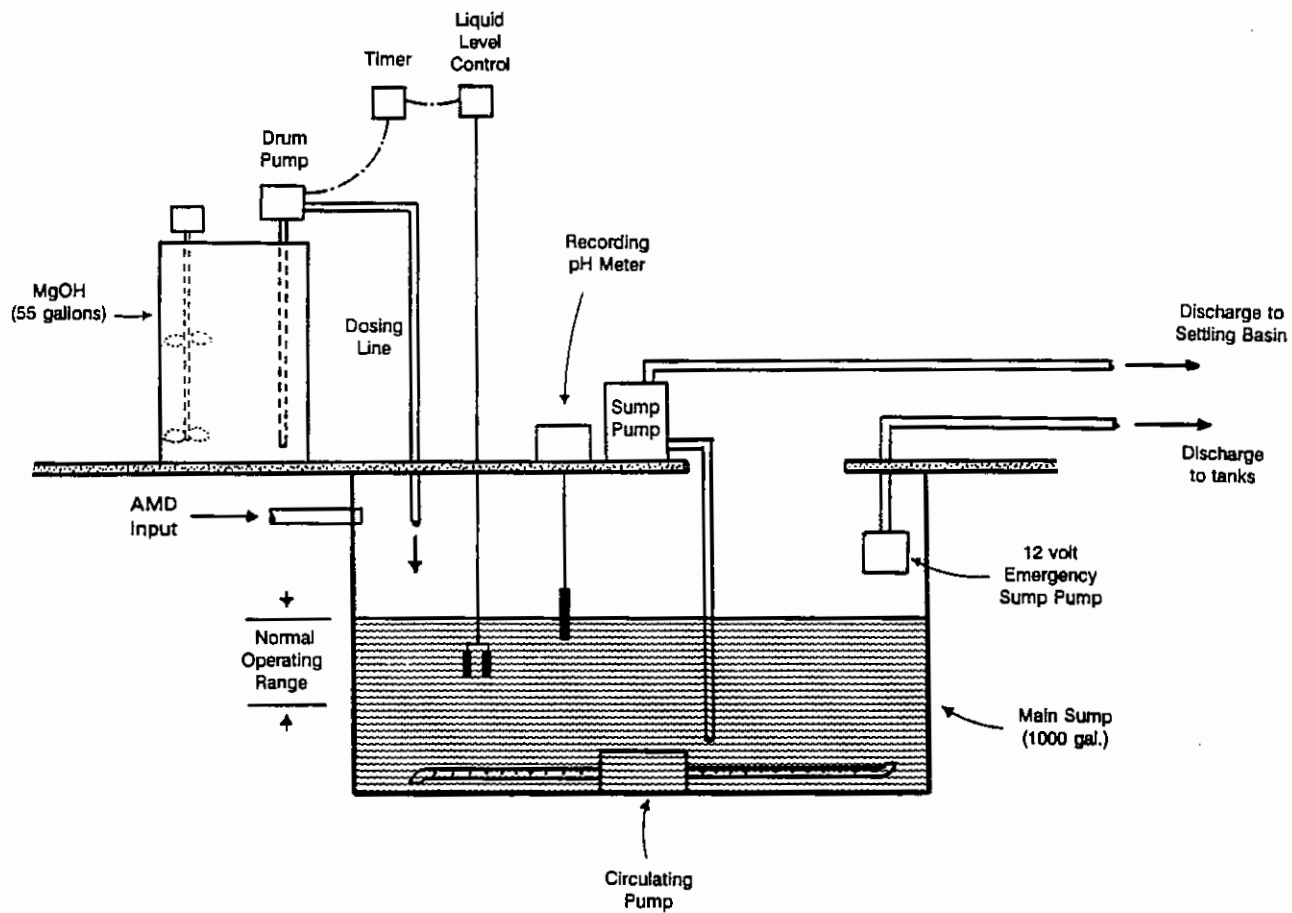
Figure 4. Schematic of the magnesium hydroxide treatment system.

liters (150 gallons) remain in the sump after the pump shuts off.

Rather than install a separate treatment tank, a plan was developed which uses the existing collecting sump for treatment. To maximize contact time between the leachate and the magnesium hydroxide, the alkaline material has to be added immediately after the sump is emptied. Therefore, a second liquid-level control switch activates a timer when the sump begins to fill. The timer energizes the metering pump which then pumps a predetermined quantity of magnesium hydroxide slurry (58% $Mg(OH)_2$ by weight) into the sump. This dose is calibrated to treat the 750 liters of test pile drainage that flows into the sump before the next pump-out cycle (Figure 4).

Magnesium hydroxide rapidly settles from solution. Once it settles, its treatment capacity is greatly diminished, so in order to maximize the reaction rate and the treatment efficiency, a high capacity (280 - 450 l/min) submersible pump equipped with a flow distribution system has been included to continuously circulate the water in the sump. This pump also keeps the sludge suspended so it can be pumped to the settling basin with each pump-out cycle.

