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Scale Inhibitors and Slow-Release Polymers for Mine Water Treatment Systems

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm^3	cubic centimeter	in	inch
cm/min	centimeter per minute	L	liter
cps	centipoise	lb	pound
ft	foot	mg/L	milligram per liter
g	gram	pct	percent
gal	gallon	ppb	part per billion
gal/h	gallon per hour	ppm	part per million
gal/min	gallon per minute	psi	pound per square inch
h	hour	ton/d	ton per day
hp	horsepower		

SCALE INHIBITORS AND SLOW-RELEASE POLYMERS FOR MINE WATER TREATMENT SYSTEMS

By T. E. Ackman,[1] G. R. Watzlaf,[1] T. J. Fox,[2] and R. L. P. Kleinmann[3]

ABSTRACT

Scale inhibitors and slow-release polymers were tested by the Bureau of Mines at mine drainage treatment facilities. The scale inhibitors were investigated to determine their effectiveness in controlling gypsum ($CaSO_4$) scale; the polymers were investigated to determine their effectiveness for increasing settling rates of suspended iron hydroxide.

Two types of scale inhibitors were tested at a site having a severe $CaSO_4$ scaling problem. Both proved to be effective in controlling scale formation; in addition, one caused the dissolution of $CaSO_4$ deposits.

Slow-release polymers were tested at three mine drainage treatment facilities. These gelatinous polymeric flocculants were found to be convenient and easy to use, but only effective when pH could be controlled.

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INTRODUCTION

Mine drainage, from both surface and underground mining operations, must meet established State or Federal water quality standards before being discharged from a mine property into natural waterways. Raw mine drainage rarely meets these quality criteria and, therefore, it is often necessary to treat these waters to reduce suspended solids, adjust pH, and precipitate high levels of inorganic compounds such as iron prior to discharge from the mine site.

The Bureau of Mines has studied the potential benefits of using chemical additives to control two specific problems: the buildup of $CaSO_4$ (gypsum) scale and the poor settleability of iron hydroxide sludge at certain acid mine water treatment plants. Two scale inhibitors that distort the crystal lattice of gypsum, and a slow-release, sludge-settling polymer were tested in the laboratory and at mine sites in southwestern Pennsylvania. Their selection was based on demonstrated success in other mining industry applications (i.e., copper beneficiation, boiler and cooling tower operation, and battery recycling).

In this report, two separate studies are presented. A study concerning the inhibition of scaling is presented first, followed by a study of flocculation of iron hydroxide precipitates with gelatinous polymers. Background information concerning polymers can be found in the appendix.

INHIBITORS TO CONTROL CALCIUM SULFATE SCALE

When lime is used to treat acid mine drainage (AMD), the calcium in the lime slurry often forms a gypsum ($CaSO_4$) precipitate (scale) after reacting with sulfate in the water. This scale precipitates on equipment and in ponds, becomes a maintenance problem, and may obstruct critical treatment equipment (fig. 1).

FIGURE 1. - Gypsum scale on rake.

Gypsum scaling is a common occurrence in most lime or limestone AMD treatment plants and depends upon the sulfate concentration of the treated water; however, the degree of buildup is site-specific and depends upon the chemical composition of the mine water. Gypsum scale will typically build up in sludge thickeners: on rakes, center wells, discharge troughs, weirs, and side walls. Descaling of this equipment is generally expensive and time-consuming. Often, excavation is required for access to clogged underground pipelines that may be so severely plugged that replacement is necessary. In treatment plants with severe calcium sulfate scaling, the use of piping is not practical owing to the frequency of required cleaning; therefore, flumes are used instead of piping where possible. Pumps often suffer additional wear and tear due to the increased head losses they must overcome as scaling gradually reduces the diameter of inlet and outlet lines. In severe cases, AMD treatment plants periodically have to be shut down to allow maintenance crews to remove scale.

Severe scale buildup can be prevented by chemical agents that distort growth of gypsum and calcium carbonate crystals and thus limit seed crystal formation on solid surfaces. Two types of inhibitors were selected for evaluation in this study on the basis of their effectiveness in other scale-inhibiting applications. Type 1 consists of a chelating agent and a polyelectrolyte. The chelating agent inhibits crystal growth and the polyelectrolyte softens and removes existing scale. In the type 2 inhibitor, a phosphonate compound is the active crystal-distorting agent.

TEST SITE

The test site in this study was an AMD treatment plant located in Greene County, PA. The raw water from the mine is typical of acid mine drainage in this area with a pH of 4 to 5, and an average sulfate concentration of 5,000 ppm (table 1). Raw water pumped from the mine is held in a large surface holding pond. The water is then pumped at a flow rate of approximately 2,300 gal/min to the aeration unit where raw water and lime slurry are mixed and aerated to oxidize ferrous iron to ferric iron. The aeration tank effluent subsequently travels down a long (300-ft) flume where part is channeled for the makeup of the lime slurry and the rest enters the clarifier. In the quiescence of the thickener, the ferric iron sludge settles to the bottom, and the clarified overflow is transported by flume to the polishing pond. In the polishing pond, any remaining settleable iron flocs are removed before discharge of the effluent to a nearby stream. Figure 2 is a schematic of the treatment system. Historically, a severe gypsum problem has occurred during thickener operations at this treatment plant.

TABLE 1. - Quality of raw water from treatment plant in Greene County, PA

Temperature..................°C..	22
pH (av)........................	4.3
Analysis, ppm:	
Al........................	31.5
Ca........................	1,000
Fe (total)................	740
Mg........................	704
SO_4........................	5,200

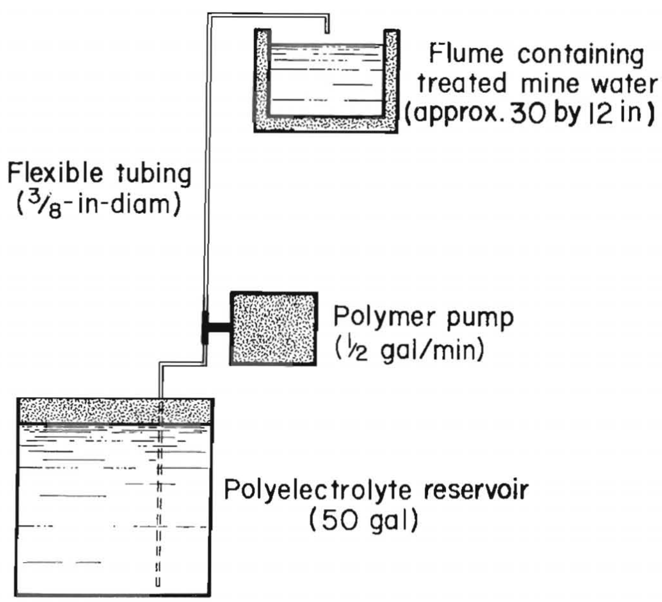

FIGURE 2. - Schematic of polymer pump system.

TEST PROCEDURES

A simple pumping system was used to add the scale inhibitors to the treatment system. A diaphragm metering pump delivered liquid inhibitor from a storage vessel to the aerated effluent (fig. 3).

Type 1 inhibitor, part chelating agent and part polyelectrolyte, was developed to prevent fresh scale buildup and to promote softening of existing scale in boiler water systems. The agent was added to the water in accordance with the manufacturer's suggested dosage of 0.5 gal of additive per ton of lime used in slurry makeup. At this plant, lime usage averaged 20 tons/d, which represented a feed rate of 0.5 gal/h. Tests were conducted over two 48-h periods.

Type 2 inhibitor, a phosphonate compound, has been successfully used in copper beneficiation to inhibit scale formation in high-pH treatments circuits. The manufacturer provided enough material for a 6-h test at a dosage of 10 ppm at the treatment plant site.

Performance was monitored in two ways. Water samples were analyzed for pH, total iron, aluminum, magnesium, calcium, and sulfate. In addition, samples of the gypsum scale were viewed through the microscope to monitor crystal growth at intervals of 2, 24, and 48 h. The second sampling method consisted of the use of materials commonly used in the construction of treatment plants; namely, stainless steel and polyvinyl chloride (PVC) (fig. 4). Sections of 2-in-diam PVC pipe and 4-in-sq stainless steel plates were weighed and then immersed in the treated water to provide a surface for gypsum crystallization. After submersion for 24 or 48 h, these representative materials were removed and reweighed, with the increase in weight taken to represent the rate of scale buildup. Four sampling points, (A, B, C, D) and raw water (fig. 4) were used to monitor the effectiveness of the treatment.

RESULTS

A scale inhibitor feed rate of 0.50 gal/h at the pump was maintained for the

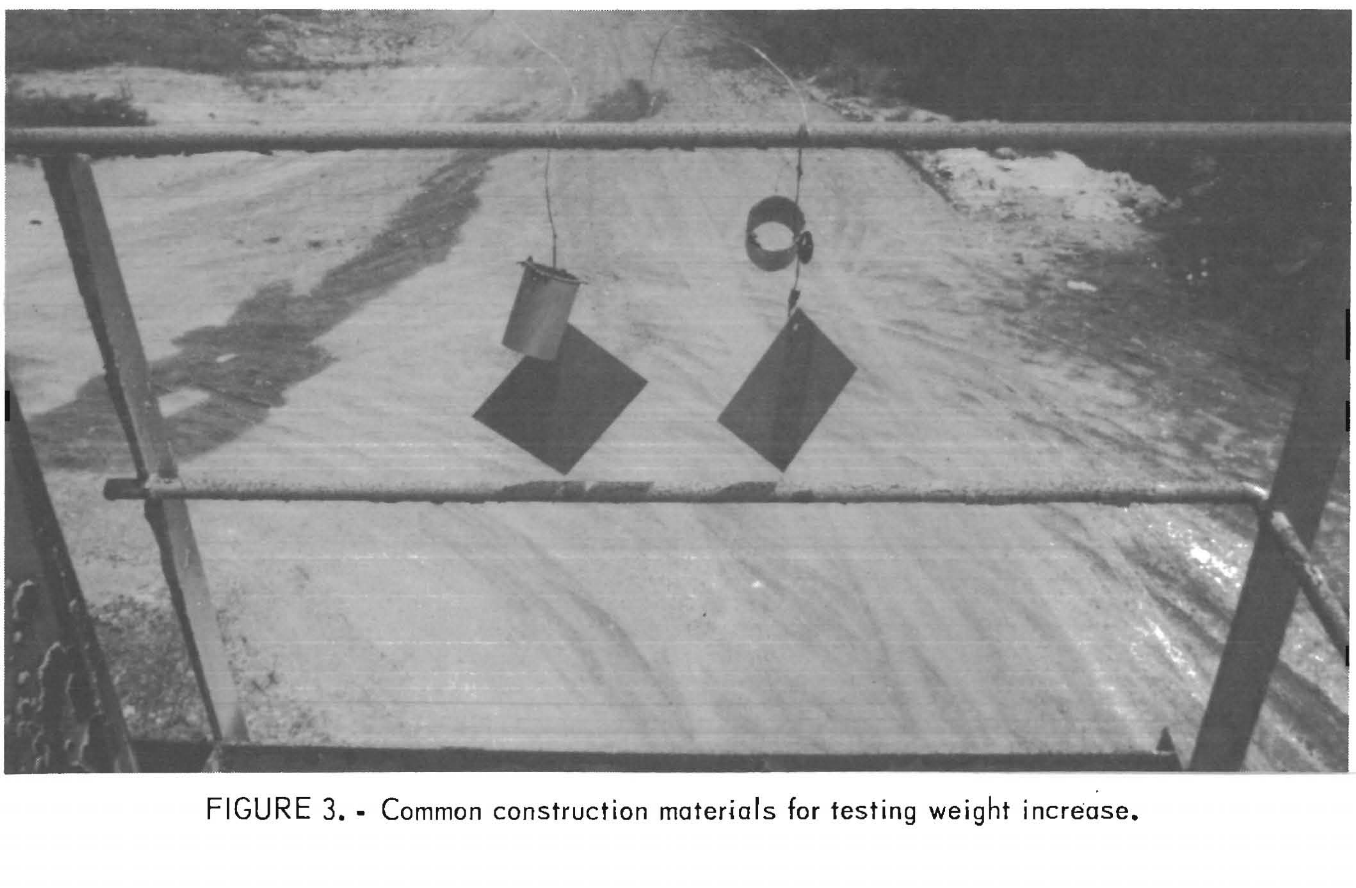

FIGURE 3. - Common construction materials for testing weight increase.