Magnesium hydroxide slurry is purchased in 55 gallon drums. A drum mixer is used to mix the slurry on a regular basis to keep the solution well mixed because of the relatively low usage rate of 75 to 110 liters per month. Failure to keep the slurry well mixed results in separation of the slurry into its solid and liquid components.

Field Results

Based on the laboratory results for the drainage representing the combined flow of the test piles, a magnesium hydroxide dose between 1.0 - 2.0 g/l appeared to be appropriate. During 1991 adjustments and improvements were made to the treatment system. Based on these results,

an initial dose of 1.7 g/l was used in 1992. This dose was increased to 2.2 g/l toward the end of the field season to provide better treatment at high flow rates.

A continuous recording pH meter was used periodically in 1992 to record the pH in the sump. Although the data is somewhat limited during high flow periods, a general trend is apparent from the existing data (Figure 5). When the contact time in the sump is greater than about 6 hours, pH is maintained above 8, and suitable treatment is achieved. However, during periods of high flow (3.7-8.5 l/min) and with contact time of 100-200 minutes (1.5-2.5 hours), pH is increased, but only to around 7. While this pH increase is sufficient to remove copper from solution, significant quantities of nickel still remain.

The system is presently being evaluated to determine how performance during periods of high flow can be improved. Data from the laboratory tests were used to develop an approximate relationship for the dosage required to raise pH above 8 for a given contact time in the sump (Figure 6). Contact time is inversely proportional to the flow rate and is defined as the time it takes for 750 liters of drainage to flow into the sump.

Field data generally agrees with the laboratory results. When dosage and contact time were adequate, pH generally exceeded 8 and plot to the right of the laboratory line (overdose), and when dosage and contact time were not adequate, pH was less than 8 and the points plot to the left of the line (underdose; Figure 6). This data therefore provides an initial relationship to establish a flow-proportional dosing system.

This type of dosing system should correct the present problems of underdosing at high flow and overdosing at low flow, and provides a more cost-effective method of adequately treating all of the drainage.
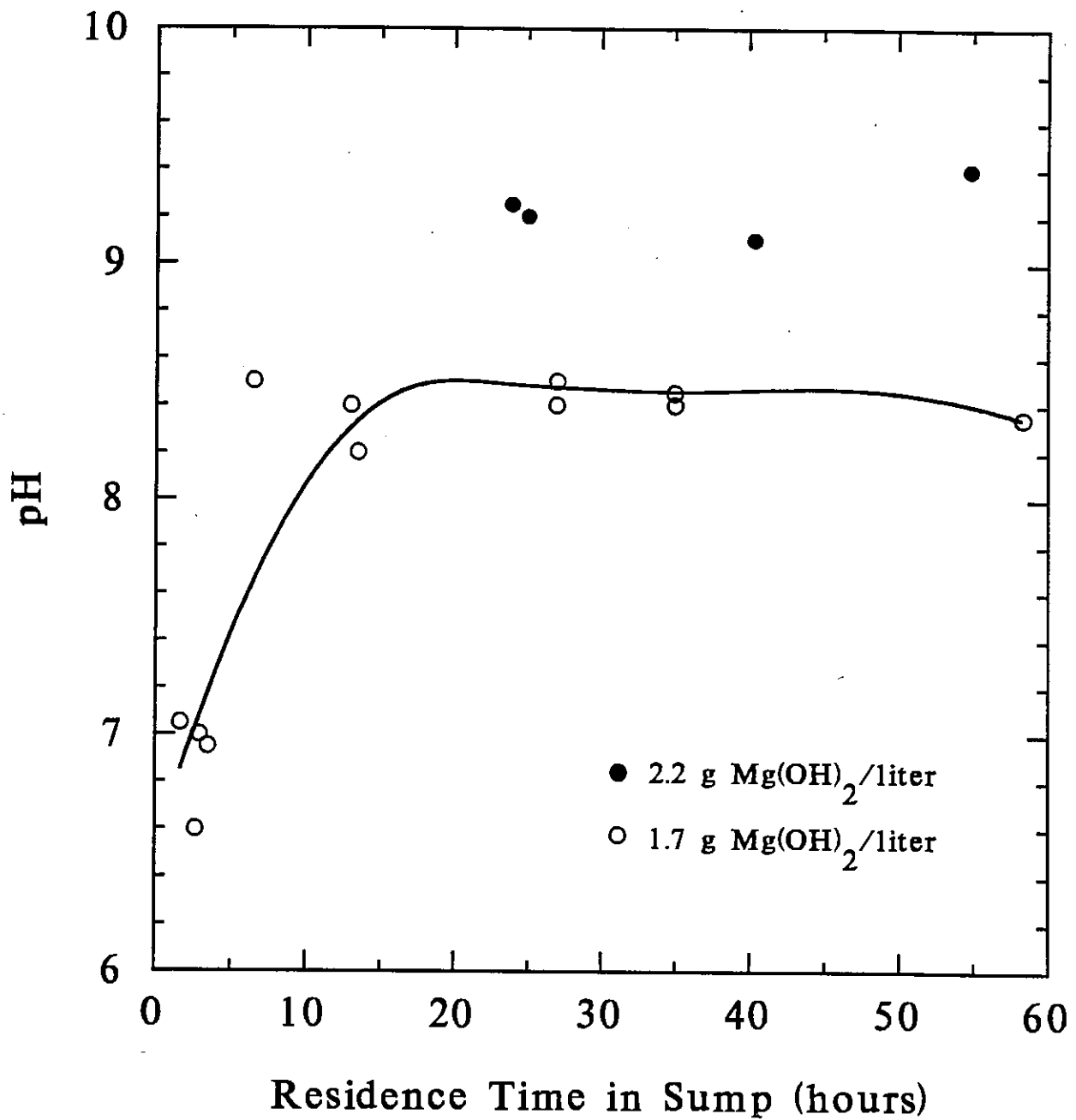
Figure 5.   Field treatment data, 1992; pH of treated drainage as a function of contact time.