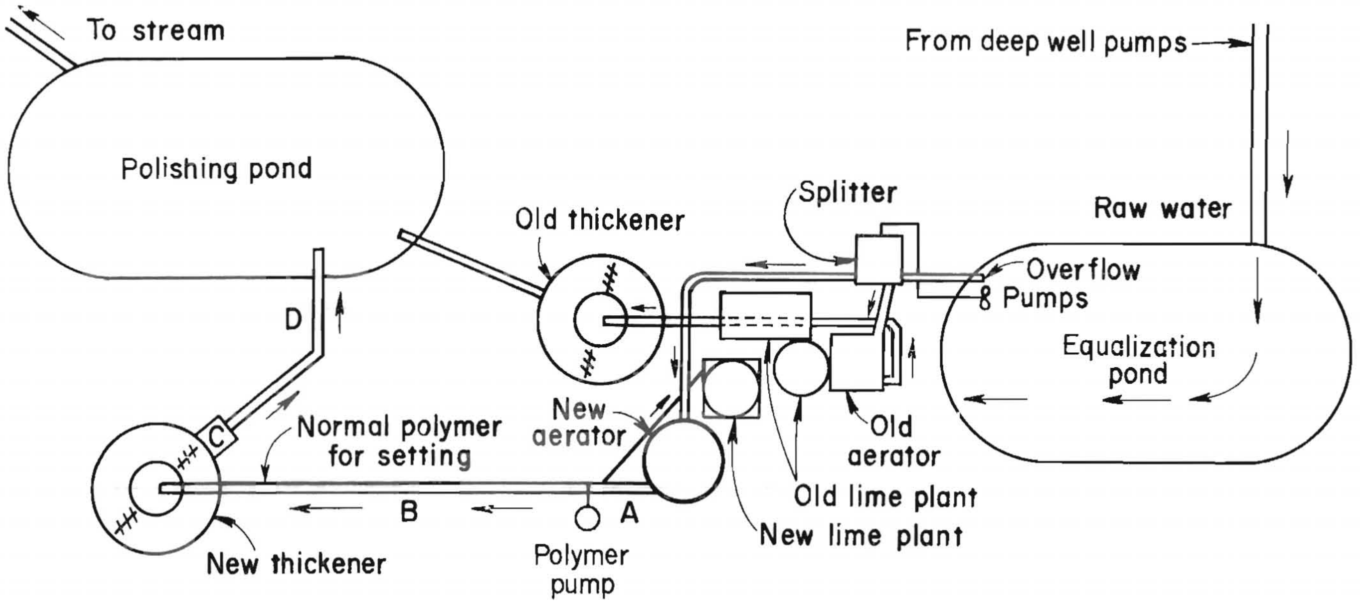

FIGURE 4. - Schematic of Greene County, PA, AMD treatment plant with sampling locations.

duration of the type 1 test. Water samples and material samples (weight increases) were taken at 24- and 48-h intervals, analyzed, and compared with samples collected from the existing system prior to the study. (Figures 5-6 and table 2 show the data for the 24-h interval.) Baseline chemical analysis data of the existing system showed that sulfate concentration in the treated water typically decreased throughout the system as some of the sulfate combined with excess calcium to form $CaSO_4$ (gypsum) scale. This was substantiated by the finding that in the absence of a scale inhibitor, the weight change for the samples of representative materials showed an increase in scale weight throughout the system. After addition of the scale inhibitor to the treatment system, the trend was reversed. The weight change for the samples of representative materials decreased in scale weight throughtout the system while the chemical analyses of the water revealed an increase in sulfate concentration in solution. The decrease in the formation of scale throughout the system indicates that the chelating agent effectively inhibits crystal growth. The increase in sulfates in solution indicated that some of the existing scale was being softened and returned to solution.

Figures 7-8 and table 3 show the results of the type 2 inhibitor test. The weight increase of the representative material samples showed a reduction in scale buildup of approximately 40 pct after the polymer was added to the system.

CONCLUSION

The use of commercially available scale inhibitors to control the formation of gypsum scale in mine water treatment plants is a potentially effective technique for the coal mining industry. This investigation indicated that both types, chelating agents and phosphonates, successfully reduced the formation of fresh gypsum scale. Further refinement of feed rates, based on the site-specific quality of the mine water, may result in complete scale elimination. Treatment circuits employing scale inhibitor additives can be fully automated and should not interfere with neutralization or aeration of mine water. Without the downtime and labor requirements normally associated with the manual removal of scale, the total cost of mine water treatment can be significantly reduced.

TABLE 2. - Analysis of treatment plant water with and without type 1 scale inhibitor, parts per million

	Raw water	A	B	C	D
WITHOUT INHIBITOR					
Constituents:					
Al	31.5	ND	NAp	ND	ND
Ca	1,000	1,500	NAp	1,740	1,860
Fe (total)	740	5.6	NAp	.19	.15
Mg	704	761	NAp	638	658
SO_4	5,200	5,000	NAp	5,000	4,200
pH	4.3	8.8	NAp	8.3	8.3
TYPE 1; FEED RATE = 0.5 gal/h					
Constituents:					
Al	20.4	1.4	1.8	ND	ND
Ca	NA	NA	NA	NA	NA
Fe (total)	625	20.5	3.4	0.1	0.1
Mg	609	662	662	630	630
SO_4	5,000	5,500	10,000	7,500	6,000
pH	4.9	8.5	8.9	8.6	8.4

NA Not analyzed. NAp Not applicable. ND Not detected.

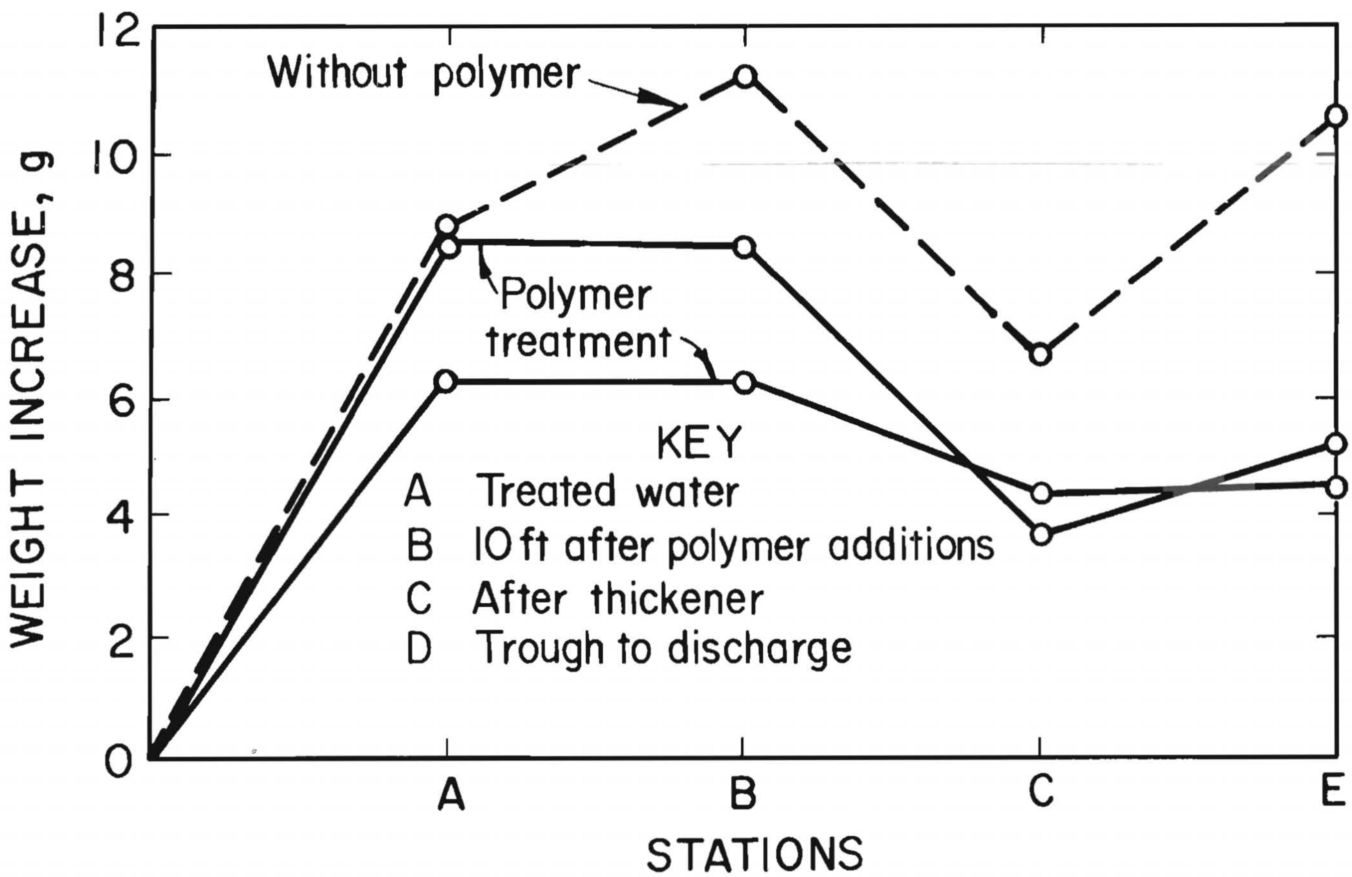

FIGURE 5. - Weight increase for steel plate, 24-h contact time.

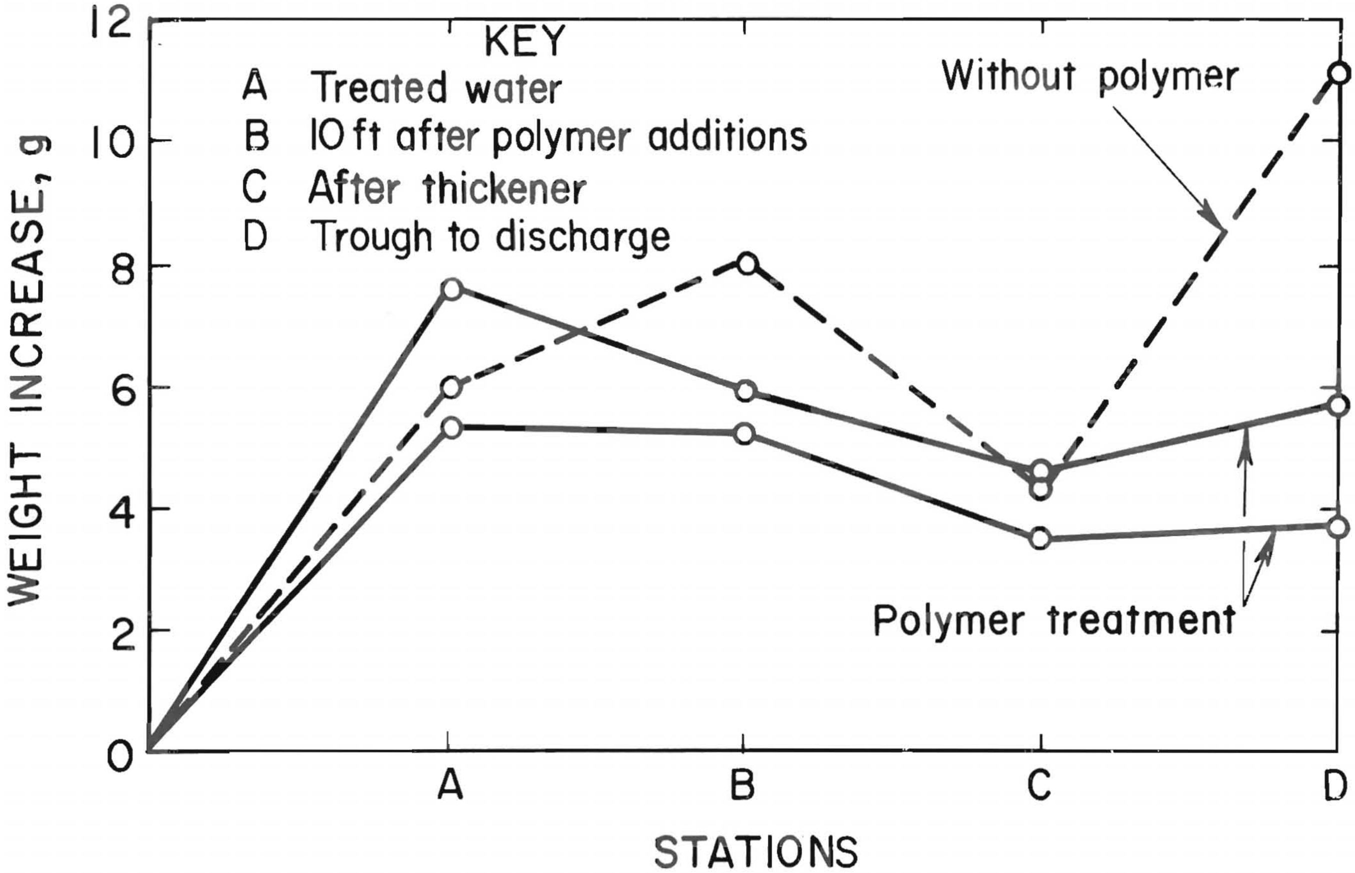

FIGURE 6. - Weight increase for PVC pipe, 24-h contact time.