The curve represents a least-squares fit through the open circles (dosage = 1.7 g/l) using an algorithm developed by McLain (1974).
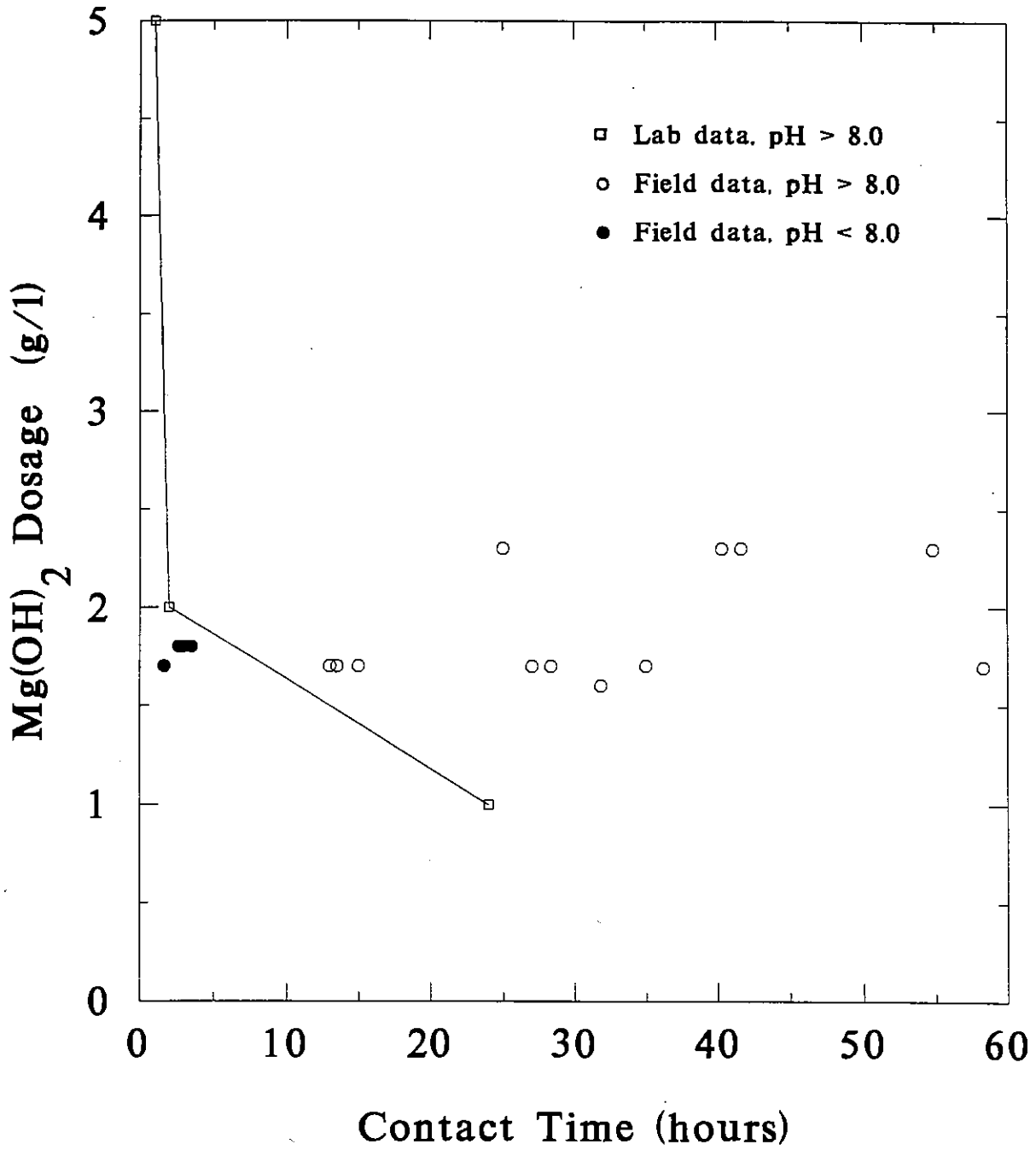
Figure 6.   Relationship between magnesium hydroxide dosage and contact time.

Conclusions

Magnesium hydroxide can effectively neutralize and remove metals from acid mine drainage. Although more expensive than other forms of alkaline material, such as lime and sodium hydroxide, the benefits of its use, particularly for small operations at remote sites, can outweigh the additional cost.

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