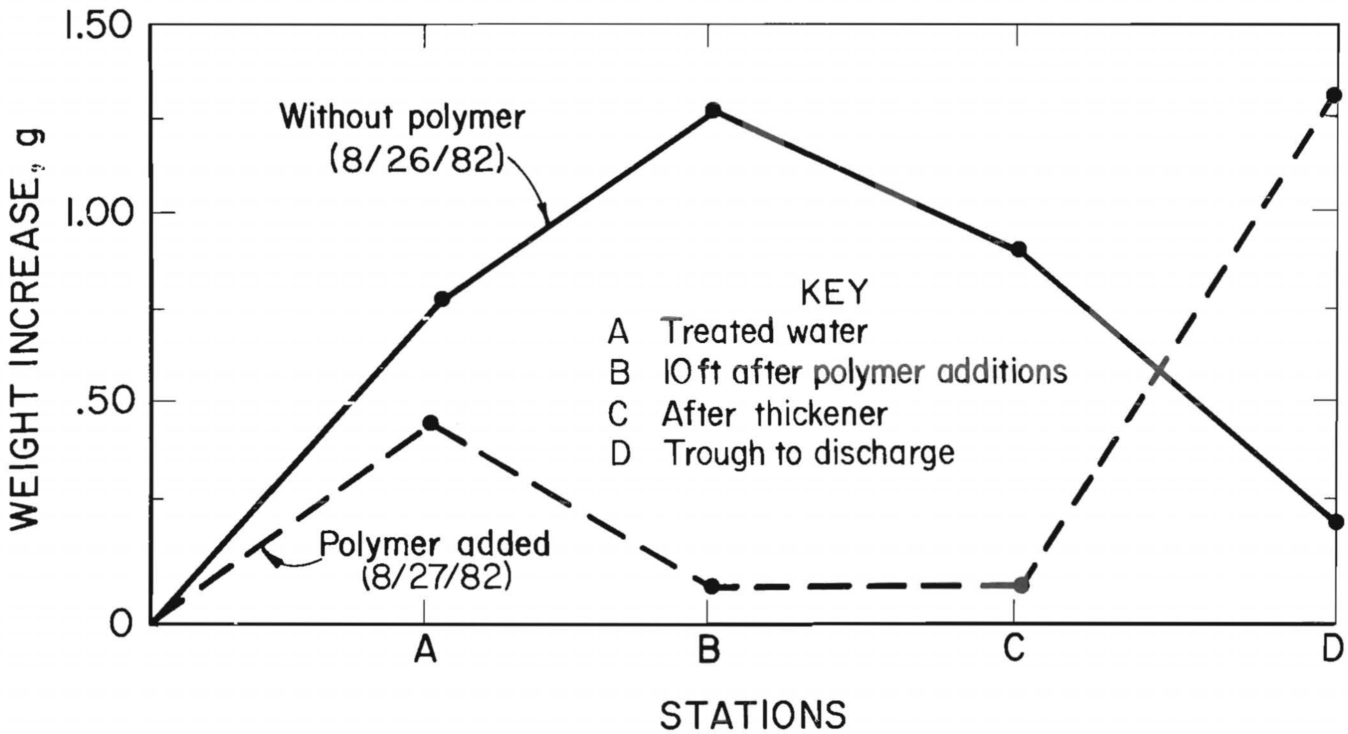

FIGURE 7. - Weight increase for steel plate, 6-h contact time.

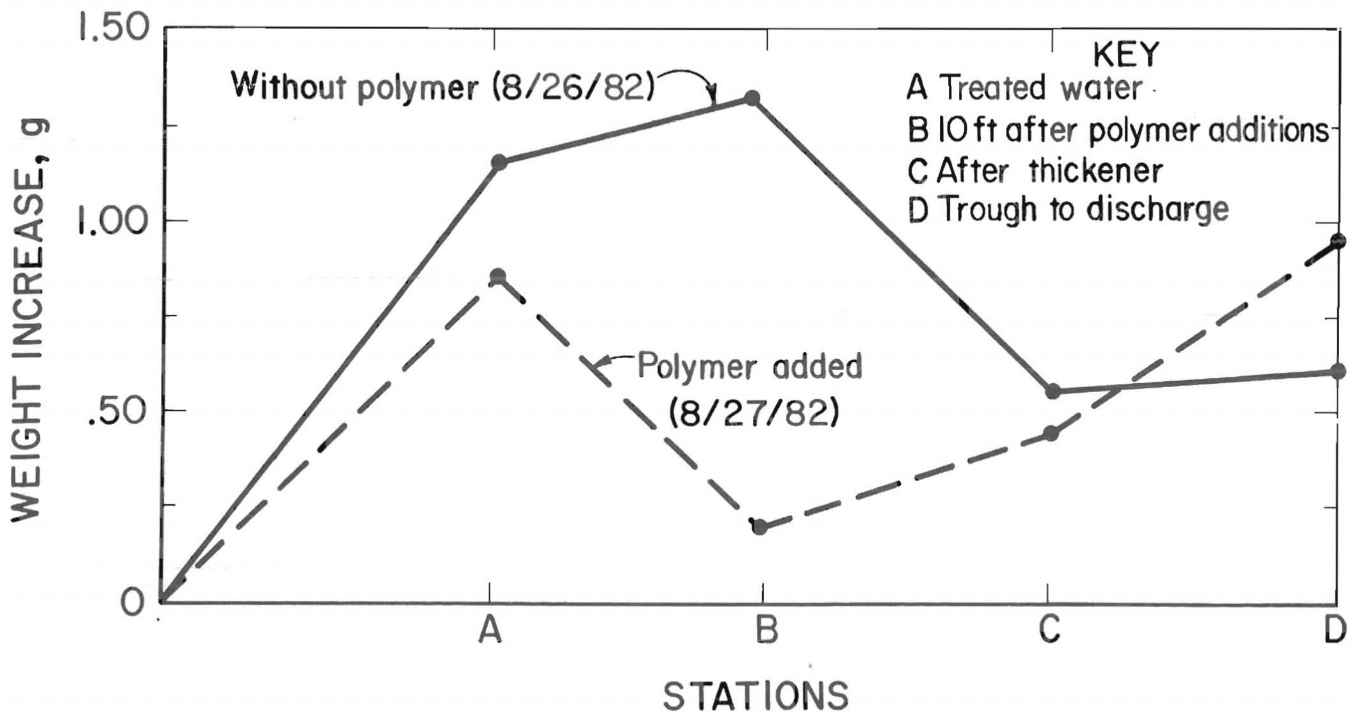

FIGURE 8. - Weight increase for PVC pipe, 6-h contact time.

TABLE 3. - Analysis of treatment plant water with and without type 2 scale inhibitor, parts per million

Station	A	B	C	D
WITHOUT INHIBITOR				
Constituents:				
Al	49.2	ND	ND	ND
Fe (total)	ND	1,080	0.75	0.64
Mg	914	745	679	675
Ca	ND	1,835	2,073	2,147
SO_4	6,800	5,200	5,800	12,200
pH	ND	5.5	6.4	6.5
TYPE 2; FEED RATE = 1.5 gal/h				
Constituents:				
Al	ND	0.69	ND	ND
Fe (total)	1,040	1,080	0.57	0.60
Mg	745	733	733	737
Ca	1,935	1,947	2,172	3,146
SO_4	6,800	7,600	6,800	5,800
pH	8.4	7.5	6.5	6.6

ND Not detected.

POLYMERIC GEL TO INCREASE SETTLING RATES OF SOLIDS IN COAL MINE DRAINAGE

Settleable solids, such as those produced by neutralization of AMD, are typically removed from the treatment system by gravitational settling. Because individual mine waters have different settling characteristics, they require different detention times for adequate reduction of sludge solids. It has been previously shown that by adding a polymeric flocculant, settling rates can be increased, thereby decreasing the required detention time of the system (1-3).[4] A decrease in the required detention time enables the mine operator to utilize smaller or fewer ponds and to clean existing ponds less frequently.

Normally, flocculants are purchased in liquid or powdered form. A composition and distribution system similar to the one shown in figure 9 is commonly used. This system requires clean makeup water, feed pumps, storage tanks, a source of power, and personnel to monitor and maintain the system (4).

An alternative approach to conventional liquids and powders is a new gelatinous form of polymeric flocculant. This polymeric gel is conventionally sold as 40 lb cylindrical "logs." These logs are 9 in. in diameter by 18 in long. As with traditional liquid and powdered polymers, various cationic, anionic, and nonionic formulations are available. The principle advantage of the gel logs is their ease of use. They are placed directly in the stream or channel so that water flows over them, gradually dissolving the flocculant. Dosage is regulated by the number of logs used and, to some extent, velocity of water flow. Thus, unlike conventional polymer systems, the gel log system is easy to install, requires no electricity or auxiliary equipment, and needs minimal operator attention.

In addition to the advantages of installation and operation, it has been determined that the gel logs are effective at very low polymer concentrations (5-6). Polymer dissolved from the gel logs was effective at 50 to 200 ppb in laboratory studies, as opposed to liquid and powdered polymers, which require 1 to 5 ppm (5-6). This greater efficiency may be realized because the gelatinous flocculants dissolve slowly, which permits the polymer molecules to fully uncoil. During the preparation of liquid and powdered flocculants, conventional mixers tend to shear the long polymer molecules, which reduces their effectiveness.

The gel log has been used successfully to help settle suspended solids from coal mine runoff (5). The current study was based on the possibility that this form of polymeric flocculant could be used to decrease the settling time of iron hydroxide sludge at acid mine water treatment facilities, reducing operating costs.

PRELIMINARY TESTS

The specific ionic character of the mine water must be identified in order

[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

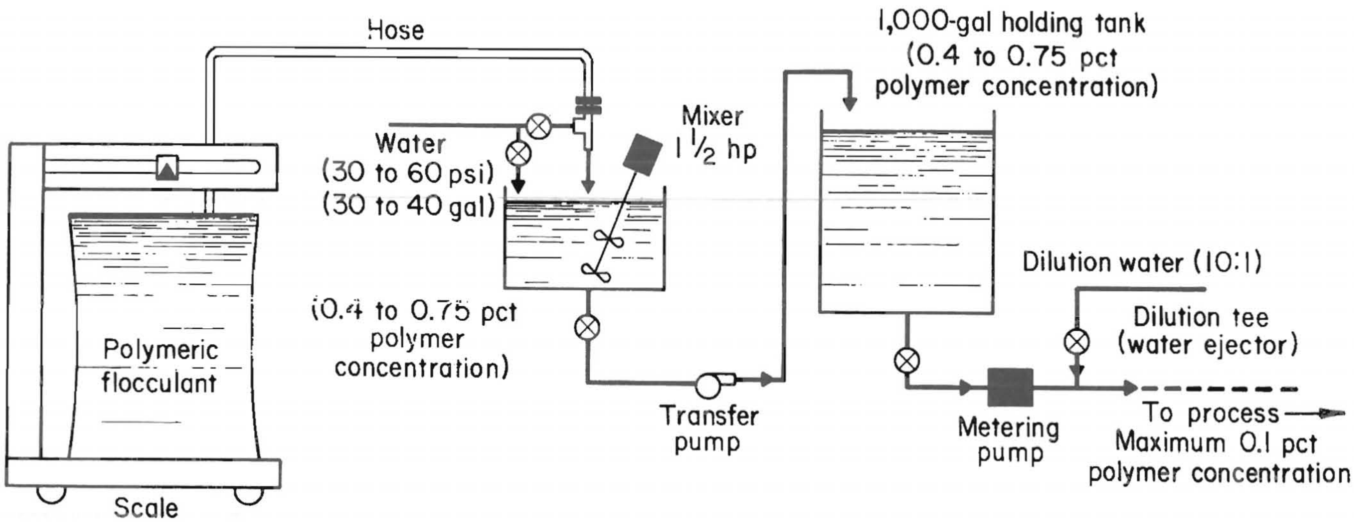

FIGURE 9. - Conventional polymeric flocculant makeup and distribution system.

to choose an effective gel log. Eight polymeric flocculants were evaluated using treated mine water from two field sites. These flocculants differed with respect to their ionic functionalities, strengths of ionic functionality, and viscosity characteristics. Eight 0.5-pct stock solutions were prepared from powdered flocculants that correspond to available gel log formulations. Each flocculant was added dropwise to 1-L mine water samples while the mixture was slowly stirred using a multiple-spindle stirrer. Flocculation, when it occurs, is readily apparent. In general, anionic polymers performed much better than cationic and nonionic polymers. For the mine waters tested, a medium anionic polymeric solution was the most effective.

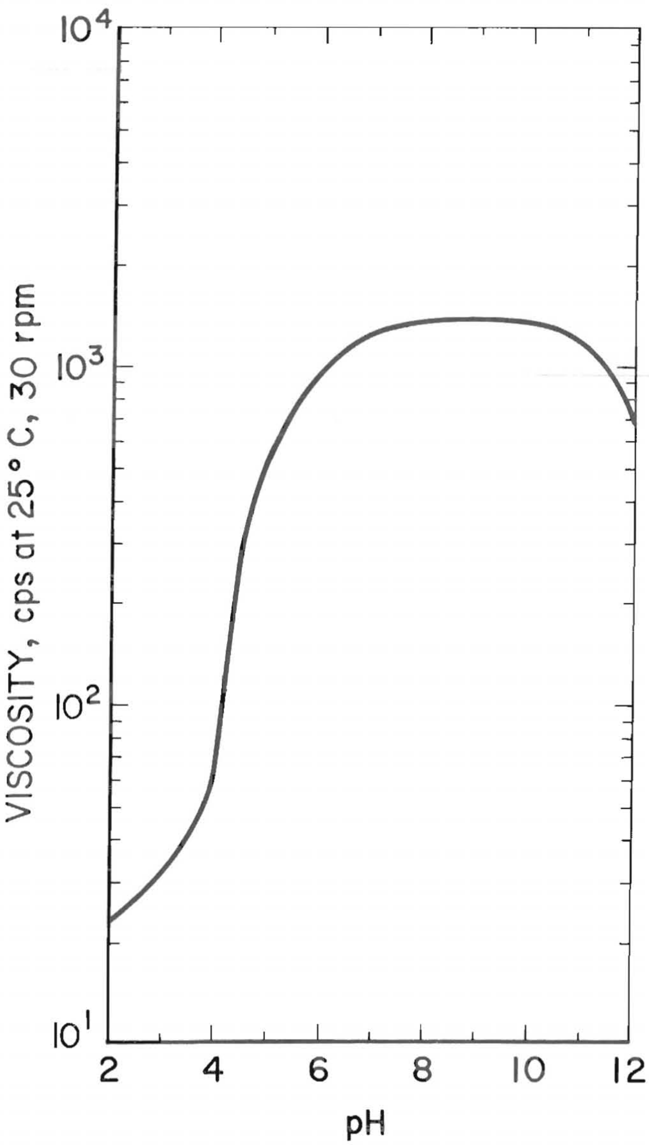

FIGURE 10. - Effect of pH on viscosity of polymer.

Untreated mine water (pH 2-3) was brought directly from the site to the laboratory to determine the most effective pH for the chosen gel flocculant. As shown in figure 10, the viscosity of the polymer, and thus its effectiveness, varies with pH (7). The effective pH range of the medium anionic flocculant was tested by adding various amounts of quicklime (CaO) to mine water to provide pH values of 5, 6, 7, 8, 9, and 10. It was found that the polymer was most effective at pH 8.

In another test, various dosages of the powdered polymer were added to treated mine water having a pH of 8. The minium effective dosage was found to be 0.75 ppm. However, previous studies (5-6) indicate that gel logs may be effective at much lower concentrations.

FIELD TESTS

Gel logs were tested at three mine drainage treatment facilities in southwestern Pennsylvania. These facilities represent a wide range of water quality and treatment technology. Table 4 presents the treatment data.

TABLE 4. - Summary of mine drainage treatment facilities

Neutralizing agent......	None	CaO	NaOH
Type of operation[1]......	UG	UG	S
Water quality: pH......	7.2	3.0	3.9
Analysis, mg/L:			
Acidity (as $CaCO_3$)....	NAp	955	486
Alkalinity (as $CaCO_3$).	387	NAp	NAp
Ferrous iron..........	ND	9.2	([2])
Total iron............	28	180	360
Flow.......... gal/min..	600	400	([1])

NAp Not applicable. ND Not detected.
[1] Seasonal. [2] Not available.

NOTE.--S = Surface. UG = Underground.

No Neutralizing Agent

This underground operation is located in Washington County, PA. The untreated mine water has a pH of 7.2, 387 mg/L alkalinity (as $CaCO_3$), no detectable ferrous iron, and 28 mg/L total iron. The water is pumped from the mine at a rate of 600 gal/min. Since the discharge at this site constitutes the headwaters of a stream, as opposed to discharging into a stream, the mining company is required to meet an effluent standard of 1.5 ppm (average for 30 days) of total iron. This poses a problem since the iron at this site does not settle easily and remains suspended.

Three gel logs were placed in a pipeline between the two settling ponds. A fourth log was positioned beneath the discharge end of the pipe with water flowing directly onto it. Floc formation was observed in the second pond shortly after the water had contacted the gel logs.

Samples were taken before and after the water contacted the gel logs. Another sample was taken at the discharge of the second pond. The samples were brought back to the laboratory for settling and analysis. A portion of the supernatant liquid was taken from each sample after 18, 24, and 48 h of settling, and analyzed for total iron. As shown in table 5, the gel logs reduced the concentration of total iron for each period of settling, in effect, reducing the required detention time.

TABLE 5. - The effects of gel logs on low concentrations of total iron, parts per million

Location[1]	Total iron at--			
	0 h	18 h	24 h	48 h
1................	2.1	1.1	0.74	0.56
2................	2.1	.74	.70	.48
3................	.78	.74	.43	.39

[1]Locations defined:

1 - Immediately before gel logs between first and second ponds.

2 - Immediately after gel logs; influent to second pond.

3 - After gel logs; second pond effluent.

Lime as Neutralizing Agent

Mine water at this Greene County, PA, site originates from an underground operation and has an untreated pH of 3.0, 955 mg/L acidity (as $CaCO_3$), 9 mg/L ferrous iron, and 180 mg/L total iron. The treatment plant consists of a holding pond, lime slaker, flume and settling pond. The plant treats approximately 400 gal/min.

Field test procedures involved the following. Gel logs were wrapped in chicken wire (fig. 11) and were positioned in the flume (fig. 12). The logs were partially immersed, which provided maximum scouring by the flowing water. Figure 12 shows proper installation with good scouring action. The positioning is important because very little polymer will be dissolved if the logs are completely immersed. Samples of the treated water were taken from the flume before and after contact with the gel logs. Sludge settling tests were performed according to Standard Methods (8). Both pH and temperature were monitored during these tests.

FIGURE 11. - Gel logs being wrapped in chicken wire.

FIGURE 12. - Gel log installation in flume.

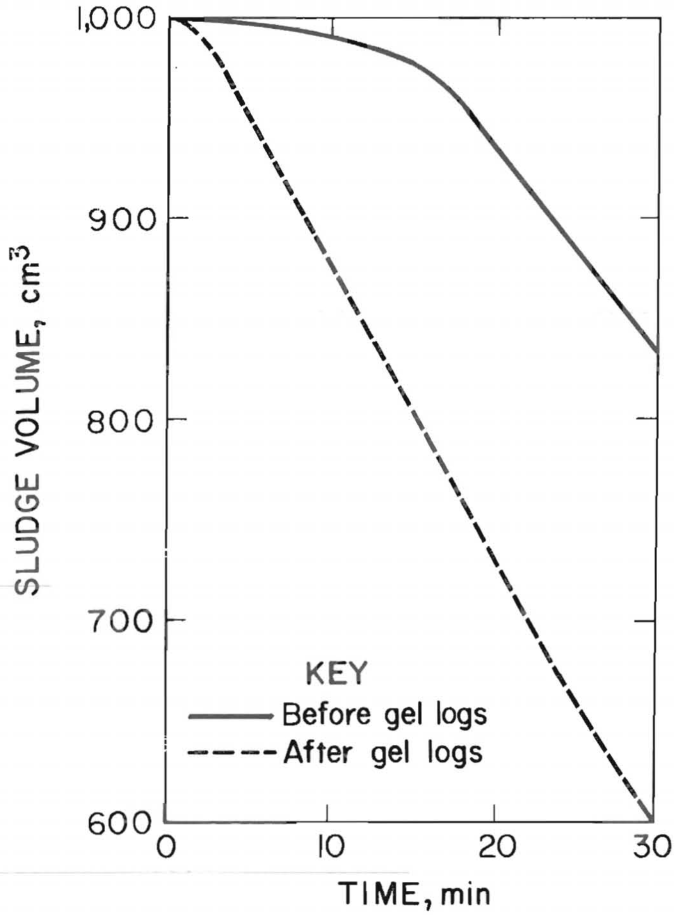

FIGURE 13. - Settling rates of sludge before and after adding polymer.

Gel logs were added one at a time in an attempt to find the minimum effective dosage. Although a total of eight gel logs were installed in the flume at one time, little or no flocculation was observed in the settling tests. Analysis of the treated water indicated that pH of the treated mine water ranged between 4.2 and 12.2. Laboratory analysis of the quicklime used at this plant indicated that the lime was of inconsistent quality, which accounted for the pH variation.

Sodium Hydroxide as Neutralizing Agent

The third site is a surface operation located in Allegheny County, PA. The untreated mine water has a pH of 3.9, and contains 486 mg/L acidity (as $CaCO_3$) and 360 mg/L total iron. The acid water is being pumped out of the pit and treated with 50 pct sodium hydroxide (NaOH) solution. The amount of sodium hydroxide is regulated to yield a pH near 8. The treated water travels down a trough cut in the spoil and then through three settling ponds. Three gel logs were placed in the trough leading to the first settling pond.

Samples were taken before and after the water contacted the gel logs. The gel logs increased the rate of settling (i.e., the slope of the curve shown in figure 13) from 0.19 cm/min to 0.46 cm/min over a 30-min settling period. Once again, the detention time requirement was decreased.

CONCLUSION

Polymeric flocculants in gel log form were examined at three sites. Two of the sites had good pH control, and maintained a pH between 7 and 8. At these sites, the gel logs noticeably improved settling of the iron hydroxide sludge. The other site had poor pH control; pH ranged from 4.2 to 12.2. No improvement in sludge settleability was found at this site.

Before gel logs are used, a simple laboratory test should be performed to select the ionic functionality best suited for the site. Based on our experience, anionic polymer gel logs will provide better flocculation over the pH range 6 to 9 than nonionic or cationic polymers, but the specific anionic polymer gel log (ionic strength, viscosity characteristics) must be selected based on individual mine water composition.

The advantages of gel logs over conventional systems are (1) no electrical requirement, (2) no equipment needed, (3) possibly effective at lower dosages, (4) low maintenance, and (5) easy installation. At sites where a steady pH was maintained, polymeric flocculants in gel log form proved beneficial.

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APPENDIX.--BACKGROUND

"Polymeric flocculants," are water-soluble, vinyl-addition polymers with a molecular weight of 100,000 or greater, capable of promoting flocculation of solids in liquid suspension. Other commonly used terms are polymers, polyelectrolytes, flocculants, and coagulant aids. Most polymeric flocculants are structured on an acrylic monomer backbone. A monomer is a basic chemical unit that can react itself or with another monomer to form a long-chained molecule called a polymer. Anionic polymers have the highest molecular weight and are the most linear in nature, with few side branches to the polymer molecule. This is an important characteristic for efficient flocculation of treated acid mine drainage.

Flocculation is an irreversible kinetic process in which two reactions (shown in figure A-1) take place: (1) charge neutralization and collision, followed by (2) bridging and agglomeration. Normally, a particle in suspension will not be attracted to a similar particle because their net surface charges are alike. No collision will occur. When a polymeric flocculant of the proper functionality, or charge density, is added to the system, its structure is attracted to the particles and will neutralize their surface charge so that collisions will occur between the suspended particles. The second reaction takes place when the polymeric flocculant bridges among several particles and pulls them together to form a larger, faster settling particle (6).

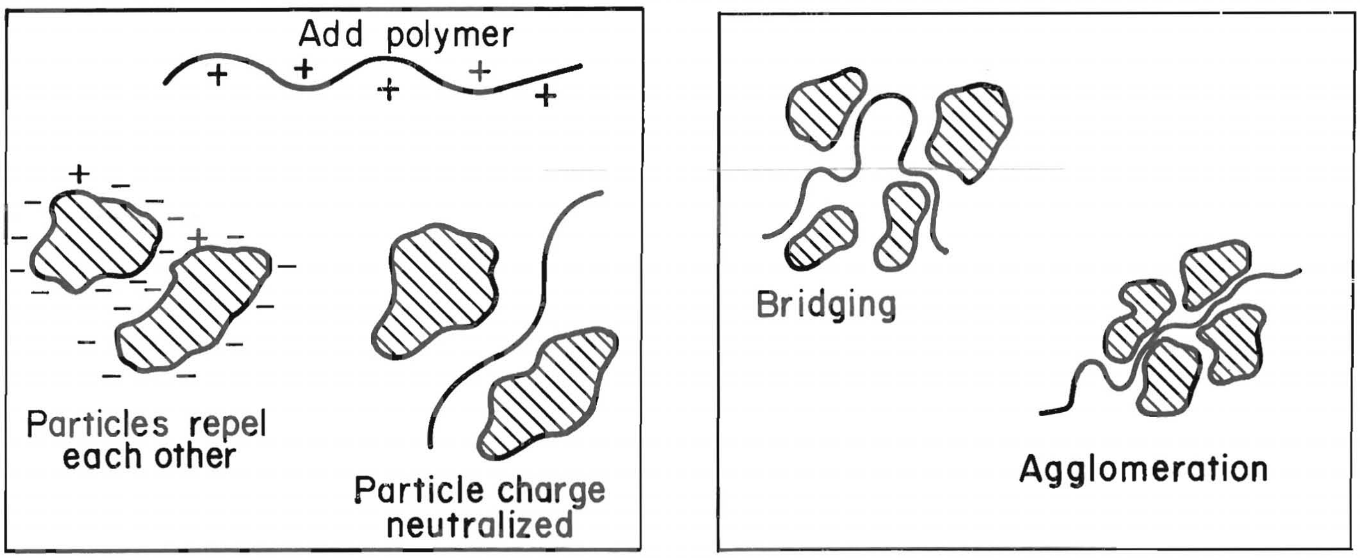

FIGURE A-1. - Charge neutralization, bridging, and agglomeration of particles using polymeric flocculant.